

## Upgrading Furfurals to Drop-in Biofuels: An Overview

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**ABSTRACT:** Biomass is a promising feedstock for the next generation drop-in liquid fuels and renewable chemicals, and hence the development of economically viable technologies for the production of commodity and specialty chemicals from sustainable biomass have received significant attention in recent years. Although biomass transformation into drop-in biofuels involves multiple processing steps in which biomass is first depolymerized and converted to furfurals (5-hydroxymethylfurfural, furfural), catalytic upgrading of furfurals is the most important step in achieving end products of the desired fuel properties. Several research papers have been published in the past decade reporting homogeneous and heterogeneous catalytic processes for upgrading furfurals to relevant drop-in fuel candidates such as, 2,5-dimethylfuran (DMF), 2-methylfuran (2-MF), 5-ethoxymethylfurfural (EMF),  $\gamma$ -valerolactone (GVL), ethyl levulinate and long chain hydrocarbon alkanes. Although process technologies for the production and upgrading of some of these fuel compounds have been reviewed, a concise overview on production methodologies for all relevant furan based fuel compounds, including long chain hydrocarbon alkanes, from furfurals is worth publishing for further advancement. This perspective article is aimed at presenting an up to date analysis of the reported catalytic technologies for upgrading furfurals into long chain hydrocarbons with special emphasis on the condensation reactions for producing high carbon chain precursors and catalytic systems for their subsequent deoxygenation to achieve high yield and selectivity in fuel grade hydrocarbons. The current state-of-the-art on upgrading furfurals to DMF, 2-MF and EMF are also analyzed.

**KEYWORDS:** 2-Methylfuran, 2,5-Dimethylfuran, 5-Ethoxymethylfurfural,  $\gamma$ -Valerolactone, Drop-in biofuels, Long chain hydrocarbons, Furfurals, Hydrodeoxygenation



### INTRODUCTION

Driven by high global demand for petrochemical products and fossil fuels, and the resulting demand–supply imbalance of nonrenewable resources, researchers are banking on the production of energy from biorenewable feedstock such as grains, sugar beet and oil seeds. However, because of additional land requirements and adverse effect on food and fiber crops production, it was soon realized that the first generation biorenewable feedstock based on edible crops would not achieve the desired targets for petrochemical substitution and economic growth.<sup>1,2</sup> Therefore, the current research efforts of bioenergy production are being focused on utilization of earth abundant nonfood lignocellulose such as wood chips, waste biomass and municipal wastes. Lignocellulose can be converted into different forms of fuels via biological and chemical pathways.<sup>3</sup> Most common forms of fuel compounds produced via chemical pathways are 2,5-dimethylfuran (DMF), 5-ethoxymethylfurfural (EMF),  $\gamma$ -valerolactone (GVL) and long chain hydrocarbons.<sup>4–6</sup> These furan based compounds are superior fuels in comparison to ethanol because of their higher

energy density and higher octane values.<sup>7</sup> Although production of deoxygenated fuels is desirable, complete removal of oxygen via deoxygenation of furfurals or furan based molecules is a major challenge. Catalytic hydrothermal liquefaction of cellulose and saccharides can offer hydrocarbons of low carbon chain length, but access to long chain hydrocarbons requires advanced synthetic strategies. Recent studies have shown that aldol condensation of furfurals with ketones to form an intermediate condensation product and subsequent hydrodeoxygenation (HDO) of the aldol intermediate is a viable strategy to produce long-chain hydrocarbons.<sup>8–13</sup>

The conversion of carbohydrate fractions of lignocellulose to advanced fuels involves multiple steps such as (i) acid catalyzed isomerization and dehydration of carbohydrates to furfurals, (ii) catalytic HDO or etherification of furfurals to fuel grade furanic molecules,<sup>14,15</sup> (iii) aldol condensation of furfurals with ketones

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
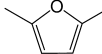

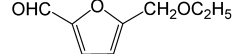
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Table 1. Classification of Biofuels<sup>a</sup>

Generation	Feedstocks	Examples
first generation	sugar, starch, vegetable oils, or animal fats	ethanol, biodiesel, biosyngas, biogas
second generation	nonfood crops, wheat straw, corn stover, wood, solid waste, energy crop	ethanol, bio-oil, DMF, biohydrogen, biodiesel
third generation	algae	biodiesel

<sup>a</sup>Adopted from ref 30.

Table 2. Properties of Gasoline and Biomass Derived Fuels

Properties	Gasoline	Ethanol	DMF	2-MF	EMF
<b>Chemical formula</b>	C <sub>6</sub> -C <sub>9</sub>				
H/C ratio	1.795	3	1.333	1.2	1.27
O/C ratio	0	0.5	0.17	0.2	0.37
Density @ 20°C (kg/m <sup>3</sup> )	745	791	890	913	1100
Research Octane Number (RON)	97	107	101	103	-
Motor Octane Number (MON)	85.7	89	88.1	86	-
Energy density (MJ/L)	31.9	21	29.3	28.5	30.3
Initial boiling point (°C)	32.8	78.4	92	64.7	274

to form carbon precursors with high carbon density and (iv) catalytic HDO of the precursors using a metal catalyst. Alternatively, aldol condensation and hydrogenation steps can be coupled in a single step using a bifunctional catalyst containing both basic as well as hydrogenation sites.<sup>16–20</sup> This approach of self and cross condensation results in the formation of up to C<sub>15</sub> or higher carbon chain length hydrocarbons.<sup>21</sup>

Recently, the U.S. Department of Energy has initiated an integrated biorefinery approach for upgrading lignocellulose and biomass intermediates into drop-in biofuels with high carbon efficiency. Consequently, several research articles have been published describing different reaction methodologies and HDO processes for improving the yield and selectivity of the desired end products, namely furan based fuel molecules and distillate range hydrocarbons. These literature papers have improved our understanding on the relationship of the catalytic properties with yields and selectivity of the desired products and mechanistic insights of the processes.<sup>22–28</sup> In the present paper, we critically analyze the current state of this technology area.

## ■ CLASSIFICATION OF BIOFUELS

Biofuels are a promising replacement for petroleum based fuels due to their ability to (i) provide sustainable supply, (ii) improve carbon efficiency and (iii) reduce the environmental carbon footprint. Biofuels can be classified into first, second and third generation on the basis of the nature of feedstock and technology used for their production (Table 1).<sup>29,30</sup>

Although the first generation biofuels can reduce CO<sub>2</sub> emissions, there are considerable economic and environmental limitations.<sup>31</sup> The most common disadvantage is an inevitable rise of food prices due to a decrease in arable land for food production as the production capacity of biofuels increases.<sup>32</sup> The production of the second generation biofuels from lignocellulose such as, wood chips, hardwood, corn cob, rice

straw and wheat straw does not compete with food production.<sup>33–35</sup> However, the conversion of cellulosic biomass into biofuels in the present scenario is not cost competitive because of high pretreatment, capital and operational costs.<sup>36</sup> For the third generation biofuels, microorganisms, primarily algae biomass, are used as feedstock. Although the later process of biodiesel production from microorganisms does not compete with arable land usage and hence algae biomass can play a vital role in solving the food-versus-fuel problem, the amount of biomass in the microalgal culture is very low, which makes the harvest of algal biomass relatively expensive.<sup>37–41</sup> The fourth generation biofuel (for example biogasoline), involving microbial conversion of genetically engineered crops, not only meets the energy demand but also is promising for CO<sub>2</sub> trapping. This process differs from the second and third generation biofuels production, as CO<sub>2</sub> is captured at all stages of production, such as processes like oxy-fuel combustion.<sup>42</sup> The latter process is capable of replacing the conventional fuel as well as minimizing CO<sub>2</sub> emission.

## ■ ADVANTAGES OF FURANIC BIOFUELS

Biodiesel and ethanol have been promoted over the past decade as a sustainable substitute for fossil fuels. However, it becomes evident that the production of these fuels from corn and soybeans competes with food production by engrossing agricultural crop land. Thus, the production of drop-in fuel compounds from low cost base sustainable feedstock has received significant attention. Drop-in fuels include DMF, 2,5-dimethyltetrahydrofuran (DMTHF), 2-methylfuran (2-MF), EMF, ethyl levulinate (EL), distillate range hydrocarbons and aromatic aviation fuel additive. Among these biofuels, 2-MF and DMF have comparable fuel properties to those of conventional gasoline (Table 2).

## ■ UPGRADING FURFURALS INTO FURANIC BIOFUELS

Furfurals derived fuels have attracted significant attention in recent years due to their environmental, economic and strategic advantages. These fuels are synthesized via hydrogenation, oxidation, etherification, alcoholysis and aldol condensation followed by HDO techniques. For the sake of length and cohesion, we chose to review the recent literature reports on DMF, 2-MF, EMF and GVL production methods in this section.

