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# Chemical Compositions and Properties of Lignin-Based Jet Fuel Range Hydrocarbons

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# 24 Abstract

25 Sustainable aviation fuels remain the only near, mid, and likely long term solution for lowering the carbon emissions of commercial and military aviation. 26 27 Determination of sustainable aviation fuel's chemical compositions and prediction of their properties is a critical first step for further research and development leading to 28 the final certification process. Our analytical results showed that the lignin-based jet 29 fuel (US patent 9,518,076 B2) consists of mainly paraffinic hydrocarbon species. 30 31 They can be further classified into several classes, including n-paraffins, iso-paraffins, mono-, di-, and tri-cycloparaffins of which the majority contains carbon numbers in 32 the range of 7 to 20. The very high concentration of polycycloparaffins along with the 33 34 relatively low content of monocycloparaffins contribute to the high boiling point of the sample. Reducing the boiling point will require cracking and further hydrotreating 35 of the lignin-based jet fuel range hydrocarbons to increase monocycloparaffins ratio 36 close to the coal-based jet fuel compositions (e.g., JP-900). Also, this lignin-based jet 37 fuel contain very low aromatics concentration which illuminates favorable energy 38 content, energy density, possible low emissions, and very high-performance 39 characteristics might meet drop-in specifications. 40

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# 42 Keywords

43 Hydrodeoxygenation; Lignin; GC×GC-FID/TOF-MS; Lignin-based jet fuel (LJF);
44 sustainable aviation fuel (SAF); pre-screening;

#### 45 **1. Introduction**

46 The deleterious effects of climate change via anthropogenic carbon emissions are becoming clearer, more frequent, and intense [1]. The sensitivity of aviation 47 transportation to specific energy and energy density of fuels implies significant input 48 of aviation emission to the GHG emissions related to transportation. In response, the 49 International Civil Aviation Organization (ICAO) has established a Carbon Offsetting 50 and Reduction Scheme for International Aviation (CORSIA), which sets voluntary 51 52 carbon reduction standards during Phase 1 (through 2026) and mandatory standards during Phase 2 (2027 and beyond). Sustainable Aviation Fuel (SAF) is identified as 53 the only near to mid-term solution for reducing carbon emissions. Projections suggest 54 55 that greater than 30% of total jet fuel consumption by 2040 will need to be SAFs to meet ICAO commitments. Based on projected increase in flight travel, on a global 56 basis, this quantity is greater than the total jet fuel consumed currently. 57

58 In 2017, US-based SAF production was credited with approximately 2 million 59 gallons of Renewable Identification Numbers (RINs), or less than one-hundredth of a 60 percent of total jet fuel consumption. However, the lack of any clear high-volume cost-competitive SAF encourages continued research and development in innovative 61 technologies [2]. However, SAFs remain the only real alternatives for the commercial 62 aviation industry and the military, both facing ambitious near-term targets of 63 greenhouse gas reduction. A broad range of renewable alternative jet fuel possesses 64 performance characteristics and chemical compositions essentially identical to 65 conventional jet fuel. Although most SAF technologies are still in the early stages of 66

research, development, and approval, biojet fuel is the most promising alternative
energy source as both short- and long-term solutions to replace fossil crude oil derived
jet fuel for the airline industry.

Currently, there are five well-developed renewable conversion technologies 70 71 leading to the production of SAFs, which meet the current ASTM D7566 standard specifications [3] and certifications in preparation [4, 5]. Indeed, there are many more 72 technologies in exploratory discussions [6-20]. Notably, Jet A/A-1 and the five 73 approved biojet fuels differ in composition, with the variance of compositions and 74 properties being much broader from bio-routes vs. conventional fuel routes. The 75 approval of these fuels as part of the ASTM D4054 process depends on the 76 compatibility of fuel with existing equipment while complying with tests under the 77 78 ASTM D4054 approval and evaluation testing. Nominally, this approval and evaluation process investigates compatibility, consistency, and operability. 79

Materials compatibility requirements are extensive. Lubrication, swelling, static dissipation, and many other metrics must be satisfied by the approved fuel. In some cases, the use of additives can facilitate meeting material compatibility requirements. In other cases, such as swelling, the bulk composition of the fuel is 'tailored' to meet compatibility. The minimum aromatic limit of alternative jet fuels has been set to above 8 vol% for this reason, which contributes to a limited 50/50 blend of alternative/conventional fuel.

