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Sustainable production of furan-based oxygenated fuel additives from pentose-rich biomass residues

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ABSTRACT

The emission of carbon monoxide, greenhouse gases (e.g., carbon dioxides), hydrocarbon, and particulate matter can be reduced by applying oxygenated additives as a blend to combustible hydrocarbon fuels. However, conventional oxygenates, such as dimethyl ether and methyl *t*-butyl ether, are sourced from non-renewable feedstocks. This study presents a critical review on the catalytic synthesis of furanic compounds, as an alternative to the conventional oxygenated fuels, from highly abundant lignocellulosic biomass (LCB). This study aims to evaluate the potential of production of furan-based oxygenated fuel additives (e.g., 2-methyl furan, 2-methyl tetrahydrofuran, alkyl levulinates, ethylfurfuryl ether, ethyl tetrahydrofurfuryl ether, tetrahydrofurans) from LCB via the C5-sugars pathway (through furfural); the fuel properties and the performance of furanic fuels in SI or CI engine. The review showed that selecting solvents and catalysts is critical in improving the yield of furanic compounds and reducing the generation of intermediates. The biphasic system for the one-pot conversion of LCB (dehydration and hydrogenation) into furans could facilitate the final product separation and improve final product yield. The combination of Brønsted/Lewis acid catalysts or heterogenous catalysts is promising for effectively converting LCB (alcoholysis) into alkyl levulinates. The use of biomass-based furan fuel additives could potentially have a substantial positive impact on the life cycle analysis of furan/fuel blends due to the availability of lignocellulosic biomass-based feedstocks and improving the sustainability of fuel additives synthesis sourced from LCB waste.

Introduction

Fossil fuels, such as gasoline and diesel, are significant contributors to air pollution and global warming due to particulate matter (PM) emissions and greenhouse gases (GHG) such as CO_2. The application of oxygenated additives, such as alcohols, ethers, and furans, in transportation fuels can increase fuel combustion efficiency and reduce emissions of GHG and soot or PM [1,2]. Oxygenated fuel additives must be a low-carbon composition fuel with less GHG emission than fossil fuels during its life cycle, including alcohols, ethers, and furans [3]. The combustion of alcohols and ethers as fuels is substantially cleaner than gasoline due to less emission of CO and nitrogen oxides (NO_x) and low pollutant contents, such as sulfur [4]. Alcohols and ethers also consist of carbon atoms that may provide fuel energy. In addition, the resulting fuels blended with oxygenated additives possess higher oxygen content that enhances fuel combustion due to the elevation of the oxygen to fuel ratio [5]. The oxygenated fuel additives would also improve engine performance by boosting the octane number of fuels [1]. Furthermore, the ignition temperature of fuel blended with oxygenated additives is expected to be relatively reduced due to the increase in ignition probability and the reduction in the ignition delay [5].

Biodiesel, alcohol such as ethanol/bioethanol, dimethyl ether (DME), diethyl ether (DEE), and methyl *t*-butyl ether (MTBE) have been extensively investigated to be used as alternative fuels and oxygenated fuel additives [3]. The blend of *n*-pentanol as an oxygenate additive with diesel resulted in a dramatic decrease in soot emission [6]. DEE as an oxygenated fuel additive in the fuel blend of cottonseed biodiesel-diesel

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Abbreviations: CAPEX, Capital expenditures; OPEX, Operating expenses.

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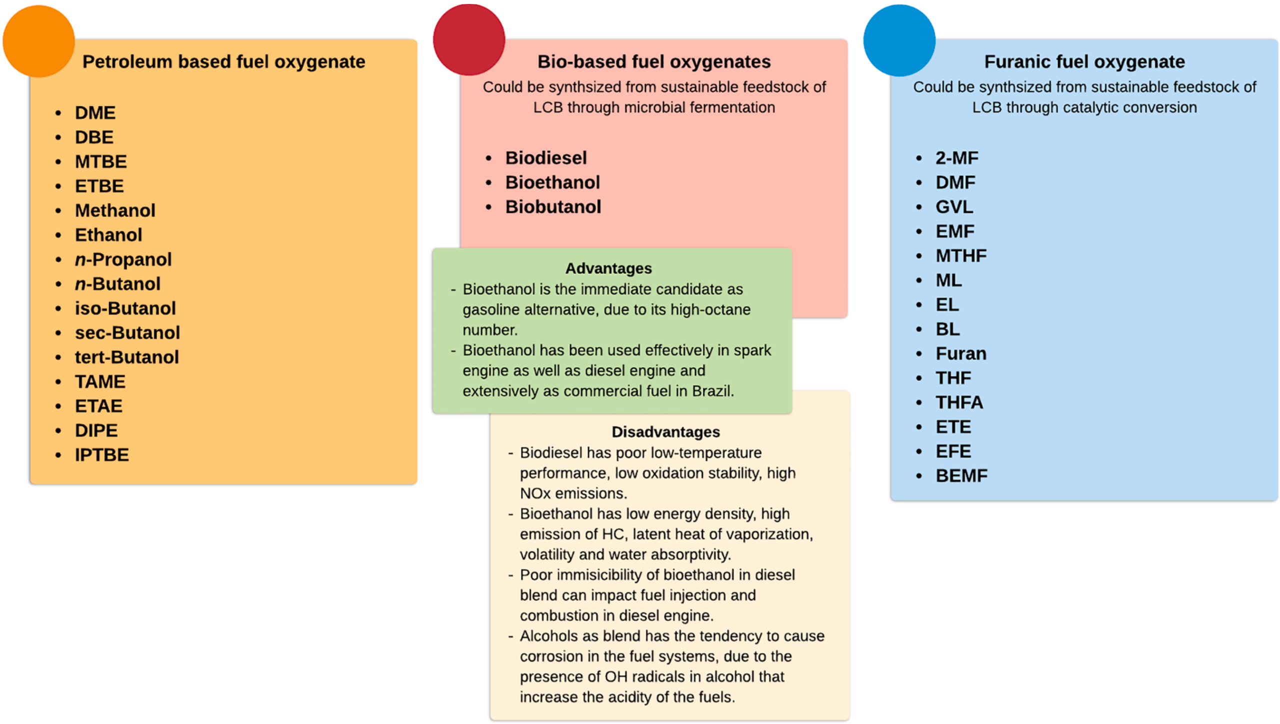
Nomenclature

2-BTHF	2-butyltetrahydrofuran
2-ETHF	2-ethyltetrahydrofuran
2,3-DHF	2,3-dihyrofuran
2,5-DHF	2,5-dihyrofuran
2-MF	2-methylfuran
AC	activated carbon
BEMF	bisethoxy methyl furan
BL	butyl levulinate
BRON	blend research octane number
BTE	brake thermal efficiency
ClMF	5-(chloromethyl)furfural
CO	carbon monoxide
CTH	catalytic transfer hydrogenation
DBE	dibutyl ether
DCN	derived cetane number
DHF	2,3-dihydrofuran
DICI	direct-injection compression-ignition
DIPE	diisopropyl ether
DME	dimethyl ether
DMF	2,5-dimethylfuran
DMTHF	2,5-dimethyltetrahydrofuran
EF	5-methyl furoate ethyl ester
EFE	ethylfurfuryl ether
EL	ethyl levulinate
EMF	5-ethoxymethylfurfural
ETBE	ethyl *t*-butyl ether
ETE	ethyl tetrahydrofurfuryl ether
FAL	furfuryl alcohol
GO	graphite oxide
GVL	γ-valerolactone
HC	hydrocarbon
HHCI	homogeneous charge compression ignition
HMF	5-hydroxymethylfurfural
HPW	phosphotungstic acid
IMEP	Indicated mean effective pressure
IPTBE	isopropyl *t*-butyl ether
LA	levulinic acid
LCB	lignocellulosic biomass
LHV	lower heating value
ML	methyl levulinate
MMF	5-methoxymethylfurfural
MOF	metal organic framework
MTBE	methyl *t*-butyl ether
MTHF	2-methyltetrahydrofuran
NO_x	nitrogen oxides
PL	propyl levulinate
PM	particulate matters
SI	spark ignition
TAEE	*t*-amyl ethyl ether
TAME	*t*-amyl methyl ether
TFA	tetrahydrofurfuryl alcohol
THF	tetrahydrofuran
ULSD	ultra-low sulphur diesel
XMF	5-(halomethyl)furfural



Petroleum based fuel oxygenate

- DME
- DBE
- MTBE
- ETBE
- Methanol
- Ethanol
- *n*-Propanol
- *n*-Butanol
- iso-Butanol
- sec-Butanol
- tert-Butanol
- TAME
- ETAE
- DIPE
- IPTBE

Bio-based fuel oxygenates

Could be synthsized from sustainable feedstock of LCB through microbial fermentation

- Biodiesel
- Bioethanol
- Biobutanol

Advantages

- Bioethanol is the immediate candidate as gasoline alternative, due to its high-octane number.
- Bioethanol has been used effectively in spark engine as well as diesel engine and extensively as commercial fuel in Brazil.

Disadvantages

- Biodiesel has poor low-temperature performance, low oxidation stability, high NOx emissions.
- Bioethanol has low energy density, high emission of HC, latent heat of vaporization, volatility and water absorptivity.
- Poor immisicibility of bioethanol in diesel blend can impact fuel injection and combustion in diesel engine.
- Alcohols as blend has the tendency to cause corrosion in the fuel systems, due to the presence of OH radicals in alcohol that increase the acidity of the fuels.

Furanic fuel oxygenate

Could be synthsized from sustainable feedstock of LCB through catalytic conversion

- 2-MF
- DMF
- GVL
- EMF
- MTHF
- ML
- EL
- BL
- Furan
- THF
- THFA
- ETE
- EFE
- BEMF

Fig. 1. Different types of oxygenated compounds as fuel additives, including commercial, oxygenates from the petroleum-based product, bio-based oxygenates and the benefits and drawbacks of its application, and furanic compound oxygenates [3–5,8,12,14,72,171]. Among the petroleum-based oxygenates are alcohols, dimethyl ether (DME), dibutyl ether (DBE), methyl *t*-butyl ether (MTBE), ethyl *t*-butyl ether (ETBE), *t*-amyl methyl ether (TAME), *t*-amyl ethyl ether (TAEE), diisopropyl ether (DIPE) and isopropyl *t*-butyl ether (IPTBE).

resulted in the emission reduction of HC, smoke, and NO_x [7]. Even though the use of oxygenated biofuels, like biodiesel and bioethanol, as a transportation fuel is promising to overcome the environmental challenges caused by the use of petrol fuels, the practical application of these fuels is not feasible due to the restriction of these alternative fuels. For instance, the drawbacks of biodiesel can be attributed to some of its fuel properties performance as biodiesel has poor low-temperature performance, low heating value, low oxidation stability, low volatility, high NO_x emissions, high viscosity, and non-feasible production economics and supply-chain [8–11]. Ethanol has low energy density, increased emission of total hydrocarbon (HC), high latent heat of vaporization, high volatility, and high water absorptivity [8,12]. Even though the application of alcohols as oxygenate fuel additive typically reduces the emission of soot, the addition of alcohols such as ethanol into diesel could lead to higher HC emission due to the extreme cooling effect of ethanol in the blends [13]. The production of bioethanol requires high energy consumption [14]. The benefits and drawbacks of using bio-based fuel oxygenate, including biodiesel and bioethanol, as fuel additives are outlined in Fig. 1.

The alternatives to the most commonly used oxygenated fuels are furanic compounds, which can be synthesized from hexose or pentose sugars through catalytic conversion. The furanic compounds could be used as fuel additives due to the high degree of oxygenation as the result of the presence of oxygen bonds in the compounds. The use of furans as oxygenated fuels is promising as various furanic compounds have high heating value, prominent detonation resistance, low water solubility, and excellent volatility [3], as shown in Table 1. 2,5-dimethylfuran (DMF), a furanic oxygenate, was reported to reduce soot or PM emission much better than other oxygenates, in descending order, alcohols, ketones, and others due to enhancing combustion and thermal efficiency [15].

Opportunity exists on valorizing lignocellulosic biomass into furans, allowing the sustainable production of furan-based oxygenated fuels. Lignocellulosic biomass is abundant and primarily sourced from agro-industry residues. The top five crops produced in 2019 globally were corn, sugarcane, wheat, paddy rice, and oil palm fruit, which generated substantial carbohydrate-based residues (Fig. 2) [16]. The abundance of lignocellulosic biomass could have impact on the economics of agro-industries due to the requirement of managing its disposal in compliance with local environmental regulations. Due to the high composition of cellulose and hemicellulose, the opportunity to convert lignocellulosic biomass into furanic compounds (Fig. 2) can be integrated with the biorefinery of any particular agro-industry, potentially improving the sustainability and profitability of the agro-industries [17]. For instance, the production of methyl levulinate (ML), a furan-based oxygenate, from direct conversion of softwood bark biomass allows for the low production cost of ML at a large scale either due to low CAPEX or OPEX [18].

Fig. 3 presents the potential pathways of synthesizing furan-based oxygenated compounds from lignocellulosic biomass through furfural and 5-hydroxymethylfurfural (HMF), including 2-methyl furan (2-MF), 2,5-dimethylfuran (DMF), levulinic esters, γ-valerolactone (GVL), 5-ethoxy methyl furfural (EMF), 2-methyl tetrahydrofuran (MTHF), levulinic acid (LA), methyl levulinate (ML), ethyl levulinate (EL), ethyl tetrahydrofurfuryl ether (ETE) and ethyl furfuryl ether (EFE). The catalytic synthesis of derivatives of HMF and furfural from hexoses and pentoses, respectively, have been reviewed extensively. However, limited studies examined the production of furan-based fuels directly from lignocellulosic biomass. Most review studies focused on synthesizing individual furan-based fuels, furfural derivatives fuels only, or HMF derivatives fuels only from monosaccharides, mainly from glucose and fructose. Lang et al. and Natsir and Shimazu reviewed the synthesis of furfural-based fuels and fuel additives via etherification from furfural and HMF [19,20], where direct synthesis from carbohydrate or its monomers were not discussed in detail. The review on catalytic synthesis of liquid fuels from lignocellulosic biomass by Jing et al. and Li et al. focused on the production of HMF, furfural, LA, and GVL [21,22].

Table 1
Physical and chemical properties of fuel and fuel additives.

