



Review article

Recent progress in production of fuel range liquid hydrocarbons from biomass-derived furanics *via* strategic catalytic routes



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ABSTRACT

Lignocellulosic biomass (LC) has gained a substantial interest in replacement of the existing primary transportation fuels. This review basically emphasizes the recent progress in upgradation of biomass-derived furan compounds into traditional fuel grade liquid hydrocarbons. The article starts with a brief introduction about the existing commercial technologies for the production of furanics from LC-biomass followed by envisaging the state of furan platform in manufacturing of several possible expedient fuel and commodity chemical-precursors. Subsequently, the review switches to recent advancements in the catalytic upgradation of 5-hydroxymethyl furfural (HMF) and furfural to diesel and jet fuel range alkanes. After that, the key challenges associated in the commercial production of furanic-fuels have been addressed to some extent. Overall, this piece of survey attempts to focus the advances in the catalytic routes to fuel precursor alkanes from biomass/carbohydrate derived furans.

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1. Introduction

These days, creating energy security without eco-conflicts is one of the crucial aspects due to the exhausting fossil fuel reserves, skyrocketing prices of primary fuels and also spate in eco-pollution. The incessant supply of liquid hydrocarbon fuels has become a prime episode as the transportation sector is the largest sole consumer of crude oil [1]. In the year 2010, United States (US) refined a total of 7 billion barrels of petroleum fuel to meet the gasoline, diesel and jet fuel demands [2]. All these alarms have steered the world towards the development of biomass based transportation energy systems as alternatives by considering their aptitude in low greenhouse gas discharges. Consequently,

extensive research efforts are going on throughout the globe to efficiently convert the profusely available lignocellulosic biomass into a range of liquid transportation fuels [3–5]. An advisory committee of US department of energy (DOE) has forecasted that ~20% of liquid green fuels will be produced from lignocellulose by 2030 [6]. In the face of significant research taking place on the conversion of lignocellulosic residues into 2G fuels such as bioethanol (energy density 6.1 kW h L⁻¹) [7] and butanol, the available infrastructure for LC-conversion requires time to make it economically and technically practicable.

The high content of oxygenated groups in carbohydrates could facilitate them to involve in numerous chemical reactions for the production of valuable chemical entities, however, such condition is deleterious to convert them into liquid fuels [9–14]. Direct production of fuel grade liquid alkanes from LC-biomass has profound opportunity to meet with the future transportation hydrocarbon

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Nomenclature

HMF	hydroxy methyl furfural
FA	furfural
LC	lignocellulose
LA	levulinic acid
HDO	hydrodeoxygenation
EMF	ethoxy methyl furfural

MPs	melting points
MIK	methyl isobutyl ketone
THF	tetra hydro furan
GVL	γ -valarolactone
2-MTHF	2-methyl tetra hydro furan

fuel supplies [8]. The C₅ and C₆ sugars of holocellulose can be exploited for the production of various fuel chemical intermediates by converting them into platform chemicals including furfural (FA), 5-hydroxy methyl furfural (HMF), levulinic acid (LA), acetic acid etc. [15,16]. Ample research and review reports are available on the production of biomass-derived furan compounds [17–19]. However, limited literature addressed the sustainable upgradation of these platform entities into hydrocarbon jet fuels and possible additives for gasoline and diesel fuels [20–22].

The current contribution is an account of recent advances and results in the field of transportation fuels/liquid alkanes synthesis from biomass-derived furans through catalytic processes, emphasizing the optimal conditions to achieve better yields and key challenges in terms of commercial and technical aspects.

2. Furanics-platform

From last few decades, the spark-engine vehicles have been running on gasoline fuel, however in more recent times the fuel experts have proposed special biomass-based fuels to replace such

traditional fuels [22]. Furan compounds are identified as an excellent fuel additives and starter entities for the production of numerous commodity chemicals. The structural and chemical intricacy of lignocellulose complex demonstrates that a combinatorial treatment processes may be required to enhance the yields of furanic products from the desired biomass. The structure of lignocellulose involves two different carbohydrate polymers namely cellulose (40–45%), made up of β -D-glucose units, and hemicellulose (25–35%) containing xylose, glucose, arabinose, mannose and galactose [23,24]. These polymeric carbohydrates are protected by lignin (15–20%) sheath. In general, furanics are readily formed by the acid-catalytic triple dehydration of C₅ and C₆ sugars that are obtained by the hydrolysis of hemicellulosic and cellulosic components of LC-biomass, respectively [23]. The heterocyclic oxygenate compounds (furan) produced from hydrodeoxygenation (HDO) of monomeric sugars are compatible for gasoline blending. Among these compounds, HMF and furfural represent a potential carbon-neutral feedstock for the production of diesel and jet fuel range liquid hydrocarbons [25–33]. The energy density of ethoxy methyl furfural (EMF), a furfural derivative, is

Table 1
Comparison of physical and chemical properties of furanic fuels with traditional fuels and biofuel (ethanol) [34–39].