Figures of Merit (FOM) operability limits are primarily determined, like swelling,
by the bulk properties of a fuel. Density, viscosity, surface tension, volatile properties,

and Derived Cetane Number (DCN), capture nearly all combustion-related operability
variance associated with alternative fuels [21]. Traditional Jet-A specifications in
addition to newer efforts bound potential SAF deleterious operability limits providing
higher fidelity biojet screening tools. While the ASTM approval process does not
evaluate performance from the perspective of added benefit to end consumers, SAFs
and biojet fuels do offer considerable monetizable performance benefits [22].

Performance from the perspective of a given mission can be found via increases 95 in specific energy, energy density, and thermal stability with a reduction in emissions. 96 Increases in specific energy have the opportunity to benefit any mission. Energy 97 density increases have the potential to benefit missions with fuel tank volume 98 limitations as well as increasing the performance of a fuel on a per volume basis. 99 100 Thermal stability, however, has perhaps the most significant benefit, although efforts are still needed to quantify these benefits. Specific energy of an unstrained molecule 101 scales closely with the hydrogen-to-carbon ratio of fuel. Hence, fuels with a high 102 degree of saturation, n- and iso-paraffins, have higher specific energies than the other 103 common hydrocarbon classes found in jet fuel. Interestingly, cycloparaffins have both 104 higher specific energies and energy densities than conventional fuels [22], with 105 preliminary swelling studies suggesting they could also facilitate the removal of 106 aromatics[23]. 107

Hydrocarbons found in jet fuel can be categorized as paraffins, olefins,
naphthenes, and aromatics [24], each of which contains a different number of carbon
atoms. Since biomass and crude oil are both converted to a mixture of hydrocarbon

compounds, taking a look at the elemental profiling of various biomass and crude oil 111 compositions is an efficient way to understand the different chemical compositions of 112 jet fuels and conversion efficiency in biomass and crude oil refineries [25-28]. For 113 example, the oxygen content in biomass is much higher than that of crude oil, thus 114 requires more energy input to effectively remove excess oxygen and produce 115 hydrocarbons consisting of only carbon and hydrogen atoms. This is one of the 116 reasons why hydrotreating is needed in nearly all biojet fuel conversion pathways, and 117 the cost and availability of these industrial processes are considered a risk in the 118 research and development of biojet fuel [29]. What is more, understanding the 119 different element compositions is extremely useful for estimating the potential 120 abundance of air pollutants that are emitted during fuel combustion. 121

122 The lignin-based jet fuel (LJF) refers to the lignin-substructure-based hydrocarbons which were produced through a catalytic process of the 123 depolymerization of lignin into monomers and dimers via the cleavage of C-O-C 124 bonds without disrupting the C-C linkages [12, 13, 15, 19, 30-34] and followed by a 125 hydrodeoxygenation (HDO) process that catalyzed by the bifunctional catalyst 126 Ru/H<sup>+</sup>-Y or a super Lewis acid and Ru-M/H<sup>+</sup>-Y (M= Fe, Ni, Cu, Zn) [18, 35-39]. The 127 resulting hydrocarbons are primarily  $C_{12}$ - $C_{18}$  cyclic structure hydrocarbons in the jet 128 fuel boiling point range with carbon yields of around 30 wt% from lignin. The 129 lignin-based jet fuel offers unique potential advantages compared to other varieties of 130 biojet fuels [35]: a) uses low-cost raw materials from biorefinery wastes without 131 conflicting with food or other biofuel production; b) has higher thermal stability; c) 132

has higher energy density; d) produced at lower cost; and e) reduces greenhouse
emissions. These impressive benefits are vital steps forward on the path for producing
biofuels from lignin and may lead to the commercial development of new biojet fuels
suitable for industrial applications.