Fuel additive	Chemical formula	Research octane number	Motor octane number	Cetane number	Kinematic viscosity at 40 °C (mm^2 /s)	Stoichio-metric air/ fuel ratio	Density at 20 °C (kg/ m^3)	Lower heating value (MJ/ kg)	Heat of vaporization (kJ/kg)	Auto-ignition tempera-ture (°C)	Initial boiling point (°C)	Flash point (°C)	Reference
Diesel	$C_{12} - C_{25}$	20–30	20–30	40–55	2.6	14.3	826	42.5	270–301	180–220	180–370	65–68	[12,82,130,131]
Biodiesel	$C_{12} - C_{24}$	–	–	47–52	4.0	12.5	870	38.81	300	363	262–359	166	[132,133]
Gasoline	C_4–C_{12}	63–99	85.7	10–15	0.469	14.46	720–780	42.9	373	420	38–204	−43	[8,12,19,47,131,134]
Isooctane	C_8H_{18}	100	100	15.2	1.81	691.9	691.9	44.3	307.63	418	99	4.5	[47,135–137]
Methanol	CH_4O	130	102	<5	0.747[a]	6.4	791	20.0	1200	464	64	16	[133,134,138]
Ethanol	C_2H_6O	109	90	8	1.5[a]	8.95	785	26.9	919.6	434	78	13	[12,14,19,29,30,134]
n-butanol	$C_4H_{10}O$	100	91	25	2.22	11.2	810	33.1	600	343	118	34	[3,82]
MTBE	$(CH_3)_3COCH_3$	116	102	<6	0.47	11.5	746	38.2	300	443	55	–33	[3,138,139]
ETBE	$C_6H_{14}O$	116	105	8	0.45	12.1	770	39.3	300	310	73	−19	[3,138,140]
DMF	C_6H_8O	101.3	88.1	9	0.525	10.79	889.7	32.89	332	286	92	−1	[8,47,130,141]
ML	$C_6H_{10}O_3$	100	–	7.8	1.84[a] (25 °C)	–	1051	22.38	332.5	–	194	–	[117,142]
EL	$C_7H_{12}O_3$	110	102	<10	1.5	8.12	1012.4	24.34	306.7	425	206	90–94	[75,116,143]
BL	$C_9H_{16}O_3$	98	–	14	1.5		974	27.4	277.3[a]	–	232	–	[82,142]
2-MF	C_5H_6O	103	86	17	4.00	10.05	913.2	31.2	358.4	450	64.7	-22	[47,142,143]
MTHF	$CH_3C_4H_7O$	86	73	23.5	0.56	11.2	854	33.5	364.43	270	78	−12	[29,30,65,131,142,143]
DMTHF	$C_6H_{12}O$	82	–	17.2	0.47	11.73	830	37.35	348	–	92	27	[131,142,144]
THF	$(CH_2)_4O$	–	–	<32	0.47	–	889.2	34.88	410	336.5	66	−14	[69,70]
EFE	$C_7H_{10}O_2$	89		18.4	0.95	9.29	986	29.28	277	–	136.5	41.5	[19,117,125,142,143]
ETE	$C_7H_{14}O_2$	–	–	80–90	0.91	–	939.6	30.70	–	–	156	42.5	[117,125]

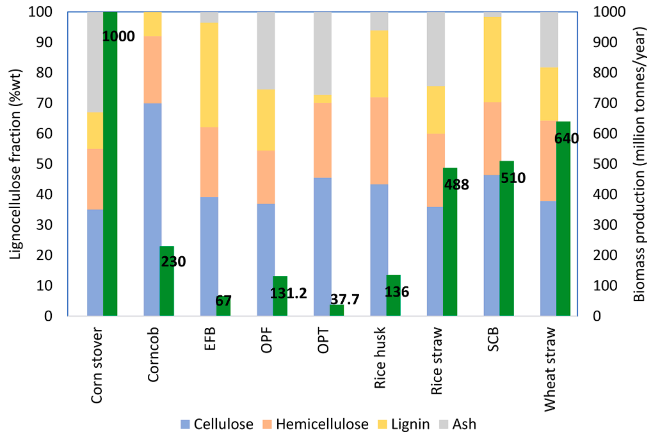


Fig. 2. Annual production of top agro-industrial lignocellulosic biomass worldwide and the weight fraction of cellulose, hemicellulose, lignin, and ash. (The data was taken from the following year; 2017 for corncob, EFB (oil palm empty fruit bunch), rice husk, rice straw, SCB (sugarcane bagasse), wheat straw; 2014 for corn stover; 2009–2010 for OPF (oil palm frond) and OPT (oil palm trunk) [172–174]).

This study presents the review of the potential of production furan-based oxygenated fuel additives lignocellulosic biomass, from pentose-based pathway (through furfural) and the fuel properties of the furan-based oxygenated fuels. This study's strategy is to review the catalytic synthesis of the furanic oxygenated fuels from furfural or HMF, as furfural and HMF can be derived from lignocellulosic biomass. This was followed by the review on the selection of catalysts for the synthesis and the direct synthesis of furanic oxygenated fuels from lignocellulosic biomass.

The use of biomass-based furan fuel additives could potentially positively impact the life cycle analysis of furan/fuel blends due to the sustainability of lignocellulosic biomass-based feedstock and the reduction of toxic and pollutant emissions. In addition, the development of fuel additives from the biomass will allow the utilization of lignocellulosic biomass waste to synthesize higher value products, which will subsequently improve the sustainability of fuel additives production.

Biomass-derived pentose-based furanic oxygenated fuels

Two important chemical precursors can be derived from the degradation of lignocellulosic biomass, 5-hydroxymethylfurfural (HMF) and furfural (furan-2-carbaldehyde). HMF and furfural have been identified as the US National Renewable Energy Laboratory revisited "Top 10" platform chemicals from biomass by Bozell and Petersen due to the plethora of chemicals and fuels that could be derived from these compounds [23].

HMF is generated from dehydration of hexoses such as glucose and fructose, while furfural is from dehydration of pentoses such as xylose and arabinose. Hexoses have wider applications than pentoses, especially in microbial fermentation for efficient production of biological products, including biofuels (e.g., bioethanol, biobutanol, etc.) and biochemicals (e.g., lactic acid, succinic acid, etc.). Although some microorganisms can also metabolize pentoses, their biological conversion efficiency is much lower than hexoses [24,25]. Therefore, the chemical conversion of xylose to value-added products such as furfural and furfural derivatives is likely more attractive than biological conversion.

Hemicellulose in lignocellulosic biomass, such as sugarcane bagasse and palm oil empty fruit bunch (Fig. 2), is the major source of pentoses [10,26,27]. Hemicellulose is a short and highly branched polymer of pentoses and hexoses, such as xylan, mannan, β-glucans, and xyloglucans [28]. Hemicellulose has substantially less polymerization and stability relative to cellulose, allowing it to be easily degraded under heat

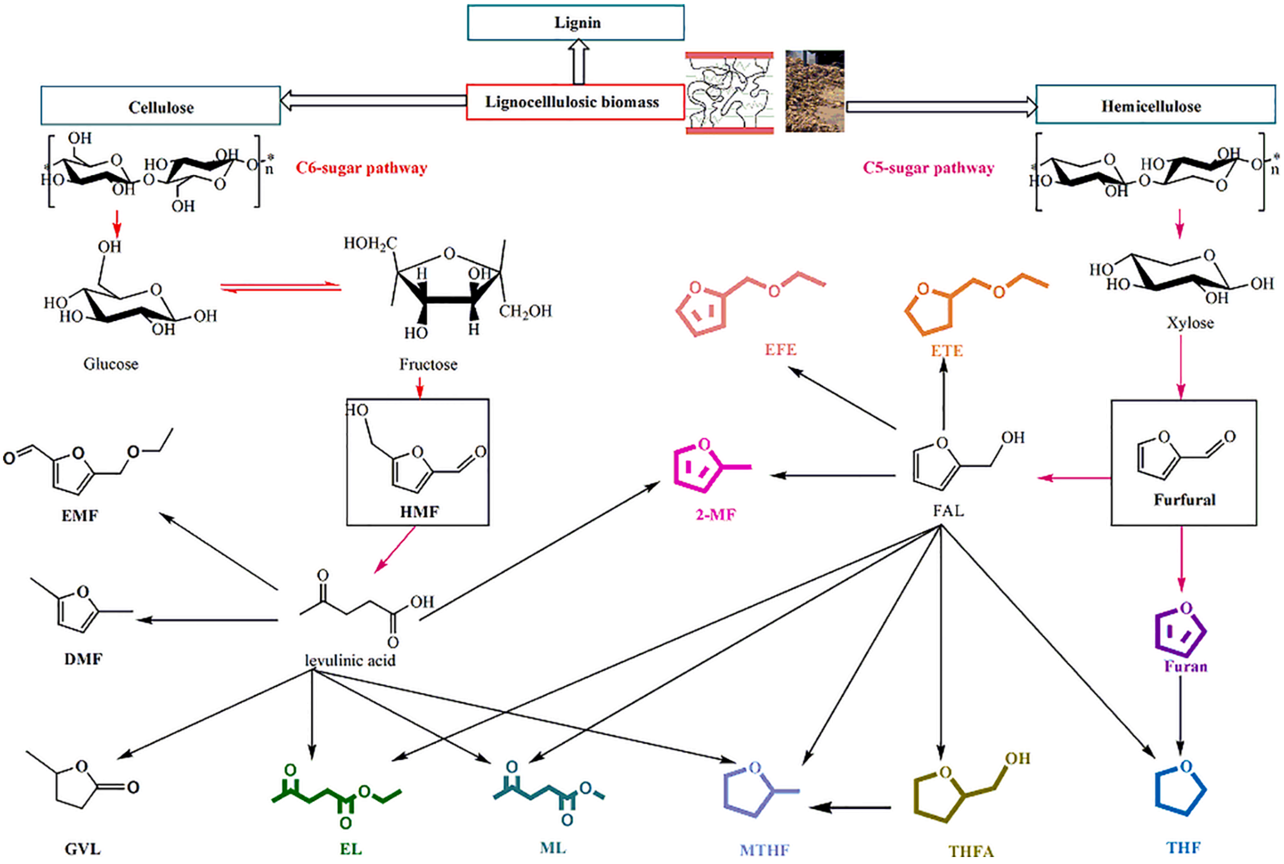
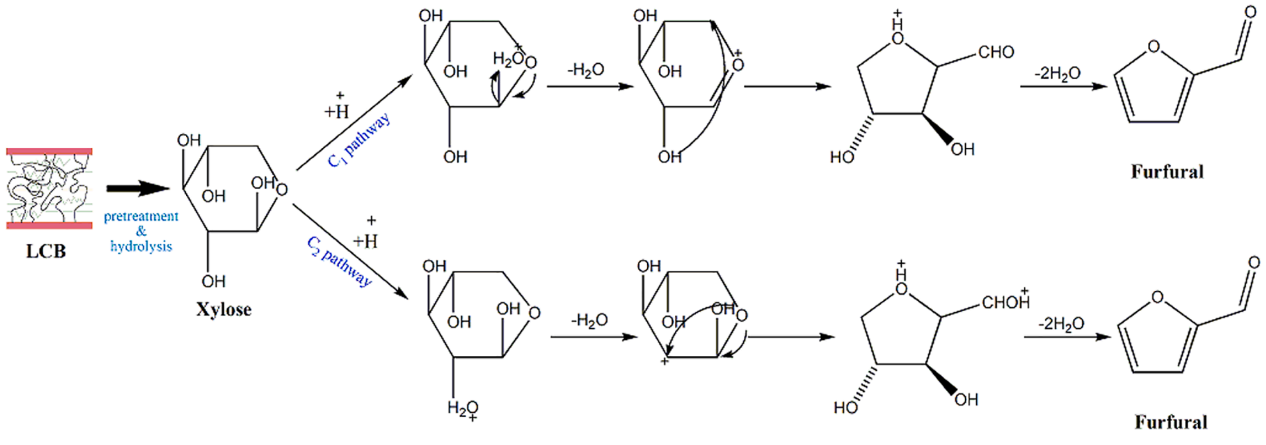


Fig. 3. The prospect of the production of furanic-based fuels via hexose- and pentose-based (C6 and C5 sugar respectively) pathway of lignocellulosic biomass.

treatment [28]. For example, Xylan in lignocellulosic biomass can be readily hydrolyzed to xylose, followed by dehydration to produce furfural at enhanced temperatures in the presence of acid catalysts, such as H_2SO_4. Fig. 4(a) shows the mechanism of xylose degradation into furfural through direct rearrangement of the pyranose structure after protonation of the oxygen atom (either at C1 atom or C2 atom) and dehydration [29]. During commercial furfural production from lignocellulosic biomass, furfural is continuously separated from the reactor by steam stripping to avoid further furfural degradation by acid catalyst into furfural-derivatives [30].

Furfural itself is not suitable as fuel additives due to its instability and low energy content resulting from high oxygen to carbon ratio [31]. However, as one of the platform molecules, the opportunity exists to convert furfural into various value-added chemicals and fuel additives. Fuel additives and precursors that could be synthesized from furfural include furan, furfuryl alcohol (FAL), furfuryl esters, 2-MF, MTHF, THF, and TFA (Fig. 4(b)) [32]. As furfural is a heteroaromatic molecule with furan ring and aldehyde functional group, the conversion of furfural revolves around modifying the aldehyde group [33]. Among the aldehyde group reactions are reducing furfural to alcohols by H2 or Meerwein-Ponndorf-Verley (MPV) hydrogen transfer, decarbonylation, and oxidation carboxylic acid and acetalization [33]. For the hydroxyl group of furfural, the functional group's reaction is only hydrogenolysis of the C-O bond, oxidation to aldehyde or acid, etherification, acetalization, esterification, and halogenation reactions [33]. Catalytic transfer hydrogenation (CTH) is the typical conversion method for furfural through MPV reaction that involves the use of solvent as hydrogen donor (e.g., secondary alcohol as reacting solvent) [33]. The drawback of the CTH reaction is the generation of stoichiometric by-products from the dehydration of H_2 donor and potential acetalization between the

(a) Possible pathways of synthesizing furfural from lignocellulosic biomass (LCB) through different oxygen protonation either at C1 atom or C2 atom [29].



(b) Various furan-based, dihydrofurans, and tetrahydrofuran-based fuels can be derived from furfural [49]. (Furfuryl alcohol, FAL; Dihydrofuran, DHF; ethyltetrahydrofuran, ETHF; butylltetrahydrofuran, BTHF)

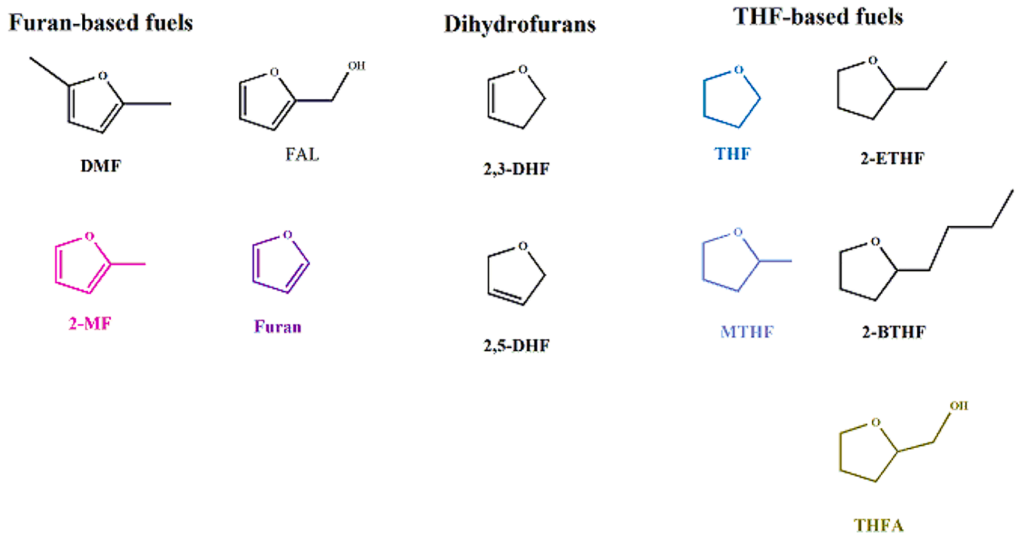


Fig. 4. (a) Possible pathways of synthesizing furfural from lignocellulosic biomass (LCB) through different oxygen protonation either at C1 atom or C2 atom [29]. (b) Various furan-based, dihydrofurans, and tetrahydrofuran-based fuels can be derived from furfural [49]. (Furfuryl alcohol, FAL; Dihydrofuran, DHF; ethyltetrahydrofuran, ETHF; butylltetrahydrofuran, BTHF).

aldehyde function group and the solvent [33]. Most formation of furanic compounds from furfural through hydrogenation is via FAL as intermediate, as the result of a reaction of the aldehyde group of furfural [29,34]. The conversion of furfural into furanic compounds is performed using a heterogeneous catalyst due to easy separation. Nobel metal-based catalysts are the most commonly applied for the conversion of furfural due to their excellent catalytic activity and stability under acidic, basic and aqueous conditions; however, it is costly [35]. Therefore, exploring other cheaper solid catalysts with efficient catalytic activity is crucial for improving the overall economics of furanic fuel synthesis. During dehydration of xylose for furfural production, the organic solvent is added into an aqueous solution containing a heterogeneous catalyst to form a biphasic system [28]. In the biphasic system, furfural converted from xylose in the aqueous phase will be continuously extracted into the organic phase at the top phase [28]. Subsequently, the formation of undesirable intermediates from the side reactions will be suppressed, where the equilibrium shifts the reaction systems towards the production of furfural [28]. As the results, the yield of furfural could be improved.

