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Review Article

Sustainable aviation fuels from biomass and biowaste via bio- and chemo-catalytic conversion: Catalysis, process challenges, and opportunities

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Abstract

Sustainable aviation fuel (SAF) production from biomass and biowaste streams is an attractive option for decarbonizing the aviation sector, one of the most-difficult-to-electrify transportation sectors. Despite ongoing commercialization efforts using ASTM-certified pathways (e.g., lipid conversion, Fischer-Tropsch synthesis), production capacities are still inadequate due to limited feedstock supply and high production costs. New conversion technologies that utilize lignocellulosic feedstocks are needed to meet these challenges and satisfy the rapidly growing market. Combining bio- and chemo-catalytic approaches can leverage advantages from both methods, i.e., high product selectivity via biological conversion, and the capability to build C-C chains more efficiently via chemical catalysis. Herein, conversion routes, catalysis, and processes for such pathways are discussed, while key challenges and meaningful R&D opportunities are identified to guide future research activities in the space. Bio- and chemo-catalytic conversion primarily utilize the carbohydrate fraction of lignocellulose, leaving lignin as a waste product. This makes lignin conversion to SAF critical in order to utilize whole biomass, thereby lowering overall production costs while maximizing carbon efficiencies. Thus, lignin valorization strategies are also reviewed herein with vital research areas identified, such as facile lignin depolymerization approaches, highly integrated conversion systems, novel process configurations, and catalysts for the selective cleavage of aryl C-O

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J. Zhang et al. / Green Energy & Environment xxx (xxxx) xxx

bonds. The potential efficiency improvements available via integrated conversion steps, such as combined biological and chemo-catalytic routes, along with the use of different parallel pathways, are identified as key to producing all components of a cost-effective, 100% SAF. © 2024 Institute of Process Engineering, Chinese Academy of Sciences. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co., Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

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1. Introduction and background

A global push toward a carbon-neutral economy is inevitable due to rapidly accelerating climate change. Among these efforts, the aviation industry has committed to reducing its carbon footprint, as it alone generates ~13% of transportation greenhouse gas (GHG) emissions [1], with limited available electrification options due to energy density challenges associated with battery technology. Furthermore, aviation emissions are expected to grow to approximately 1.8 billion tonnes of CO₂ annually by 2050, almost doubling those during 2019 [2]. Therefore, in order to meet current commitments from the industry to achieve net-zero carbon emissions in 2050 requires ~8.2 billion tonnes of CO₂ reduction in total [2], posing a grand challenge to aviation.

It is difficult to decarbonize the aviation sector via electrification as is being done for light-duty transportation. New electric aircraft may help to alleviate emissions associated with short-range flights, however, the use of batteries in longhaul cargo and large passenger aircraft is currently infeasible due to energy density limitations (e.g., lithium-ion batteries in modern electric vehicles enable energy densities of 0.72 MJ/ kg vs. jet fuel possessing 43 MJ/kg) as well as poor battery performance at low temperatures (like those found in the upper atmosphere) [3]. As a result, the aviation industry has started implementing strategies targeting technology development in aircrafts, improvement in operations and infrastructure, as well as increasing the production and uptake of sustainable aviation fuels (SAFs) [2]. While continuous advancements in aircraft and engine technology, coupled with flight and ground logistics optimization, can aid in decarbonization, they alone fall short of meeting CO₂ emission reduction targets. SAFs from renewable, carbon-based feedstocks (e.g., biomass and biowastes) are the only near-term solution for the global aviation industry. More than 100 billion liters of annual SAF production are needed globally to meet these targets [2,4], however, SAF production is currently less than 0.1% of this globally [4]. This vast supply-demand gap creates significant opportunities for SAF research and development (R&D), demonstration, and commercialization.

Bio-feedstock diversity requires the development of various conversion technologies to meet the SAF grand challenge. Seven pathways have been thus far certified by ASTM D7566 [5], namely, gasification and Fischer–Tropsch (FT) synthesis, hydroprocessed esters and fatty acids (HEFA), synthesized isoparaffin (SIP), Fischer–Tropsch synthetic paraffinic kerosene with aromatics (FT-SPK/A), alcohol-to-jet (ATJ), catalytic

hydrothermolysis (CH), and hydroprocessed hydrocarbons hydroprocessed esters and fatty acids (HH-SPK or HC-HEFA). These pathways can be categorized into four technology groups based on which feedstocks are utilized, i.e., gas-based, alcoholbased, lipid-based, and sugar-based technologies.

Within these technologies, commercial SAF production currently relies on waste oil conversion with processes such as HEFA [6]. Unfortunately, given the limited availability of the waste oils, current planned and ongoing biorefinery construction projects are aiming to expand to utilizing other ASTM-certified pathways, such as FT and ATJ [6]. Despite these efforts, the near-term predicted production capacity is still limited [6]. Further conversion technologies are required to increase production to meet the rapidly growing market. Additionally, current SAF production costs are generally at least two or three times higher than those for petroleum-based jet fuel [4,7]. Thus, significant R&D efforts are needed to create a variety of new economically viable and environmentally friendly technologies available for converting diversified feedstocks to meet the large SAF market demand.

Several recent reviews on SAFs have primarily focused on ASTM-certified pathways [7–12], as well as the progress [13–15] and challenges [16,17] associated with lipids, waste fats [18], and oilseeds [19–22], and their upgrading [23] to SAF or other compounds [24,25]. Likewise, conventional ATJ (dehydration-oligomerization-hydrogenation) and gasification-FT synthesis have been reviewed by Okolie et al. [26].

These certified pathways are not the focus of our review. Instead, we aim to discuss alternative conversion pathways that have the potential to expand feedstock sources/supplies, improve production volumes, lower production costs, and meet the challenges associated with biomass collection. This review focuses on the hybrid bio- and chemo-catalytic conversion of the carbohydrate fraction of lignocellulose, as well as the valorization of waste lignin, to produce SAF. The state of technology, i.e., existing challenges and R&D opportunities associated with the discussed pathways, will be identified to guide future research.

2. Types of jet fuel and their properties

2.1. Aviation turbine fuel specifications

Aviation turbine fuel specifications vary based on geographic location and application (e.g., civilian or military). Civilian aviation fuels typically follow Jet A (USA), Jet A-1 (Canada and Europe), DEF STAN 91-91 (UK), TS-1 (Russia),

or RP-3/No. 3 (China) specifications [27]. Jet A and Jet A-1 specifications are maintained by ASTM International via the ASTM D1655 specification. The predominant difference between Jet A and Jet A-1 is the freezing point, which is required to be no greater than -40 and -47 °C, respectively [28]. The most notable variation between the other specifications is the flash point allowance of TS-1 fuels, which are allowed to be as low as 28 °C vs. 38 °C in the case of Jet A, Jet A-1, and DEF STAN 91-91 [29]. The combination of the strictest of these specifications is the Aviation Fuel Quality Requirements for Jointly Operated Systems, which is a combination of Jet A-1 and DEF STAN 91-91.

Current turbine fuel specifications ensure that fuels are dropin. Drop-in fuels are vertically compatible with existing infrastructure, aircrafts, and engines. Fuels that meet these specifications are ensured to be acutely safe. Some examples of acute safety concerns include the ability of a fuel to remain a liquid at operating conditions as well as not coke/degrade rapidly in an aircraft fuel system. Perhaps the most complex of these acute safety issues is the operability limits of a fuel. Engines and fuels need to operate at both cold and sub-atmospheric conditions. Categorically, the three most critical operability events for fuel evaluation are cold start, lean blowout, and altitude reignition [30]. Cold start refers to the event that an aircraft is 'cold soaked' on a runway and must start the auxiliary power unit and main engines [31]. Meanwhile, lean blowout refers to conditions under which fuel ceases to convert chemical energy to thermal energy in the combustor due to low fuel to air ratios [32]. Finally, the most critical event is altitude re-ignition. Here, an engine needs to be relit at altitude, where conditions are likely very cold along with low ambient pressures.

Alternative jet fuels, such as SAF for civilian aviation, follow more stringent specifications and qualification processes than conventional fuels. SAF is not yet approved at 100% synthetic compositions, with the exception of an approved Sasol fuel under DEF STAN 91-091 [33,34]. Instead, alternatives are approved as blend components to be mixed with a qualified ASTM D1655 fuels. Qualified alternative blend components are described in either DEF STAN 91-091, ASTM D7566, or, in the case of coprocessing technologies, in ASTM D1655. Most currently approved routes fall under ASTM D7566 [35]. Approved blend components in ASTM D7566 have an associated Annex that describes blend limits, acceptable feedstocks, processing technologies, and additional specifications relevant to that annex [35]. For an alternative fuel blend component to reach an aircraft, it needs to first meet the respective ASTM D7566 annex. The component then, once blended with a conventional fuel, must meet ASTM D1655 specifications. Coprocessing is allowed in ASTM D1655 Annex A1 with mono-, di-, and triglycerides, free fatty acids, and fatty acid esters at coprocessing blend limits of $\leq 5\%$ v [28].

2.2. Chemical composition and physical properties of conventional aviation fuel

Conventional aviation turbine fuels can be composed of innumerable chemical species of yet-to-be-determined

isomeric compositions. However, qualified conventional fuels must meet three categorical criteria related to composition, properties, and feedstock source. ASTM D1655 specifies that a qualified fuel is "derived from conventional sources" with conventional sources defined there-in [28]. The remaining portion of ASTM D1655 scopes qualified compositions and properties [28]. These scoped properties and compositions are the result of decades of experience, focused on incremental improvements to properties and compositions critical for the evolution of the industry.

Conventional fuels are primarily constrained by their respective distillation temperatures and volatilities. The maximum distillation temperature requirements for both Jet A and Jet A-1 are a T_{10} and T_{90} of 205 and 300 °C, respectively [36]. Meanwhile, the maximum allowable volatility is defined as a flash point of 38 °C. Beyond distillation temperatures and volatility requirements, aviation turbine fuels are subject to additional bulk property limits. Properties like density, viscosity, heat of combustion, and freeze point ensure the safe operation of an aircraft [37].

The compositional variations of conventional fuels are substantial. For example, some fuels are reported to contain as low as 4–8 wt% aromatics and as high as 60% cycloalkanes [38]. Upper limits on composition are especially important for certain fractions such as n-alkanes, which have high freeze points relative to their carbon numbers, and aromatics, which are limited to lower concentrations due to their elevated energy densities as well as pollution concerns [39]. The upper bound for other hydrocarbon types is less clear as high concentrations of iso- and cyclo-alkanes in conventional fuels are not associated with known deleterious performance effects.