In this study, a series of analytical approaches including comprehensive 137 two-dimensional gas chromatography (GC×GC) with both mass spectrometry and 138 flame ionization (FID) detection was applied for identification and quantification of 139 species in lignin-based jet fuel. Followed by a detailed discussion on estimating 140 141 Lignin-to-Jet FOM operability performance characteristics, and suggestions on how to fine-tune this flexible catalytic process will allow unfettered access to the most 142 important hydrocarbon classes that are innate to aviation jet fuel. The viability of the 143 144 new biofuel will be assessed through qualification and performance testing.

145

#### 2. Materials and Methods

# 146 **2.1 LJF sample preparation**

LJF sample was prepared via a hydrodeoxygenation process we developed in previous studies [17]. First, corn stover was soaked in <1 wt% NaOH solution at 80-90°C, to deacetylate the biomass and extract soluble sugars, acetate, ash, and lignin components. The soluble reactive lignin in the black liquor was precipitated and extracted into 50-250 mM NaOH solution and then precipitated and collected for the hydrodeoxygenation processing [17]. Then, noble-metal catalyst (Ru/Al<sub>2</sub>O<sub>3</sub>), solid acid (H<sup>+</sup> Z-Y), and collected lignin were added into the reactor. After sealing the

vessel, H<sub>2</sub> was used for flushing out the air in the reactor for at least 3 times, and then 155 the reactor was pressurized to 4 MPa at room temperature. The reactor was then 156 157 heated to reach the reaction temperature (250 °C) where the reaction time was started. After the various reaction times, the vessel was plunged into cold water to cool. The 158 headspace gas was then exhausted, and the volume was measured using the water 159 displacement method. A gas sample was extracted and analyzed by GC-MS for 160 qualitative and quantitative analysis. Then all the liquid phase and solid residues were 161 transferred into a centrifuge tube. Product was extracted from the reaction mixture 162 163 using ethyl acetate. Then a sample was acquired from the organic phase for further analysis [36]. 164

# 165 **2.2 Two-dimensional Gas Chromatography (GC×GC)**

A preliminary fuel sample was acquired via rotary evaporation to remove the large quantity of extraction solvent. An extra distillation process was conducted via a set of equipment meant for ASTM D 86 [37] to remove the residual solvent. The distillation was stopped when the bottom flask temperature was kept at 200 °C for about 10 min while the vapor temperature was never able to research higher than 40 °C.

The GC×GC analyses were conducted on two independent systems: GC×GC-FID (Agilent 6890 GC) and GC×GC-TOF-MS (Agilent 7890 GC coupled to a Pegasus IV time-of-flight mass spectrometer (LECO corp. Instruments, Mississauga, ON, Canada)). Data handling, including contour plotting, GC×GC peak collection, retention time measurements, and peak volume calculations were performed using ChromaTOF ver. 4.50.8 software provided by LECO Instruments.

GC×GC-FID: the instrument was equipped with a 'normal' column combination set. 177 The primary column was a VF-5HT (30 m  $\times$  0.32 mm  $\times$  0.1  $\mu$ m; Agilent J&W), and 178 the secondary column was a BPX-50 (1.25 m  $\times$  0.1 mm  $\times$  0.1  $\mu$ m; SGE Analytical 179 Science). GC×GC-FID was equipped with a split/splitless injector and a 180 liquid-nitrogen-cooled quad-jet cryogenic modulator (Leco Instruments, Mississauga, 181 ON, Canada). The modulation period was set at 6 s for all experiments. A 0.1-µL 182 sample was injected at 340 °C at a 50:1 split ratio. The carrier gas was helium (grade 183 5.3, Linde, Edmonton, AB). The separations were started at 50 °C, reaching 360 °C at 184 185 3 °C/min, with a hold time of 1 min at the beginning and 5 min the end of the run. The secondary oven and modulator were kept 10 °C and 50 °C above the main oven 186 temperature, respectively. Detection was performed by flame ionization detector (FID) 187 188 operated in tandem with sulfur chemiluminescence detector (SCD) (355 Dual Plasma, Sievers Inc. Boulder, CO, USA). Hence, in addition to the general hydrocarbon 189 response, it is possible to provide detailed sulfur speciation. A series of n-paraffins 190 191 (C5-C30) was analyzed to establish a correlation between retention time and boiling point. 192