**2,5-Dimethylfuran (DMF).** DMF is generally obtained via HDO of HMF. As shown in Table 2, DMF has superior fuel properties over ethanol in terms of energy density ( $29 \text{ kJ cm}^{-3}$ ) and oxygen content. Additionally, the higher boiling point ( $92 \text{ }^\circ\text{C}$ ) and lower water miscibility of DMF make it less volatile and suitable to blend with gasoline. Zhong et al.<sup>43</sup> tested 99.8% DMF in a single-cylinder gasoline direct-injection (GDI) research engine. The test results showed comparable combustion and emission properties of DMF to that of commercial gasoline.<sup>44</sup>

The transformation of  $\text{C}_6$ -monosaccharides to DMF is a two-step process involving acid catalyzed isomerization and dehydration of monosaccharides to HMF followed by HDO of the resultant HMF.<sup>45</sup> A two-step process involving HCl catalyzed dehydration of fructose to HMF and subsequent HDO of HMF with Cu/Ru catalyst gave 71% DMF at  $220 \text{ }^\circ\text{C}$  and 6.8 bar  $\text{H}_2$ .<sup>46</sup> Due to the presence of chloride ion, the hydrogenation catalyst deactivated after a few cycles, thus making this process less sustainable. Under similar reaction conditions, Binder and Raines reported<sup>47</sup> maximum 49% yield of DMF from Cu/Ru catalyzed HDO of HMF. Chidambaram and Bell<sup>48</sup> reported a process for HMF hydrogenation to DMF in EMIMCl/acetonitrile solvent in which maximum 17% DMF yield was achieved over a Pd/C catalyst at  $120 \text{ }^\circ\text{C}$  for 1 h. Recently, Lu et al.<sup>49</sup> reported 93% DMF yield from HMF using a high Ru/ $\text{Co}_3\text{O}_4$  catalyst loading (40 wt %) at  $130 \text{ }^\circ\text{C}$  and 7 bar  $\text{H}_2$  pressure. Nishimura et al.<sup>50</sup> developed a  $\text{Pd}_x\text{Au}_y/\text{C}$  bimetallic catalyst and compared its HMF hydrogenation activity with the Pd/C and Au/C catalysts. The  $\text{Pd}_{50}\text{Au}_{50}/\text{C}$  catalyst in the presence of HCl as cocatalyst exhibited high activity for hydrogenation of HMF, giving 96% DMF yield in tetrahydrofuran (THF) at  $60 \text{ }^\circ\text{C}$  for 6 h. Similarly, we have recently reported HDO of HMF with different bimetallic catalysts (Pd/C, Ru/C, Ni/C, Pd/C/ $\text{ZnCl}_2$ , Ru/C/ $\text{ZnCl}_2$ , Ni/C/ $\text{ZnCl}_2$ ). Among the investigated catalysts, bifunctional Pd/C/ $\text{Zn}^{2+}$  catalyst achieved maximum DMF yield (85%).<sup>51</sup> The production of HMF and furfural from various sources of lignocellulose and upgrading furfurals into 2-MF and DMF with high yields (>90%) have also been reported.<sup>52</sup>

Utilization of in situ hydrogen, generated via a catalytic transfer hydrogenation (CTH) pathway, for HMF HDO has been reported by many research groups. Thananathanachon et al.<sup>53</sup> showed Pd/C catalyzed HDO of HMF using formic acid as a hydrogen source, giving 70% DMF yield. Formic acid has also been reported as a hydrogen source in a subsequent communication in which DMF was prepared from lignocellulosic biomass and carbohydrates with a moderate yield (up to 32%).<sup>6</sup> Recently, Vlachos et al.<sup>54</sup> used 2-propanol as a hydrogen source for HMF HDO using Ru/C catalyst and achieved 80% DMF yield at  $190 \text{ }^\circ\text{C}$  over 6 h reaction time. In all of these methods, the key step has been the hydrogenolysis of C—O to C—H in the presence of a noble metal catalyst. The most recent

technological development for DMF production includes ruthenium-based hydrotalcite catalyzed HDO of HMF and hydrogenation of 5-(chloromethyl) furfural (CMF).<sup>55–58</sup>

**2-Methylfuran (2-MF).** 2-MF is an important furfural derived fuel candidate obtained from the hemicellulose fraction of biomass. It is a versatile chemical intermediate used for the production of pesticides, perfumes and antimalarial drugs.<sup>59</sup> The energy density of 2-MF is superior to ethanol and similar to DMF (Table 2). The boiling and flash points of 2-MF are lower than DMF which resolves engine ignition problem. Additionally its latent heat of vaporization is higher than DMF which provides high power output to direct injection spark-ignition (DISI) engine during testing.<sup>60,61</sup> Wang and co-workers examined combustion and emission characteristic of 2-MF in a single cylinder DISI engine<sup>62</sup> and compared these characteristics with DMF, ethanol and gasoline. 2-MF production from xylose is a two-step process involving acid catalyzed conversion of xylose to furfural, followed by catalytic HDO of furfural. Vapor-phase hydrogenation of furfural with  $\text{SiO}_2$  supported Cu/Fe bimetallic catalyst at 1 bar  $\text{H}_2$  is reported to produce 2-MF as a major product with excellent yield (98%).<sup>63</sup> A comparison of silica supported monometallic (Ni) and heterobimetallic (Ni—Fe) catalyst for the vapor phase conversion of furfural at 1 bar  $\text{H}_2$  and  $210\text{--}250 \text{ }^\circ\text{C}$  showed that furanic alcohol is formed as the primary product with monometallic species; however, bimetallic species offered 2-MF as a major product via C—O hydrogenolysis.<sup>64</sup> Fe suppresses decarbonylation activity of Ni while promoting C=O hydrogenation and C—O hydrogenolysis. DFT analysis suggests that the stability of  $\eta^2\text{-(C,O)}$  surface species is higher on Ni—Fe catalyst than on pure Ni which results in rapid hydrogenation of  $\eta^2\text{-(C,O)}$  species to form 2-MF on the bimetallic alloy due to a strong interaction between the carbonyl O and the oxophilic Fe atom. On the pure Ni surface,  $\eta^2\text{-(C,O)}$  species converted to a surface acyl species, which can then produce furan and CO after decomposition. The vapor phase hydrogenation of furfural to 2-MF is an exothermic reaction ( $142 \text{ kJ mol}^{-1}$ ) and hence difficulty in controlling temperature affects the yield of the desired product and also deactivates the catalyst rapidly. In addition, this approach requires pressurized hydrogen and gaseous reagent, which increases process cost. Zhu et al.<sup>65</sup> demonstrated catalytic coupling process for hydrogenation of furfural in a fixed bed reactor over Cu—Zn bimetallic catalyst with excellent yield of 89% at  $212 \text{ }^\circ\text{C}$ . Yang and co-workers investigated catalytic coupling process to obtain 2-MF over trimetallic Cu—Zn—Al catalyst in which catalytic hydrogenation (furfural to 2-MF) and dehydrogenation (1,4-butanediol to  $\gamma$ -butyrolactone,  $\Delta H = +62 \text{ kJ mol}^{-1}$ ) processes were coupled to utilize the released heat from the hydrogenation reaction for the dehydrogenation step and hence dramatically reduced the heat of exothermic of the furfural hydrogenation process to  $80 \text{ kJ mol}^{-1}$ .<sup>66</sup> The performance of the Cu—Zn—Al catalyst decreased when the catalyst was calcined at higher temperature ( $750 \text{ }^\circ\text{C}$ ). To overcome this difficulty, Sun et al.<sup>67</sup> described hydrogenation of furfural to 2-MF over polymer-supported  $\text{Pd}^{\text{II}}$  complex which offered 100% yield of 2-MF at  $18 \text{ }^\circ\text{C}$  under 1 bar  $\text{H}_2$  pressure. Nudelman et al. reported hydrogenation of furfural to 2-MF with Pd/C catalyst at room temperature and 2 bar  $\text{H}_2$  pressure.<sup>68</sup> Vapor phase HDO of furfural oxygenates with molybdenum carbide ( $\text{Mo}_2\text{C}$ ) catalyst reported to produce 2-MF with 50–60% selectivity.<sup>69a</sup> The same authors have also reported liquid phase catalytic transfer hydrogenation of

