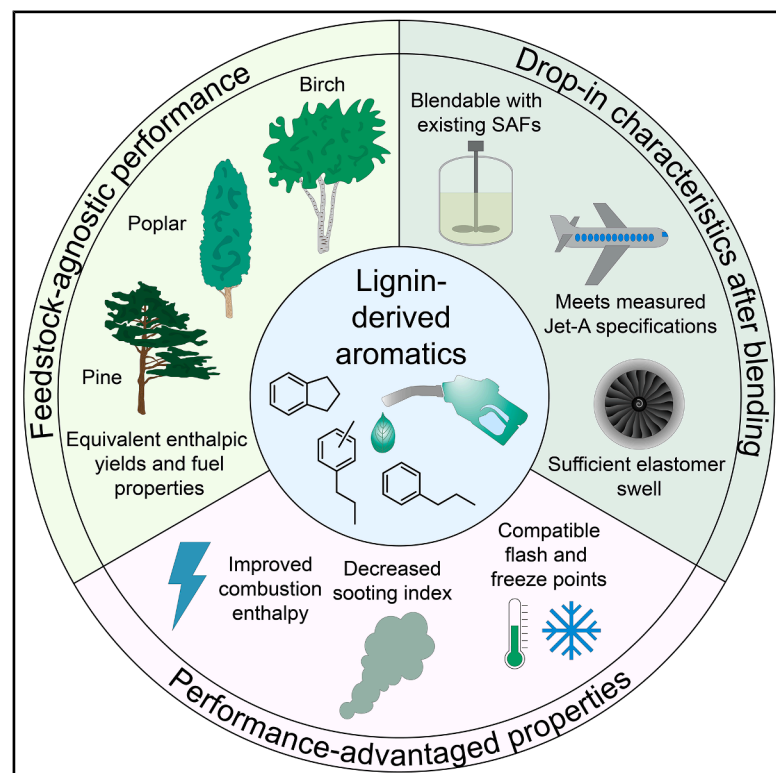


Drop-in sustainable aviation fuels enabled by feedstock-agnostic lignin deoxygenation

Graphical abstract



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In brief

Webber et al. demonstrate that the sequential reductive catalytic fractionation and hydrodeoxygenation of lignin enables drop-in sustainable aviation fuels after blending with conventional synthetic paraffinic mixtures. They further evaluate the process to be feedstock agnostic, resulting in similar enthalpic yields and distillate properties across multiple woody biomass sources.

Highlights

- Scaled RCF-HDO enables rigorous fuel property testing
- Blending with conventional SPKs generates drop-in-compatible aviation fuels
- Similar enthalpic yields result across multiple biomass sources
- Identical fuel properties result after distillation, regardless of feedstock



Article

Drop-in sustainable aviation fuels enabled by feedstock-agnostic lignin deoxygenation

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SUMMARY

Current sustainable aviation fuels (SAFs) require blending with petroleum-derived fuels due to incomplete hydrocarbon distributions, most notably a lack of aromatics. Lignin, the most abundant renewable source of aromatics, is a promising feedstock for addressing this limitation. Here, we demonstrate a sequential reductive catalytic fractionation and continuous hydrodeoxygenation process that converts multiple woody feedstocks into aromatic hydrocarbons at up to 93% of the theoretical carbon yield. Blending these products with commercial SAFs produces drop-in compatible fuels with elastomer swell performances equivalent to conventional aviation fuels. The process is adaptable across multiple biomass sources, yielding aromatic hydrocarbons with consistent enthalpic efficiencies and fuel properties. These findings establish a scalable route to 100% drop-in SAFs, leveraging lignin-derived aromatics within the existing biofuels infrastructure.

INTRODUCTION

Lignin has long been targeted as a source of renewable carbon for the production of chemicals and fuels, but it remains predominantly combusted in biorefineries for heat and power generation.^{1–7} Meanwhile, the demand for biofuels is increasing, particularly in the aviation sector, where high-energy-density requirements preclude near-term electrification.^{8,9} A critical challenge in sustainable aviation fuel (SAF) deployment is the existing blend wall, which primarily arises from the limited aromatic content within existing certified SAFs.¹⁰ This necessitates the blending of these mixtures with petroleum-derived jet fuel to meet required performance specifications. In this context, lignin is a promising feedstock for producing SAF blendstocks due to its aromaticity and high energy density.^{11–22} The catalytic conversion of lignin to SAF could thus provide a route to decarbonize an inherently carbon-intensive transportation sector by enabling 100% drop-in fuel formulations.