193 <u>GC×GC-TOF-MS</u>: experiments were carried out using an Agilent 7890A GC 194 coupled with LECO Pegasus® 4D system. The system incorporates LECO's 195 Consumable-Free (CF) thermal modulator (dual stage quad-jet). The average phase 196 column set comprised of a combination of a primary non-polar VF-5HT column (30 197  $m \times 0.32 \text{ mm} \times 0.1 \mu \text{m}$ ; Agilent J&W) and a mid-polar secondary column BPX-50 198 (1.1  $m \times 0.1 \text{ mm} \times 0.1 \mu \text{m}$ ; SGE Analytical Science). A 0.2- $\mu$ L sample was injected at

340°C at a 50:1 split ratio via split/splitless injector. A constant flow rate (1.5 mL/min) 199 of helium (grade 5.3, Linde, Edmonton, AB) was used as the carrier gas. The oven 200 temperature was held initially at 40 °C for 2 min and raised at 3 °C/min to 340 °C and 201 held for 2 min. The modulation period was set to 10, and the modulator and secondary 202 oven were kept 30°C and 10°C above the central oven temperature, respectively. 203 Compounds eluting from the secondary oven were passing to TOF-MS through the 204 transfer line, and the ion source operated at 350 °C and 200 °C, respectively. The 205 detector voltage was set to 1550V, and the TOF-MS was operated in electron impact 206 207 ionization mode (70 eV) scanned in the mass range of 45–500 mu at an acquisition rate of 100 spectra/s. 208

209

#### 210 **3. Results and discussions**

The LJF samples were analyzed using GC×GC analysis coupled with FID and TOF-MS detectors. All quantitative analyses provided in this study for hydrocarbons were based on the FID response. The FID response is linear over an extensive range of concentrations and proportional to the mass flow rate of carbon.

215 **3.1.** Hydrocarbon characteristic for the LJF sample

Qualitative chromatographic analysis of the LJF sample was investigated with the use of GC×GC-TOF-MS and GC×GC-FID technique. Therefore, hydrocarbons' components were tentatively identified by comparing their mass spectra with those from the NIST library (2018) and Wiley mass spectra library (Wiley Registry 8<sup>th</sup> edition) using a minimum similarity value of 700 as the criterion.

In this study, the separation of components in GC×GC -FID was achieved using 221 'normal' column configuration, wherein the first non-polar column separates 222 223 primarily by volatility and the second semi-polar column separates the constituent compounds by polarity/polarizability and volatility. This approach enables accurate 224 separation of cycloparaffins into one-, two-, three-, and four ring subgroups, as well 225 as improved differentiation from other hydrocarbon classes. The column sets and 226 GC×GC parameters were adjusted to achieve the best possible separation of sample 227 components. 228

Figure 1 shows a 'normal' GC×GC-FID contour plot with simplified hydrocarbon regions superimposed on the chromatogram obtained for the sample under the condition specified in the experimental section. Peaks are displayed as spots in the retention plane described as the first-dimension retention time on the x-axis and the second-dimension retention time shown on the y-axis. Signal intensity is illustrated by the color intensity. Light gray color represents the baseline and dark blue color represents the most intense peaks in the chromatogram.