Table 3. Selected Physical Properties of Various Oxygenates<sup>a</sup>

Chemical properties	Methanol	Ethanol	MTBE	ETBE	GVL	2-MeTHF
MW (g mol <sup>-1</sup> )	32.04	46.07	88.15	102.17	100.12	86.13
Carbon (wt %)	37.5	52.2	66.1	70.53	60	69.7
Hydrogen (wt %)	12.6	13.1	13.7	13.81	8	11.6
Oxygen (wt %)	49.9	34.7	18.2	15.66	32	18.7
Boiling point (°C)	65	78	55	72–73	207–208	78
Melting point (°C)	–98	–114	–109	–94	–31	–136
Density (°C)	0.7910	0.8	0.74	0.742	1.05	0.86
Flash point (°C)	16.1	14	–33	–19	96	–11
Energy density (MJ/L)	16	21	31	32	27.7	28.5

MTBE = Methyl *t*-butyl ether, ETBE = ethyl *t*-butyl ether and 2-Me-THF = 2-methyl tetrahydrofuran. <sup>a</sup>Adopted from ref 91.

furfural over Ru/C and Ru/RuO<sub>2</sub>/C catalysts.<sup>69b,c</sup> Corma et al. designed a remarkable synthesis process for the production of diesel with ten to eighteen carbon atoms from 2-MF.<sup>70</sup> High quality diesel fuel was obtained through two consecutive catalytic steps that involve hydroxyl alkylation/alkylation and hydride oxygenation with an overall yield of 96%. An oxygenated C<sub>13</sub> fuel precursor was derived from condensation of 2-MF with acetone over a mixed oxide catalyst followed by HDO into C<sub>13</sub>/C<sub>14</sub> jet fuel range alkanes.<sup>71,72</sup>

**5-Ethoxymethylfurfural (EMF).** 5-Ethoxymethylfurfural (EMF) is an attractive biofuel alternative having desirable fuel properties. Its energy density (30.3 MJ L<sup>-1</sup>) is higher than that of ethanol (21 MJ L<sup>-1</sup>) and similar to gasoline (31.9 MJ L<sup>-1</sup>) and diesel (33.6 MJ L<sup>-1</sup>).<sup>73</sup> Avantium has blended up to 20% EMF as an additive with regular diesel, and it was found that EMF can reduce SO<sub>x</sub> emission, solid particulate contamination and soot formation. The researchers also observed that the engine ran smoothly for many hours using EMF blended fuel. EMF can also be used as a flavor and aroma ingredient in wines and beers.<sup>74</sup> It is synthesized by acid catalyzed etherification of biomass derived HMF and ethanol. Lanzafame et al.<sup>75</sup> studied etherification of HMF and ethanol over different mesoporous silica materials. The catalytic activities of Brønsted acidic H<sub>2</sub>SO<sub>4</sub> and Amberlyst-15 have also been reported for etherification of HMF with ethanol, although these reactions produced 4-oxopentanoate (EOP) as a main product instead of EMF. Recently, Liu and co-workers<sup>76</sup> demonstrated direct conversion of fructose into EMF (43%) using MCM-41 supported 12-tungstophosphoric acid (MCM-41-HPW) catalyst. Balakrishnan et al. reported H<sub>2</sub>SO<sub>4</sub> and *p*-toluene sulfonic acid catalyzed etherification of HMF and ethanol, which produced 75 and 81% EMF, respectively at 75 °C for 24 h.<sup>77</sup> At a higher temperature (120 °C), EL was obtained as a sole product. Recent studies have shown direct conversion of glucose to EMF using AlCl<sub>3</sub> catalyst, giving 57% EMF and 11% EL at 160 °C, and cascade catalysis for the production of 2,5-bis-(alkoxymethyl)furan from HMF over a Lewis acid zeolite catalyst.<sup>78</sup>

Risagar and co-workers developed a successive dehydration and etherification process for the conversion of fructose to EMF and EL using sulfonic-acid-functionalized “task specific” ionic liquid catalyst.<sup>79</sup> Inspired by this work, our research group reported a one-pot synthesis method for direct transformation of cellulose and lignocellulosic biomass into a mixture of EMF and EL (9:1) with 24% yield.<sup>6</sup> Zr(O)Cl<sub>2</sub>/CrCl<sub>3</sub> was used as a catalyst in the latter method to perform sequential hydrolysis, dehydration and etherification reactions in ethanol at 120 °C for 15 h in the presence of 9 wt % 1-butyl-3-methylimidazolium chloride [BMIM]Cl ionic liquid additive. Under comparable

conditions, we also reported etherification of HMF that produced 29% EMF and EL at 9:1 ratio for 8 h.<sup>6</sup> Heteropolyacids (HPAs) were effective catalysts for the conversion of lignocellulosic biomass into biofuels because of their Brønsted acidity, well defined structure, high proton mobility and the ability to accept and release electrons. Furthermore, high solubility of HPAs in polar solvent and good thermal stability in solid state renders HPAs as potentially promising bifunctional acid catalysts in homogeneous and heterogeneous systems.<sup>80</sup> We found that Brønsted acidic *N,N*-dimethylacetamide methanesulfonic acid, *N*-methylpyrrolidone methanesulfonic acid ionic liquid and silica supported HPAs catalysts gave moderate yield (58%) of EMF from weed biomass, based on its glucane content, under microwave and conventional heating condition.<sup>8</sup>

H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> catalyst was also used for the conversions of fructose, sucrose and inulin into EMF with 76, 33 and 62% yields, respectively, under microwave assisted heating.<sup>81</sup> Improved yield of EMF from fructose was noted in the presence of THF as a cosolvent. A similar EMF yield (64%) has also been reported from phosphotungstic acid catalyzed conversion of fructose at 140 °C for about 2 h.<sup>82</sup> In recent years, the use of carbon graphene-based materials has received considerable interest for biomass conversion. Graphene oxide (GO) prepared by Hummers method was reported as a highly efficient catalyst for oxidation of benzylic alcohol and ring-opening of epoxides.<sup>83,84</sup> Wang et al. have achieved 92% EMF yield from etherification of HMF over GO at 100 °C for 12 h.<sup>85</sup> Under comparable reaction conditions, fructose, sucrose and inulin produced 71, 34 and 66% EMF, respectively. When GO was replaced by flake graphite and reduced graphite oxide (R-GO), no reactions were noted, suggesting that the functional groups of GO catalyst played a crucial role in the etherification process.

**γ-Valerolactone (GVL).** γ-Valerolactone (GVL) is a biomass derived renewable chemical that can be employed as food additives, solvent, bio-oxygenate and precursor for HVCs.<sup>86,87</sup> GVL can also be used as a fuel additive that exhibits excellent fuel properties, as compared in Table 3.<sup>88</sup> It is reported that GVL blended diesel fuel reduced CO and smoke emission in automobile exhausts.<sup>89</sup> GVL is usually produced via selective hydrogenation of levulinic acid as shown in Figure 1. In one pathway, LA is first dehydrated to angelica lactone which is subsequently converted into GVL by hydrogenation. The acid catalyst required in this pathway also catalyzed the coke formation from angelica lactone and thus lower the yield of GVL.<sup>90</sup> In the second pathway, LA is hydrogenated to form γ-hydroxyvaleric acid that is then converted into GVL by eliminating a water molecule via intramolecular esterification.

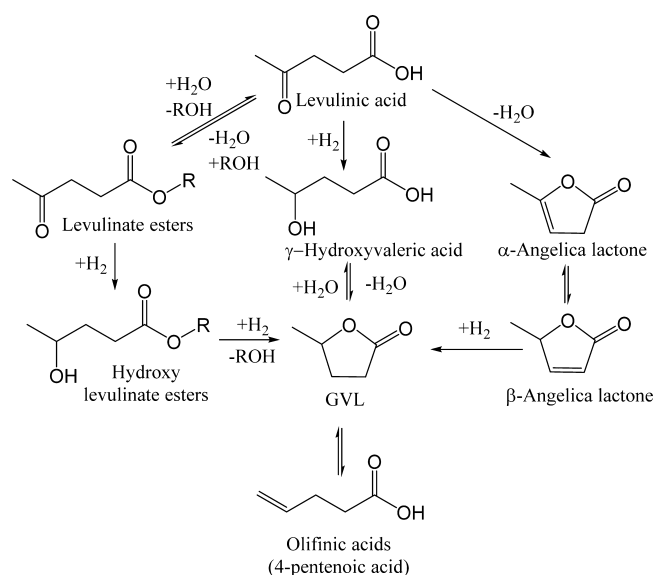


Figure 1. Reaction pathways to produce GVL (adopted from ref 92).

Several homogeneous and heterogeneous metal catalysts have been developed for the production of GVL from LA. Among homogeneous catalysts, Ru–phosphine based catalyst achieved maximum yields.<sup>95</sup> Osakada et al. have shown that  $\text{RuCl}_2(\text{PPh}_3)_3$  catalyzed conversion of LA achieved 99% yield

of GVL at 12 bar  $\text{H}_2$  and 180 °C for 24 h.<sup>94</sup> Hydrogenation of LA to GVL has also been reported by several other groups.<sup>95–98</sup> In case of heterogeneous catalyzed reactions, hydrogenation of LA with a combination Ru/C and Amberlyst A70 catalysts offered maximum GVL yield (99%) in 3 h at 5 bar  $\text{H}_2$  and 70 °C.<sup>99</sup> The yields and selectivity of GVL using reported heterogeneous catalysts are summarized in Table 4.