Trace compounds (or lack thereof) are also critical to turbine aviation fuels. Alkenes and heteroatoms, for example, are associated with deleterious behavior such as coking and thermal instability [40]. These substances react and form products that can accumulate in fuel channels and valves. The accumulation of these products eventually leads to required engine maintenance. Additionally, heteroatoms can cause issues related to freeze point, material compatibility, and heat of combustion [41,42]. As a result, turbine aviation fuels generally need to be devoid of these contaminants.

2.3. Qualification and evaluation of hydrocarbons from alternative sources

Conventional fuel feedstock use, traditional fuel processing methodologies, and adherence to aviation turbine specifications sufficiently restrict available fuels for most commercial applications. Deviation from any one of these three constraints implies a potential for deleterious effects. For this reason, the process of approving an alternative fuel blendstock via an ASTM D7566 annex is highly stringent. The formal evaluation process for alternative fuels currently follows ASTM D4054, which will be described in greater detail in subsequent paragraphs [43]. This evaluation process requires significant amount of neat, unblended product (there have been several notable exceptions to this requirement, such as the approval of ASTM D7566 Annex

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A5 [ethanol-to-jet] and A7, which was evaluated using Fast Track [and subsequently approved at $\leq 10\%$ v]) [44].

These testing volume requirements for ASTM D4054 are relatively high for many nascent fuel production technologies. As a result, an additional pre-ASTM evaluation process has been developed. This process is often referred to as prescreening and is described in more detail elsewhere [45,46]. Prescreening is not a requisite for qualification as an ASTM D7566 pathway, but notionally, the process consists of a tiered α and β evaluation targeting potential deleterious operability effects. This is important as full evaluation of these effects is the most expensive stage of the ASTM D4054 evaluation process. Tier α evaluates the candidate fuel's chemical composition (by multidimensional gas chromatography) and distillation temperatures (ASTM D2887) [47]. Leveraging the gas chromatography data, the candidate's key operability properties can be predicted with less than 1 mL of fuel [48]. These measurements and predictions can be compared to both ASTM specification limits and properties of known conventional fuels of varying quality. When larger fuel volumes are available, these key operability properties are tested with scaled ASTM methods under a more rigorous Tier β evaluation process. The experimental data from Tier β , like the predictions in Tier α , are compared against conventional fuels and relevant specifications [44].

Beyond prescreening, the formal evaluation process for an alternative fuel is rigorous and comprehensive, ensured using a diverse body of stakeholders who formally ballot and critique candidates. There are currently two paths for a candidate to become an ASTM D7566 annex. Either a candidate undergoes the traditional Tier 1–4, 2-Phase process or a modified Fast Track process (Tier 1–2, 1-Phase) [46]. A schematic of the 4-Tier evaluation process is provided in Fig. 1. Meanwhile, the Fast Track evaluation process is composed of only Tiers 1 and 2, a Phase 1 research report, and an original equipment manufacturers (OEM) review. These results are sent to the Federal Aviation Administration for subsequent review [46]. Fast Track approved fuels are limited to blends of $\leq 10\%$ v with a certified ASTM D1655 fuel [28,44].

Tiers 1 and 2 of ASTM D4054 focus on the specification and fit-for-purpose behavior of a candidate pathway. These test results compare with the requirements laid forth in ASTM D7566, which are more rigorous than those of ASTM D1655 [28,35]. Tiers 3 and 4, following the recommendations from the OEM's responses to the Phase 1 research report, involve rig component and full-scale aircraft tests to evaluate any potential operability concerns noted. These Tier 3 and 4 tests can consume significant volumes of fuel (> 40,000 L) and involve high fuel generation costs beyond the capital expenditures associated with scale-up [45]. The motivation for these tests is to de-risk the candidate fuel if approved as an ASTM D7566 fuel.

3. Conversion pathways and the state of technology

3.1. Overview of biomass conversion

Biomass is primarily composed of cellulose, hemicellulose, lignin, extractives/volatiles, and ash [49]. These components

vary significantly in both content and composition among various biomass feedstocks [49,50]. For example, lignin content in herbaceous biomasses such as miscanthus is 9–13%, while woody biomasses have much higher lignin contents, e.g., 28% for pine [50]. Even for the same feedstock type, composition can vary significantly depending on plant genotype, growing conditions, harvesting time, collection techniques, and transport/storage conditions [49]. These large variances among feedstocks warrant matching conversion technologies for specific feedstocks to maximize both process yield and energy efficiency.

Generally, biomass conversion processes first utilize fractionation/deconstruction technologies to generate intermediates (e.g., sugars, lignin, syngas, or bio-oil), which can be subsequently upgraded, either biologically or thermocatalytically, to synthesize jet-range hydrocarbons (Fig. 2). Based on the conversion technology and feedstock, conversion pathways can be categorized into the following groups: hybrid bio-/chemo-catalytic, lignin valorization, sugar aqueous phase processing, thermochemical conversion, and lipid upgrading. Lipid upgrading, thermochemical conversion, and sugar aqueous phase processing have been discussed in previous reviews, and are therefore not presented here [13–15].

A hybrid bio-/chemo-catalytic pathway functions by integrating biomass pretreatment, hydrolysis, biological upgrading, and thermocatalytic conversion to maximize process yields toward jet-range hydrocarbons. The upstream pretreatment, hydrolysis and biological conversion are only briefly discussed herein, with the majority of the discussion being centered around the catalytic upgrading of generated intermediates including alcohols, diols, C=O containing compounds, and terpenes. Lignin valorization is also discussed, with a focus on biomass fractionation, lignin depolymerization, and hydrodeoxygenation (HDO) of lignin-derived bio-oils.

3.2. Hybrid bio-/chemo-catalytic pathways

3.2.1. Alcohol-to-jet pathways

Alcohols are important platform molecules for producing large quantities of SAF due to their commercial availability and established infrastructure, as well as emerging opportunities in alcohol synthesis from industrial waste gases. The major biomass-derived alcohol on the market today is ethanol. In 2019, US annual fuel ethanol production reached >15 billion gallons with corn starch as the primary feedstock (93.5% of total production) [51]. Aside from ASTM-certified ethanol and butanols, herein we broadened ATJ to include the conversion of diols to SAF. To do so, we use the conversion of 2,3-butanediol (2,3-BDO) to SAF as an example to demonstrate potential opportunities in this space.

The certified ATJ pathway under D7566 Annex A5 uses ethanol or isobutanol as feedstocks. The conversion process includes the initial dehydration of ethanol or isobutanol, followed by olefin oligomerization, hydrotreating, and fractionation. Such ATJ processes have been reviewed by Xie et al. [52], and are therefore not discussed herein. On the other hand, direct synthesis of butene-rich olefins from ethanol, Guerbet



Fig. 1. The nominal ASTM D4054 evaluation process for fuels above 10%v blend limits with approximate fuel and cost requirements (excluding fuel production) [43].



Fig. 2. Overview of biomass conversion to SAF. HDO: hydrodeoxygenation; HMF: 5-hydroxymethylfurfural; LA: levulinic acid; CH: catalytic hydrothermolysis. This review focuses on routes represented in red letters.

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J. Zhang et al. / Green Energy & Environment xxx (xxxx) xxx

coupling, alcohol conversion to aromatic hydrocarbons, and direct conversion of diols to olefins represent alternative routes to generate intermediates that can also be upgraded to SAF. A renewable hydrogen source is needed to have a low carbon intensity score for the overall process for these routes except for the ethanol to aromatic. Fig. 3 maps out various potential alcohol-based pathways for SAF production.

3.2.1.1. Ethanol conversion to C_{3+} olefins (ETO). There are four major ETO pathways: an ethylene-based pathway over Brønsted acid zeolites, an acetone-based route over metal oxides, a butadiene-based pathway over transition metal modified oxides or Lewis acid zeolite/hydrogenation catalyst composites, and a butyraldehyde intermediate-based pathway over Lewis acid zeolites. The key process steps and intermediates for these pathways are summarized in Fig. 4.

Conventional Brønsted acid zeolites (e.g., H-ZSM-5) or modified H-ZSM-5 catalysts (e.g., P-modified H-ZSM-5) can convert ethanol to ethylene via dehydration, which can be subsequently oligomerized and cracked to form C_{3+} olefins [53]. In general, both propene and butenes are generated with propene as the major olefin product. Significant aromatics and light paraffins are also typically formed due to the presence of strong Brønsted acid sites and zeolite shape selectivity, restricting C_{3+} olefin yields to <50% [54,55]. The second ETO route is based on ethanol conversion to propene and/or isobutene over metal oxide catalysts with unique acid-base properties (e.g., $Zn_xZr_yO_z$ [56] and Y/ZrO₂). In these systems, ethanol is first dehydrogenated to form acetaldehyde, followed by oxidation, ketonization to acetone, and conversion to either propene or isobutene. Zn_xZr_yO_z primarily forms isobutene while other oxide materials (e.g., Y/ZrO₂, Nb/CeO₂) [57] produce propene. Significant CO₂ formation also results due to C-C bond cleavage during acetone formation and its

subsequent conversion to isobutene, limiting the maximum theoretical C₃₊ olefin yield to 69% assuming complete conversion to isobutene from ethanol. Another possible route for generating olefins from ethanol is based on a butadiene intermediate, where the reaction proceeds via dehydrogenation, Meerwein-Ponndorf-Verley aldol condensation, (MPV) reduction, dehydration to butadiene, and hydrogenation to 1and 2-butenes. For example, a Ag/ZrO₂/SiO₂ catalyst has been reported to generate ~69% selectivity toward C_{3+} olefins along with a ~19% ethylene selectivity at near complete ethanol conversion, in the presence of hydrogen, at 673 K [58]. A composite catalyst of Zn-Y/Beta and single-atom alloy Pt- Cu/Al_2O_3 was also able to selectively produce butene-rich C_{3+} olefins (78% selectivity at 94% conversion) from ethanol using only in situ-generated hydrogen [59]. Finally, the butyraldehyde-based pathway follows similar initial reaction steps as the butadiene-mediated pathway (dehydrogenation followed by aldol condensation). However, crotonaldehyde is instead hydrogenated to butyraldehyde rather than proceeding through crotyl alcohol. It has been reported that a Cu-Zn-Y/Beta catalyst is capable of selectively converting ethanol to butenerich C3+ olefins (88% selectivity) at 100% ethanol conversion [60].