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The separation of components presented in Figure 1 illustrate the ordered structure of the GC×GC system, especially its chemical structural sense behind the repeating bands in the chromatogram. It is worth to note, that chemical families elute together in a band, which allows for straightforward identification. The structured layout of the contour plot allows peaks to be assigned quickly without the use of individual standards. This form of tentative identification was used to assign the major chemical classes in the chromatograms of the samples. Further, a more detailed

template was developed for sample evaluation by close examination of MS results and 244 subsequent translation to the co-generated FID file. The classification template 245 included the following hydrocarbon classes: paraffins (isoparaffins and normal 246 paraffins), cycloparaffins (mono-, di-. tri-. and tetra-cycloparaffins), 247 naphthenebenzenes (indans/tetralins), polar compounds (esters, cyclohexanols, and 248 cyclohexanones), and region with unknown heavier hydrocarbons. 249

To enhance the visibility of detailed hydrocarbon group speciation, the complex 250 two-dimensional chromatograms have been converted from a series of co-eluted 251 252 peaks into a series of color-coded bubbles to discriminate detailed hydrocarbon types. Peak areas obtained after preprocessing with ChromaTOF software were transferred 253 into MATLAB® and subjected to further processing. The first-dimension retention 254 255 time was converted into a boiling point using a correlation established between the boiling point of n-paraffins and their retention time. This exercise allowed for the 256 presentation of GC×GC-FID maps in the boiling point domain. Additionally, 257 258 component peaks found in chromatograms were presented in bubble plot form where the size of the bubble is related to the component concentration, and color is assigned 259 to specific HC compound type. Figure 2 presents the upgraded bubble plot 260 representation of GC×GC-FID chromatogram of liquid product. 261

As shown in Figure 2 paraffins are seen to be separated from cycloparaffins. Mono-, di- and polycycloparaffins are organized in well-separated bands. Within these bands, a roof-tile structure is observed where each tile was representing particular hydrocarbon type with the same number of carbon atoms. Quantification of

hydrocarbon classes was performed by the FID response of the compounds in each 266 hydrocarbon class. Figure 3 summarizes the results of the GC×GC analysis completed 267 268 for the analyzed sample. Cycloparaffins are the most abundant group and constitute about 77 wt% of the total hydrocarbon content in the product. Dicycloparaffins are the 269 significant constituents followed by tricycloparaffins, monocycloparaffins, and 270 tetracycloparaffins. Generally, the paraffinic content is low. Cycloparaffins will have a 271 beneficial effect on busting the octane number in gasoline fraction. On the other hand, 272 they will decrease the cetane number in diesel fraction. 273

274 Semi-quantitative analysis was accomplished for polar compounds (esters, cyclohexanones, and cyclohexanols) using normalized peak areas. In such cases, we 275 assumed a uniform response of 1.0 for each polar compound in the FID (this 276 277 assumption holds for mixtures containing only hydrocarbons). Neither response factor nor external calibration standards were used to calculate the concentrations of polars 278 in the analyzed sample. The structure of GC×GC chromatograms allows getting more 279 detailed information on the sample composition than that provided by a simple 280 group-type separation. Figure 4 shows the distribution in weight percent of two 281 hydrocarbon types by carbon number for the hydrodeoxygenated sample. We can 282 observe that paraffins (in general) and n-paraffins in particular with odd carbon 283 number (i.e., C15, C17, C19) have higher abundance than even carbon number 284 paraffins (... C16, C18). 285

Figure 5 presents comparison of the simulated distillation (SimDis) (ASTM
D2887) data of lignin-based jet fuel, a fractionated lignin-based jet fuel, a fractionated

and 50/50 wt% blend with an average Jet A, and a range of jet fuels with extreme 288 operability properties. The SimDist data on the neat lignin-based jet fuel illustrates 289 290 that ~45 wt% of the fuel is within the jet fuel distillation range. This hypothetical fraction (45 wt%) is then compared to a range of D2887 data from Jet A fuels with 291 extreme on spec distillation temperatures [38]. While technically within specification 292 limits, fuels exceeding this distillation range would not likely be approved via ASTM 293 D4054, as heavier distillation profiles imply poor operability limits and lighter cuts 294 add uncertainty. The final line in Figure 5 illustrates a hypothetical blend of a 50/50 295 296 by mass blend of the lighter 45 wt% lignin-based fuel with an average Jet A fuel. This blend, once more, illustrates that a 50/50 blend with the jet fuel has distillate 297 temperatures above the experience range of conventional Jet A fuels. The implication 298 299 being, any blend limit approved would need lower blend thresholds than 50 wt% or the jet cut from this lignin-based would need to be limited to a lighter fraction (<45 300 wt%). 301