Chia et al.<sup>106</sup> developed metal oxide based catalysts ( $\text{ZrO}_2$  and  $\gamma\text{-Al}_2\text{O}_3$ ) to produce GVL. The authors adopted Meerwein–Ponndorf–Verley reaction for hydrogenation of LA using secondary alcohols as solvent as well as hydrogen donor. It was found that  $\text{ZrO}_2$  catalyzed reaction achieved the highest GVL yield (92%) using 2-butanol as  $\text{H}_2$ -donor. The activity of metal oxide catalysts decreased after 100 h of operation, but regained activity upon calcination in air at 450 °C. Tang and co-workers<sup>107</sup> also developed an effective method for the conversion of EL into GVL using low-cost  $\text{ZrO}_2$  as a catalyst and supercritical ethanol as a hydrogen donor, which produced 82% GVL at 250 °C for 3 h. Similarly, other non-noble metal based catalysts have also been developed for GVL production. For instance, Hengne et al. reported Cu/ $\text{ZrO}_2$  and Cu/ $\text{Al}_2\text{O}_3$  catalysts for the hydrogenation of LA and its methyl esters in water and methanol with excellent selectivity in GVL.<sup>108</sup> Recently, a continuous process for hydrogenation of LA with metal hydroxide catalysts have been reported.<sup>109</sup> Among these,  $\text{ZrO}(\text{OH})_2 \cdot x\text{H}_2\text{O}$  catalyst offered the best performance, producing ~94% GVL from LA. Hydrotalcites

Table 4. Summary of GVL Yields and Selectivity Using Reported Heterogeneous Catalysts<sup>a</sup>

entry <sup>(ref.)</sup>	catalysts	reaction conditions <sup>b</sup>	T (°C)	conv. (%)	GVL selec. (%)	GVL yield (%)
1 <sup>93</sup>	5 wt % Ir/C	batch reaction, 1,4-dioxane, $\text{H}_2$ (55 bar), LA	150	49	97	47
2 <sup>93</sup>	5 wt % Rh/C	batch reaction, 1,4-dioxane, $\text{H}_2$ (55 bar), LA	150	30	95	28
3 <sup>93</sup>	5 wt % Pd/C	batch reaction, 1,4-dioxane, $\text{H}_2$ (55 bar), LA	150	30	90	27
4 <sup>93</sup>	5 wt % Ru/C	batch reaction, 1,4-dioxane, $\text{H}_2$ (55 bar), LA	150	80	90	72
5 <sup>93</sup>	5 wt % Pt/C	batch reaction, 1,4-dioxane, $\text{H}_2$ (55 bar), LA	150	13	80	10
6 <sup>93</sup>	5 wt % Re/C	batch reaction, 1,4-dioxane, $\text{H}_2$ (55 bar), LA	150	7	80	6
7 <sup>93</sup>	5 wt % Ni/C	batch reaction, 1,4-dioxane, $\text{H}_2$ (55 bar), LA	150	2	20	0.4
8 <sup>100</sup>	$\text{CuO/Cr}_2\text{O}_3$	vapor phase, LA	200	100	100	100
9 <sup>101</sup>	5 wt % Ru/C	vapor phase, $\text{H}_2$ (1 bar), LA	265	100	98.6	98.6
10 <sup>101</sup>	5 wt % Pd/C	vapor phase, $\text{H}_2$ (1 bar), LA	265	100	90	90
11 <sup>101</sup>	5 wt % Pt/C	vapor phase, $\text{H}_2$ (1 bar), LA	265	100	30	30
12 <sup>102</sup>	$\text{PtO}_2$	batch reaction, diethyl ether, $\text{H}_2$ (2–3 bar), LA	25			87
13 <sup>103</sup>	Re “black”	batch reaction, no solvent, $\text{H}_2$ (148 bar), LA	106	100	71	71
14 <sup>104</sup>	5 wt % Ru/C	batch reaction, methanol, $\text{H}_2$ (12 bar), LA	130	90	95	86
15 <sup>104</sup>	5 wt % Pd/C	batch reaction, methanol, $\text{H}_2$ (12 bar), LA	130	17	38	6
16 <sup>104</sup>	Raney Ni	batch reaction, methanol, $\text{H}_2$ (12 bar), LA	130	18	30	5
17 <sup>104</sup>	Urushibara Ni	batch reaction, methanol, $\text{H}_2$ (12 bar), LA	130	45	5	2
18 <sup>105</sup>	5 wt % Ru/ $\text{TiO}_2$ (Tronox)	batch reaction, ethanol/water, $\text{H}_2$ (12 bar), LA	130	0	0	0
19 <sup>105</sup>	5 wt % Ru/ $\text{TiO}_2$ (Degussa P25)	batch reaction, ethanol/water, $\text{H}_2$ (12 bar), LA	130	81	87	71
20 <sup>105</sup>	5 wt % Ru/C	batch reaction, ethanol/water, $\text{H}_2$ (12 bar), LA	130	99	89	89
21 <sup>105</sup>	5 wt % Ru/ $\text{Al}_2\text{O}_3$	batch reaction, ethanol/water, $\text{H}_2$ (12 bar), LA	130	94	80	76
22 <sup>105</sup>	5 wt % Ru/ $\text{SiO}_2$	batch reaction, ethanol/water, $\text{H}_2$ (12 bar), LA	130	98	76	75
23 <sup>106</sup>	$\text{MgO/Al}_2\text{O}_3$	batch reaction, 2-BuOH, 20 bar He, BL	150	17		14.6
24 <sup>106</sup>	$\text{MgO/ZrO}_2$	batch reaction, 2-BuOH, 20 bar He, BL	150	12.6		8.0
25 <sup>106</sup>	$\text{CeZrO}_x$	batch reaction, 2-BuOH, 20 bar He, BL	150	19.7		15.8
26 <sup>106</sup>	$\gamma\text{-Al}_2\text{O}_3$	batch reaction, 2-BuOH, 20 bar He, BL	150	37.9		29.6
27 <sup>106</sup>	$\text{ZrO}_2$	batch reaction, 2-BuOH, 20 bar He, BL	150	>99.9		84.7
28 <sup>106</sup>	$\text{ZrO}_2$	batch reaction, 1-BuOH, 20 bar He, BL	150	60.5		42.8
29 <sup>106</sup>	$\text{ZrO}_2$	batch reaction, EtOH, 20 bar He, BL	150	98.2		49.2
30 <sup>106</sup>	$\text{ZrO}_2$	batch reaction, IPA, 20 bar He, BL	180	93.2		80.5

<sup>a</sup>BL = butyl levulinate, IPA = isopropyl alcohol. <sup>b</sup>Second entry is solvent.