Hemicellulose-derived fuel additives: Furfural derivatives

2-Methylfuran (2-MF) and furan

Synthesis of 2-MF oxygenate from LCB

2-MF has a similar chemical structure to DMF, with only one alkyl group fewer than DMF. 2-MF fuel properties are as competitive as DMF, as it has a higher RON than gasoline. 2-MF can be derived from lignocellulosic biomass via selective hydrodeoxygenation of furfural, with (Pathway II) or without (Pathway I) furfuryl alcohol as the intermediate (Fig. 5). The main pathway of synthesizing 2-MF is via hydrogenolysis of the side C-O bond from furfural and furfuryl alcohol (FAL) [33]. Another possible route of synthesizing 2-MF from furfural is through 2-(isopropoxy ethyl)furan as the intermediate (Pathway III-Fig. 5) [33].

The synthesis of 2-MF from furfural can be performed in the gas or liquid phase due to the high vapor pressure of furfural [36]. The production of 2-MF from furfural in the gas phase via hydrogenation has been performed at high temperatures (200–300 ℃) and low pressure using Cu-based catalyst, which includes Cu/Al_2O_3, Cu-/$FeCr_2O_4$, Raney-Cu, with furfuryl alcohol as the intermediate [20]. However, it has been reported that the catalysts deactivated rapidly in this reaction, possibly due to thermal polymerization of and coking of furfuryl alcohol [20,37]. In addition, ressurized H_2 and high-temperature required for the reactions in the gas phase are costly [19].

The liquid phase conversion of furfural is favorable as the process is more compatible with furfural production the upstream [36]. The hydrogenolysis of furfural in the liquid phase for a high yield of 2-MF production can be conducted under mild conditions (room temperature and low H_2 pressure), with the use of polar solvents (e.g., methanol, ethanol, 2-propanol) [20,36]. In catalytic transfer hydrogenation (CTH), molecular H_2 is replaced by hydrogen donors such as alcohols. CTH reaction is favorable, as alcohols are non-corrosive, can be used as solvents, and sustainably sourced from biomass [36]. The catalysts used for this process are transition metal catalysts (e.g., Cu/SiO_2, Cu-Co/Al_2O_3,

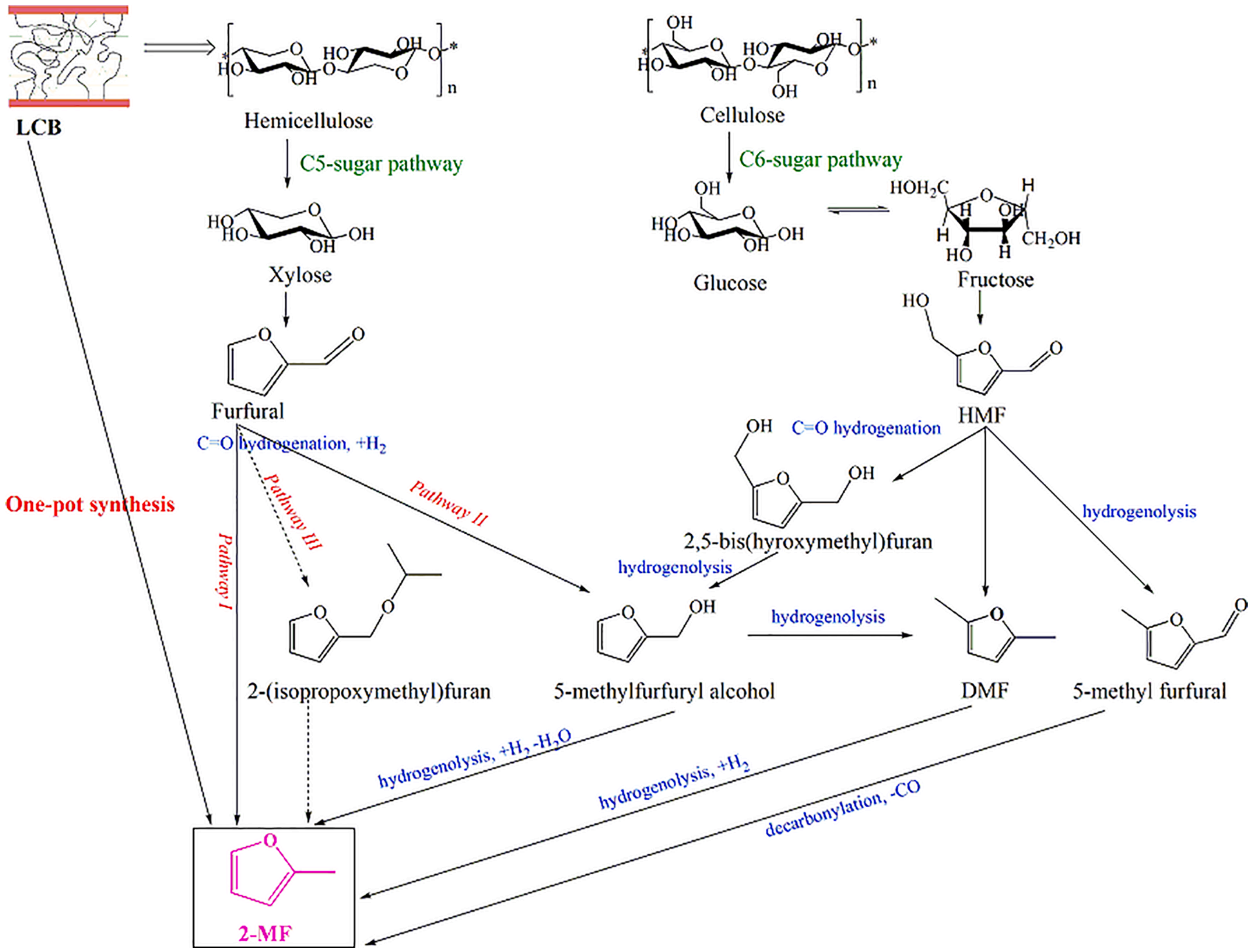


Fig. 5. Pathways for synthesizing 2-methyl furan (2-MF) from lignocellulosic biomass (LCB) directly via one-pot synthesis or indirectly via C5- and C6-sugar pathways through furfural, 2-(isopropoxy ethyl)furan, furfuryl alcohol, 2,5-dimethylfuran (DMF) and 5-methyl furfural [19,20,33].

Cu-Ni/TiO_2, Ni-Cu/Al_2O_3), noble metal catalysts (including Ir/TiO_2, Rh-Sn/SiO_2, Ru/C, Ru/Co_3O_4, Ru/$NiFe_2O_4$, Pd/C, Pd^{II}-poly(acrylonitrile-vinyltriethoxysilicon), Pt/C, Pt–Ge/SiO2, Pt-Sn/SiO_2), or bimetallic catalysts [19,20,36,38]. Cu-based catalysts can selectively cleave the C=O bond of the furan ring through hydrogenation, with the C—C bond remaining intact [39]. Some of these catalysts were recyclable, such as Ru/C, with no significant reduction in furfural conversion after repeated used, however, the yield of furfuryl alcohol as intermediate elevated at the expense of 2-MF formation [36]. Pd-based catalyst can be utilized for high yield production of 2-MF by controlling the oxidation state of Pd [33]. This can be achieved by conducting a reaction under mild conditions at low pressure or low temperature or adding a second metal active in the hydrogenation [33]. The mechanism for the conversion of furfural to 2-MF through furfuryl alcohol as intermediate using noble metal catalyst supported on metal oxides involves (1) furfural adsorption on catalysts via interaction between C=O of furfural and the oxygen vacancies of the metal oxide or the furfuryl bonds to one atom of noble metal, (2) hydrogen (first) interaction with carbonyl carbon for the formation of alkoxy intermediate, (3) breakage of C-O bond, (4) hydrogen (second) interaction with oxygen and methyl group, and lastly (5) desorption of 2-MF from the surface of the catalyst [19].

However, the reaction for the synthesis of 2-MF in the liquid phase may lead to undesired side reactions owing to the ring hydrogenation of 2-MF or furfuryl alcohol to form MTHF or THA decarbonylation of furfural to furan [20,40]. Decarbonylation and ring-opening can be suppressed through enhancing catalyst activity when metal electron density or the formation of new active sites increases, which will enhance the hydrogenation of the C=O group [36]. A metal catalyst such as Cu can reduce decarbonylation and ring hydrogenation owing to its full valence *d*-band [40]. However, Cu has a low activity for H_2 activation and more vital interaction with furfural rather than furfuryl alcohol, which renders the conversion from furfuryl alcohol intermediate to 2-MF to be slow [40]. The side reaction can be reduced using acid co-catalysts, effective solvent, and halide anions such as $CaCl_2$ and HCl [20]. The bimetallic system provides a solution to the drawback of using a single metal catalyst; in addition, the bimetallic system is cheaper than using noble metal catalysts. The addition of a co-metal catalyst can alter the adsorption configuration of furfural. The furan ring was deterred by an atomic co-metal catalyst that enhanced the interaction of the catalyst with carbonyl O, subsequently preventing the carbonylation reaction [19,29]. The addition of co-metal catalysts, such as Co to Cu catalysts, increased the activity of the bimetallic system due to the hydrogen spill-over effect and provided metal-Lewis acid sites as active sites from the generation of CuO_x [19].

However, the price of furfural is estimated to be five times more than ethanol, which will render the production of 2-MF from furfural is not economically competitive relative to ethanol, a promising biofuel candidate [30]. There are limited studies on the one-pot synthesis of 2-MF directly from lignocellulosic biomass, potentially reducing the number of processing steps, such as complicated separation and purification processes [41]. The strength of Brønsted solid acid catalyst must be high to break β-1,4-glycosidic bonds and depolymerize them into water-soluble sugars [41]. The production of 2-MF from corn-cob was reported involving two-step processes of (1) dehydration of C5 sugar-rich corn-cob liquor using Amberlyst 70, a solid acid catalyst, with N_2, was continuously fed into the reactor to separate furfural and water as condensate, and (2) hydrogenation of furfural using Cu-Co/γ-Al_2O_3 catalyst at 220 ℃ and 3 MPa of H_2 pressure for four hours [30]. Wang et al. reported simultaneous DMF and 2-MF in one-pot synthesis from lignocellulosic biomass of bagasse, birch, cornstalk, pine, and poplar in the biphasic system of NaCl in THF/H_2O under mild conditions [41]. Furfural and HMF formed in the upper organic phase were directly used to convert into 2-MF and DMF, respectively [41].

Synthesis of furan oxygenate from LCB

Furan is the simplest form of furanic fuel with unsaturated cyclic ether. Furan is also a significant intermediate in synthesizing other alkylfuran oxygenates [42], including DMF and THFA. Furan can be produced from LCB indirectly via the C5-sugar pathway through furfural. Furan is derived from lignocellulosic biomass through the decarbonylation of the aldehyde group from biomass-derived furfural and the release of C=O (Pathway I-Fig. 6) [29]. In the conventional production of furan, furoic acid is generated as the intermediate (Pathway II-Fig. 6) [29]. The reaction process involves the use of catalysts, including noble metal catalysts (Pd/C, Pd/Al_2O_3) at high temperatures or metal oxide catalysts (Ni/SiO_2) [29,33,36,43]. The selectivity towards furan formation from furfural can be enhanced through reaction conditions that favor acid formation [36]. The industrial production of furan is undertaken through decarbonylation of furfural, either in the vapor phase or the liquid phase, where the former offers feasible separation and catalyst recycling [33]. However, there are no studies on the direct conversion of LCB into furan to date.

Fuel properties and engine performance of 2-MF and furan oxygenates

Table 1 depicts the basic fuel properties of 2-MF. 2-MF can be used as fuel by blending with gasoline without modifying the engines, as 2-MF/gasoline blend does not negatively affect engine gear [20]. 2-MF has a higher octane number, higher thermal efficiency, and lower aldehyde emission relative to gasoline [14,30]. The lower heating value of 2-MF (27.63 MJ/L) is superior to ethanol (21.09 MJ/L) and comparable to gasoline (RON 95) (31.05 MJ/L) (Table 1) [44]. 2-MF also possesses lower fuel consumption than bioethanol owing to its higher energy density than ethanol [12]. Compared to DMF, 2-MF has lower flash points at −22 ℃ relative to 16 ℃ for DMF and higher latent heat of vaporization (Table 1). The low flashpoint of 2-MF, in addition to higher rates of vaporization and higher combustion stabilities, enables 2-MF to overcome cold engine start problems, which typically occur with bioethanol fuel [14]. The superior latent heat of vaporization of 2-MF will lead to higher power output in DI engines [14]. The water solubility of 2-MF is negligible, which renders it ideal for storage as it may avoid water contamination risk [12].

The ignition studies of DMF, 2-MF, and furan in spark-ignition (SI) engines showed that DMF has a longer ignition delay relative to furan and 2-MF [45]. The study by Xu et al. also demonstrated that furan exhibited the most negligible reactivity than DMF and 2-MF from the ignition properties in the high-temperature range and at a constant fuel load [46]. Furan possesses superior chemical stability due to the double alkylation bond, whereas 2-MF has greater reactivity due to a mono alkylation bond [45]. 2-MF was reported to lead to a 61% reduction of HC emission and improved knock resistance compared to gasoline (RON 95) [44]. The study of laminar flame propagation of 2-MF/isooctane blend reported that the blend at 50% 2-MF has burning velocities that were very close to 2-MF and isooctane, specifically at 393 K [47].

The addition of 2-MF, furfuryl amine, *p*-cresol, and furfuryl alcohol in gasoline for application in SI engines (4-cylinder, four-stroke turbocharged engine) resulted in lower CO and HC emissions than gasoline due to improved anti-knocking properties (Fig. 7(a)) [48].

The application of diesel/2-MF blend in the direct-injection compression-ignition (DICI) engine showed that 2-MF enhanced brake thermal efficiency (BTE), prolonged ignition delay, and shortened combustion period [12]. 2-MF was reported to have better knock suppression than gasoline and DMF due to a more compacted chemical structure of 2-MF relative to gasoline (longer hydrocarbon chain), resulting in the faster combustion of 2-MF in DICI [14]. This could be explained by the tendency of the fuel to break down easily upon exposure to high temperatures as the hydrocarbon chain length increases [14]. The superior knock suppression ability of 2-MF also led to higher thermal efficiency by 3% relative to gasoline and DMF [14]. The fuel consumption of 2-MF is also lower than ethanol by 30% [14]. 2-MF also has less PM, formaldehyde, and acetaldehyde emissions than gasoline [14].