#### **302 3.2.**

#### Estimating the LJF combustion performance characteristics

In general, jet fuels are evaluated based on the quality and operability performance characteristics. Energy content (specific energy and energy density), thermal stability, and emissions nominally determine the utilitarian quality of jet fuel. However, operability performance characteristics largely determine the blending limits and the ability of a fuel to eclipse the approval and evaluation process for alternative jet fuels (ASTM D4054). This cost and duration of this approval process hinges on three operability FOM evaluation criteria that measure a fuel's ability to hold stabile combustion (lean blowout (LBO)) and the ability of a fuel to evolve tostable combustion (cold ignition and altitude relight).

These FOM criteria are the focus of previously reported National Jet Fuels Combustion (NJFCP) work [38], which has related statistically correlated fuel physical properties to FOM behavior. Nominally, one chemical property and four physical properties, see Table 1, determine more than 90% of all combustion variance across diverse fuel and hardware architecture characteristics.

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# 318 3.3. Estimating the LJF FOM operability performance characteristics

The reported LJF is composed of approximately nine major compositional 319 categories of interest to combustion and aircraft operability, Figure 6. Three 320 321 compositional categories, n-paraffins, iso-paraffins, and monocycloparaffins, are found in high concentrations in conventional jet fuels and would likely not cause any 322 operability issues (~21 wt%) when the carbon numbers blended are matched to the jet 323 range, see Figure 7 and 8. Bicyclicparaffins compose up to approximately 17/32 wt% 324 of conventional/LTJ fuel [39]. Higher concentrations of bicyclic compounds are 325 associated with higher surface tension, poorer ignition performance, and significant 326 uncertainty surrounding conformational variance on the autoignition propensity of the 327 molecules as determined by the DCN of the fuel [22, 40]. Approximately 19 wt% of 328 the bicyclocparaffins fall in the molecular weight range of a typical Jet A. The 329 remaining 13 wt% of the bicyclic compounds would need additional identification 330

and testing to bound the potential deleterious operability effects associated with theseheavier molecules.

Tetra and tri-cyclic molecules are atypical for conventional Jet A fuel, respectively. Tricyclic molecules, when identified, are in minimal concentrations (<0.2 wt%) and high concentrations found here would very likely impact the operability limits of a fuel. Tetra- and tri-cyclic compounds would likely need to be removed from the LTJ, or approved blend limits would likely be low for the fuel.

Aromatics are associated with lowering the durability of an aircraft combustor and specific energy of fuel while increasing the emissions. Correspondingly, the Jet-A specification (ASTM D1655) limits the maximum concentration of aromatics to less than 25 vol% and of naphthalenes to less than 3 vol%. Lignin-based jet fuel has very low aromatic concentrations, potentially facilitating low particulate matter emissions.

The last compositional category, heterocyclic, are not permissible in jet fuels. They are associated with low energy content, compatibility issues, poor thermal stability, and high freeze points. These molecules would need to be removed entirely from the fuel as a process to enable approval. Finally, all the deleterious compositional categories can be removed by distillation fractioning. Lighter hydrocarbon species (<C16) found here could potentially be blended in Jet-A.

349

#### 4. Towards A High-Performance LJF

350 Improvements to the lignin-based jet fuel, from the combustion perspective, can 351 be gained via the removal of aromatics and heteroatoms and producing a lighter/lower molecular weight fuel. The removal of heteroatoms will benefit multiple performance and operability properties. The removal of aromatics, moreover, will increase the specific energy of a fuel. Figure 6 illustrates the specific energy and energy density of molecules and classes common in a conventional fuel. The LJF is heavily composed of cycloparaffins, which tend to have higher energy densities and specific energies relative to conventional fuel.