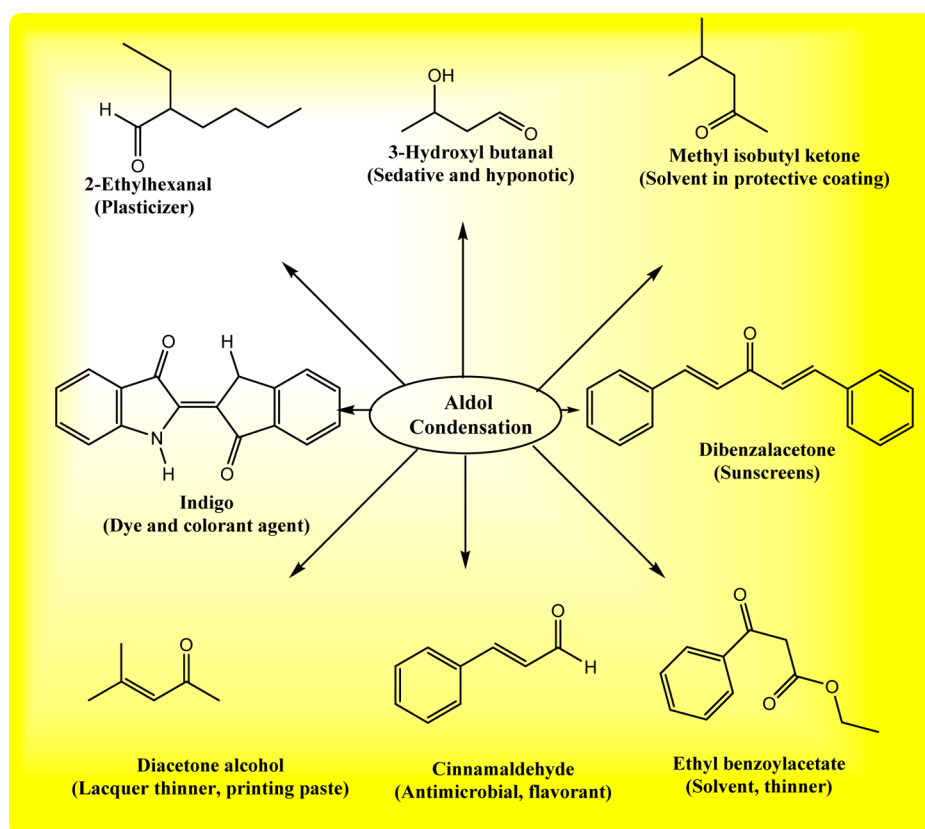
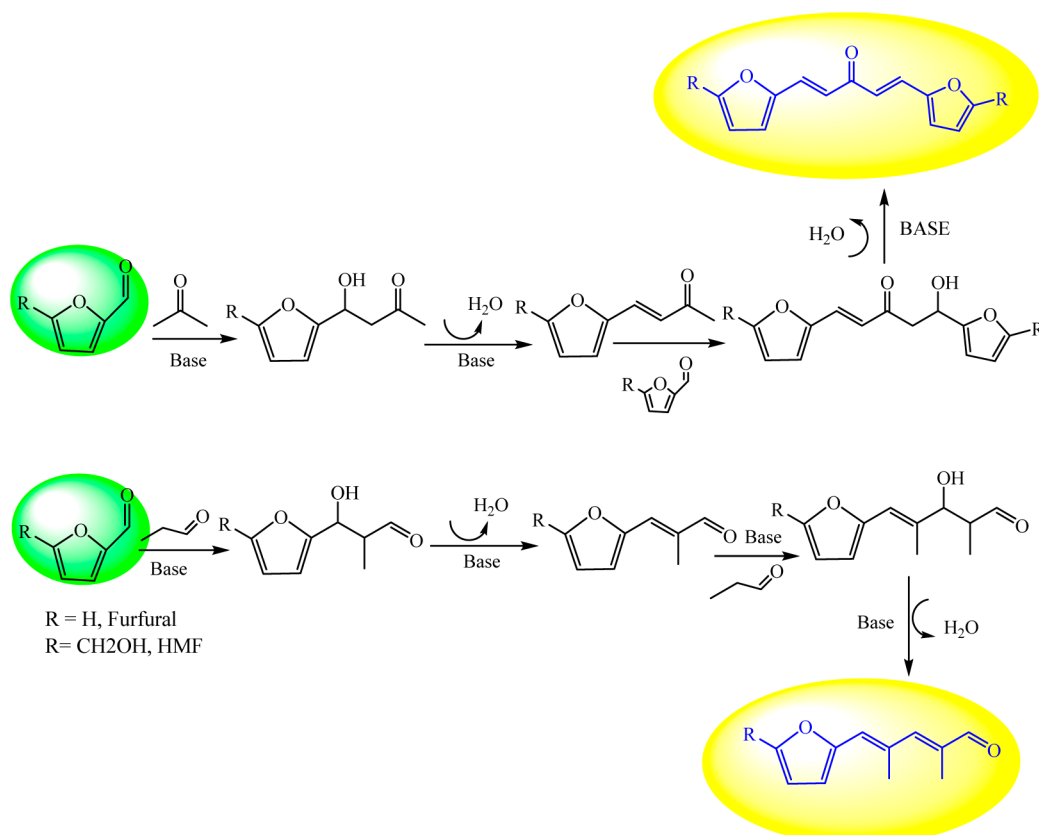
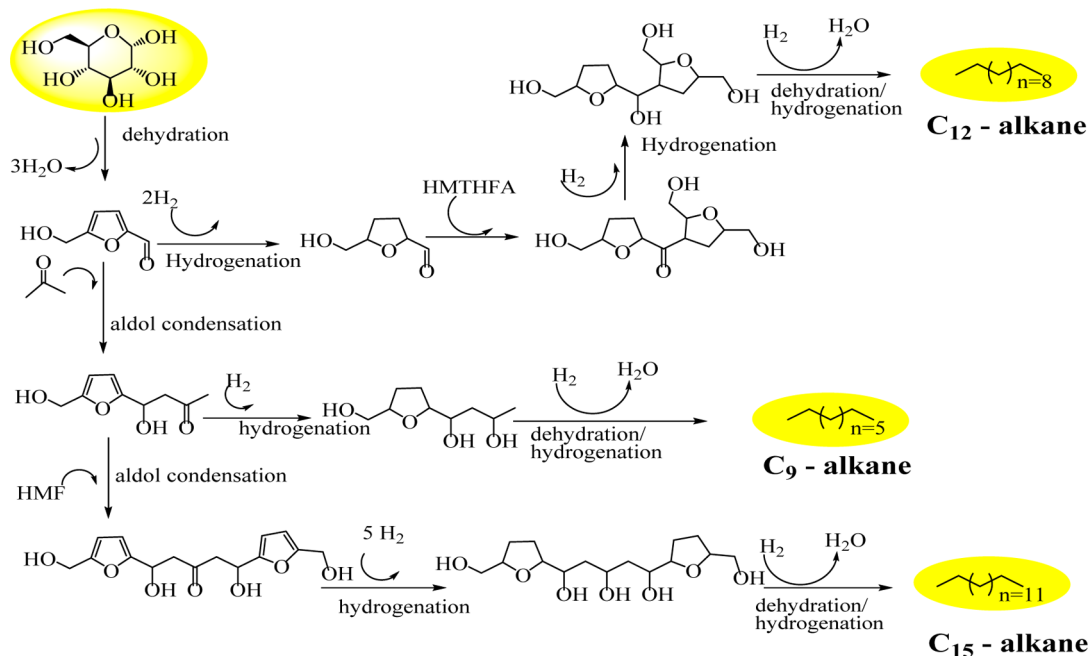
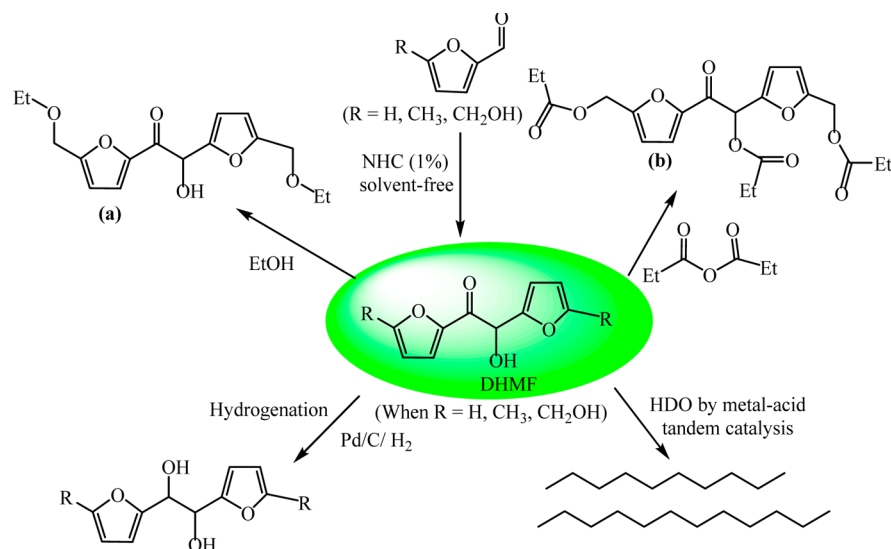


Figure 2. Different aldol condensation products and their applications.

Scheme 1. Base Catalyzed Aldol Condensation of Furfurals with Acetone or Propanal<sup>a</sup>



<sup>a</sup>Modified from scheme in ref 111.

Scheme 2. Pathways to Convert HMF into Alkanes<sup>a</sup><sup>a</sup>Modified from ref 21.Scheme 3. Upgrading of HMF into Chemicals, Oxygenated Diesel and Alkane Fuels<sup>a</sup><sup>a</sup>Modified scheme in ref 115.

derived Cu–Al, Cu–Cr and Cu–F catalysts have also exhibited excellent activity, enabling 91% GVL at 200 °C for 10 h.<sup>110</sup>

### LONG CHAIN HYDROCARBONS VIA ALDOL CONDENSATION

C–C bond formation via aldol reaction involves condensation of an enol or enolate of an aldehyde or ketone with another carbonyl molecule in polar solvents in the presence of acid or base catalysts. Condensation reaction is a key step for the production of different HVCs such as, methyl isobutyl ketone (MIBK), 4-methoxybenzalacetone, 3-hydroxybutanal and dibenzalacetone (Figure 2). In the context of drop-in biofuels production, biomass derived furfural, HMF or tetrahydrofurfural

undergoes condensation reactions with a suitable carbonyl reactant to produce high carbon containing precursors, which are subsequently hydrodeoxygenated into fuel grade alkanes. Several reaction methodologies for the production of aldol products via base catalyzed condensation of HMF and furfural with acetone or propanal have been reported (Scheme 1).