Other alkylated furans, including 2-ethylfuran (2-EF), 2-butylfuran

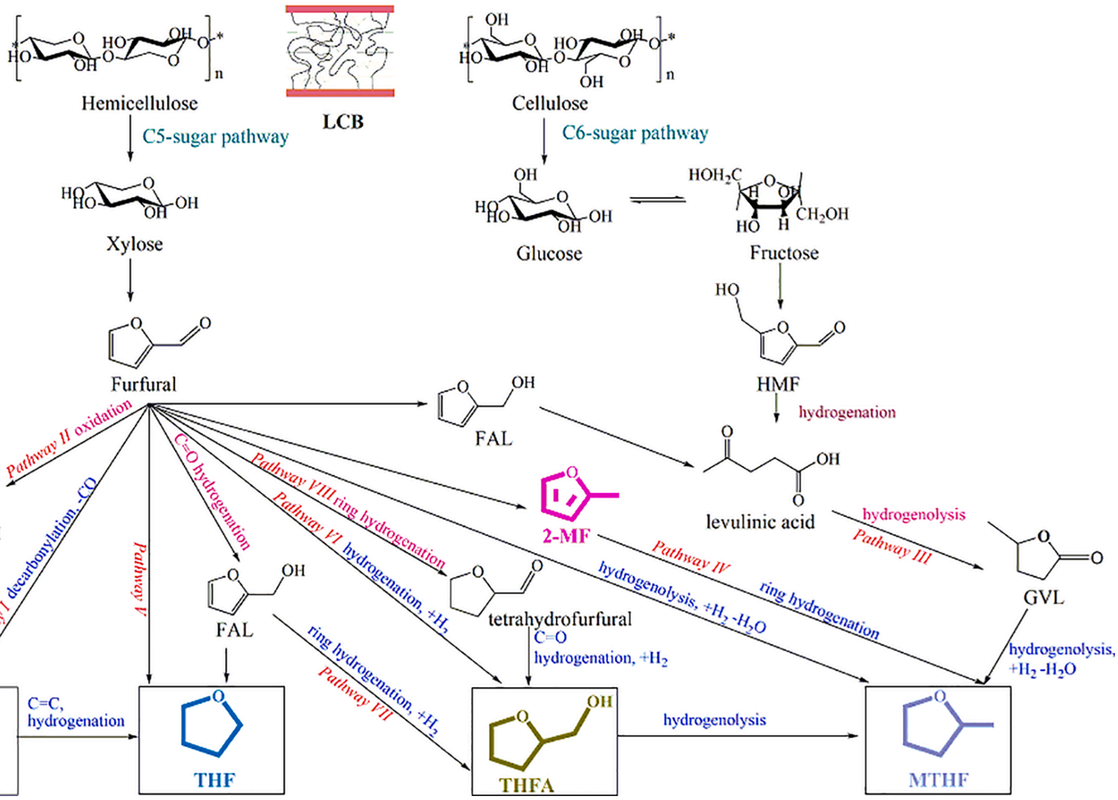


Fig. 6. The pathways for synthesizing furan, tetrahydrofuran (THF), tetrahydrofurfuryl alcohol (THFA), and 2-methyltetrahydrofuran (MTHF) from lignocellulosic biomass (LCB) indirectly via furfural (C5-sugar pathway) [29,33]. However, there are no studies on the direct conversion of these oxygenates from LCB.

(2-BF), and dihyrofurans (DHFs) such as 2,3-DHF and 2,5-DHF, also have the potential to be used as fuel additives (Fig. 4(b)). The derived cetane number (DCN) of these alkylated furans and dihyrofurans have been assessed, where furan, 2-MF, 2-EF, 2-BF, DMF, 2,3-DHF, 2,5-DHF, and FAL were reported to have DCN of 7.0, 8.9, 10.2, 13.1, 10.9, 20, 15.5 and 10.8, respectively [49]. Therefore, as the DCN values were lower than the DCN of RON 90 fuel at ~23, all the alkylated furans and dihyrofurans were suitable for application in the SI engines.

2-Methyltetrahydrofuran (MTHF) and tetrahydrofurans (THFs)

Synthesis of MTHF from LCB

MTHF is a principal component of P-series fuel, where MTHF acts as co-solvent to ethanol, as it could substantially reduce ethanol vapor pressure when it was co-blended with ethanol in fuel [50,51]. In addition, MTHF may provide a solution due to the limitation of GVL as a fuel additive, including elevated water solubility, blending limit for application in conventional combustion engines, corrosiveness in storage, and low energy density relative to conventional fuels [51].

MTHF can be synthesized from lignocellulosic biomass indirectly through biomass-derived levulinic acid, GVL, and 2-MF (Fig. 6). The synthesis of MTHF through furfural via the routes of (1) levulinic acid involves hydrogenation of levulinic acid into GVL (Pathway III-Fig. 6), the reduction of GVL, and the dehydration of the resulting 1,4-pentanediol into MTHF; (2) 2-MF via hydrogenation with the use of, for instance, Ni-based catalyst (Pathway IV-Fig. 6) [20,29]. The hydrogenolysis of GVL via various catalysts, including Ni-MoO_x/Al_2O_3 and Cu/Al_2O_3-OG, yielded MTHF as a by-product with high selectivity towards the production of 1,4-pentanediol and catalysts of Co/SiO_2 (Lewis acid), Ni/Al_2O_3, and Cu/Al_2O_3 with MTHF as the main product [52–55]. The consumption of external H_2 in converting levulinic acid to MTHF is 3 mol [56]. MTHF was also produced as a by-product in converting furfural into 2-MF, using Cu-Co/γ-Al_2O_3 catalyst in DMTHF solvent at 3 MPa at 220 ℃ [30].

There are incredibly scarce studies on the one-pot conversion of lignocellulosic biomass into MTHF. One-pot conversion from biomass-derived furfural, not directly from lignocellulosic biomass, was performed into MTHF via two-stage packing in a single reactor, involving a two-stage process of converting furfural into a single reactor 2-MF using Lewis acid such as Co-based catalysts, followed by conversion into MTHF using Ni-based catalysts [57].

Synthesis of tetrahydrofuran (THF) from LCB

THF is a non-toxic solvent with various applications as intermediates in commercial chemical production, such as butyrolactone and polytetrahydrofuran [33]. THF is one of the saturated cyclic ether oxygenates, which also include MTHF and DMTHF (Fig. 4(b)) [58]. 2,3-dihydrofuran (DHF) has a similar structure to furan and THF with the presence of a C═C bond (Fig. 4(b)) [42]. The use of THF as a fuel oxygenate favorable, as its lower heating value (~28.5–29.5 MJ/L) is similar to gasoline (~31.6 MJ/L) and superior to ethanol (~21.3 MJ/L) [58]. The lower heating value of THF is also comparable to biodiesel at more than ~35 MJ/kg (Table 1).

THF is synthesized conventionally from the reaction of petroleum-based feedstock, such as butadiene acetoxylation, propylene oxide process, maleic anhydride hydrogenation, *n*-butane-maleic anhydride process, and Reppe process [33]. Therefore, the opportunity to synthesize THF from furfural as renewable feedstock is favorable, as furfural can be derived from a sustainable source of LCB. THF can be synthesized directly from furfural, without a furan intermediate (Pathway V-Fig. 6), through decarbonylation and hydrogenation using various noble metal catalysts at temperatures 220–250 ℃, such as Pd/SiO_2, Pd/C, and Pd-B/C [33]. Catalytic hydrogenation of furfural into THF, directly without multiple steps through FAL, has been performed with the use of ruthenium(II) bis(diimine) complexes (26% selectivity), 3% of Si–MFI molecular sieve supported Pd (selectivity of 95%), Ni/SiO_2 (94% yield)

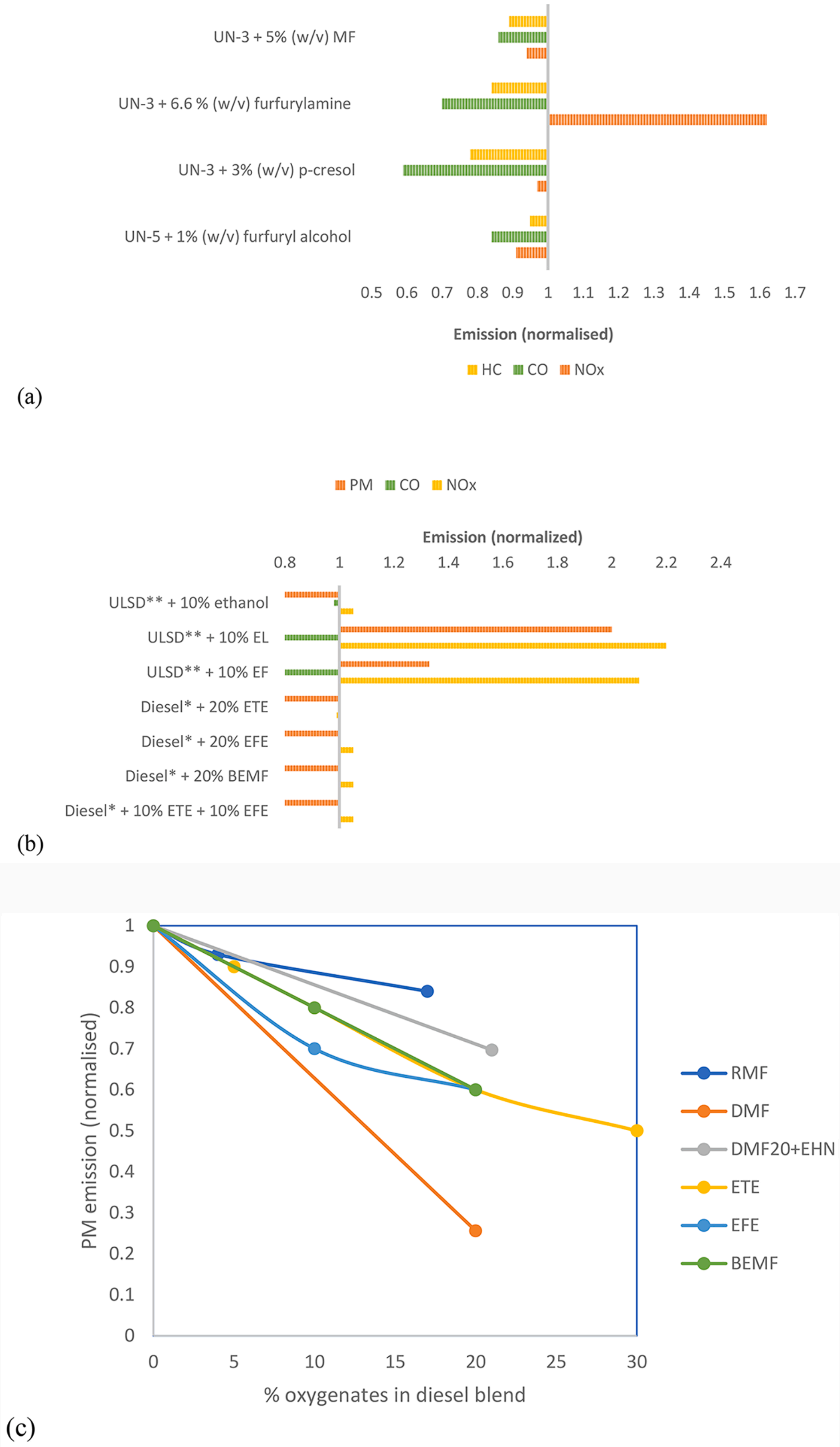


Fig. 7. (a) Emissions of HC, CO, and NO_x from fuel blend of oxygenating (2-MF, furfuryl amine, *p*-cresol, and furfuryl alcohol (FAL)) blended with the unleaded gasoline of UN-3 and UN-5 in SI engine with five hp engine load [48]. (b) Emission of PM, CO, and NO_x from various oxygenate/diesel blends with ULSD (ultra-low sulphur diesel) and diesel as the reference fuel [120,125]. (c) PM emission of various oxygenate/diesel blends at various ratios [125,130,175], with the emission value normalized based on diesel fuel as the reference fuel.

catalyst [29,59–61]. The conversion of furfural using Pd/MFI was highly effective with 100% furfural conversion due to Pd particles' confinement in the molecular sieve and the cavities of the Si-MFI molecular sieve [60]. A high yield of THF (92%) was achieved with 95% conversion of furfural using Pd catalyst supported on metal nanoparticles (Pd (trioctylphosphine)/mesoporous-carbon beads-H_2O_2) at a relatively lower temperature of 100 ℃ and pressure of 1.0–1.4 MPa [62].

Synthesis of tetrahydrofurfuryl alcohol (THFA) from LCB

Tetrahydrofurfuryl alcohol (THFA) is another cyclic ether used as biofuel. As a green solvent, THFA is a biodegradable, transparent, non-toxic, mild odor, high boiling point solvent that is completely miscible in water [29,63]. THFA is an intermediate in the conversion of furfural into MTHF. THFA can be generated from furfural directly (Pathway VI-Fig. 6) or indirectly through FAL as an intermediate via liquid/gas phase hydrogenation (Pathway VII-Fig. 6) [33]. The synthesis of THFA from FAL involves the hydrogenation of furfural at the aldehyde functional group to FAL and subsequently the hydrogenation of FAL at the furan ring to THFA [33]. Another pathway for synthesizing THFA from furfural is via tetrahydrofurfural as an intermediate (Pathway VIII-Fig. 6), where furfural undergoes ring hydrogenation to tetrahydrofurfural, followed by C═O hydrogenation of tetrahydrofurfural into THFA [33]. There are, however, no reported studies on the one-pot synthesis of THF and THFA from LCB to date.

Fuel properties and engine performance of MTHF and alkylated tetrahydrofurans

MTHF is a fuel extender that can be blended with up to 30% gasoline without modifying the current internal combustion engine [56]. Therefore, even though the lower heating value (LHV) of MTHF is lower relative to gasoline (Table 1), the LHV can be compensated by its greater specific gravity, which may lead to similar mileage obtained using gasoline [56].

Furthermore, 10% MTHF blended with gasoline blend was tested in a four-cylinder SI engine, which showed comparable power output to unleaded gasoline, better than MTBE-, ethanol- and methanol-gasoline blend [66]. MTHF blend also possessed a lower air–fuel ratio than gasoline, possibly attributed to high density and energy (BTU (British Thermal Unit)) values of MTHF that lead to similar fuel properties to gasoline [66]. Furthermore, the laminar burning velocity of MTHF at 0.56 m/s, stoichiometric ratio, and 120 ℃ was shown to be comparable to ethanol and more rapid than iso-octane, which indicated fast-burning properties and the possibility of enhancing engine thermal efficiency [67].

Although MTHF has a low cetane number, the blend of MTHF with dibutyl ether (DBE) is suitable for use in compression engines [64]. MTHF was 60 times more soluble in water than biodiesel [64]. The laminar flame test showed that MTHF reduced liquid penetration length by 60% and soot emission relative to diesel fuel in compression engines [65]. The isomers of MTHF, 3-methyl tetrahydrofuran (3-MTHF), and 2,5-dimethyltetrahydrofuran (DMTHF) are also suitable for application in diesel engines [64]. 3-MTHF was reported to be more reactive than MTHF in combustion, possibly due to the presence of two secondary α-carbon centers and four α-C–H bonds in 3-MTHF relative to one secondary α- and one tertiary α-carbon center of MTHF [68]. In a low-temperature ignition delay times study of various THFs in a rapid compression machine (RCM), 3-MTHF was shown to have two to three times lower ignition delay times than MTHF [49].

Fuel properties and engine performance of THF and THFA oxygenates

The oxidation of THF in the jet-stirred reactor reported a large generation of aldehydes, including formaldehyde, acetaldehyde, and propanal at temperatures from 527 to 1527 ℃, pressures from 202 to 1013 kPa and equivalence ratio (φ) from 0.5 to 2 [58]. The maximum burning velocity of THF was similar to ethanol and diethyl ether [58]. The auto-ignition characteristics of furan, DHF, and THF at temperatures of 800–1050 K and equivalence ratio of 0.5–2.0 showed that the ignition delay times of furan were significantly insensitive to the equivalence ratio [42]. The auto-ignition characteristics relative to the temperature change suggested that the degree of saturation was more significant than alkyl substitution in reactivity of furan, DHF, and THF [42]. The derived cetane number of THF was reported to be greater than furan, as the reactivity of furan was influenced by the ring structure [42]. In contrast, the reactivity of THF relied on the side chain properties [42].

THF/*n*-heptane blends were tested in homogeneous charge compression ignition (HCCI) engine enhanced fuel combustion and engine performance by eliminating knocking and misfiring that impeded the HCCI operating range [69]. This can be attributed to the increase in the octane number of the fuel blend due to the addition of THF [69]. However, the addition of THF to *n*-heptane fuel on the HCCI engine increased hydrocarbon and NO_x emission [69].