3.2.1.2. The Guerbet reaction. Another important C–C bond formation pathway for alcohol upgrading is the Guerbet reaction. This topic has been reviewed in detail elsewhere [52]. Thus, here we will only briefly mention the relevant catalysts and their reaction performance. This reaction primarily occurs over basic metal oxides [61], metal phosphates [62], oxide supported transition metals [63,64], and basic zeolites [63]. It generally occurs through either an aldehyde-mediated condensation pathway or a direct condensation between alcohols. Via this pathway, ethanol can be converted to butanol,



Fig. 3. Alcohol conversion pathways to jet-fuel-range hydrocarbons.

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J. Zhang et al. / Green Energy & Environment xxx (xxxx) xxx



Fig. 4. Four pathways for ethanol conversion to C₃₊ olefins.

which can undergo further condensation to form heavier alcohols. Unfortunately, competition with side reactions (e.g., dehydration) prevents a high yield of targeted alcohols via this methodology [63]. Generally, 1-butanol selectivities as high as 70-80% can be achieved when ethanol conversion is controlled below 25% on metal-loaded alumina or hydroxyapatites [65,66]. Guerbet reaction rates can be influenced through several variables related to catalyst composition and chosen reaction conditions [63]. Among them, metal doping to tune acid-base site interaction or modify catalyst properties has been shown to have a significant impact on the resulting rates [62]. For instance, Al doped into MgO increases acid site density, thereby facilitating C-C formation and dehydration while suppressing dehydrogenation due to fewer available basic sites. Cu and Ni modified porous metal oxides (PMO) lead to product site time yield of 704.6 $g_{prod}/(kg_{cat} \cdot h)$ [67].

3.2.1.3. Alcohol to aromatics. The direct conversion of alcohols (e.g., ethanol and butanol) to aromatics has been extensively studied over zeolite catalysts (particularly [metal-modified] H-ZSM-5) [55,68,69]. This route combines alcohol dehydration and oligomerization into a single step, leading to a mixture of hydrocarbons containing primarily C₆-C₈ aromatics and C₅-C₁₀ paraffins. To increase middle-distillate-range hydrocarbon yields, further alkylation of the generated aromatics would likely be required. Vertimass has demonstrated this process for ethanol conversion over Ga or V modified H-ZSM-5 catalysts, obtaining ~80% liquid C₅₊ hydrocarbon yields [54]. Due to one-step operation and the

capability to directly feed aqueous ethanol (avoiding the need for ethanol dehydration), such a process offers a costcompetitive alternative for producing aromatic-type components for use in aviation fuel.

3.2.1.4. Oligomerization of ethylene and C_{3+} olefins. The oligomerization of ethylene has been studied for several decades using both homogeneous and heterogeneous catalysts. Homogeneous catalysts have long been used to oligomerize ethylene to longer-chain linear alpha olefins, however, due to the difficulty and high cost of separating and reusing these catalysts, they are not seen as cost-effective for producing hydrocarbon fuels. Therefore, the development of heterogeneous catalysts (e.g., [Ni-modified] solid acid catalysts) has been a primary focus for producing fuels from ethylene. Generally, two-step oligomerization is required, including preliminary ethylene oligomerization to butene-rich olefins and subsequent oligomerization of these larger olefins to jetrange hydrocarbons. Ni-modified zeolites, amorphous silica aluminas, and Al-containing mesoporous silicas [70-72] have all been extensively studied for ethylene conversion, which has also been reviewed in detail by Finiels et al. [73] Niexchanged ordered mesoporous silica alumina catalysts (e.g., Ni-Al-MCM-48, Ni-Al-MCM-41) have thus far been reported to have the highest activities for these reactions, producing primarily butenes and hexenes.

Further oligomerization of C_{3+} olefins usually occurs over solid acid catalysts, such as zeolites [74], solid phosphoric acid [75], Al-form ordered mesoporous silica, or polymeric resins

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J. Zhang et al. / Green Energy & Environment xxx (xxxx) xxx

[76]. Some emerging materials such as metal organic frameworks [77] and ionic liquids [78] have also been explored for olefin oligomerization. Among known olefin oligomerization catalysts, zeolites are most commonly used today. Both medium pore zeolites (e.g., ZSM-5, ferrierite, ZSM-22, Theta-1) and large pore zeolites (e.g., Beta, mordenite, offretite) have been explored widely with two well-known industrial oligomerization processes having already been developed (i.e., Mobil's olefins to gasoline and distillate (MOGD) and Lurgi's olefins to diesel) [74]. Over zeolite catalysts, high pressures (> 30 bar) and low temperatures (typically 200-220 °C) are generally preferred to maximize selectivity to middle-distillaterange hydrocarbons, while high temperatures (> $300 \circ C$) favor cracking to generate smaller molecules with a high degree of branching [74]. On the other hand, low pressures (e.g., ambient pressure) and high temperatures (> 350 °C) lead to the generation of short-chain hydrocarbons as well as aromatics. Comparatively, polymeric acid resin catalysts are generally more reactive, which enables higher conversions (e.g., 99% 1butene conversion over Amberlyst 70 vs. 90% over H-ZSM-5) [79] at lower temperatures (e.g., 170 °C vs. 250 °C) while also decreasing cracking activity.

3.2.1.5. 2,3-BDO to SAF. One example of a diol which can be utilized for the generation of SAF-range hydrocarbons is 2,3-BDO. Compared with ethanol, this C_4 molecule can be converted into jet-range hydrocarbons with greater carbon efficiency [80]. Additionally, high value-added chemicals such as 1,3-butadiene, ketones, and epoxides can be generated as coproducts during the upgrading process, thereby offsetting the cost of jet fuel [81-83]. More importantly, 2,3-BDO is less toxic to the microorganisms in the fermentation broth, enabling production at higher concentrations (>100 g/L) [84,85]. Such concentrated broth can significantly reduce the energy input required for distillation and enhance overall energy efficiency. There are two primary routes through which this can occur: 1) the dehydration of 2,3-BDO to methyl ethyl ketone (MEK), followed by MEK self- or cross condensation with other ketones or aldehydes (e.g., furan derivatives), followed by HDO, or 2) the direct conversion of 2,3-BDO to form butenes, followed by olefin oligomerization and hydrotreating.

Using the first method, the dehydration of 2,3-BDO initially produces MEK, isobutanal, and butadiene. The distribution of these compounds depends on both catalyst selection and operating conditions. Solid acid catalysts such as H-ZSM-5 tend to primarily generate MEK, along with a small amount of isobutanol [86]. Meanwhile, Sc_2O_3 coupled with alumina [87] and SiO₂-supported cesium dihydrogen phosphate [88] can instead selectively generate butadiene. MEK can subsequently either go through self-aldol condensation to form a cyclic trimer [89] or be coupled with furan-based aldehydes to produce jet-range hydrocarbons.

In the second pathway, 2,3-BDO is instead directly converted to butene-rich olefins. This has been reported previously over Cu-modified H-ZSM-5 [90,91]. Butene-rich olefins can then be oligomerized to form jet-range hydrocarbons as discussed previously. This pathway has been demonstrated to

achieve high carbon efficiencies toward liquid hydrocarbons using corn stover as a substrate (74-82% of theoretical) [80].

3.2.1.6. Challenges and opportunities. Across all hybrid bio-/ thermo-catalytic conversion pathways there is a need for costcompetitive, low-carbon-intensity alcohols. Minimum fuel selling prices are highly dependent on the cost of these alcohols. Starch derived alcohols (e.g., ethanol) currently have far lower selling prices than cellulosic alcohols [92], however, their carbon intensities are much higher. Thus, in order to produce cost-competitive SAFs with significant GHG reduction potentials via these methodologies, it is essential to develop technologies for making cost-competitive low-carbonintensity alcohols. Moreover, the development of new processes capable of producing value-added coproducts provides another important strategy to reduce the cost of alcoholderived SAF, especially coproducts traditionally produced by petrochemical technologies. For instance, 1,3-butadiene, a crucial petrochemical product for polymer production, has suffered from production decline due to the shift in ethylene production processes from naphtha reforming to shale gas reforming. By incorporating 1,3-butadiene as a value-added product, techno-economic analysis [92] has revealed that the cost of jet fuel derived from the ethanol-to- C_{3+} olefins process can be reduced from \$2.80/GGE to \$1.70/GGE with ethanol produced from corn stover, comparable to conventional jet fuel priced at \$2.00/GGE. Another challenge arises from the inevitable hydrogen consumption during alcohol upgrading. Nearly all alcohol feedstocks undergo hydrogen loss due to deoxygenation, a process that involves dehydration to produce olefin intermediates. Additionally, the jet-range hydrocarbon derived from the oligomerization of olefins requires hydrogenation to produce alkanes. The predominant hydrogen production process, steam methane reforming (SMR), is energyintensive and results in CO₂ emissions. Utilizing conventional hydrogen from SMR would undoubtedly diminish the environmental benefits of SAF. Therefore, seeking renewable hydrogen sources, such as those from electrochemical and photochemical water splitting, is critical for SAF production. However, it is important to note that hydrogen consumption during ethanol to SAF production is relatively low (8-17 kg of hydrogen per ton of fuel).

3.2.2. Short-chain C=O containing-compounds to SAF

Biomass derived C=O containing compounds such as organic acids, esters, aldehydes, and ketones are also useful platform chemicals for producing larger hydrocarbons. Carboxylic acids can be derived from (hemi)cellulosic fractions of lignocellulose as well as other waste organic streams at high yields via anaerobic fermentation [93,94]. This can be done without the need for extensive pretreatment or additional enzymatic hydrolysis [95]. Several *Clostridium* species have been demonstrated to produce butyric acid in high concentrations from lignocellulose, along with acetic acid as a major side product [96,97]. Acetic acid can be produced either via oxidative fermentation of ethanol or direct fermentation of sugars [98]. Sugars, alternatively, can also be fermented to

lactate, a precursor of lactic acid, using *Lactobacillus* strains. Aside from biological generation, hydrothermal treatment of biomass can also generate carboxylic acids. For example, formic acid and acetic acid can be produced under hydrothermal oxidation conditions [99]. Pyrolysis of biomass also results in bio-oils containing a variety of short-chain organic acids including acetic, propionic, butyric, pentanoic, and hexanoic acids [100]. Additionally, levulinic acid is another promising building block molecule that can be derived in high yields from biomass [101]. Beyond carboxylic acids, ketones and aldehydes can also be produced during biomass conversion [102], and are extremely important intermediates for several conversion pathways.