Liquid alkanes of high carbon chain length (C<sub>7</sub>–C<sub>15</sub>) have been synthesized from carbohydrates via liquid phase aldol condensation (Scheme 2).<sup>21</sup> In this process, condensation of HMF/furfural and acetone in polar solvents (water, water–methanol or water–ethanol) over base catalysts (NaOH, MgO–Al<sub>2</sub>O<sub>3</sub>, MgO–ZrO<sub>2</sub> or CaO–ZrO<sub>2</sub>) formed C<sub>12</sub>–C<sub>15</sub> intermediates. Subsequent hydrogenation/HDO of these intermediates with noble metal catalysts (Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/C,

Ru/C and Pd/Al-MCM-41) achieved *n*-nonane (C<sub>9</sub>), *n*-dodecane (C<sub>12</sub>) and *n*-pentadecane (C<sub>15</sub>) products.<sup>16,17,112</sup> Dedsuksophon and co-workers used TiO<sub>2</sub>, TiO<sub>2</sub>-ZrO<sub>2</sub>, Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/CeO<sub>2</sub> catalysts for the conversions of furfurals to hydrocarbon fuels.<sup>113</sup> Xing et al. reported a method for the production of liquid alkane fuels from hemicellulose extract, derived from hardwood.<sup>17</sup> This process involved four steps: (i) acid catalyzed dehydration of hemicellulose to furfural in biphasic solvent, (ii) base catalyzed aldol condensation of furfural with acetone to produce furfural-acetone-furfural (FAF) dimer, (iii) low temperature hydrogenation of FAF to the hydrogenated product (H-FAF) at 110–130 °C and 55 bar H<sub>2</sub> over 5 wt % Ru/C catalyst and (iv) upgrading H-FAF into jet and diesel fuel range alkane over bifunctional Pt/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalyst. Though the above process offered only a single-component fuel; a mixture of different hydrocarbons including *n*-paraffins, isoparaffins and naphthenes can be accessible by changing reaction conditions and catalyst.<sup>28</sup> A process of HMF conversion to alkane involving aldol condensation of HMF with acetone over NaOH as a base catalyst and subsequent low temperature hydrogenation and ring opening of the aldol product in supercritical carbon dioxide (scCO<sub>2</sub>) over bifunctional Pd/Al-MCM-41 achieved C<sub>9</sub> linear alkane with >99% selectivity, although the yield of the C<sub>9</sub> alkane was quite poor (30%) due to cleavage of C–C bond during HDO step.<sup>16</sup>

Recently, Sutton et al. demonstrated a promising one-pot and multiple step technique for producing *n*-alkanes with excellent yield (90%).<sup>114</sup> Inspired by this work, Liu et al. developed a two-step process for the conversion of HMF into diesel and alkane fuels in which the first step involved solvent free self-condensation of HMF and its substituted analogues with *N*-heterocyclic carbene (NHC) catalyst at 60 °C for 1 h to produce furoin intermediates.<sup>115a</sup> Simple hydrogenation of these intermediates with Pd/C catalyst did not produce alkanes. However, when –CH<sub>2</sub>OH substituted furoin intermediate reacted with bifunctional metal–acid tandem catalyst (TaOPO<sub>4</sub> and Pt/C) at 300 °C and 35 bar H<sub>2</sub> for 3 h, linear alkanes were formed. This process produced a mixture of linear alkanes consisting of 27% *n*-decane, 23% *n*-undecane and 46% *n*-dodecane. The –CH<sub>2</sub>OH substituted furoin intermediate can also be upgraded to oxygenated biodiesel and hydrocarbon via etherification, esterification and hydrogenation, or by HDO using metal–acid tandem catalysts (Scheme 3). Recently, Wegenhart et al. also adopted similar catalytic approach for C<sub>10</sub>–C<sub>12</sub> hydrocarbons with moderate yield (71%) and high selectivity (94%).<sup>115b</sup>

Aldol condensation of HMF and acetone using homogeneous catalytic systems in monophasic solvents such as, water, methanol/water or ethanol/water are well-explored;<sup>28,116–118</sup> however, these reactions have common drawbacks involving separation and purification of the desired products. To overcome this difficulty, a biphasic system for condensation of furfural, furaldehyde, methyl furfural and HMF with ketones (acetone, dihydroxyacetone, 2-hexanone and 3-hexanone) was employed.<sup>11</sup> This biphasic system consists of a reactive aqueous phase and low boiling point organic extracting phase for facilitating easy removal of the aldol products. Many heterogeneous catalysts such as alkali oxides, alkali earth oxides, mixed oxides, phosphates and hydrotalcites have been developed to promote aldol reactions. For example, aqueous-phase aldol condensation of acetone and furfural over mixed-oxide (Mg–Zr, Mg–Al and Ca–Zr) catalysts, in which activity and selectivity of the catalyst being correlated with their

physicochemical properties.<sup>119</sup> This revealed that mixed-oxides with the highest concentration of basic sites (especially medium-strength basic sites) are the most active and selective for the C<sub>13</sub> product formation. Usage of basic catalysts, such as MgO–ZrO<sub>2</sub>, NaY and nitrogen substituted NaY (Nit-NaY), for aldol condensation of furfural and HMF with acetone or propanal in water–methanol media have also been reported. Among these catalyst, Nit-NaY catalyzed condensations achieved maximum selectivity (81%) in the desired product that contained a mixture of monomer and dimer.<sup>100</sup>

Hydrotalcite materials have also been employed for aldol condensation of furfurals with acetone.<sup>120–123</sup> A recent study on Mg–Al hydrotalcites and mixed oxides catalyzed condensations revealed excellent furfural conversion (>95%) when Mg–Al catalyst containing Mg to Al molar ratio of 3 was used.<sup>124</sup> However, this catalyst deactivated quickly because of their high sensitivity toward ambient CO<sub>2</sub>.<sup>125,126</sup> Natural dolomitic rocks have been reported as potential base catalysts for aldol condensation of furfural and acetone in the temperature range of 33–150 °C. The later reactions using activated dolomite rock showed high selectivity in C<sub>13</sub> product. Acid catalysts are seldom used for aldol condensation.<sup>127,128</sup> Kikhtyanin and co-workers reported condensation of furfural with acetone over acidic zeolites [(NH<sub>4</sub>-ZSM-5(23), NH<sub>4</sub>-ZSM-5(50), NH<sub>4</sub>-BEA(25), NH<sub>4</sub>-BEA(38), NH<sub>4</sub>-MOR(20), HSDUSY(80), HSUSY(5)] in a batch reactor at 20–100 °C.<sup>129</sup> In a subsequent report, spinel aluminate catalysts (CoAl<sub>2</sub>O<sub>4</sub>, MgAl<sub>2</sub>O<sub>4</sub>, Cu/MgAl<sub>2</sub>O<sub>4</sub> and ZnAl<sub>2</sub>O<sub>4</sub>) with high specific surface area were used for aldol condensation of HMF and acetone. Among these catalysts, Cu/MgAl<sub>2</sub>O<sub>4</sub> demonstrated the highest selectivity (78%) in aldol product.<sup>130</sup> Most recently, Li et al. developed a novel bifunctional Pd/CN@MgO catalyst for aldol condensation of furfural with acetone, and subsequent hydrogenation of the aldol adduct which gave ~95% selectivity in hydrogenation product at 120 °C and 10 bar H<sub>2</sub>.<sup>131</sup> Recently, our group developed a heterogeneous zirconium carbonate catalyst for aldol condensation of HMF with acetone and achieved 92% yield under mild reaction conditions in water (54 °C, 24 h).<sup>132</sup>

Li et al. reported a process for the production of diesel and jet fuel range alkanes via aldol condensation of furfural and 2-pentanone, followed by HDO of condensation product under solvent free conditions.<sup>133</sup> The authors employed different solid base catalysts (MgO, MgO–ZrO<sub>2</sub>, KF/Al<sub>2</sub>O<sub>3</sub>, Co Al-HT, MgAl-HT, CaO) for aldol condensation. Among these catalysts, CaO exhibited excellent activity enabling 87% C<sub>9</sub> aldol product at 130 °C for 6 h. Subsequent HDO of the aldol product was performed by using palladium supported catalysts (Pd/H-ZSM-5, Pd/H-β, Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>). Pd/H-ZSM-5 catalyst demonstrated maximum activity, giving ~90% C<sub>9</sub>–C<sub>10</sub> diesel and jet fuel range alkanes at 260 °C and 60 bar H<sub>2</sub> pressure for 24 h.<sup>133</sup>