THF has higher oxygen content (22.2%) and lower viscosity and boiling point than diesel fuel (10.8% oxygen content) (Table 1), which renders its potential to enhance the combustion of biodiesel and lower biodiesel emissions. THF is also favorable as a biodiesel additive, as it has more excellent calorific value and oxygen content than DMF and 2-MF (16.7% and 19.5% oxygen content, respectively) (Table 1) [70]. Relative to the use of ethanol as an oxygenated additive in internal combustion engines, THF is preferable due to its superior properties in energy density, viscosity, latent heat of vaporization, and boiling point [70]. THF was also added to the ethanol/biodiesel blend (2–15% ethanol) as the surfactant to enhance the poor miscibility of ethanol in biodiesel [71]. The addition of the above 2% ethanol to the biodiesel blend results in an unstable blend and phase separation. A higher amount of THF was required to add more ethanol to the biodiesel blend [71]. However, the addition of THF into ethanol/biodiesel blend resulted in drop flashpoints below 55 ℃, which is a drawback to the safety of the fuel blend due to lower security of fuel to ignite during its storage, handling, transportation, and usage [71]. However, a lower fuel flashpoint does not impact the fuel combustion in the internal combustion engine [71]. The addition of THF to the diesel blend was reported to have lower soot. Still, however, it increased NO_x emission in an engine test using a six-cylinder heavy-duty diesel engine [72]. The addition of THF was also demonstrated to increase brake-specific fuel consumption (BSFC) and lower brake thermal efficiency (BTE) of diesel blends [72]. THF/biodiesel blend was also reported to lower CO, HC, 1,3-butadiene, and benzene emission at 30% blend of THF with biodiesel, tested in a four-cylinder direct-injection compression ignition engine with the engine speed at 1800 rpm [70]. NO_x and soot emission of THF/biodiesel blend decreased at the highest THF loading [70].

THFA is used as a fuel additive through blending with diesel for cleaner fuel [29,34]. The use of levulinate esters as a fuel additive requires additional solvent, where THFA (2–5 wt%) can be used as a co-solvent to the fuel blend [34]. The derivatives of THFA could also be used as diesel fuel additives such as tetrahydro furfuryl *t*-butyl ether and ditetrahydro furfuryl polyacetal [34]. In addition, the presence of the –OH group in THFA renders better anti-knock properties of THFA relative to other THF fuels [73].

Alkylated furans (furan, 2-MF, 2-EF, 2-BF, DMF, FAL), dihyrofurans (2,3-DHF, 2,5-DHF), alkylated THFs (THF, MTHF, 2-ETHF, 2-BTHF), THFA, and *n*-heptane were tested for global ignition behavior in an Ignition Quality Tester (IQT) (Fig. 4(b)) [49]. The derived cetane number (DCN) of the fuels were measured, where fuels with a DCN higher than the minimum required cetane number for diesel fuels according to the EU standard (50) and the USA standard (40), were considered to be suitable for diesel engines [49]. On the contrary, fuels with less DCN than the cetane number of RON 90 fuel (~23) were preferable to be used for the SI engines, as fuels with low DCN have high knock resistance [49]. 2-BTHF were demonstrated to have a DCN (45.5) higher than the cetane number of diesel fuel according to the US standards, which renders it promising for diesel engine application. On the other hand, 2-ETHF with DCN of 28.1 was not suitable for either engine application, as the DCN is higher than RON 90 fuel and lower than diesel fuel [49]. THF, MTHF, and THFA were favorable for application in the SI engine, owing to its low DCN (Table 1) [49]. As the side chain length of furans and THFs increased, the DCN also increased, and the change was more significant for THFA. The increase of the number of double bonds in the furan ring led to the rise in aromaticity and reduction in fuel reactivity [49].

Alkyl levulinates: methyl levulinate (ML), ethyl levulinate (EL), butyl levulinate (BL)

Synthesis of alkyl levulinate oxygenates

Alkyl levulinates are short-chain fatty acid esters that have properties comparable to biodiesel, made of fatty acid methyl esters [74]. Alkyl levulinates, including methyl levulinate (ML), ethyl levulinate (EL), propyl levulinate (PL), and butyl levulinate (BL), are promising as bio-based fuel additives due to their properties of flash point stability, moderate flow properties, high lubrification, and low sulfur content, low toxicity [18,75]. For example, EL can be applied as an octane booster for gasoline and a fuel extender for diesel. In contrast, butyl levulinate (BL) and other higher alkyl levulinates can be used as diesel and biodiesel additives [76].

Alkyl levulinates can be produced from lignocellulosic biomass, consisting of C6- and C5-sugars, through several synthesis routes (Fig. 8). The conversion of cellulose or its C6-sugar derivatives into alkyl levulinates through (1) isomerization of C6-sugars into fructose, (2) dehydration of fructose into HMF or 5-alkoxy methyl furfural, (3) rehydration of HMF (Pathway V-Fig. 8), and (4) alcoholysis into alkyl levulinates [75,77]. The yield of alkyl levulinates from fructose is typically higher than any other hexoses, such as glucose or mannose [75], as the conversion from fructose would not require isomerization monosaccharides. The synthesis of alkyl levulinates originating from C5-sugars involves (1) alcohol esterification of levulinate acid (can be derived from C6- and C5-sugars) (Pathway I-Fig. 8), (2) conversion of furfuryl alcohol and its ethers (from C5-sugars) (Pathway II-Fig. 8), (3) by-product of MMF or EMF (depending on the reagent, ROH, used for alcoholysis) production biomass (from C6-sugars) (Pathway III-Fig. 8) and (4) direct conversion from carbohydrates [78]. Another route of synthesis of alkyl levulinates indirectly from lignocellulosic biomass is through the esterification of biomass-derived levulinic acid using acidic catalysts or alcoholysis of biomass-derived 5-(chloromethyl)furfural (ClMF) (Pathway IV-Fig. 8) [75,77]. ClMF can be synthesized from polysaccharides, including cellulose and lignocellulosic biomass in a biphasic system. At the end of reaction, the organic phase consists of 90% of ClMF less than 10% of levulinic acid [79]. The alcoholysis of biomass-derived ClMF using $HClO_4$-SiO_2 (0.551 mol%) catalyst at 90 °C for two hours with methanol, ethanol, propanol, and butanol resulted in high yield (>91%) of ML, EL, propyl levulinate, and BL, respectively [80].

Alcoholysis, a thermochemical process, is the most commonly used process for directly converting lignocellulosic biomass into alkyl levulinates. The benefits of alcoholysis are the low-temperature reaction process (<400 °C) relative to gasification and pyrolysis (400–1000 °C),

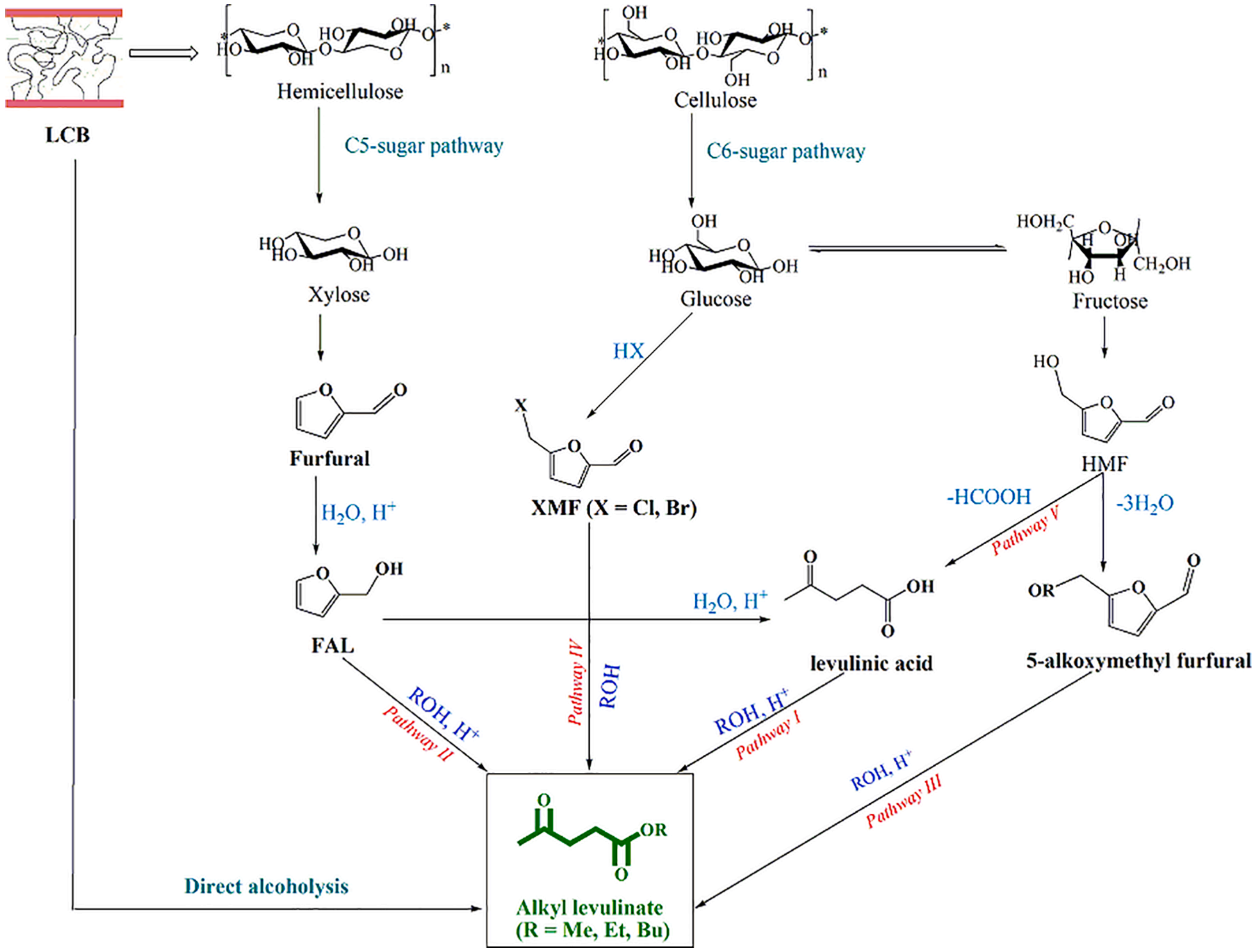


Fig. 8. The synthesis of alkyl levulinates from lignocellulosic biomass (LCB) directly or indirectly via alcoholysis (using MeOH or EtOH) of FAL through C5-sugar pathway; and 5-(halomethyl)furfural (XMF), levulinic acid, and 5-alkoxymethyl furfural (e.g., MMF or EMF) through C6-sugar pathway for the production of ML and EL respectively [78,80,118].

the short reaction time compared to the biochemical process, simultaneous partial decomposition of lignin, cellulose, and hemicellulose via solvolysis, and less formation of humins by-product as alcohol instead of water is used as solvent [81,82]. However, the alcoholysis of lignocellulosic biomass can be affected by lignin content and crystallinity, where rapid decomposition of lignin reduces the crystallinity of biomass and subsequently improves the conversion process [81]. Therefore, the major concern in using lignocellulosic biomass as the feedstock in a direct conversion into alkyl levulinates is the low yield of the main product due to recalcitrance from the complex microstructure of lignocellulosic biomass and the formation of by-products, including formate, HMF ether, and dialkyl ether from alcohol dehydration [82].

Catalysts for alcoholysis process

The combination of Brønsted acids and Lewis acids is used as catalysts to convert lignocellulosic biomass into alkyl levulinates effectively. Bases or Lewis acids catalyze aldose isomerization of glucose into fructose. Brønsted acids, such as mineral acids, catalyze fructose dehydration [78]. Therefore, using a single mineral acid catalyst, like HCl or H_2SO_4, for the conversion of glucose resulted in a lower yield of alkyl levulinates than the conversion of fructose [78]. Glucose methanolysis by Brønsted acid may result in the formation of ethyl-*D*-glucopyranoside (EDGP) as intermediate, where isomerization of EDGP into ethyl-*D*-fructofuranoside (EDFF) is difficult and rate-limiting [75]. Mixed acids, such as $Al_2(SO_4)_3$, were used as homogenous catalysts that consisted of both Brønsted and Lewis acids, where the yields of ML from glucose from these catalysts were higher relative to the use of mineral acids [78,83,84]. Besides the low cost of mineral acids, the benefit of using mineral acid catalysts is that it typically results in a high reaction rate [77]. However, these catalysts impose practical difficulties from their corrosiveness, non-recyclable, non-regeneration, toxicity, miscibility in hydrophobic solvents, and waste disposal [77]. Enzyme-like lipase (Novozym 435 from *Candida antarctica*) was employed as a biocatalyst to convert levulinic acid in *n*-butanol into BL [85]; however, enzyme-based conversion is slightly slower than conversion via other homogeneous catalysts. Table 2 summarizes the application of homogenous and heterogeneous catalysts that consists of the site of Brønsted acid, Lewis acid, or the combination of both acids.

The use of heterogeneous catalyst systems in converting carbohydrate to alkyl levulinates is more advantageous in curbing equipment corrosion, difficult catalyst recovery, and polluting effluent generations from a homogenous catalyst system [18,78]. The key factor that influences the catalyst activity of heterogeneous acid catalysts is the surface area of acids, pore size distribution, and optimum Lewis/Brønsted acid sites ratio. Among heterogeneous catalysts that have been used for the synthesis of alkyl, levulinates were Si-based catalyst (Al_2O_3/SBA-15, SBA-15-$(CH_2)_3$-SO_3H, KCC-1/Pr-SO_3H, CeO_2 and Sm_2O_3 on rice husk-derived silica, Al-TUD-1), ion-exchange resins (Amberlyst, sulfonated polystyrene-divinylbenzene), solid heteropolyacids (Nb_2O_5-$H_4SiW_{12}O_{40}$, $[MIMBS]_3PW_{12}O_{40}$, $H_3PO_4\cdot12WO_3\cdot xH_2O$/montmorillonite, $H_4SiW_{12}O_{40}$/mesoporous SiO_2, $H_4SiW_{12}O_{40}$/benzene moieties), zeolites (modified H-ZSM-5, HY zeolite, H-USY zeolite, Y-zeolite, ZrAl-mp), carbonaceous material (sulfonic acid-functionalized lignin-montmorillonite complex, sulfonated magnetic waste paper-derived carbon, sulfonated glucose-derived carbon), zirconia (ZrY6(0.5), TiO_2-ZrO_2), metal acid catalysts (α-Fe_2O_3, $AlCl_3$, metal triflate/*p*-toluene sulfonic acid, metal triflate/2-naphthalene sulfonic acid), metal–organic framework (MOF), ionic liquids and nano-catalysts (sulfated TiO_2, graphite oxide (GO), reduced GO) [77,78,86–98]. The cheap metal salt catalyst, $Al_2(SO_4)_3$, resulted in a high conversion yield into ML due to the good Brønsted/Lewis acidity of the metal catalyst [18]. The yield of EL was reported to be higher in ethanolysis catalyzed by HY zeolite than H-USY zeolite and Y-zeolite due to its high BET surface area and acid density sites [75]. The low yield of EL from Y-zeolite could result from the microporous structure of Y-zeolite that allows intermediates formed to readily diffuse out of pores [75]. Mesoporous catalysts, like TiO_2 nanoparticles, are composed of a large composition of hydrogen (acts as Brønsted acid) and oxygen adsorbed on the surface, resulting in a higher yield of ML and EL [75,99]. The application of heteropolyacids catalyst in alcoholysis resulted in a similar yield of EL relative to ionic liquids in a more rapid reaction [75]. The use of ionic liquids catalysts is more advantageous as it is recyclable and curbing corrosive and environmentally unsustainable catalysts [100]. However, the cost of the catalyst renders the process to be not economical. Microwave heating was reported to improve the conversion efficiency of biomass into alkyl levulinates, as it allows the process to be conducted with high heating rates, rapid processing time, less energy consumption [81].