Condensation reactions (e.g., aldol condensation, acetalization, etherification, esterification, and ketonization) are among the most studied approaches for C-C bond formation. This section primarily focuses on the upgrading of short-chain organic acids (C₂-C₆ volatile fatty acids [VFAs]). Particularly, microbial production of acetic and butyric acids is highly promising for generating intermediates that can be upgraded to jet-range hydrocarbons. Fig. 5 shows several potential pathways for upgrading VFA to SAF-range hydrocarbons. Although there are currently no certified processes for converting biomass derived organic acids to SAF blendstocks, C-C formation followed by HDO has been frequently reported in the literature, showing promising results for obtaining SAFrange molecules [103]. Ketonization of organic acids is one such pathway for increasing carbon chain lengths while also improving carbon-oxygen ratios of resulting products. However, it should be noted that this reaction pathway results in the loss of one carbon atom to carbon dioxide formation for each coupling operation. Formed ketones can then be converted to higher hydrocarbons suitable for SAF applications via aldol condensation and subsequent HDO/hydrotreating. Alternatively, organic acids can be upgraded via hydrogenation to alcohols, which in turn can be converted to SAF by methods described previously, thereby improving carbon efficiencies as compared to ketonization.

3.2.2.1. Ketonization of carboxylic acids. Ketonic decarboxylation of organic acids and esters is an important process allowing for C-C coupling of short chain organic acids to larger ketones suitable for conversion to SAF. Catalytic upgrading of organic acids to ketones is typically done over metal oxides and metal oxide mixtures [104]. Glinski et al. [105]. performed a systematic study of acetic, propionic, hexanoic, and heptanoic acid ketonization using 20 different metal oxide materials. All studied catalysts showed some level of ketonization activity with cerium, manganese, cadmium, and lanthanum oxides showing the highest reactivities. Experimental studies coupled with kinetic modeling for the ketonization of carboxylic acid mixtures revealed that formation rates of heavier ketones decrease with increasing chain length [105–107]. Additionally, cross-ketonization tends to be faster than homo-ketonization for carboxylic acids, while both are significantly faster than the direct ketonization of esters [107]. Investigation of acetic acid cross-ketonization with branched carboxylic acids revealed that the reaction proceeds slower than cross-ketonization using linear acids [108].

There has been extensive research focused on gaining a mechanistic understanding of ketonic decarboxylation of organic acids over metal oxides. Two different reaction pathways have been reported to occur depending on the lattice energy and basicity of utilized oxides: bulk and surface ketonization [104]. Bulk ketonization proceeds over oxides with low lattice energy, which strongly interact with organic acids to form surface carboxylate salts which can subsequently decompose to release ketones. This has been probed for acetic acid ketonization over bismuth oxide, where at low reaction temperatures bulk acetic acid concentrations decreased without product generation. Analysis of the catalyst via XRD showed the formation of bismuth (III) acetate, which can generate acetone and carbon dioxide upon decomposition [108]. In contrast, surface ketonization dominates over highlattice-energy oxides, which generate ketene, β -ketoacid, adsorbed carboxylate, acyl carbonium ion, and acid anhydride intermediates. It appears that the presence of an α -hydrogen is essential for the surface ketonization pathway to occur, as it allows for the formation of the above-mentioned species [106,108].



Ketonization of carboxylic acids can also be done over acid zeolites. However, the elucidation of the reaction mechanism

Fig. 5. Catalytic conversion pathways for acetic acid and butyric acid to jet-range hydrocarbons.

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J. Zhang et al. / Green Energy & Environment xxx (xxxx) xxx

and relevant intermediates remains challenging due to the complex nature of secondary reactions that take place in the presence of the strong Brønsted acid sites within zeolite pores. It has been hypothesized that carboxylic acid ketonization in acid zeolites involves formation of surface acyl species rather than carboxylates. Although there is no consensus on the exact reaction mechanism, it has been proposed that adsorbed carboxylic acids form reactive surface acyl intermediates which then react with adjacently adsorbed carboxylic acids, resulting in ketone generation [104]. Ketonic decarboxylation of organic acids over Brønsted acid zeolites has also been shown to be influenced by carbon chain length [104], where ketonization of smaller carboxylic acids yields ketones that favor further C-C coupling. It should also be noted that ketonization over Brønsted acid zeolites also results in the formation of significant quantities of aromatic hydrocarbons via side reactions [109].

Numerous bioderived organic acids have been reported as potential chemical building blocks for producing value-added chemicals and fuels [104,105]. Here, only a few examples of which will be discussed for upgrading to SAF. Organic acids can be categorized into simple acids (e.g., acetic, propionic, pentanoic, etc.) and organic acids containing other oxygencontaining functional groups (e.g., lactic acid). As an example for the upgrading of a simple organic acid, butyric acid ketonization over ZrO₂ has been demonstrated to generate a ~80% yield to 4-heptanone at near complete conversion (708 K and 3.8 h^{-1} WHSV) [93]. Interestingly, long-term durability and regenerability studies confirmed the catalyst can be partially regenerated via coke removal, however the impact of biogenic impurities remains an issue [103]. Another example beyond classical ketonization for the upgrading of simple organic acids is the conversion of acetic acid to isobutene via a multi-step reaction cascade. This included ketonization, aldol condensation, and C-C hydrolytic bond cleavage catalyzed over both a Zn_xZr_yO_z binary metal oxide [110] and a Lewis acidic Y/Beta zeolite [111]. The maximum yields of isobutene at optimized conditions were 50% for $Zn_2Zr_8O_z$ and 60% for Y/Beta. The weak acid-base pair sites of $Zn_xZr_yO_z$ were proposed to be responsible for ketonization and aldol condensation while residual Brønsted acid sites were involved in cracking [110]. In the case of Y/Beta, weak acidic silanol groups were identified to be necessary for both ketonization and mesityl hydrolysis while Lewis acidic Y-sites were required for aldol condensation and mesityl hydrolysis [111]. Beyond simple organic acids, more complex molecules can also be upgraded via ketonization. For example, aqueousphase catalytic upgrading of lactic acid at mild temperatures (523-537 K) has been previously demonstrated over a bifunctional Pt/Nb₂O₅ catalyst [112]. At complete conversion, an organic-rich phase was generated with an overall carbon yield of approximately 50%, primarily consisting of C₄-C₇ ketones (40-62%), acetaldehyde (2-10%), and propanoic acid (as well as its ethyl ester analogues [30%]).

3.2.2.2. Aldol condensation. After ketonization, generated compounds can subsequently undergo aldol condensation to

further increase carbon chain lengths. Aldol condensation consists of two steps: nucleophilic addition and α -substitution. For example, aldehydes and ketones containing an α -hydrogen atom can undergo aldol condensation over base-catalysts via enolate formation followed by addition to an electrophilic carbonyl group. These reactions can occur at a wide range of conditions in the presence of both homogeneous and heterogeneous acid, base, or amphoteric catalysts [98].

Aldol condensations have also been shown to be catalyzed over heterogenous Lewis acidic zeolites. This has been demonstrated to occur over acid-base pair sites within the zeolite framework via a soft enolization and α -hydrogen abstraction [113,114]. It has been suggested that Lewis acidic framework heteroatoms (e.g., Hf, Zr, or Sn) can polarize carbonyl groups and thus increase the acidity of the α hydrogen which can then be abstracted by a weakly basic oxygen atom attached to the heteroatom. This process generates an enolate intermediate coordinated by the Lewis-acid site. Investigation of "open" Lewis-acid sites, where a (metal)-OH group results from partial hydrolyzation of a (metal)-O-Si interlinkage, and "closed" Lewis-acid sites, where the metal atom is completely coordinated with the silica framework, has revealed the both sites are active toward the aldol condensation of butanal, with the former having a ~ 2.5 higher activity than the latter [115].

Microporous Brønsted acids have also been reported to catalyze aldol condensation [116]. Selective titration of Brønsted acid sites with 2,6-di-tert-butyl pyridine showed an inverse linear correlation between aldol condensation rates and cumulative titrant uptake, indicating framework protons to be viable active sites. Mechanistically, aldol condensation of both acetone and acetaldehyde over H-ZSM-5 has been demonstrated to involve enolate formation [117]. Reaction rates were determined to depend on the reactant surface coverage as well as temperature [117]. On a related note, the exploration of propanol condensation over H-MFI zeolites in the absence of molecular hydrogen revealed that there are two competing reaction pathways: intermolecular enolate formation and intramolecular C=C formation (dehydration) [118]. The latter is responsible for the formation of aromatic hydrocarbons, which are primary products under inert conditions. This observation correlates with other reports, such that Brønsted acid zeolites suffer from quick deactivation due to sequential reactions of α , β -unsaturated products over Brønsted acid sites, leading to the formation of strongly surface bound arenes [116].

Acid-base catalysts such as hydrotalcite, metal oxides, and hydroxyapatite (HAP) have also been shown to be effective for aldol condensation. Exploration of the kinetic mechanism for acetaldehyde condensation over anatase titania (TiO₂), HAP, and magnesia (MgO) has thus far implied that these materials share similar C–C coupling steps [119]. It has been reported that enolate formation is not kinetically limiting for these materials, but rather reactant adsorption and product desorption limit reactivity [119]. Investigation of acetaldehyde condensation over various metal oxides revealed that acetaldehyde can molecularly adsorb on two neighboring sites and subsequently react to form crotonaldehyde. Notably, reaction

temperature and catalyst pretreatment conditions have been reported to affect product selectivity [120]. Dumesic et al. have shown these catalysts to be effective for C–C coupling of both C_4 - C_6 ketones and secondary alcohols [121]. Using a CuMg₁₀Al₇O_x catalyst, they achieved as high as 90% conversion of methyl ketones to C_8 - C_{12} species, which can be readily converted to jet-range hydrocarbons via HDO over Pt/ NbOPO₄.