Lignin remains an underutilized component of biomass primarily due to its heterogeneity and reactivity. Conventional biomass pretreatment and fractionation techniques induce deleterious condensation reactions, compounding the challenges of lignin valorization.^{5,6} This limitation has prompted the development of lignin-first fractionation techniques, which aim to stabi-

lize lignin during extraction and facilitate subsequent depolymerization and processing.^{23–25} Among these, reductive catalytic fractionation (RCF) is a promising method that cleaves ether bonds in lignin while stabilizing reactive intermediates, producing an oxygenated, aromatic-rich oil while leaving behind a solid polysaccharide pulp.²³ Owing to their low carbon numbers and liquidity, our group has previously examined the continuous deoxygenation of neat, poplar-derived RCF oils over molybdenum carbide (Mo₂C), demonstrating stable hydrodeoxygenation (HDO) performance with unprecedented carbon yields and aromatic selectivities.¹⁶ Nonetheless, there remains motivation for designing scalable processes capable of handling variable biomass feedstocks, which pose processing challenges, such as differing ether and functional group contents, that significantly impact RCF product distributions.^{20,26}

Here, we assess the practical viability of sequential RCF-HDO as a means of generating aromatic SAF blendstocks from multiple woody biomass substrates. We initially scaled our continuous HDO process to convert ~300 g of poplar-derived RCF lignin oil into 150 mL of deoxygenated aromatic hydrocarbons at 93% of the theoretical carbon yield. These volumes enabled the rigorous measurement of critical aviation fuel characteristics, including density, viscosity, freeze/flash point, and elastomer swell.^{27,28} Blends comprising 75% paraffins—sourced from