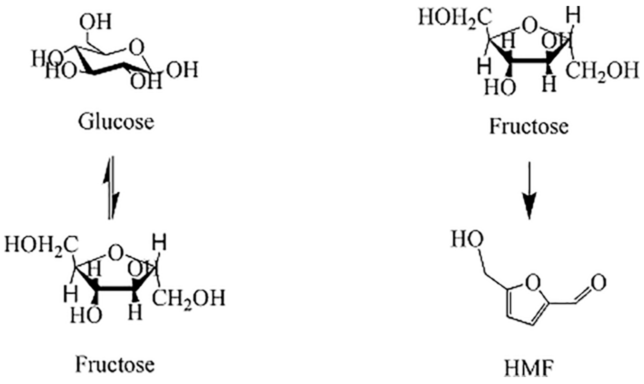
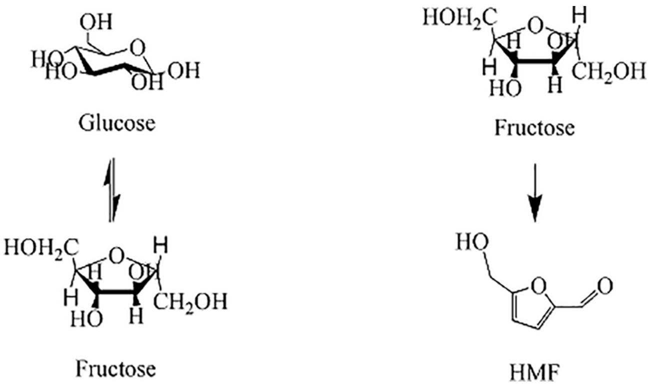
The study on the methanolysis of α-cellulose catalyzed by $Al_2(SO_4)_3$ showed that the low yield of ML was not much improved, even with doubling the reaction time from 2.5 h to 5 h due to poor depolymerization and decrystallization in methanol at 160 °C [83]. However, by doubling the reaction time and increasing the reaction temperature from 160 °C to 180 °C, the yield of ML was doubled to 44% [83]. The production of ML from the methanolysis of liquid hydrolysate of poplar wood (mainly composed of C5-sugars), where the hydrolysis of poplar wood was catalyzed by mineral acid (HCl, H_3PO_4, H_2SO_4, HPW (phosphotungstic acid), $C_7H_7SO_3H$ (sulfamic acid, *p*-toluenesulfonic acid) [101]. Poplar wood hydrolysate was converted using Amberlyst 70 in dimethoxymethane/methanol into a 30% yield of ML (the weight of ML to the weight of methyl glucoside), with the reaction taking place in the reactor heated at 140–170 °C for 120 min with 350 rpm stirring [101]. The combination of Brønsted acid (benzenesulfonic acid) and Lewis acid ($In(OTf)_3$) in methanol was utilized to catalyze direct conversion (200 °C, 5 h) of various lignocellulosic biomass including bagasse, eucalyptus and pine into ML with the yield of 67–74% [102]. The combination of catalyst systems was not affected by impurities like lignin, minerals, and ashes typically found in lignocellulosic biomass [102]. Various sulfonic acid was tested as the catalysts in the conversion of cedar powder. The use of benzenesulfonic acid, which has electron-donating substituents, resulted in 99% yield of ML from cedar powder using $In(OTf)_3$ catalyst [102]. The combination of Brønsted acids and Lewis acid metal catalyst facilitates the conversion of lignocellulosic biomass by first catalyzing the solvolysis of cellulose to sugars by sulfonic acid as Brønsted acid, followed by catalyzing alcoholysis of sugars to ML via $In(OTf)_3$ as Lewis acid catalyst [103].The production of ML from eucalyptus wood chips was conducted using H_2SO_4 catalyst at 170 °C for 20 min in co-solvent of methanol with yield of 30.9 mol% [104]. Bamboo powder was directly converted into a high yield of ML (30.75%) in subcritical methanol using H_2SO_4 catalyst (2.5 wt%) with microwave heating at 200 °C for 120 min [105]. The methanolysis of bamboo powder also resulted in the formation of glycosides and phenols (lignin derivatives) in a substantial amount [105]. ML was directly converted from corn stover via methanolysis catalyzed by H_2SO_4 at 160 °C, where microwave heating resulted in a ~25 mol% increase in the yield of ML [106]. Most conversions from lignocellulosic biomass into ML resulted in the generation of humins, black-like insoluble compounds, as by-products [102]. The generation of humins has ramifications on the yield of main products and could deposit on solid catalysts that potentially exacerbates catalyst deactivation [104]. The formation of humins can be curbed by preserving the active group of glucose and/or HMF from oligomerization [104]. The use of water as a co-solvent, along with methanol, resulted in less formation of humins in the conversion of glucose to ML [104]. The drawback in using methanol is that methanol was also consumed in other reactions, which led to a significant loss and challenging methanol recovery [104].

Conversion of LCB into alkyl levulinate oxygenates

A metal catalyst of $Al_2(SO_4)_3$ could also be used to directly convert lignocellulosic biomass softwood bark into LA and ML, with the optimal yield of ML at 62% [18]. The benefits of using the metal catalyst of $Al_2(SO_4)_3$ are attributed to its low cost and the reduction of corrosion inside the reactor relative to using a homogenous catalyst of H_2SO_4 [18].

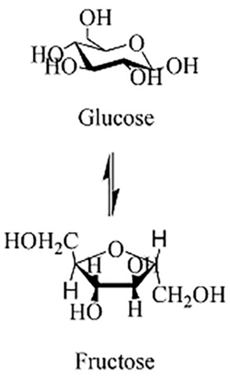
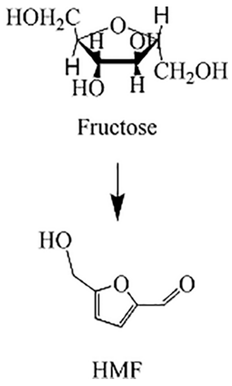
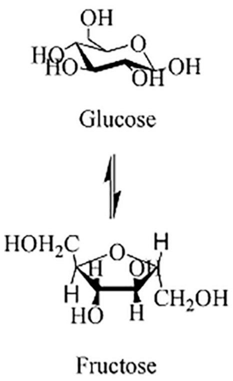
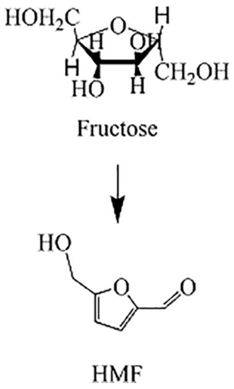
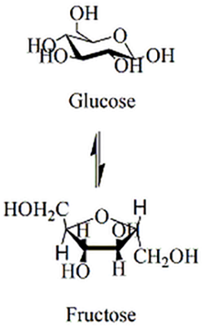
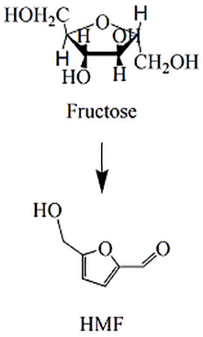
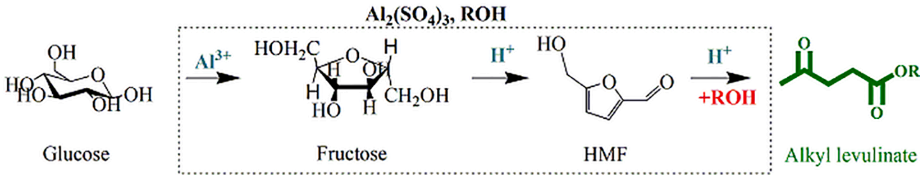
Table 2

Synthesis of alkyl levulinate catalyzed by a homogenous and heterogenous catalyst that consisted of the site of Brønsted acid, Lewis acid or the combination of both. (MOF, metal–organic framework).

Catalyst	Brønsted acid	Lewis acid	Advantage	Disadvantage	Re-erence
					
Homogenous catalyst	HCl	–	• Low cost of mineral acids • High reaction rate • Higher yield of alkyl levulinates from fructose due to Brønsted acidity; but the low yield from glucose	• Corrosion to equipment • Miscibility in hydrophobic solvents • Non-feasible separation and reusability • Polluting effluent	[77,78]
	H_2SO_4	–			
	$Fe_2(SO_4)_3$ $Al_2(SO_4)_3$		• Provides both Brønsted and Lewis acid sites	• Alcohol dehydration to a diether	[18,78,83,84,114,145–147]

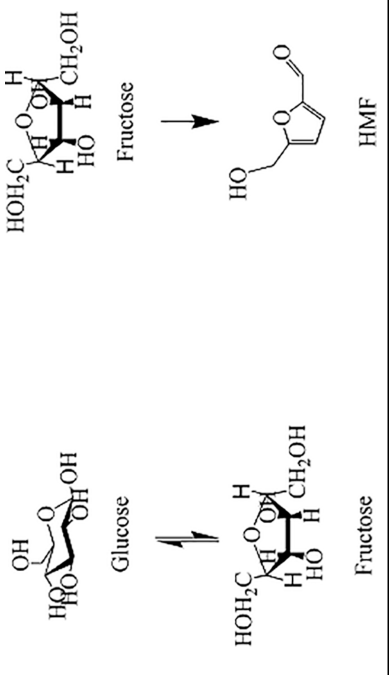
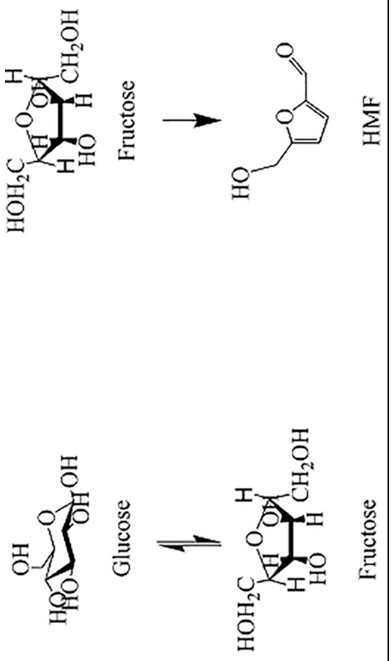
(*continued on next page*)

Table 2 (*continued*)

Catalyst	Brønsted acid	Lewis acid	Advantage	Disadvantage	Re-erence
	  	  			
	  				
	 Lipase enzyme (Novozym 435 from *Candida antarctica*)		• Reaction is specific	• Slightly slower reaction than with mineral acid catalysts	[85]
Heterogenous catalyst	–	Cu-MOF, Hf-MOF and Zr-MOF	• Feasible recovery and reusability	• Some are slightly expensive than mineral acids catalyst	[77]
	Sulfonic acid-functionalized lignin-montmorillonite complex	–			[97]
	$H_4SiW_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_5PW_{11}TiO_{40}$, K-HPW-1, $[MIMBS]_3PW_{12}O_{40}$, $H_3PO_4\cdot 12WO_3\cdot xH_2O$ supported on montmorillonite	–			[86,98,110,112,148]
	Amberlyst	–			[101]
	p-toluene sulfonic acid	$In(OTf)_3$			[102,103]

(*continued on next page*)

Table 2 (*continued*)

Catalyst	Brønsted acid	Lewis acid	Advantage	Disadvantage	Reference
					
	PW_{12}/Nb_2O_5-Si(Ph)Si $AlPW_{12}O_{40}$ $Y(OTf)_3/H_3PO_4$ H-USY zeolite	Nb_2O_5	• Exhibited synergistic effects due to Brønsted/Lewis acids site • Feasible recovery and reusability	• Some has toxicity issue	[149] [150] [151] [76]

Using directional liquefaction, ML was recovered from pyrolysis oil from lignocellulosic biomass [107,108]. Directional liquefaction involves stepwise precipitation of hydrophobic compounds from pyrolysis oil to form monosaccharides (sugar derivatives) and aromatic compounds (mainly from lignin) [107]. Pyrolysis oil derived from pine wood was stabilized using a solid acid catalyst, Amberlyst 70, with alcohol at 140–170 °C and 2 MPa [108]. The stabilized oil was further upgraded by catalytic hydrotreatment at 400 °C using $NiMo/Al_2O_3$ catalyst into levoglucosan-rich biofuel [108]. Levoglucosan can be further converted into ML using acid-catalyzed methanolysis. Directional liquefaction on bamboo, bagasse, pine, hybrid poplar, and hybrid willow biomass using H_2SO_4 catalyst [107]. H_2SO_4 catalyst could directly cleave the glycosidic bonds, β-O-4, 4-O-5, and dibenzodioxocin units [107].

EL was synthesized from levulinic acid derived from oil palm fronds (OPF) through a two-step process involving the dehydration of OPF and esterification of levulinic acid into EL (yield of 20.1% for 5 h) over-acidic ionic liquid catalyst of 1-sulfonic acid-3-methyl imidazolium tetrachloroferrate ([SMIM][$FeCl_4$]) [74]. The use of an ionic liquid catalyst is advantageous due to its reusability, environmental sustainability, and efficient reaction rate at mild process conditions. The direct production of EL from wheat straw via ethanolysis was catalyzed by H_2SO_4 (2.5 % wt) at 183 ℃ for 36 min with a yield of 17.9% [109], which was not that high due to the use of only Brønsted acid as a catalyst. Grey pinewood was converted into EL in the one-pot reaction and two-step acid hydrolysis and esterification using ethanol catalyzed by H_2SO_4 [76]. Both types of reactions resulted in similar yields of EL (~15–16%) from the pinewood [76]. The addition of H-USY zeolite in the direct ethanolysis of pine wood showed no improvement in the yield of EL, only less formation of diethyl ether (DEE) by-product [76]. Liquid fractions (light and heavy fractions) from the one-pot process of wheat straw, obtained after drying and removing unused alcohol and composed of EL in the heavy fraction, can be blended with gasoline or diesel/biodiesel fuel [76]. Direct ethanolysis of cellulose into EL catalyzed by K-HPW-1 (at 220 ℃), Brønsted acidic ionic liquid 1-(1-propyl sulfonic)-3-methylimidazolium chloride (at 170 °C for 12 h after addition of water, followed by for 12 h after addition of ethanol), $H_4SiW_{12}O_{40}$ (180 °C) resulted in the yields of EL at 14.8%, 4.93%, 19%, respectively and intermediate at 1.4% (levulinic acid), 9.87% (levulinic acid), 24% (ethyl glucosidase), respectively [110–112]. The conversion of wheat straw into EL in the one-pot reaction catalyzed by ionic liquids showed that [HSO_3-BMIM][HSO_4] catalyst at 200 °C for 60 min resulted in higher EL yield at 16.23% relative to the use of other ionic liquid catalysts of [BMIM][HSO_4] and [BMIM][Cl] [100]. Corn stover conversion into EL via ethanolysis catalyzed by H_2SO_4 at 180 °C under the initial microwave power of 600 W resulted in 12.4 wt% [81]. Furfural and ethyl *p*-hydroxybenzoate were the by-products generated from the direct conversion of corn stover [81].

BL has been synthesized from various lignocellulosic biomass via alcoholysis. Cellulose was converted into BL via five-step fed-batch hydrolysis, decolorization, extraction, esterification, and purification catalyzed by H_2SO_4 [113]. The study on one-pot alcoholysis of fructose using various metal sulfates (K, Mg, Fe, Co, Cu, Ti, Zn, Al) in butanol resulted in the highest yield of BL with $Fe_2(SO_4)_3$ catalyst [114]. 30.5% yield of BL was obtained from cellulose in the reaction using $Fe_2(SO_4)_3$ catalyst at 220 °C for 3 h [114]. The reaction mixture after the extraction process consisted of BL and levulinic acid, where BL separated, and levulinic acid was further esterified in *n*-butanol catalyzed by H_2SO_4 at 100 °C into BL [113]. Rice straw was converted into BL in a two-step process, which began with the degradation of biomass using H_3PO_4 in THF with levulinic acid and HMF as intermediates, followed by esterification of levulinic acid catalyzed by H_2SO_4 (0.5 M) in *n*-butanol for 60 min to BL (yield of 7.0%) [115].