3.2.2.3. Hydrogenation of carboxylic acids to alcohols. Alternatively, carboxylic acid hydrogenation can instead produce alcohols to serve as platform molecules for SAF synthesis. Catalytic hydrogenation of carboxylic acids and esters is challenging as a carbon atom within a carbonyl group is near its highest oxidation state and thus requires a high thermodynamic driving force to enable reactivity. Direct hydrogenation of carboxylic acids and esters to alcohols has been demonstrated over Cu, Rh, Ru, and Re based catalysts, which has been reviewed in detail by Tamura et al. [122] Among noble metals, Ru has the highest activity for the selective hydrogenation of carboxylic acids to alcohols, likely owing to its high oxophilicity [122]. Ni- and Cu-based catalysts are also effective and less expensive than noble metals, but tend to possess lower hydrogenation activities. Another major challenge facing Ni/Cu systems is metal leaching under acidic conditions. To address this, bimetallic systems have been shown to yield more active and stable catalysts for carboxylic acid hydrogenation. Aside from active metals, catalyst supports such as TiO_2 , ZrO_2 , MoO_x and FeO_x can also help to facilitate carboxylic acid hydrogenation by weakening the C= O bond via interaction with oxygen vacancies or Lewis acid centers on the support [122].

3.2.2.4. Challenges and opportunities. Carboxylic acids produced via fermentation are usually present in dilute aqueous solutions, making the separation of carboxylic acids from fermentation broths highly energy intensive. Water-tolerant catalysts that can upgrade aqueous carboxylic acid can minimize water separation and thus reduce energy consumption and cost. Additionally, base catalysts generally used for aldol condensation are very water sensitive. As a result, it is critical to understand catalyst deactivation in water and develop stable catalysts for aldol condensation. Similar to the alcohol-to-jet process, there are opportunities to cut the jet fuel cost by incorporating value-added chemical products during jet fuel production. As mentioned in section 3.2.2.1, the upgrading of acetic acid can generate isobutene as a value-added coproduct.

3.2.3. Upgrading of terpenes

Terpenes are a class of chemicals which are comprised of isoprene units $(C_5H_8)_n$ and can be categorized as monoterpenes (C_{10}) , sesquiterpenes (C_{15}) , or di-terpenes (C_{20}) , all of which can comprise numerous cyclic and acyclic forms [123]. Terpenes can be either extracted from plants or produced via the fermentation of sugars. Terpenes form a class of compounds in plants known as isoprenoids [124]. They are found in most plant taxa but occur at high concentrations in only a small subset (resin ducts in gymnosperms, glandular trichomes in *Mentha*, and oil glands in *Eucalyptus* and *Citrus*). Within a given plant species, terpene composition and concentration can also vary greatly [125], with *Eucalyptus* currently having the largest known set of terpenes synthetase genes [126]. Terpenes can be converted to higher number hydrocarbons suitable for SAF application via a combination of dehydration, oligomerization, and isomerization, depending on the specific compound. Here, the catalytic conversion of terpenes to SAF is only briefly covered. For a more detailed discussion, readers are referred to the review by Lapuerta [127], which discusses the use of heterogeneous catalysis for the upgrading of terpenes.

3.2.3.1. Catalytic conversion of terpenes to SAF. Catalytic upgrading to remove the oxygen and saturate C=C bonds is generally needed for SAF production from terpenes. The high variability in the structure of terpenes requires tailor-made, compound-specific solutions to convert a given compound into viable hydrocarbons for use in SAF, such as iso-alkanes, aromatics, or cycloalkanes. While some terpenes be upgraded in a single hydrogenation step (e.g., limonene or bisabolene), the conversion of other compounds entails additional operations such as dehydration, oligomerization, and isomerization [128]. The preservation of cyclic/strained ring systems is of particular interest due to their potential to imbue resulting SAFs with performance-advantaged properties.

The use of the isoprene-based molecules has long been studied for SAF applications, with farnesane (produced by Amyris and Total via the hydrogenation of farnesene) already having been approved for commercial use at up to 10% blend ratios with Jet-A [129]. The combustion kinetics of farnesane as well as synthesis byproducts *p*-menthane and *p*-cymene have also been studied in detail [130]. Unfortunately, *p*-cymene was shown to increase particulate formation during combustion. However, it can instead be hydrogenated to *p*-menthane, thus eliminating the aromatic ring and improving the resulting combustion behavior of the fuel. *p*-Menthane has also been produced in quantitative yields from 1,8-cineole using a biphasic system [131]. Additionally, both 1,4- and 1,8-cineole can be deoxygenated to *p*-menthane [132].

A variety of other terpenes can also be used for the generation of SAF-range hydrocarbons. For example, a similar suite of products (*p*-cymene, *p*-menthane, limonene, and terpinene) can also be obtained from pinene [133]. Alternatively, pinene has the potential to be dimerized, thereby preserving the ring-strained nature of the molecule while improving the resulting energy density of the generated blendstock. Another high-energy-density, terpene-derived fuel can also be generated via turpentine dimerization, resulting in turpentine dimer fuel (TDF). However, it should be noted that the high viscosity of this compound could limit its potential inclusion in jet fuel [134]. Meanwhile, carophyllene can be isomerized to other multicyclic sesquiterpenes [135], which have been shown to blend well with SPK [136]. The dimerization of myrcene also generates a fuel-range hydrocarbon (camphorane) with higher

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energy density than the parent terpene [137]. Finally, linalool has promise for SAF generation as it can be converted to methylcyclopentadiene, a precursor to RJ-5 fuels.

3.2.3.2. Challenges and opportunities. Reducing feedstock costs remains one of the largest barriers in the way of SAF production from terpenes. Davis et al. [138] report that the use of short rotation annual harvesting of eucalyptus leaves could be economically viable in the southern US. Similar systems are currently used in Australia for essential oil production. Alternatively, genetic improvements may pave the way for plants which can economically produce terpenes for subsequent upgrading. Terpene content, chemical form and concentrations vary greatly among individual genotypes, tissue type, and growing environment. As a result, Mewalal et al. [139] have suggested exploiting the strong genetic control of terpene content and chemistry to create process-advantaged eucalyptus for SAF production. Similarly, Peter [140] indicates there is an opportunity to breed and select for pine with high terpene concentrations.

3.3. Lignin to SAF

Lignin is another promising feedstock for the production of biofuels [50]. As synthesized in nature, lignin is made up of a complex network of C–O and C–C bonds linking multiple aromatic monolignols, including coniferyl alcohol (G unit), sinapyl alcohol (S unit) and *p*-coumaryl alcohol [141]. The utilization of lignin-derived products in jet fuel hinges on

developing effective methods for 1) extracting and depolymerizing lignin into compounds with jet-range carbon numbers and 2) reducing its oxygen content (lignin O/C ~ 0.3 -0.4 vs. jet fuel O/C < 0.03) [142]. The method used to separate lignin from lignocellulose drastically impacts the extractive structure, which in turn dictates the choice of available downstream upgrading routes. For instance, common commercial methods utilized by the pulp and paper industry today to extract lignin result in rapid re-condensation, creating a network of carbon-carbon bonded aromatics (Fig. 6) [143]. As a result, such lignins require methods enabling C-C bond cleavage for efficient depolymerization. Alternatively, "ligninfirst" methods utilize active stabilization approaches to solubilize lignin from native lignocellulosic biomass while avoiding re-condensation reactions [144,145]. This can be done by either catalytically stabilizing reactive intermediates (e.g., reductive catalytic fractionation [146]) or utilizing protection group chemistries [147] to inhibit condensation reactions (e.g., formaldehyde-assisted fractionation [148]). Active stabilization approaches enable lignin depolymerization via the hydrogenolysis of ether bonds to obtain mixtures consisting mainly of monomeric and dimeric species.

After extraction and depolymerization, further processing is required to obtain jet-range hydrocarbons, such as deoxygenation, alkylation, and hydrogenation reactions, dependent on the extracted structure and desired product composition. Fig. 6 shows several potential target compounds generated from lignin that resemble molecules present in jet fuel [36]. Note that renewable aromatics are not currently supplied by



Fig. 6. Overview of lignin structure, along with processes and reactions required to convert biomass into aviation fuels [149,150].

commercial SAF generation processes [9]. In this section, we will primarily discuss catalytic routes toward cleaving the aryl-oxygen bonds present in lignin while briefly introducing catalysts and reaction conditions that result in ring saturation.

3.3.1. Evaluating candidate catalysts/pathways using simple model compounds

One of the critical reactions for converting lignin to jet fuel is the selective cleavage of aryl-oxygen bonds in the form of hydroxy and methoxy groups attached to S- and G-units. This is commonly performed via HDO. For a more in-depth summary of the model compound HDO literature, we refer the readers to other comprehensive reviews on the topic [142,151]. Two catalyst families used to deoxygenate lignin-derived compounds stand out due to their ability to generate either cyclic alkanes or aromatic hydrocarbons using fundamentally different reaction pathways. Specifically, bifunctional systems containing both redox-active metals (e.g., Pt [152], Pd [153], Ru [154], Ni [155]) and Brønsted acid sites (e.g., H₃PO₄ [156], H-ZSM-5 [157], HBEA [153]) operate via a 3-step mechanism in which metal sites first catalyze hydrogenation of the aromatic ring, followed by an acid catalyzed dehydration of the -OH group and successive hydrogenation of the double bond [158–165]. This mechanism, while efficient for HDO, requires ring hydrogenation and cannot produce aromatic hydrocarbons without an additional dehydrogenation/re-aromatization step [166]. Alternatively, some catalysts can directly cleave aryloxygen bonds to produce aromatic compounds, as demonstrated with model compound experiments in both gas and liquid phases over Mo₂C [167], MoO₃ [168], FeMoP [169], Ru/TiO₂ [170], PdFe/C [171], PtCo/C [172], Ni₂P [173], Pd/ Nb₂O₅ [174], CoMo/Al₂O₃ [175], NiMo/SiO₂ [176], CoMoS/ Al₂O₃ [177] and Ni-ReO_x/CeO₂ [178]. Depending on the operating conditions and co-catalysts used, these processes can also produce alkanes via a subsequent hydrogenation step. Thus, when designing a process to produce jet fuel from lignin, choice of both catalyst and reaction conditions are essential for determining product selectivity.

3.3.2. Extending catalyst activity to more realistic models and identifying reaction engineering challenges

While simple models enable performing rigorous kinetic studies necessary to identify active catalysts and map reaction pathways for aryl-O bond cleavage, these compounds do not capture the complexities of lignin, motivating the study of larger and more realistic model compounds. In general, selectivity toward saturated vs. aromatic products during the deoxygenation of simple dimer models largely mirrors that seen in monomers, with bifunctional metal/acid catalysts (e.g., Ni/H-ZSM-5 [179], Ru/HZSM-5 [154]) producing cycloalkanes and others proceeding through direct deoxygenation to produce aromatics (e.g., Ru/Nb₂O₅ [180], Ru/SZ [181]). However, the functional groups present in model dimer systems can greatly influence catalyst activity. Bulut et al. [182] recently demonstrated that by shifting the reagent composition from 0 to 2 methoxy groups, the resulting selectivity of a nanoscale Ru15Ni85 catalyst changed from 91% ring hydrogenated products to 92% aromatic products. Given that adding methoxy groups creates a model more similar to real lignin, these results highlight the importance of testing catalyst systems with realistic models or real lignin feedstocks.