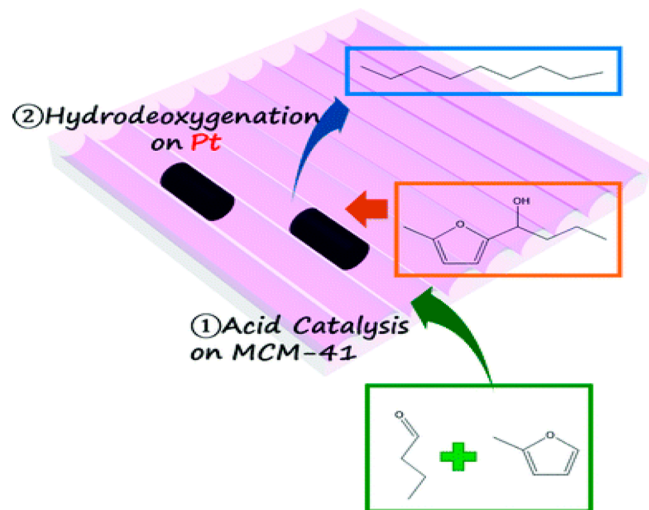
## ■ ADVANTAGES IN ACCESSING LONG CHAIN HYDROCARBONS

The recent research effort on drop-in biofuel production is more focused toward synthesis of long chain carbon precursors and their deoxygenation to hydrocarbon fuels.<sup>134</sup> The long chain hydrocarbon fuels have several advantages over biodiesel and ethanol such as high heat value, compatibility with existing energy infrastructure and hydrophobicity. Catalytic hydroxy-alkylation–alkylation (HAA) plays an important role in upgrading furfurals into drop-in fuels via condensation of 2-



MF with butanal or furfural, and subsequent HDO of the resultant adducts. Using this chemistry, Corma et al. have synthesized 2,2'-butyldiene-bis(methylfuran), a C<sub>14</sub> intermediate, with ~78% yield and 91% selectivity via *p*-toluene sulfonic acid (*p*-TsOH) catalyzed HAA of 2-MF and butanal at 50 °C under solvent free conditions.<sup>70</sup> Subsequent HDO of the resultant intermediate in a tubular reactor at 350 °C and 50 bar H<sub>2</sub> over Pt/C and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts produced C<sub>9</sub>–C<sub>14</sub> alkanes. Another report on HAA of 2-MF with a mixture of furfural and hydroxyacetone over Nafion-212 resin catalyst and HDO of the resultant intermediate adduct with Pt/ZrP catalyst demonstrated to produce C<sub>9</sub>–C<sub>14</sub> alkanes with 94% yield.<sup>135</sup> One drawback of the later process is the requirement of high temperature and high pressure for HDO for opening the furan ring of the intermediate. Inexpensive nickel catalyst, Ni/Hβ-(394), has also been developed for HDO of the intermediate adduct obtained from HAA of 2-MF and butanal, which achieved an overall ~90% carbon yield of diesel range alkanes under mild conditions.<sup>136</sup> Wen et al. found that HAA and HDO processes can be performed in a single step by utilizing a bifunctional catalyst (Pt/MCM-41) containing acidic and metallic sites to produce C<sub>8+</sub> hydrocarbons, as shown in Scheme 4.<sup>137</sup> The Pt/MCM-41 catalyst offered 96% yield of C<sub>8+</sub> hydrocarbons in a fixed bed reactor and the catalyst was stable over four consecutive cycles.

**Scheme 4. C<sub>8+</sub> Alkanes Production from 2-MF and Butanal Using a Bifunctional Pt/MCM-41 Catalyst<sup>a</sup>**



<sup>a</sup>Reproduced from ref 137.

Upgrading HMF derived GVL into liquid hydrocarbons is also possible through two different pathways.<sup>26</sup> The first pathway involves catalytic HDO of GVL at elevated pressure over a silica/alumina catalyst to produce a gas stream consisting of a mixture of unsaturated C<sub>4</sub> hydrocarbons and CO<sub>2</sub>. Subsequent oligomerization of unsaturated C<sub>4</sub> molecules of the gas stream with acid catalysts (H-ZSMS, Amberlyst 70), followed by coupling with butene enabled long chain alkanes (C<sub>8</sub>–C<sub>12</sub>). The second pathway involves catalytic dehydration and hydrogenation of GVL to pentanoic acid, and subsequent ketonization of pentanoic acid to 5-nonanone and then HDO of 5-nonanone to hydrocarbon products using ceria–zirconia catalyst (Figure 3).<sup>24</sup> However, when cellulose was used as a starting material, the process involved more steps for the

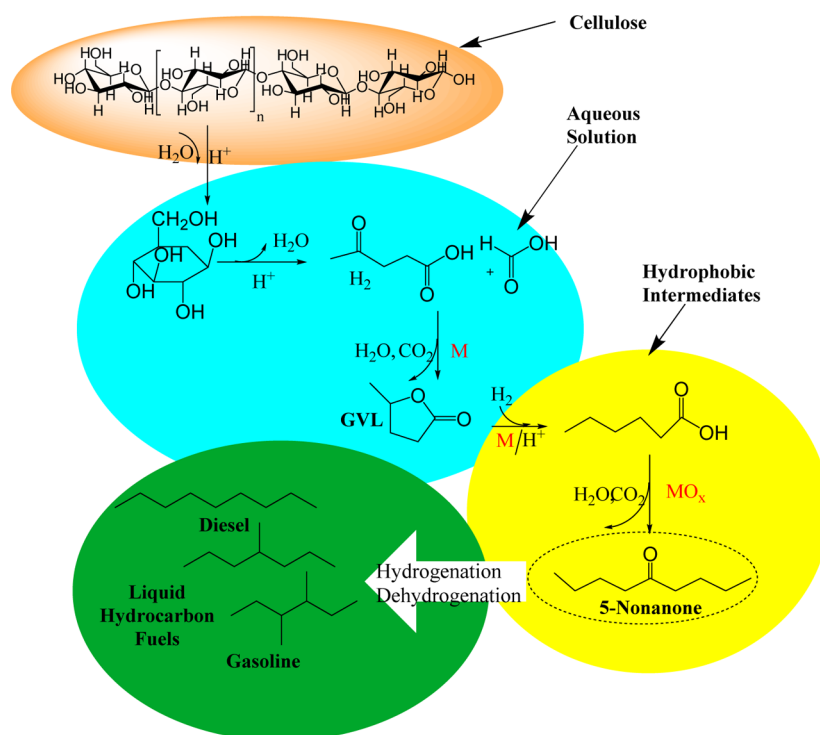
conversion of cellulose to GVL, namely (1) acid catalyzed hydrolysis of cellulose to glucose, (2) catalytic conversion of glucose to levulinic acid, (3) reduction of levulinic acid to GVL using the process generated formic acid (in step 2) as a hydrogen source.

Due to its hydrophobic nature, separation of 5-nonanone from the process stream is easier which makes it a promising precursor for the production of different long chain hydrocarbons.<sup>92</sup> Catalytic HDO of 5-nonanone to nonane with bifunctional Pd/Nb<sub>2</sub>O<sub>5</sub> catalyst has been reported.<sup>25</sup> Further upgrading of 5-nonanone with USY-zeolite catalyst resulted in a mixture of branched C<sub>9</sub> alkenes via isomerization and aromatization steps. Another report on hydrogenation of 5-nonanone with Ru/C catalyst produced 5-nonanol, which was then dehydrated over an acid catalyst (Amberlyst 70) to form a mixture of C<sub>9</sub> olefins.<sup>138</sup> To increase carbon chain length, the resultant C<sub>9</sub> olefins were further oligomerized to C<sub>18</sub>–C<sub>27</sub> olefins using Nafion SAC 13 solid acid catalyst.

Electrochemical methods for transformation of HMF derived levulinic acid to hydrocarbon fuels have also been reported.<sup>139–141</sup> Deoxygenation of oxygenated furanic biomass components is a key step in accessing hydrocarbons of different chain lengths. However, mechanisms for the deoxygenation processes are not well-defined. In the presence of H<sub>2</sub>, how C–O bond cleaves and hydrogenates to form C–H bond for a substrate derived from biomass would be an interesting topic of investigation. In this process, key features to look at would be (1) adsorption of oxygenated substrates on the solid catalyst containing active metal center, (2) activation of H<sub>2</sub> and dissociation into highly active atomic hydrogen, (3) attack of C–O bonds by the weakly held H<sub>2</sub>. To find convincing answers for the above possible events occurring during deoxygenation, detailed mechanistic studies are essential. A summary of different catalytic approaches for long chain hydrocarbon preparation is listed in Table 5.