One-pot alcoholysis of the cellulose-rich feedstock of *Eucalyptus nitens* into BL in *n*-butanol catalyzed by diluting H_2SO_4 (1.2 wt%) at 190 °C for 120 min with the highest yield of BL at 49 mol%, which was higher than that under microwave heating [82]. *Eucalyptus nitens* were pretreated with autohydrolysis to remove hemicellulose and water-soluble extractive and HCl-catalyzed acetic acid treatment (Acetosolv method) for delignification [82].

Fuel properties and engine performance of alkyl levulinate oxygenates

The anti-knocking index values or octane number of ML at 106.5, EL at 107.5, and BL at 102.5 showed that alkyl levulinates are comparable to diesel as fuel (Table 1) [75]. ML is less miscible in gasoline, which renders the cold flow properties of the blend is not favorable [75]. The EL blend was reported to substantially reduce PM emission [116]. 10% blend of EL showed similar IMEP and engine efficiency with the reference fuel (Euro95 gasoline) [117]. ML and EL were reported to have greater knock resistance quality than Euro95 gasoline [117]. Engine tests performed on EL, BL, ketones, and valeric esters added with 30 wt% of heptane showed EL reduced NO_x emission due to the decrease in the overall premixed combustion temperature [118].

EL and BL have good solubility in diesel range fuels [75]. ML/diesel blend has lower NO_x emissions than EL/diesel blend [75]. EL/diesel blend has a lower cloud point, pour point, and cold filter plugging point than diesel fuels [75]. The blend of EL at 10% was reported to have the longest ignition delay relative to diesel fuel, E85, and B10, which led to the highest CO and noise emissions [119]. Despite that, the EL blend resulted in similar engine efficiency to diesel and a 50% reduction of soot emission based on the Euro 6 emission levels [119]. The EL blend (10%) was tested in a diesel engine (4-cycle 2012 Ford 6.7 L), along with E20 and 5-methyl furoate ethyl ester (EF) blend (10%), as shown in Fig. 7(b) [120]. The emission test showed that the oxygenated fuel additive could lower CO emission; however, the NO_x emission was higher Fig. 7(b) [120]. EL has a short lifespan (4 days) due to its quick degradation via OH radicals, reducing the negative impact on the environment from the unburned hydrocarbons [75]. The addition of EL into diesel was reported to increase the cloud point of the diesel fuel, even though EL has an extremely low melting point, as EL was in a separate liquid phase in diesel blend at low temperature [116].

As ML is completely miscible in water and can be separated from gasoline at room temperature, the use of higher chain alkyl levulinate esters in the blend is favorable [116]. Diesel blended with 20% (*v/v*) levulinates, BL was deemed better than EL in terms of its lower solubility in water that renders BL to remain completely soluble in diesel blend at the diesel cloud point, in contrast to EL that tends to form a separate liquid phase in diesel blend [94,116]. The use of BL as fuel resulted in cleaner combustion, as BL decreases vapor pressure and enhances fuel's lubricity, conductivity, and cold flow properties [94]. BL and butanol have a lower cetane number than diesel fuel, which makes these compounds exhibit higher ignition delays in engine application [82]; therefore, their use as fuel may require cetane enhancers [94].

The blend of ultra-low sulfur diesel (ULSD) with EL at 10%, EL at 10% and 5% biodiesel, and BL at 20% was tested in a Cummins ISB 2008 engine, with each blend was added with a cetane enhancer that resulted in blend fuels with cetane numbers of 45.0, 44.5 and 43.4, respectively [116]. HC, CO, and noise emissions of BL blended with diesel were higher than diesel; however, the BL blend led to a significant reduction in soot emission, like EL [121]. EL and BL blends were reported to reduce the engine-out smoke number substantially due to its high oxygen content and slightly raise BSFC due to its low energy density relative to ULSD [121]. The use of BL as sole fuel was not feasible, as it cannot ignite without blending with fast igniting fuel components, such as *n*-tetradecane [121]. Testing was performed over the heavy-duty diesel transient cycle, where EL blends resulted in no change in NO_x emission, but the BL blend has a 4.5% increase in emission [116].

The fuel performance test of the ternary mixture from one-pot butanolysis of corn stover consisting of BL, DBE, and unreacted *n*-butanol (BuOH), blended with diesel (10%, 20%, and 30% (*v/v*)), was conducted in two-cylinder diesel engines (Lombardini LD 625/2) [82]. At full power, the engine test was performed at different rpm values (1500, 2000, and 2500 rpm) [82]. The emission of CO and soot from BL/DBE/BuOH/diesel blends was lower than diesel alone due to the elevation in combustion oxygen availability in the blends, which minimizes the low air access zones resulting in the formation of CO and soot [82]. In addition, the reduction of CO and soot emission in the diesel blend could be attributed to the droplet explosion formed when the blend was introduced in a hot ambient at the end of the compression stroke, which may increase spray fragmentation and mixing [82].

Ethylfurfuryl ether (EFE) and ethyl tetrahydrofurfuryl ether (ETE)

Synthesis of EFE and ETE oxygenates from LCB

EFE has the potential to be used as furanic-based fuels. The production of EFE and its application has been patented by Shell [34]. ETE can be blended with gasoline up to 30 wt% [34]. The stability and octane number of EFE is greater than FAL, which makes it more promising as a fuel additive [34]. EFE is derived from furfural via a two-step reaction involving catalytic acetylation of furfural with the use of catalysts such as Pd-H, followed by catalytic hydrogenolysis of 2-(diethoxymethyl)furan under low-pressure H_2 gas [19]. Fig. 9 depicts different reaction pathways for the synthesis of EFE from furfural. The synthesis of EFE from furfural can also be achieved through the etherification of furfuryl alcohol with ethanol [117]. This pathway involves the use of a bifunctional hydrogenation catalyst and a strong Brønsted acid catalyst and requires a high reaction temperature (>100 °C) [32]. The drawback of the high reaction temperature is the possibility of ring-opening of furan-group in the chemical structure of EFE that may lead to the production of LA or its esters [32]. The high reaction temperature also leads to high energy consumption [122]. This conversion can also be inefficient due to the conversion of furfuryl alcohol into insoluble humins as the by-product [122]. EFE can also be produced directly from furfural in one-pot synthesis in ethanol via catalytic reductive etherification [32]. The synthesis of EFE via etherification was performed using various catalysts, including Pd nanoparticles (supported on TiO_2, Al_2O_3, SiO_2, and active carbon) and HZSM-5 [32,122,123]. Optimal yield EFE (up to 81%) from furfural was obtained at low reaction temperature (60 °C) and H_2 pressure (0.3 MPa) using Pd/C catalyst, with furfuryl alcohol and MTHF as the main by-products [32]. Using a bimetallic catalyst system of Pt/Mo supported on activated carbon (AC) led to 92% conversion of furfural with 80% and 20% selectivity towards the formation EFE and FAL, respectively [35]. The conversion of furfural into EFE with 100% was achieved with the use of monometallic Mo/AC [35]. The etherification of furfuryl alcohol using HZSM-5 catalyst with orthoesters, like triethyl orthoformate, as a sacrificial reagent allowed reaction at mild condition with minimal production of humins as the by-product [122]. EFE is also an intermediate product of EL production from FAL [124].

Ethyl tetrahydrofurfuryl ether (ETE), also known as ethoxymethyl tetrahydrofuran ether, has a cetane number of 80–90, making it suitable a diesel fuel additive [124,125]. YXY fuel, formulated by Avantium, contained ETE, EFE, and bisethoxy methyl furan (BEMF) to produce fuels with superior properties to biodiesel, bioethanol, and other conventional fossil fuels [125]. ETE can be derived from furfural via hydrogenation of furfural into furfuryl alcohol, followed by reduction and esterification into ETE (Fig. 9) [117,125]. Direct conversion of ETE from furfural involves complete hydrodeoxygenation with 6 mol of hydrogen was consumed [124]. The synthesis of ETE from EFE involves ring-hydrogenation [20,125].

Fuel properties and engine performance of EFE and ETE oxygenates

The use of ETE and EFE as fuel blends is promising because its lower heating values are high at ~30 MJ/L, comparable to gasoline (Table 1) [125]. In addition, EFE possesses a high BRON at ~110 (Table 1) [123]. Therefore, EFE will be more suitable for the SI engines due to its octane number. On the contrary, ETE was reported to have a high cetane number (>80) [125], which makes it suitable for application in diesel engines [20].

ETE, EFE, and BEMF of YXY fuel were reported to reduce PM

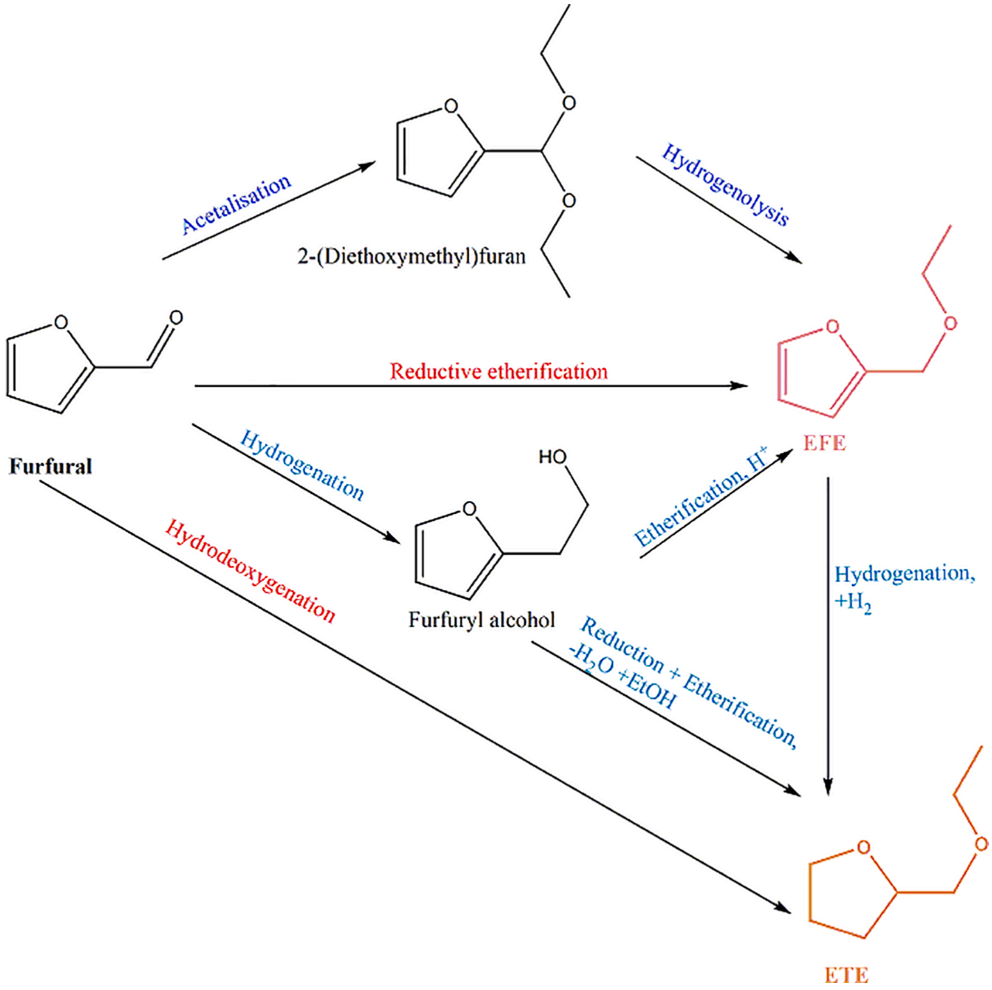


Fig. 9. The synthesis of ethylfurfuryl ether (EFE) and ethyl tetrahydrofurfuryl ether (ETE) from furfural [32,117,124]. However, there are no studies on EFE and ETE's direct conversion from lignocellulosic biomass.

emission (Fig. 7(c)), based on a diesel engine test on the PACCAR PR 9.2 L 183 kW engine [125]. The addition of 30% (*v*/*v*) of ETE into the diesel blend resulted in a significant reduction in PM and smoke emissions and the only slight change in NO_x emission and maximum cylinder pressure (MPa) [125]. An equal blend of EFE and ETE at 10% (*v*/*v*) each in diesel resulted in better NO_x emission than EFE alone blended with diesel and superior HC emission than at 20% (*v*/*v*) ETE/diesel blend [125]. Fuel consumption, however, increased with the addition of EFE and ETE at 10% (*v*/*v*) each to diesel blend, which was expected due to the lower energy content of furanic fuels relative to diesel fuel [125]. 10% EFE diesel blend was shown to have the best performance in knock limited spark timing in the engine, right behind 10% EL diesel blend [117]. The anti-knock quality results agreed with their derived cetane number [117]. The reactivity of EFE is higher than shorter chain furans [117].

Integrated biorefinery of the production oxygenated fuels from lignocellulosic biomass processing for circular bioeconomy

Some furanic fuels derived from furfural were reported to be synthesized directly from lignocellulosic biomass, as shown in Table 3. However, there are limited studies on the direct conversion of lignocellulosic biomass into furfural derivatives. This could be attributed to the formation of many furfural derivatives that can only be synthesized through the C5-sugar pathway. Therefore, direct conversion of lignocellulosic biomass could potentially lead to the substantial generation of by-products resulting from the degradation of C6-sugars, which could complicate the recovery of furfural derivatives as the main product. Table 2 shows that only alkyl levulinates have been synthesized directly from lignocellulosic biomass, which could also be produced from the C6-sugars pathway (Fig. 8). Therefore, integrating furfural derivative fuels production with the biorefinery of lignocellulosic biomass processing could be more cost-effective.

The pretreatment-based fractionation of lignocellulose to cellulose-rich fraction, pentose-rich fraction, and lignin fraction is more attractive from the view of biorefining. Pentoses (C5-sugar monosaccharides) and furfural are generated as by-products from industrial lignocellulosic biomass processing. The pretreatment of lignocellulosic biomass is significant in overcoming the recalcitrance of the biomass's lignocellulosic complex structures that hinder the C6-sugars from cellulose fraction to be accessible for further enzymatic and biological reaction. During the pretreatment of lignocellulosic biomass for further utilization in microbial fermentation of various bio-based chemicals and fuels (e.g., bioethanol, biobutanol, lipids), dilute sulfuric acid, the liquor generated is rich in pentoses [26]. Acid-catalyzed strategies are typically applied in the industrial processing of bioproducts for the pretreatment of lignocellulosic biomass as the raw materials [126]. The pentose-rich liquor can be easily separated from the cellulose-rich pretreated-biomass. The solid phase is required for the next processing step before the microbial fermentation. C5-sugars (pentoses) derived from hemicelluloses are typically not feasible for industrial fermentation processes, as microorganisms generally could not assimilate C5-sugars through the conventional biochemical pathways of glycolysis and tricarboxylic acid (TCA)

Table 3
Summary of oxygenated furan-based fuels production indirectly from lignocellulosic biomass via furan-based platform chemicals (e.g., furfural) and directly via one-pot synthesis.