More complex substrates also reveal the reaction engineering challenges present when processing real lignin. Simple monomeric compounds such as phenol [183-185], guaiacol [167,184,186,187], and propylguaiacol [156,188] can be studied using liquid-phase batch reactions in HDO compatible solvents (hexadecane [186], water [156], neat liquid feeds [185]), liquid phase flow reactions [152], or vapor-phase [167,183,184,187] flow reactions. Vapor-phase reactions eliminate the need for an HDO-compatible solvent and allow for rigorous kinetic studies paired with in situ catalyst characterization. However, dimer models are significantly less volatile compared to monomers, requiring high temperatures for vaporization which can lead to chemical degradation. Furthermore, accurate dimer models with many oxygen functional groups are often not fully soluble at room temperature in HDO compatible solvents such as alkanes (e.g., dodecane) or water. As a result, nearly all model dimer HDO studies have been performed using rapidly stirred batch reactions where complete solubility is unnecessary. One flow reaction involving a dimer model was demonstrated for Pd/C in methanol, which could fully solubilize a complex dimeric model, but only hydrogenolysis reactions occurred and minimal HDO was observed [189], similar to a batch-mode dimer study in methanol using a Zn/Pd/C catalyst [190]. The use of oxygenated solvents that fully solubilize lignin dimers limits HDO reactivity for catalysts and risks solvent degradation instead. Despite the associated challenges, these realistic lignin model studies are essential to bridge the gap between model compounds and real lignin.

3.3.3. The conversion of real lignin feedstocks

Starting with raw biomass, there are three fundamental steps that must be taken to produce aviation fuels from lignin – biomass fractionation (separating lignin from polysaccharides), lignin depolymerization (breaking down the lignin polymer into fuel-range molecules), and bio-oil upgrading (mainly deoxygenation to produce hydrocarbons) (Fig. 7). As follows, we will first discuss methods to produce bio-oils through biomass fractionation and subsequent depolymerization. We will then discuss deoxygenation of bio-oils and highlight other "one-pot" methods beginning with extracted lignin and combine the depolymerization and deoxygenation steps, or start with whole biomass and combine all three.

3.3.3.1. Isolation of lignin via biomass fractionation. Processes that perform fractionation, depolymerization, and valorization independently begin with a biomass fractionation technique to obtain an isolated lignin. Minimally modified native lignin, such as milled wood lignin [191] and cellulolytic enzyme lignin [192], can be isolated from lignocellulosic biomass by ball milling followed by dioxane extraction or extended enzymatic hydrolysis (typically for 72 h). However, the yield of lignin extracted under mild conditions is generally lower than those obtained with standard methods [145].

13

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J. Zhang et al. / Green Energy & Environment xxx (xxxx) xxx



Fig. 7. A lignin to aviation fuel valorization chain comprises biomass fractionation, lignin depolymerization, and bio-oil upgrading. The processing strategies also can use combinatorial approaches wherein two steps occur simultaneously in a single process.

Conversely, significantly restructured technical lignin streams can be obtained via traditional pretreatment technologies (e.g., alkali [193] and organosolv [194]), which utilize harsh conditions to achieve high lignin yields but result in re-condensation to form a large network of C–C bonded aromatics. Meanwhile, several other recently developed methods such as deep eutectic solvent [195], ionic liquid [196], cosolvent enhanced lignocellulose fractionation [197], mild organosolv [198], or formaldehyde-assisted fractionation [148], can generate extracted lignin substrates with various degrees of restructuring. The effect of extraction conditions on lignin structure, as well their advantages and challenges in terms of lignin isolation, will not be discussed herein. For a more indepth discussion on the topic, we refer the reader to the following review [199].

3.3.3.2. Production of lignin-derived bio-oils via lignin depolymerization. Starting with an isolated lignin, the subsequent depolymerization step is responsible for breaking lignin macromolecules into smaller liquid fractions termed bio-oils. This process can be accomplished by several biological (e.g., bacterial treatment [200]), physiochemical (e.g., electrochemical [201], photochemical [202]), and thermochemical methods (e.g., solvolysis [203], hydrogenolysis [204], pyrolysis [205], oxidative depolymerization [206], hydrothermal liquefaction [207]) that act to cleave lignin interlinkages (mainly C-O-C bonds, and occasionally C-C bonds [208]). While many of the above techniques can generate bio-oils, some of them show more promise for the generation of aviation fuel than others. For example, ideally, some oxygen should be removed during depolymerization when trying to generate a deoxygenated fuel, making oxidative depolymerization more targeted for chemical synthesis. Meanwhile, hydrothermal liquefaction of lignin in water at either subcritical or supercritical conditions generally produces a lowquality oil with significant char formation [209]. On the other hand, both hydrocracking and lignin pyrolysis have the potential to produce aviation fuels from highly carbon-linked

technical lignin, as these conditions are required to facilitate the necessary C–C bond activation. However, these techniques often result in lower molecular weight products (C_6 - C_9) and require subsequent alkylation to achieve jet-range hydrocarbons [142]. Here we will mainly focus on reductive lignin depolymerization via hydrogenolysis to non-pyrolytic lignin bio-oil.

During hydrogenolysis, pressurized hydrogen facilitates the cleavage of C-O ether bonds in lignin, commonly performed using monometallic catalysts (e.g., Pd [210], Pt [211], Ru [212], Rh [213]) embedded on a support material in the presence of oxygenated solvents (e.g., isopropanol, ethanol, methanol) and pressurized hydrogen. These conditions often result in a combination of hydrogenolysis, hydrogenation, and HDO reactions occurring simultaneously, with direct hydrogenolysis generally favored over ring hydrogenation to obtain aromatic hydrocarbons [199]. However, hydrogen-free catalytic reductive depolymerization of lignin has also been shown utilizing alternative reducing agents (e.g., hydrosilanes) or sourcing hydrogen from the solvent or biomass [214]. Numerous works have derived the hydrogen necessary for lignin hydrogenolysis from alternative sources (e.g., isopropyl alcohol [215,216], ethylene glycol [217], glycerol [217,218], etc.). Furthermore, other works have looked at deriving the requisite hydrogen from biomass derived compounds. For example, Samec et al. have demonstrated the use of hemicellulosic sugars as a hydrogen source for lignin depolymerization [219]. Other works have also demonstrated the use of lignin-derived hydrogen for C-O bond hydrogenolysis, such as that afforded by the reforming of cleaved methoxy species [220,221]. Overall, the use of alternative hydrogen sources for lignin hydrogenolysis is likely to have a positive effect on the overall life cycle assessment for a given process due to the high carbon footprint associated with hydrogen derived from conventional processes such as SMR.

Metal-free hydrogenolysis has also been demonstrated using hydrosilanes and $B(C_6F_5)_3$ as a reductant and Lewis acid catalyst, respectively [222]. In addition, Ford et al. [223]

recently revealed that lignin can be depolymerized in a novel ethanol/isopropanol media without the addition of a catalyst, resulting in comparable monomer yields compared to reactions using precious metal catalysts. State-of-the-art catalytic depolymerization of lignin using various catalyst and solvent systems has been extensively studied and summarized in several critical reviews [199,223–225].

Because hydrogenolysis mainly cleaves C-O bonds, the yields of monomeric products in the resulting bio-oils are limited by the content of C-O-C ether bonds in the lignin substrate [226]. As a result, tuning a process in a cellulosic biorefinery to maximize the ether bond content of lignin feedstocks allows for a more carbon-efficient process [227]. For this reason, native feedstocks are generally favored over their technical counterparts when attempting to valorize lignin [228]. And while it is possible to tune the structure of lignin via genetic modification [211], preventing extensive lignin degradation/condensation typically has a larger impact and is an important consideration when choosing a biomass fractionation method. As mentioned previously, lignin degradation/condensation can be minimized during fractionation by 1) using mild pretreatment conditions, 2) chemical stabilization, and/or 3) removing reactive intermediates via flow-through extraction. The first route 1) is the least energy-intensive, however, the resulting lignin yield is often negatively impacted. Meanwhile, 2) chemical protection strategies utilizing irreversible reactions such as aldol condensation [229] or reversible reactions such as acetalization [148], have been increasingly studied in recent years to protect lignin from severe structural alteration during extraction. These protection strategies have been summarized in several recent reviews and perspectives [144,145,147,230]. Strategy 3) will be discussed later.

3.3.3.3. Combined biomass fractionation and lignin depolymerization. Biomass can also be directly converted to a biooil in a single step, allowing for the elimination of chemical pretreatments. Xia et al. converted raw woody biomass directly into a mixture of liquid alkanes using a multifunctional Pt/NbOPO₄ catalyst in cyclohexane under relatively mild conditions (190 °C, 5 MPa H₂) [231]. The cellulose, hemicellulose, and lignin fractions were converted to hexane, pentane, and alkylcyclohexanes, respectively. Similarly, Liu et al. utilized a catalyst system involving LiTaMoO₆ and Ru/C to directly convert raw lignocellulosic biomass to alkanes (from cellulose) and bio-oils (from lignin) in a one-pot reaction [232]. The obtained bio-oil phases contained primarily monophenols and a small number of C6-C19 hydrocarbons, showing great potential for producing aviation fuel directly from raw biomass via one pot conversion.

In recent years, an emerging lignin-first biorefinery technology known as reductive catalytic fractionation (RCF) has received significant attention due to its ability to combine both biomass fractionation and lignin depolymerization into a single step while minimizing condensation reactions through catalytic stabilization of reactive intermediates [233,234]. RCF typically relies on a polar, protic solvent [235] (optionally including water [236] or acid [237]) to facilitate the selective extraction of lignin fragments from whole biomass as well as a metal catalyst (e.g., Ru [233], Pd [238], Ni [239], Zn-Pd [240], Rh [241], CuPMO [242]) and H₂ (or reducing equivalents from the solvent [239,243] or extracted hemicellulose [216]) to depolymerize and stabilize extracted lignin in situ [244,245]. RCF results in a low molecular weight, lignin-derived bio-oil and a solid, delignified, carbohydrate-rich pulp, which has been demonstrated as a viable feedstock for enzymatic hydrolysis [243] and subsequent fermentation to ethanol [234]. Compared to sequential isolation-depolymerization, where chemical stabilization strategies are necessary to achieve high monomer yields, RCF is capable of directly converting native lignin into its component C_{0} phenolic monomers at near theoretical yields [216,244], thereby demonstrating its potential for the production of aviation fuels. On the other hand, some current challenges associated with RCF include difficult catalyst regeneration, product separation, and solvent utilization. The multidisciplinary nature of RCF and future research opportunities have been summarized in a recent article [246].