358 Perhaps of greatest importance in utilizing the current LJF as a jet fuel is bringing the fuel more into the conventional jet fuel carbon number range and distribution. As 359 Figure 8 shows, the average molecular weight of an average jet fuel is much lower 360 than the currently reported LTJ. This increased molecular weight would likely 361 correspond to off-spec viscosity, surface tension, freeze point, and distillation curve 362 values. Decreasing the average molecular weight would bring these values closer to 363 364 spec, increase approved blend levels, and improve the overall specific energy of the fuel by increasing the hydrogen-to-carbon ratio of the fuel. 365

366

# 367 **5. Conclusion**

The current interest in aviation turbine fuels produced from non-petroleum feedstocks has prompted the aviation fuels community to develop an evaluation and approval process to support the deployment of alternative jet fuels, with the current work the first expression of early prescreening of alternative jet fuels. This process utilizes Tiers  $\alpha$  and  $\beta$  to coordinate the evaluation of data and the establishment of 373 specification criteria for new alternative jet fuels[41]. However, one of the most 374 consistently noted challenges in the development of alternative aviation fuels is the 375 lack of clear screening and evaluation methods for novel fuels. This lack of a 376 well-defined accepted criteria or specification inhibits more rapid fuel development, 377 investment, and enables "dead-end" pursuits.

Up until recently, aviation fuel primarily has been a petroleum distillate. Standards 378 have been developed for the distillate, providing bounds on the natural variation due 379 to source and process, but not specifying the chemical composition or all the key bulk 380 381 and trace fuel characteristics required for a fuel to be fully fungible. Conventional aviation fuels serve as the basis for the entire infrastructure of refining, fuel transport, 382 filtration, testing, purchase, and refueling. The inherent assumption of these fungible 383 384 petroleum-based fuels has resulted in standards that are not always suited to evaluate alternative processes and alternative sources, as the variance in properties, 385 compositions, and is greater than variation in petroleum fuels. Whereas specifications 386 and predictive tools that detail acceptable chemistries, properties (bulk and trace), and 387 estimate blend limits are what are desired by the developers. 388

The data from these tests revealed some of the properties of our fuel produced from lignin. Despite the similar carbon number range, the properties of our product fuel are not that close to jet fuel. The very high concentration of dicycloparaffins in the lignin jet fuel sample along with the relatively low paraffin and monocycloparaffin content contributed to the high boiling point. The boiling range this high is not fit for commercial jet or diesel fuels that are on the market, but it may be fit for blend stock.

Traditionally, aromatics, including naphthalenes, are deemed as an additive to an 395 impact the cetane number, polycyclic aromatic hydrocarbon emission, smoke point, 396 397 and many other properties of a fuel.[42] Dicycloparaffins also have a higher volumetric energy density than monocycloparaffins and linear paraffins.[43, 44] This 398 makes the fuel potentially a replacement additive for high energy density molecules 399 and a potential candidate for mimicking the swelling characteristics of aromatics [23]. 400 It's also well known that synthetic paraffinic jet fuels usually have a lower density 401 which negatively affect the fuel efficiency. By blending our fuel with synthetic jet 402 403 fuels, an on-specification density jet fuel can also be produced. Thus, although the lignin to jet fuel process was proved not able to provide usable conventional 404 standardized aviation fuel out of the one-pot reactor, the analytical data did show that 405 406 the fuel we produced may be an excellent high energy content fuel additive or possible high energy fuel for the specific application. Overall, the LJF hydrocarbons property 407 ranges may offer great opportunities for increasing fuel performance, higher fuel 408 409 efficiency, reduced emission, and lower costs.