## CONCLUDING REMARKS

Biomass conversion to biofuels is a major buzzword in the transportation sector. This paper summarizes recent advances in upgrading lignocellulosic biomass derived furfural platform chemicals into drop-in biofuels, including DMF, 2-MF, EMF, GVL and long chain hydrocarbons. Over the past few years, significant advances have been made on the production of advanced biofuels with new catalysts design and process conditions optimization. However, many of these commercial processes for biofuels production are inefficient and suffer from several problems including low yield and high production cost. The kinetics and mechanism for key steps such as lignocellulose hydrolysis, dehydration of sugars and deoxygenation of aldol products are not well established. Currently, the conversion of lignocellulose into jet and diesel fuel range alkanes involves multistep processes, but one-pot synthesis of alkanes directly from lignocellulose has yet to be developed. A one-pot synthesis approach will significantly reduce separation steps for products produced in intermediate steps and hence the overall production costs. Specially designed multifunctional materials would play a major role in the development of such processes. Technically, removal of oxygen from oxygenated furanic compounds would increase the RON of the resulting fuels. New strategies of chemical deoxygenation of furanics or other oxygenated biomass components is a challenging area of R&D. Important new directions would be the following: (1) Deoxygenation of mono- and polysaccharides using strong



**Figure 3.** Strategy for the conversion of cellulose into liquid hydrocarbon fuels.  $H^+$ : acid sites; M = metal sites;  $MO_x$  = metal oxide sites (modified from ref 25).

**Table 5.** Summary of Long Chain Hydrocarbon Yield Using Heterogeneous and Homogeneous Catalyst

entry <sup>(ref.)</sup>	catalyst	substrates	solvent	$H_2$ pressure (MPa)	$T$ ( $^{\circ}C$ )	$t$ (h)	C content in pdts	total HC yield (%)
1 <sup>17</sup>	Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	hemicellulose	THF	5.51	260	1.1	C <sub>12</sub> , C <sub>13</sub>	91
2 <sup>70</sup>	Pt/C and Pt/TiO <sub>2</sub>	2-MF		5	400	1	C <sub>9</sub> , C <sub>12</sub> , C <sub>14</sub>	96
3 <sup>113</sup>	Pd/Al <sub>2</sub> O <sub>3</sub>	HMF		6	120	6	C <sub>8</sub> , C <sub>12</sub>	32
4 <sup>114</sup>	La(OTf) <sub>3</sub>	HMF	HOAc <sup>a</sup>	2.07	200	15	C <sub>9</sub>	74
5 <sup>137</sup>	Pt/ZrP	2-MF		6	350	2	C <sub>1</sub> -C <sub>11</sub> , C <sub>14</sub> -C <sub>15</sub>	94
6 <sup>138</sup>	Pd/C	GVL			370		C <sub>1</sub> -C <sub>8</sub> , C <sub>9</sub> -C <sub>13</sub>	79.5
7 <sup>139</sup>	Ni/H $\beta$ -(394)	LA		6	230		C <sub>1</sub> -C <sub>8</sub> , C <sub>9</sub> -C <sub>15</sub>	~90
8 <sup>140</sup>	Pt/MCM-41	LA		3.5	230	20	C <sub>8</sub> -C <sub>14</sub>	96
9 <sup>141</sup>	Pd/C and La(OTf) <sub>3</sub>	glucose	HOAc	2.06	250	16	C <sub>12</sub>	78
10 <sup>142</sup>	Ni-W <sub>x</sub> C/C	2-MF		6	350	2	C <sub>1</sub> -C <sub>4</sub> , C <sub>5</sub> -C <sub>8</sub> , C <sub>9</sub> -C <sub>15</sub>	93
11 <sup>143</sup>	Ni-Mo <sub>2</sub> C/SiO <sub>2</sub>	2-MF		6	300	2	C <sub>1</sub> -C <sub>4</sub> , C <sub>5</sub> -C <sub>8</sub> , C <sub>9</sub> -C <sub>15</sub>	77
12 <sup>144</sup>	Ni/SiO <sub>2</sub> -ZrO <sub>2</sub>	hemicellulose		5	250	0.75	C <sub>8</sub> -C <sub>15</sub>	83
13 <sup>145</sup>	Pt/Al <sub>2</sub> O <sub>3</sub>	furfurylidene-acetone	hexane	2.5	220	24	C <sub>8</sub>	~32
14 <sup>146</sup>	Ir-ReO <sub>x</sub> / SiO <sub>2</sub>	LA		5.4	220	7	C <sub>7</sub> -C <sub>10</sub>	88

<sup>a</sup>HOAc = acetic acid.

Lewis acids via the cleavage of multiple nonactivated C–O bonds. (2) Design surfaces with advanced features for the concerted multielectron-transfer (CMET) based deoxygenation. (3) Design multifunctional catalysts for cascade catalysis in one-pot reactions/processes.

We anticipate that one of the most promising strategies for drop-in biofuel is the ring-opening of furfurals and preservation of the carbon backbones that may lead to the production of different classes of liquid fuels. For the production of high energy density precursors for hydrodeoxygenation processes, condensation of ketones for forming larger oligomeric products will be essential. In this context, selective condensation of furfurals derived ketones (for example, 2-pentanone) can be foreseen as a promising pathway to promote a platform for jet-fuel production. During this process, access to furfural alcohol

is an important step that requires hydrogenation of furfural in either gas- or liquid-phase. The gas-phase hydrogenation processes require high energy for furfural vaporization and produce large amount of byproducts. Thus, liquid phase hydrogenation can be more affordable, though the latter process requires high pressure of  $H_2$ .

Another key area of technology development for the conversion of furfurals and other substrates to fuel additives should be the energy efficiency for the conversions processes. In this regard, strategies for utilization of solar energy for furfurals conversion into ketones that are relevant for making long chain hydrocarbons will be an important advance.

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### Notes

The authors declare no competing financial interest.

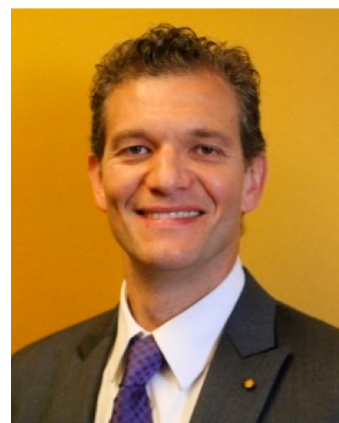
### Biographies



Dr. Ashish Bohre received his Ph.D. in 2012 from Dr. H. S. Gour Central University, India. He then joined as a postdoctoral research associate in the chemistry department of University of Delhi under the supervision of Prof. Basudeb Saha. His current research includes the synthesis of catalytic materials for lignocellulose deconstruction and upgrading biomass intermediates into drop-in biofuels and renewable chemicals.



Dr. Saikat Dutta received his Ph.D. from IISc, India. He was postdoc researcher in Taiwan and in University of Delhi, India before working at the Department of Chemistry, University of Florida, USA as a Fulbright Postdoctoral Fellow. He was an independent scientist and PI funded by Department of Science and Technology, India before joining research group of Prof. K. C.-W. Wu at the Department of Chemical Engineering, National Taiwan University. His current research projects in Functional Mesoporous Materials Laboratory of Prof. Wu are mainly focused on emerging areas of materials chemistry centering on electrosorption and electrochemical charge storage applications of metal–organic frameworks derived functional nano-materials and enzymatic strategies of biopolymer conversions towards chemicals and fuels.



Dr. Abu-Omar completed his Ph.D. from Iowa State University and postdoc from Caltech. He is the R. B. Wetherill Professor of Chemistry and Professor of Chemical Engineering at Purdue University, the associate director of the Center for Catalytic Conversion of Biomass to Biofuels (C3Bio), an Energy Frontiers Research Center, and the director of the Negishi-Brown Institute for Catalysis (NBIC). Mahdi is the founder and president of Spero Energy, Inc., a green specialty chemicals company and a technology provider for the manufacture of high value renewable chemicals from biomass. He is the author or coauthor of more than 120 original research papers in peer-reviewed journals. Dr. Abu-Omar is a Fellow of the American Association for Advancement of Science (AAAS).



Dr. Basudeb Saha received B.S. and M.S. in chemistry from Calcutta University and a Ph.D. from Indian Association for the Cultivation of Science. He is currently a research scientist at Purdue University, and also serves as the Chief Technology Officer of Spero Energy, Inc. Prior to joining Purdue University, he served as an Associate Professor at University of Delhi and worked in the polyurethane business R&D division at Dow Chemical Company. His current research is in the area of synthesis of functionalized catalytic materials and their utilization in sustainable chemical processes. He is the author or coauthor of 62 journal articles and four patents, and a recipient of the Dow WRAP award.

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