Oxygenated furan-based fuels	Type of biomass	Biomass	Conversion process	Reference
BL	LCB	*Eucalyptus nitens*	Alcoholysis in n-butanol under microwave heating. Catalyst: H_2SO_4	[82]
		Rice straw	Pretreatment of biomass with H_3PO_4 in THF, followed by esterification using H_2SO_4 in n-butanol.	[115]
	Cellulosic biomass	Microcrystalline cellulose	Fed-batch hydrolysis, decolorization, extraction, esterification and purification. Catalyst: H_2SO_4	[113]
		Cellulose	Esterification using $Fe_2(SO_4)_3$ in n-butanol for 3 h at 220 ℃.	[114]
2-MF	LCB-based furfural	Corncob	Two-step process. Dehydration of corn-cob liquor using Amberlyst 70 into furfural, followed by hydrogenation using Cu-Co/γ-Al_2O_3 for 4 h.	[30]
	(Indirectly. LCB -derived furfural)	Corncob	Furfural from dehydration using HSC(sucralose-based carbonaceous material) SO_3H for 175 ℃ in 30 min in GVL/water system.	[152]
		Corncob	Furfural and HMF from dehydration using porous polytriphenylamine–SO_3H (SPTPA) for 175 ℃ in GVL.	[153]
		Corncob, sugarcane bagasse	Furfural from dehydration using Al–Beta zeolite in GVL.	[154]
EL	LCB	Corn stover	Alcoholysis of ball-milled biomass using H_2SO_4 under microwave irradiation in ethanol at 160 °C.	[155]
			Catalyst: H_2SO_4, in ethanol microwave-assisted at 190 °C for 30.4 min.	[156]
		Corn stover, poplar wood rice straw, rape straw, wheat straw	Alcoholysis. Catalyst: H_2SO_4	[81]
		OPF	Catalyst: [SMIM][$FeCl_4$], in ethanol heated at reflux temperature (78.4 °C) for 7 h.	[74]
		Pine wood	Direct ethanolysis using H_2SO_4 and H-USY zeolite at 190–205 ℃.	[76]
		Sugarcane bagasse	Catalyst: $[DMA]^+[CH_3SO_3]^-$, in ethanol.	[157]
		Wheat straw	Liquefaction using [HSO_3-BMIM][HSO_4] in ethanol at 200 °C for 60 min.	[100]
			Catalyst: 2.5% H_2SO_4 in ethanol at 183 °C for 36 min.	[109]
	Cellulosic biomass	Cellulose	Catalyst: 1-(1-propylsulfonic)-3-methylimidazolium chloride, in water at 170 °C for 12 h, followed by ethanolysis at 170 °C for 12 h.	[111]
			Catalyst: K-HPW-1 at 220 ℃	[110]
	(Indirectly. LCB-derived LA)	EFB, mesocarp fiber	Two-step process. Depolymerisation in $InCl_3$-[HMIM][HSO_4], esterification in ethanol.	[158–160]
EL and ML	LCB	Eucalyptus, Pinus, softwood chips, wood pulp	Catalyst: $Y(OTf)_3/H_3PO_4$ at 180 °C for 2 h.	[151]
	Cellulosic biomass	Cellulose	Two-step process. Catalyst: $H_4SiW_{12}O_{40}$ or $H_3PW_{12}O_{40}$	[112]
	(Indirectly. LCB-derived BMF)	Wood	Two-step process. Catalyst: $CaCO_3$, in ethanol	[161]
	(Indirectly. LCB-derived LA)	Bamboo, corncob, corn stalk, and corn straw	Two-step process. LA from biomass pretreated via cooking with active oxygen (MgO) and solid alkali, followed by hydrolysis using 2% H_2SO_4.	[162]
ML	LCB	Bagasse, eucalyptus, pine	Catalyst: $In(OTf)_3$ (Lewis acid), benzenesulfonic acid (Brønsted acid), in methanol at 200 °C for 5 h under N_2 (0.5 MPa).	[102]
		Bagasse, bamboo, eucalyptus, pine, poplar, straw	Microwave-assisted liquefaction using H_2SO_4 at 180 °C for 40 min.	[163]
		Bagasse, bamboo, hybrid willow, hybrid poplar, pine	Liquefaction in methanol at 200 °C for 10 min. Catalyst: H_2SO_4	[107]
		Bamboo	Methanolysis. Catalyst: H_2SO_4, at 200 °C for 10 min.	[164]
		Bamboo	Methanolysis. Catalyst: H_2SO_4, at 200 °C for 120 min.	[105]
		Corn stover	Methanolysis. Catalyst: H_2SO_4, at 160 °C under microwave dielectric heating.	[106]
		Eucalyptus wood chips	Methanolysis. Catalyst: H_2SO_4	[104]
		Laurus nobilis L. pruning waste	Two-step processes, autohydrolysis at 160 °C for 45 min. Followed by reaction, catalyst: $Al_2(SO_4)_3$ under microwave irradiation.	[147]
		Core OPT	Methanolysis. Catalyst: H_2SO_4	[165]
		Paper sludge	Methanolysis at $\leq$230 °C in dimethyl ether. Catalyst: H_2SO_4	[166]
		Pine wood	Pyrolysis using acid-catalyzed Amberlyst70.	[108]
		Poplar wood	Aqueous solution phase from methanolysis. Catalyst: Amberlyst, in methanol/DMM	[101]
		Poplar, softwood bark, sorghum	Catalyst: H_2SO_4, in methanol	[167]
		Rice straw	Pyrolysis in methanol and ethanol. Catalyst: Amberlyst 70	[168]
		Softwood bark	Metal catalyst: $Al_2(SO_4)_3$ (0.067 mol/L) at 200 °C for 5.67 h with biomass loading of 2.5 wt%.	[18]
		Wheat straw	Two stage pre-treatment using decanol. Alcoholysis using copper sulfate.	[169]
	Cellulosic biomass	Cellulose	Alcoholysis of ball-milled biomass at 170 °C in 45 min. Catalyst: $Al_2(SO_4)_3$	[145,146]
		Cellulose	Methanolysis at 160 °C for 20–30 min with microwave heating. Catalyst: $AlPW_{12}O_{40}$	[150]
		Cellulose	Methanolysis for 2 h with microwave assistance. Catalyst: $H_5PW_{11}TiO_{40}$	[148]
		Microcrystalline cellulose	Catalyst: $In(OTf)_3$ and *p*-toluenesulfonic acid for 5 h at 180 °C.	[103]
		α-cellulose	Catalyst: $Al_2(SO_4)_3$ for 5 h at 180 °C.	[83]
		Duckweed	Liquefaction at 170 °C for 5 h in methanol. Catalyst: $[C_3H_6SO_3HPy]HSO_4$	[170]

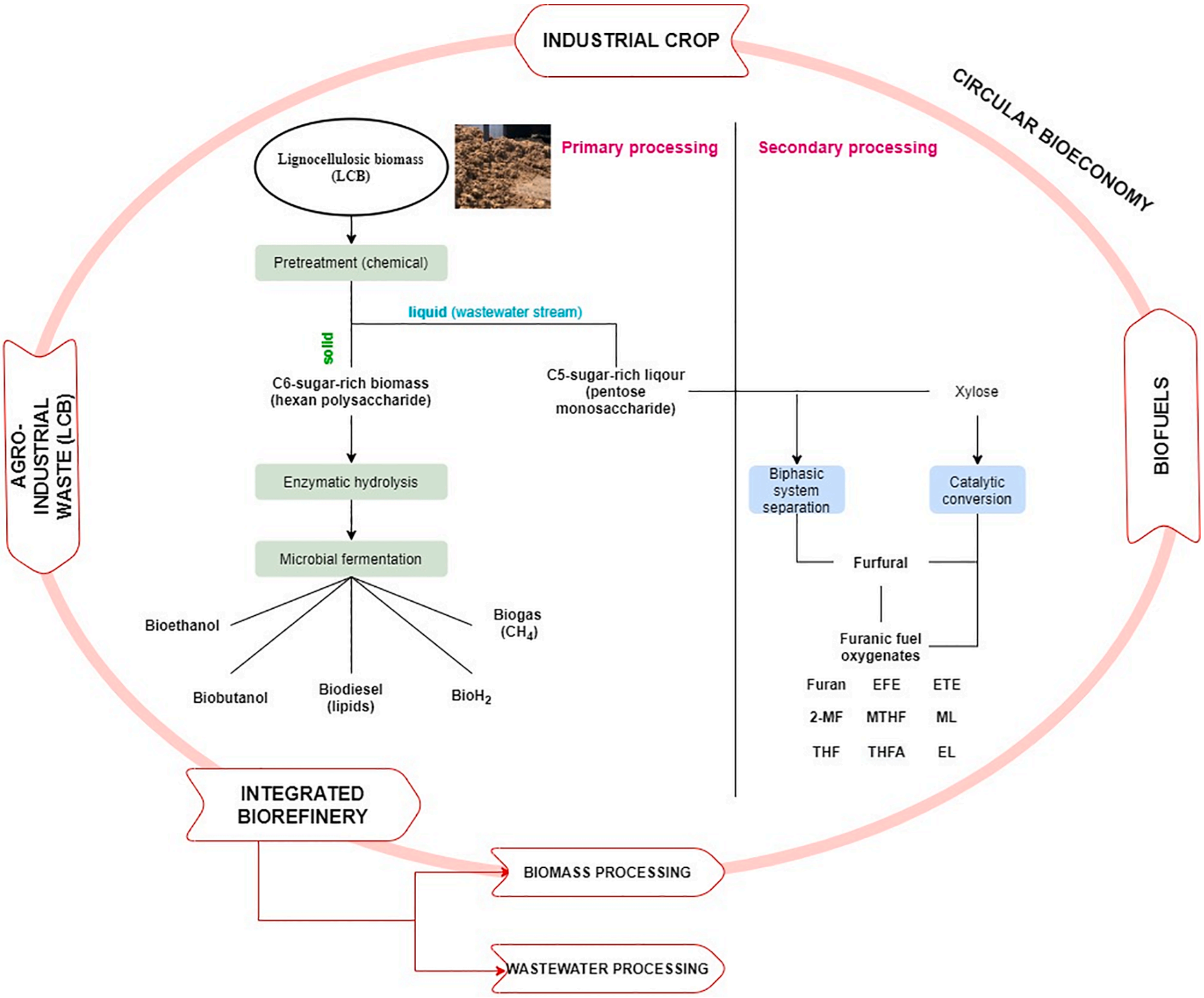


Fig. 10. The prospect of integrating pentose-based oxygenates with biorefinery of lignocellulosic biomass processing as the strategy for circular bioeconomy.

cycles [24]. Depending on the severity of the pretreatment process, furfural could be generated as the undesirable pentose degradation product under harsh pretreatment process [25], as furfural could inhibit microbial growth. The inhibition effect by furfural will significantly impact the bio-product yield from the microbial fermentation of lignocellulosic biomass [17]. Therefore, the generation of furfural in lignocellulosic biomass treatment is considered a bottleneck for microbial fermentation in lignocellulosic biomass processing. However, the opportunity exists in the re-utilization of pentose or furfural to produce oxygenates through the biorefinery of lignocellulosic biomass processing.

The concept of circular bioeconomy involves the recovery of all the products from raw material processing with no water discharge and higher value product generations for a sustainable economy [127,128]. The establishment of biorefineries for processing lignocellulosic biomass, a highly abundant waste, is a sustainable and economical approach in producing chemicals and fuels, which is significant for achieving a circular bioeconomy [129]. The US Department of Energy identified furfural in 2010 as a key target compound from biorefinery of biomass processing [129]. Integrating the conversion of furfural and pentose sugars into higher-value products, such as oxygenated fuel additives, with the biorefinery of lignocellulosic biomass processing will enhance the overall economics and sustainability of the production of bio-based chemicals and fuels. For instance, the production of bioethanol from wood chips by Lignol Energy Corporation using ethanol–organosolv pretreatment process for the biomass, followed by enzymatic hydrolysis, was estimated to be economically adverse [126]. However, the economics of the bioprocessing of wood chips could be improved with the production of chemicals and furfural from pentoses sugar [126]. Fig. 10 shows the prospect of integrating pentose-based oxygenates with biorefinery of lignocellulosic biomass processing as the strategy for circular bioeconomy. Furfural and its derivatives can be derived from the secondary wastewater processing from the primary processing. Efficient removal of furfural from the wastewater stream for higher-value products allows for process optimization and cost-effective operation of the lignocellulosic biomass processing.

Conclusions

The fuel properties of furanic compound derivatives include unsaturated cyclic ether (2-methyl furan (2-MF), furan, ethyl tetrahydrofurfuryl ether (ETE) and ethyl furfuryl ether (EFE)), saturated cyclic ether (2-methyl tetrahydrofuran (MTHF), tetrahydrofuran (THF), tetrahydrofurfuryl alcohol (THFA)), short-chain fatty acid esters (methyl levulinate (ML), ethyl levulinate (EL), butyl levulinate (BL)) are comparable to the commercial oxygenates. Furthermore, these furanic compounds are currently synthesized from furfural directly or indirectly via furfural derivatives such as furan and furfuryl alcohol (FAL) as furfural is a degradation product of xylose, which is one of the monosaccharides from pentoses of lignocellulosic biomass (LCB). Therefore, the opportunity exists for sustainable synthesis of furanic oxygenates from a low-cost feedstock of lignocellulosic biomass that is highly abundant as agro-industrial solid residues. The prospects of the production of furanic compound derivatives as oxygenated fuel additives from lignocellulosic biomass are as follows:

- The conversion of furanic compounds from lignocellulosic biomass in one-pot synthesis could improve the economics of furanic compounds production. The one-pot synthesis of furanic compounds from lignocellulosic biomass is through the degradation of pentoses in the C5-sugar pathway. However, there are limited studies on the one-pot conversion process of LCB-derived furanic compounds.
- The direct conversion of lignocellulosic biomass into furans (2-MF) involves dehydration and hydrogenation using solid acid catalysts. However, using the biphasic system for the one-pot conversion could facilitate the final product separation and improve final product yield. Therefore, selecting aqueous and organic solvents for the biphasic systems is crucial.
- The direct conversion of lignocellulosic biomass into alkyl levulinates involves direct alcoholysis using the combination of Brønsted/Lewis acid catalysts or heterogenous catalysts for efficient conversion.
- Furanic fuels with DCN less than the cetane number of RON 90 fuel (∼23) are suitable for SI engines application, as the fuels are highly knocking resistant. On the other hand, furanic fuels with DCN higher than the minimum required cetane number for diesel fuels according to the standard of the EU (50) and the USA (40) are suitable for diesel engines.
- The furfural production from lignocellulosic biomass could be integrated with the biorefinery of lignocellulosic biomass processing for cost-effective furanic fuels production. The concept of biorefinery integration is a strategy for circular bioeconomy by curbing waste production and converting the wastes into higher-value products.

However, there are challenges to the production of furanic compound derivatives as oxygenated fuel additives from lignocellulosic biomass, which could be summarized as the following:

- The direct conversion from LCB could result in the production of intermediates due to a mixture of hexoses and pentoses in LCB, which leads to the generation of different derivatives, which are HMF- and furfural-based oxygenates, respectively. The generation of intermediates could reduce the yield of the target oxygenate products. Therefore, even though LCB provides cheap feedstock for the production of the oxygenates, the low yield could have a negative impact on the economics of the production. This could be remedied by integrating the production of the oxygenates with the biorefinery development.
- The production of the oxygenates from pentoses only could lead to the production of intermediates which could lower the yield of the oxygenates. Even though some intermediates from the catalytic conversion could also be used as oxygenates, the separation process could be costly. For instance, MTHF could be generated as a by-product from furfural conversion into 2-MF. Therefore, selecting catalyst with high selectivity towards target oxygenates is vital.
- The direct synthesis from LCB requires catalytic conversion, where the use of catalysts with excellent activity and stability, such as noble metal catalysts, is crucial. However, catalysts such as noble metals are expensive.
- There are limited studies on the engine performance of the mixture of the furanic oxygenates (main product and by-products), which could improve the economics of furanic oxygenated fuel additive production due to reduction steps in downstream processing.

CRediT authorship contribution statement

Farah B. Ahmad: Conceptualization, Investigation, Writing – original draft. **M.A. Kalam:** Writing – review & editing, Supervision. **Zhanying Zhang:** Writing – review & editing. **H.H. Masjuki:** Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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