Property	Diesel	Gasoline	Jet A-1	(Bio) Ethanol ^a	Furan based fuels					n-Alkane blends		
					MTHF	DMF	MF	GVL	EL	Octane	Tridecane	Pentadecane
Formula	–	–	–	C ₂ H ₅ OH	C ₅ H ₁₀ O	C ₆ H ₈ O	C ₅ H ₆ O	C ₅ H ₈ O ₂	C ₅ H ₁₀ O	C ₈ H ₁₈	C ₁₃ H ₂₈	C ₁₅ H ₃₂
Molecular weight	–	–	–	46.06	86.13	73.09	82.1	100.1	86.13	114.2	184.3	212.4
Cetane number/Octane number	42–50	90–100	–	10	23	23	24	25	5	64	90	96
Net heat of combustion (MJ L ⁻¹)	35.8	30–33	34.7	–	28.2	30.1	27.6	26.2	28.2	33.5	35	38
Net heat of combustion (MJ kg ⁻¹)	43.1	41–44	43.5	29.7	32.8	33.8	31.2	24.2	32.8	44	46	49
Latent heat of vaporization (kJ kg ⁻¹)	230	352	330	846	375.3	330.5	358.4	543.9	375.3	298	508	543
Lower flammability limit (%)	–	1.4	0.6	3.3	1.5	–	1.9	–	1.5	1.0	0.6	–
Upper flammability limit (%)	–	7.6	4.6	19	8.9	–	14	–	8.9	7.0	4.7	–
Auto ignition temperature (°C)	316	257	246	363	–	–	–	–	–	206	202	207
Flash point closed cup (°C)	75	43	37	13	270	286	450	96	270	13	79	132
Vapor pressure at 20 °C (kPa)	–	50–100	21	5.95	13.6	–	18.5	–	13.6	1.47	0.081	4.57
Reid vapor pressure (kPa)	<0.1	54–103	6.5–7	2.3	–	13.4	18.5	–	–	–	–	–
Boiling point (°C)	180–360	27–225	176–287	78	78	94	64.7	218–220	78	125	235	270
Melting point (°C)	–	–40	–48	2.3	–136	–63	–91	–12.5	–136	–56	–55	10
Viscosity 20 °C (cSt)	1.3–3.6	0.37–0.44	0.25	78	1.52	–	–	–	1.52	–	–	–
Specific gravity (20 °C)	0.84–0.87	0.69–0.79	0.77–0.83	–114	0.855	0.888	0.913	1.0794	0.855	0.7	0.76	0.77
Water solubility in compound (% v/v at 20 °C)	0.05	Neg ^b	Neg ^b	60	5.1	–	–	Misc ^c	5.1	Neg ^b	Neg ^b	Neg ^b
Compound solubility in water (% v/v at 20 °C)	0.05	Neg ^b	Neg ^b	Misc ^c	12.1	0.26	0.3	Misc ^c	12.1	Neg ^b	Neg ^b	Neg ^b
Density (kg/m ³)	845–870	850	775–840	790	–	900	–	1.05 (g/cm ³)	–	703	750	760
<i>Exhaust characteristics</i>												
Aromatics (%)	–	11 (PAC)	25	–	–	–	–	–	–	–	–	–
SO ₂ (normalized)	1.0	7.1	–	–	–	–	0.83	–	–	–	–	–
NO _x (ppm)	160	1.72	–	–21.9 ^b	–	–	162	–	–	–	–	–
Total particulate matter = Soot (mg/Nm ³)	6.1	–	–	–	–	–	5.1	–	–	–	–	–
CO ₂ (%)	2.4	3.8	–	14.9 ^b	–	–	2.5	–	–	–	–	–
O ₂ (%)	17.8	15.1	–	0.26 ^b	–	–	17.7	–	–	–	–	–

Note: MTHF, 2-Methyltetra hydrofuran; DMF, Dimethyl furan; MF, 2-Methylfuran; GVL, γ -Valarolactone; EL, Ethyl levulinate.

^a The values furnished are for E15-gasoline (15%v/v of ethanol blend).

^b Neg – Negligible.

^c Misc – Miscible.

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