3.3.3.4. Upgrading of lignin-derived bio-oils. The main objective of a bio-oil upgrading process is to selectively remove oxygen-functionalities from the mixture. This can be achieved by a variety of processes such as zeolite-catalyzed cracking and/or HDO [247,248]. As discussed earlier, HDO of lignin can occur through two distinct pathways, direct cleavage of aryl C-O bonds or ring hydrogenation followed by acid-catalyzed dehydration. There have been numerous studies using various lignin feedstocks and catalysts utilizing both the indirect (e.g., Pt, Pd, Rh, Ru) [210] and direct pathways (CoMo, MoO₃, Mo₂C) [183,249,250]. The preservation of aromatic functionalities is of particular importance for aviation fuels, as conventional jet fuels contain 8-25% aromatic hydrocarbons by volume. Other examples of catalyst systems with this capability are PdFe/C [171], MoO_x/CNT [251], Ru/ Nb₂O₃ [252], Ru/Al₂O₃-zeolites [253], as well as several nickel-based catalysts [239,249,254-259]. There have also been several HDO studies using bio-oils generated from RCF [260,261]. The integration of RCF and HDO is a potentially promising route for the production of aviation fuels [262]. As an example of the indirect HDO pathway, Leal et al. designed an efficient catalytic system using Ni/Nb₂O₅ for the HDO of an RCF-derived lignin oil and reported obtaining primarily cycloalkanes [263]. On the other hand, Huang et al. produced a bio-oil via a RCF process catalyzed by Ru/SiC and subsequently converted it to jet fuel ranged aromatic hydrocarbons at ambient pressure over a MoO_3 catalyst [264]. For a more elaborate discussion on the effects of catalyst choice on lignin HDO the reader is referred to these dedicated reviews [199,265-267].

Beyond the chosen catalyst system, product distributions can also be heavily affected by the specified reaction temperature, hydrogen pressure, reaction media (e.g., aqueous vs. organic), and reactor configuration (e.g., flow-through vs. batch). Ideally, an HDO process should be performed at mild

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conditions to avoid unnecessary cleavage of aliphatic C–C bonds, which can lead to smaller ($<C_9$) hydrocarbons. Although, in the event harsh conditions are required, transalkylation and coupling reactions that involve the formation of new C–C bonds can be used to increase average hydrocarbon size [188]. However, these processes require additional systems which act to further increase the total cost of a potential upgrading process [268,269]. In addition, the extent of these types of coupling reactions can be difficult to control due to the potential formation of oversized macromolecules unsuitable for use in aviation fuel.

3.3.3.5. Combined depolymerization and upgrading of isolated lignin. Lignin depolymerization and subsequent oil upgrading can also be combined into a single step. For example, Yang et al. successfully obtained jet-range hydrocarbons via a onepot depolymerization/HDO approach using Ru/C-ZnCl₂ [270], Ru-Cu/HY zeolite [271], Ru/Al₂O₃-zeolite Y [253], and Hf(OTf)₄/Ru/Al₂O₃ [272]. Meanwhile, Ford et al. [273-275] reported that a Cu₂O-PMO catalyst can be used to disassemble organosolv lignin, cellulose, and even whole woody biomass while utilizing hydrogen transferred from supercritical methanol at 300 °C. A similar catalyst (e.g., CuMgAlOx) also demonstrated excellent deoxygenation efficiency for bio-oil with low ring-hydrogenation activity in other supercritical systems (e.g., ethanol) [276]. While studies carrying out twostep vs. one-pot conversion of lignin all require similar operating temperatures and pressures, hydrocarbon product yields and properties differ considerably. Two-step conversion processes typically result in higher carbon efficiencies compared to one-pot conversion processes (30-50 wt% vs. 10-30 wt%) [277]. The other advantage of two-step conversion processes is that since aromatics and cycloalkanes can be produced separately at high selectivity via the use of different catalysts and process parameters, they could potentially be post-synthetically blended at different, controllable ratios to achieve desired aviation fuel properties.

3.3.4. The importance of process configuration

Most of the processes discussed above (e.g., biomass fractionation, lignin depolymerization, HDO, etc.) have been conducted in batch. This configuration leads to a major drawback in which the onset of catalyst deactivation (e.g., sintering, poisoning, leaching) typically results in higher concentrations of unsaturated lignin intermediates and, thus an increased likelihood of condensation reactions [146]. These reactions lead to the formation of high molecular weight species that further hinder subsequent upgrading processes. To address these issues, continuous flow-through reactors capable of separating reactive intermediates have been developed for several lignin conversion processes [219,278-280]. In one flow-through extraction/depolymerization study, solubilized lignin fragments were constantly removed from the heating zone during extraction, thereby limiting potential lignin condensation/deposition. During depolymerization, the catalyst showed negligible changes in its textural properties compared to the fresh catalysts, which was attributed to the

continuous removal of heavier components from the reaction system [281]. Furthermore, the potential combination of novel lignin stabilization strategies and flow-through reactor configurations could result in even higher potential monomer yields [282]. For example, Román et al. [146,203] conducted a series of studies for flow-through RCF by conducting the solvolysis and reduction steps in interlinking reactor beds. These developments are vital for the potential scale-up of lignin conversion technologies and their implementation in industrial applications. The latest developments in flowthrough lignin depolymerization have been summarized in a recent review [283].

3.3.5. Challenges and opportunities

Lignin valorization technologies have significant potential for aviation fuel applications. Fig. 8 summarizes some of the potential pathways towards aviation-range hydrocarbons using various lignocellulosic substrates. To fully unlock the potential of these substrates, the following challenges need to be addressed. First, facile lignin depolymerization strategies need to be developed to generate high yields of monomers and dimers from raw biomass while limiting the formation of undesired condensed oligomers. This depends on efficient lignin extraction techniques capable of fully extracting the available lignin from biomass while limiting the structural modification of native lignin structure. Meanwhile, the development of highly integrated systems and novel process configurations capable of combining the extraction, depolymerization, and upgrading steps required for hydrocarbon generation is essential for improving potential process economics. Further studies on potential catalyst candidates capable of stably and directly cleaving aryl C-O bonds to generate aromatic hydrocarbons are also beneficial in order to attain sufficient aviation fuel properties while removing the current need for SAFs to be blended with non-renewables.

4. SAF products, 100% synthetic SAF and technology readiness levels

4.1. Types of SAF products and maximum blending level

Although there is significant interest in developing 100% SAF, all pathways discussed herein result in the generation of blendstocks, where each pathway alone cannot generate a fuel which mimics the distinctive characteristics of conventional aviation fuel. The compositions of each potential blendstock will determine the maximum allowable blending level with petroleum-derived jet fuel.

For conventional ATJ, iso-paraffinic hydrocarbons are generally primary products, with a higher level of branching resulting for isobutanol as compared to ethanol. Comparatively, with ethanol, there are opportunities to produce higher concentrations of n-paraffins. Jet-range aromatics can also be produced via alcohol conversion over Brønsted acid zeolites followed by alkylation to improve carbon numbers. Therefore, more than 70% of conventional aviation fuel can be obtained via the ATJ approach. However, the current maximum allowable

J. Zhang et al. / Green Energy & Environment xxx (xxxx) xxx



Fig. 8. Catalytic conversion of lignin and biomass to aviation fuel [231,232,241,250,252,253,263,264,270-272].

blending level is 50% for ethanol-derived SAFs. Aside from ATJ, sugar fermentation to farnesene followed by hydroprocessing yields farnesane, a blend component with a maximum blend level of 10%. For the other hybrid pathways, such as the upgrading of 2,3-BDO and organic acids, the technologies are still in their infancy. As such, allowable blend limits have yet to be determined. In terms of generable products, recent efforts have demonstrated primarily iso-paraffin production from 2,3-BDO [80], and a mixture of n-paraffins, iso-paraffins, and cycloalkanes from the ketonization, aldol condensation, and HDO of volatile fatty acids [284].

Meanwhile, lignin valorization utilizes the cyclic nature of the polymer to synthesize primarily aromatic and cycloparaffinic fractions for SAF. These fractions are generally produced via the HDO of lignin-derived aromatic monomers and dimers, leading to products with carbon numbers ranging from 6 to 9 and 12–18, respectively. Since petroleum jet contains molecules with carbon numbers between 8 and 16, with the majority falling between C_{10} - C_{13} , additional efforts in further upgrading the HDO fraction (e.g., alkylation) could help to improve yields of "ideal" molecules for use in SAF. Lignin valorization is also still at an early development stage, with yet-to-be-determined maximum blending levels.

4.2. En route to 100% synthetic SAF

Globally, there are numerous efforts striving towards netzero aviation emissions. The European green fuels law for aviation (known as ReFuelEU) mandates that 2% SAF be used in all flights departing from EU airports in 2025, 6% in 2030, and subsequently increasing gradually to 70% by 2050 [285]. Meanwhile, the US SAF Grand Challenge identified the goal of replacing all petroleum jet fuel with SAF (~35 billion gallons per year) by 2050 [286]. Net-zero fuels have been supported by the global aviation industry for some time, with the International Air Transport Association (IATA) developing goals on improving fuel efficiency and reducing CO₂ emissions for over a decade. The aviation industry has also embraced SAF, with numerous takeoff agreements now in place as private industry has responded to this increased market pull. However, to increase SAF content above the current 50% blend limit to 100%. policies and regulations governing these limits will need to be increased. Encouragingly, multiple demonstration flights have been performed using 100% SAF, including both business and commercial airliners [287,288]. However, the majority of current SAF production routes do not confer all the necessary properties for Jet A, thus still requiring blending with conventional fuel. Additional pathways to provide a complete Jet A replacement, which can stand alone as a drop-in substitute for petroleum jet, are still under development. Beyond resembling petroleum jet, moving towards a 100% SAF also provides an interesting opportunity to develop fuels that are both backwards compatible with current infrastructure while at the same time potentially achieving performance-advantaged properties such as the ability to burn cleaner and enable improvement in turbine design for future aircrafts. We believe that a strategy to utilize several of the routes described above to produce different components (i.e., n-alkanes, iso-alkanes, cyclo-alkanes, aromatics) is the most likely near-term pathway to a 100% SAF.