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544 **Captions:** 

545 Figure 1. A 'normal' GC×GC-FID contour plot of sample. The x-axis represents

retention time on the primary column, while the y-axis shows retention time on the

secondary axis. Eight major hydrocarbon regions: paraffins (A), monocycloparaffins

548 (B1), dicycloparaffins (B2), tricycloparaffins (B3), tetracycloparaffins (B4),

549 cyclohexanols (C), cyclohexanons (D), and naphthobenzenes (E). Label (F) indicate

550 location of heavier unknown components.

**Figure 2.** A bubble plot representation of 'normal' GC×GC-FID contour plot of

sample. The bubble size and colour are related to the compound concentration and

553 hydrocarbon type, respectively. Green labels at the bottom of the map indicate the

- position of n-paraffins. The magenta line depicts the SimDist curve calculated based
- 555 on GC×GC data.

**Figure 3**. Summary of GC×GC-FID hydrocarbon composition (wt%).

**Figure 4**. Distribution of n-paraffins (a) and iso-paraffins (b) by carbon number for

558 hydrodeoxyganated sample.

**Figure 5.** Simulated distillation curves of lignin jet fuel compared to reference jet fuels [H5-ASTM D2887 ref]. Operability characteristics of a jet fuel scale to first order with the distillation curve of the fuel, with higher distillate temperatures conferring decreased operability. The color map region bounds distillate properties found in conventional fuels with ASTM D2887 data from reference fuels. The upper and lower color map regions represent a 'worst' and 'best' case fuel for operability of a conventional jet fuel, respectively.

**Figure 6**. Conventional fuel specific energy and energy density from the PQIS

567 database (red symbols) [39]. Contour lines surrounding the conventional fuels

describe the probability density of the fuel samples. The far right solid blue line

represents the Pareto values for the conventional fuels. Other symbols series represent

570 specific molecules and their classes that conventional fuels are composed of.

571 Lignin-based jet fuel is composed of large fractions of monocycloalkanes and

572 dicycloalkanes. Plot reproduced from Kosir et al. [22].

Figure 7: Compositional categories of the reported Lignin-to-jet fuel. The inner fill
represents the fraction of the correspondingly coloured compositional class that is
within the jet fuel range (~35 wt% of the total composition).

Figure 8. Composition of lignin-based jet fuel with respect to carbon number for
molecular classes common in conventional jet fuel. A carbon number range and
distribution of an average jet fuel is highlighted in light blue, and the average carbon
number of this conventional fuel is represented as a solid vertical blue line.<sup>5</sup> For the

molecules illustrated here, the lignin-to-jet fuel has on average a much higher average carbon number than conventional fuel, with the distribution being spread over a wider carbon range. 











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645 Figure 7: Compositional categories of the reported Lignin-to-jet fuel. The inner fill

- represents the fraction of the correspondingly coloured compositional class that is
- 647 within the jet fuel range ( $\sim$ 35 wt% of the total composition).





Figure 8. Composition of lignin-based jet fuel with respect to carbon number for molecular classes common in conventional jet fuel. A carbon number range and distribution of an average jet fuel is highlighted in light blue, and the average carbon number of this conventional fuel is represented as a solid vertical blue line.<sup>5</sup> For the molecules illustrated here, the lignin-to-jet fuel has on average a much higher average carbon number than conventional fuel, with the distribution being spread over a wider carbon range. 

Table 1: Key Operability Properties which are strongly correlated to the approval andevaluation process of SAFs [21].

Property Category	Property	Impact on FOM	Physically limiting
			process
	DCN	LBO limit	Autoignition for
Cnemicai			combustion stabilization
Physical	Viscosity	LBO, Cold Ignition,	Spray angle and primary
		Altitude Relight	break-up
	Distillation	LBO, Cold Ignition,	Correlated with many
	curve	Altitude Relight	physical properties;
			impacts fuel volatility
	Density	LBO, Cold Ignition,	Spray mixing and
		Altitude Relight	atomization
	Surface	LBO, Cold Ignition,	Secondary spray break-up
	tension	Altitude Relight	and atomization