Beyond regulation, production volume must also be significantly increased. At present, the capability to replace all

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jet fuel with SAF does not exist. Current US SAF production stands at 7 million gallons per year, while to achieve the US SAF Grand Challenge, a 650-fold increase in output is needed. This will be a monumental challenge considering the variability in available feedstock composition as well as their locations and distributions. For example, in an assessment of corn stover supplies in the U.S., about half of the corn stover supply is assessed to be available with minimal cost variability in a conventional biomass logistics system [289]. In an assessment of impacts of variability in corn stover feedstock quality attributes on overall biorefinery operating effectiveness, it was found that a modeled supply logistics subsystem met a 55% minimum carbohydrate specification 64.7% of the time, and that feedstock properties other than yield were the most significant contributors to increased feedstock and biofuel cost [290].

4.3. Technology readiness levels for several SAF pathways

ATJ pathways are currently approaching commercial implementation. For example, Lanzajet's facility in Georgia is expected to produce 10 million gallons of SAF and renewable diesel per year. Gevo also operates low-carbon jet fuel production facility in Silsbee Texas with 100,000 gallons per year. Other companies like Vertimass, Byogy, Swedish Biofuels AB, and Prometheus Fuels also all have commercialization activities at different stages for ATJ conversion. Meanwhile [54], beyond these activities, the majority of the other hybrid pathways and lignin valorization are at far lower TRL (1–3), including new ATJ pathways, C_2 - C_4 organic acid upgrading [284], 2,3-BDO upgrading to SAF [80], etc.

5. Techno-economic assessment (TEA) considerations for SAF production

In ATJ-based biorefineries, capital expenditure (CAPEX) [291], conversion efficiency to SAF (or liquid hydrocarbon fuels) [292], and alcohol production cost are the major factors impacting economic performance. Process intensification is one opportunity to reduce CAPEX, for example, directly upgrading of aqueous alcohols to minimize separation costs [54], or one-step conversion of ethanol to C_{3+} olefins to avoid the need for ethanol dehydration [92], CAPEX for the hydrotreating step is usually the highest among all the alcohol conversion steps. As a result, processing oligomerization liquid in either a larger central hydrotreating facility or coprocessing with petroleum feeds could further reduce the requisite capital investment for ATJ technologies. The price of the alcohols used as feedstock, which is dependent on the feedstock employed to synthesize them, also significantly impacts the process. For example, starch-derived alcohols (e.g., ethanol) have lower market prices than cellulosic alcohols, e.g., the 10-year average corn ethanol price is \$1.80/gal vs. a corn stover ethanol price of \$2.54/gal [92]. In such routes, catalysis has an indirect effect on economics via catalyst performance, as this determines fuel yields from

generated alcohols. Thus, a majority of catalysis efforts in this space are focused on developing selective catalysts for alcohol and intermediate conversion [60,92], increasing rates to minimize reactor size, and ensuring SAF compatibility for the product mix within ASTM specifications.

The economics of converting C=O-containing molecules, mainly that of volatile fatty acids (VFAs) [293–295], has also been investigated in the scientific literature. The low loadings required for the typical catalytic steps lead to catalysis having a relatively low impact over SAF selling prices. VFA procurement cost associated with potential carbon credits appear to dominate the economic performance of the process. Tracing a parallel with the ATJ route, the numerous catalytic reactions required to upgrade carboxylic acids also indirectly dominate the economic performance of the pathway through defining the obtainable yields of fuels from feedstock sugars.

For terpene-derived SAF, feedstock supply and unit operations have been identified as the main drivers of plant economics [296,297]. Estimated selling prices for SAF produced using terpenes as intermediates are still above those currently practiced for conventional jet fuel. While the path to lower processing costs passes directly through maximizing both fermentation yields to terpenes and catalytic yields to SAF, broader changes applied to a biorefinery approach are also required, such as adding value to lignin in the form of coproducts and process integration with more established facilities.

TEA studies for lignin-to-SAF routes point to the possibility of deploying this route on an industrial scale [298–300]. Catalysis is an important piece of this route since the conversion of lignin to hydrocarbons is dictated by the performance of the multiple catalysts involved, especially in the deconstruction reaction, and the use of noble metal catalysts may significantly influence both CAPEX and operating expense (OPEX). Other variables, such as CAPEX, discount rates, and feedstock/H₂ prices, also largely impact predicted economic performance. In a scenario of large adoption of SAF in the near-to-medium term, lignin obtained after the deconstruction of lignocellulosic biomass in biorefineries could be used as a feedstock for conversion into aromatics and cycloalkanes to complement paraffinic SAF, while other fractions (cellulose, hemicellulose) could give rise to high added-value coproducts to enhance the economic performance of a given process.

6. Conclusions and outlook

The production and use of low-carbon intensity aviation fuels generated from either biomass or waste feedstocks is considered one of the only near-term solutions to addressing the long-term climate impacts of aviation. Herein, SAF conversion technologies at various development stages have been reviewed with focus on hybrid processing. Moving forward, several critical challenges must be met, including lowering SAF production costs and carbon intensities through technology development while simultaneously promoting commercial deployment of existing technologies.

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High SAF production costs are still one of the major barriers which limit their large-scale deployment. Typically, feedstock costs are one of the main cost drivers contributing to this dilemma. Thus, efforts in exploring alternative, low cost feedstocks while improving feedstock productivity are generally beneficial. Conversion efficiency improvements are also extremely important for maximizing product yields. On another note, since CAPEX is usually a large contributor to overall plant costs, leveraging existing facilities could help to dramatically reduce the burden of initial investment. For example, the retrofitting of existing ethanol biorefineries for SAF production in the countries where ethanol production infrastructure has been established (e.g., the US and Brazil) is an extremely promising opportunity. Furthermore, leveraging petrochemical facilities to co-process bioderived fuel intermediates is another potential avenue to lower initial capital investment.

Another major opportunity is the utilization of multi-step processing. Here, two or more conversion steps are utilized in sequence, taking advantage of the properties of a given feedstock to determine viable conversion processes. This is especially relevant to hybrid processing, where biomass is typically first fractionated into a lignin-rich and carbohydrate-rich fraction. The carbohydrates can then be fermented into alcohols and subsequently catalytically upgraded to hydrocarbons. Meanwhile, the lignin-rich fraction can also be upgraded to different hydrocarbon blendstocks. These sequences, if planned correctly, may allow for higher efficiencies and lower processing costs due to process efficiency improvements such as incomplete purification [54] between stages.

Another crucial strategy is to capitalize on revenues from coproducts, analogously to what is currently done in petroleum refining. Significant revenue can be made from chemical coproducts despite much lower requisite production volumes compared to fuels. The oxygenated nature of biomass can be leveraged to produce useful chemical products, potentially serving as either direct drop-in petroleum replacements or functional replacements with improved or equivalent properties [301,302]. A diverse network of chemical products and materials should be targeted, considering various feedstocks and conversion technologies, to avoid rapid market saturation.

Government policies such as carbon credits or carbon taxes will also be critical for large-scale SAF deployment as SAF production cannot yet compete with petroleum jet. Such policies are currently only constrained to selected regions and countries, such as ReFuelEU in Europe [285], Renewable Identification Numbers (RINs) in the US [303,304], the Low Carbon Fuel Standard in California (US) [305], the Climate Commitment Act in Washington (US) [306], the Greenhouse Gas Reduction Act in British Columbia (Canada) [307], as well as other various policies in the European Union [308] and Brazil [309]. Thus, further well-established and widespread government policies are urgently needed to accelerate commercial deployment.

Aside from improving SAF production cost, carbon intensity is another important metric to consider as the overall purpose of deploying SAF is to reduce GHG emissions. Unfortunately, efforts focused on reducing carbon intensity generally result in increased production costs. For example, when utilizing low-carbon-intensity feedstocks such as municipal solid waste, there are typically additional costs associated with pretreatment steps. As a result, these tradeoffs between costs and LCA benefits should be carefully evaluated for each considered technology.

Overall, current SAF production is still very limited in scale. Less than 7 million gallons of SAF are generated annually in the US, a far cry from the 35 billion gallons per year of domestic jet fuel demand predicted for 2050 [286]. Thus, multiple conversion technologies and feedstocks should be encouraged to promote a diversified technology and feedstock portfolio capable of scaling with increasing demand. Deployment of new conversion technologies at commercial scale is the only viable path to keep pace with this rapidly growing market. Meanwhile, R&D efforts focused at lowering SAF production costs and maturing infant technologies for should be further encouraged. Overall, this monumental effort will require significant cooperation between governments, private industry, universities, and research institutions.

CRediT authorship contribution statement

Junyan Zhang: Writing - review & editing, Writing original draft. Matthew S. Webber: Writing - review & editing, Writing - original draft. Yungiao Pu: Writing - review & editing, Writing - original draft. Zhenglong Li: Writing - review & editing, Supervision, Funding acquisition, Conceptualization. Xianzhi Meng: Writing - original draft. Michael L. Stone: Writing - original draft. Bingqing Wei: Writing - review & editing, Visualization. Xueqi Wang: Writing - review & editing, Visualization. Sainan Yuan: Writing - review & editing. Bruno Klein: Writing - original draft. Bhogeswararao Seemala: Writing – original draft. Charles E. Wyman: Writing - original draft. Karthikevan K. Ramasamy: Writing - original draft. Mike Thorson: Writing - original draft. Matthew H. Langholtz: Writing – original draft. Joshua S. Heyne: Writing - original draft. Aibolat Koishybay: Writing - original draft. Shiba Adhikari: Writing - original draft. Sufeng Cao: Writing - review & editing. Andrew D. Sutton: Writing - original draft. Gerald A. Tuskan: Writing - review & editing, Writing original draft. Yuriy Román-Leshkov: Writing - review & editing. Arthur J. Ragauskas: Writing - review & editing. Tao Ling: Writing - review & editing. Brian H. Davison: Writing review & editing.

Declaration of competing interest

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20

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J. Zhang et al. / Green Energy & Environment xxx (xxxx) xxx

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J. Zhang et al. / Green Energy & Environment xxx (xxxx) xxx

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23

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