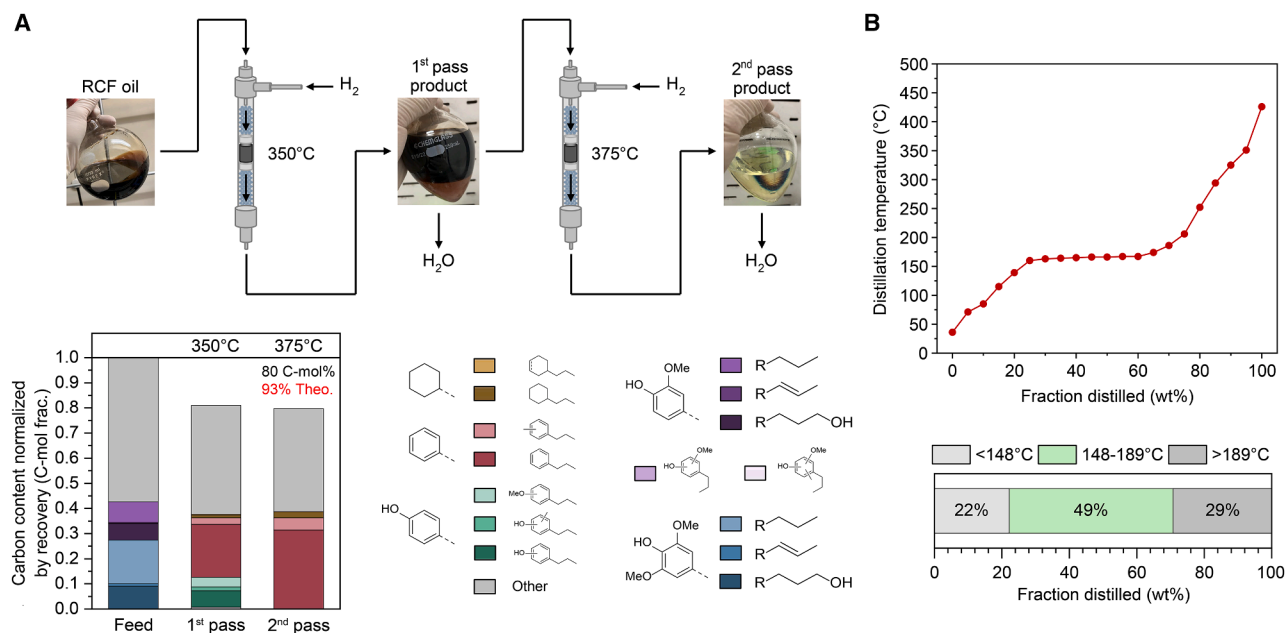


Figure 1. Scaled generation of deoxygenated lignin oil

(A) Representative schematic and quantified carbon balances for the scaled dual-pass deoxygenation reaction. Note that “other” refers to the balance of carbon quantified via CHN analysis but not quantified by GC-FID.

(B) SIMDIST results and calculated volatility fractions for the deoxygenated product mixture. Deoxygenation reaction conditions: ½-inch OD reactor, 8.66 g Mo₂C, 0.3 mL/min lignin oil, 270 mL/min H₂, 900 psig. Steady-state samples are products collected after 1 h time on stream. The RCF oil feedstock was generated using the following conditions: 300 g biomass, 30 g 5 wt % Ru/C, 3 L 2:1 (vol/vol) MeOH/H₂O, 7.5 L batch reactor, 225°C, 30 bar H₂, 80% of maximum stirring, 3 h reaction time after heating over 90 min.

Tabulated data are provided in [Data S1](#).

either the hydroprocessed esters and fatty acids (HEFAs) or ethanol-to-jet (ETJ) pathways—and 25% lignin-derived aromatics met all measured ASTM: D7566 specifications for aviation fuels and matched petroleum-based jet fuel with respect to elastomer swell performance.^{10,28} We subsequently demonstrated that lignin-derived aromatic hydrocarbons can be successfully produced from an array of woody feedstocks (including poplar, pine, and birch biomass). Interestingly, while simulated distillation (SIMDIST) revealed distinct volatility trends across the resulting crude products, the distilled jet-range fractions exhibited uniform carbon distributions and predicted fuel properties. This underscores the robustness of this approach for processing varying biomass sources, including mixed forestry residues. Overall, these results reinforce sequential RCF-HDO as a flexible, robust, and scalable pathway toward a 100% drop-in SAF by integrating lignin-derived aromatic hydrocarbons into the existing aviation biofuel infrastructure.

RESULTS AND DISCUSSION

Production of deoxygenated lignin oil for Tier β property testing

To enable distillation, blending, and rigorous property testing of lignin-derived aromatic hydrocarbons for SAF, we required 150 mL of deoxygenated product.²⁷ To accomplish this, poplar biomass ([Table S1](#)) underwent RCF over commercial Ru/C at 225°C and 30 bar H₂ in a 7.5 L batch reactor, using a

2:1 (vol/vol) MeOH/H₂O solvent to achieve optimal RCF performance.^{26,29} Reaction products from approximately ten batches were combined to generate ~300 g of RCF oil for subsequent deoxygenation. Heteronuclear single-quantum coherence (HSQC) nuclear magnetic resonance (NMR) spectroscopy ([Figure S1](#)), combined with a measured monomer-to-oil ratio of 47 wt % (including p-hydroxybenzoate derivatives), confirmed complete cleavage of β-O-4 interlinkages, indicating the effectiveness of RCF in producing a highly depolymerized lignin oil.³⁰

For deoxygenation, we constructed a ½-inch outer diameter (OD) downflow reactor with a throughput of 0.3 mL/min RCF oil. A dual-pass HDO reaction was conducted to minimize RCF oil degradation while maintaining stable catalytic reactivity ([Figure 1A](#)).¹⁶ The first reaction pass was conducted at 350°C, achieving partial deoxygenation by removing most methoxy and some phenolic functional groups. After separating the aqueous phase, the partially deoxygenated product was processed over a fresh catalyst bed at 375°C to remove any remaining oxygen-containing functionalities. Monomer concentrations were quantified via gas chromatography with flame ionization detection and mass spectrometry (GC-FID/MS) ([Figure S2](#); [Table S2](#); [Data S2](#)), with the reaction profiles shown in [Figure S3](#). The entire process yielded 130 g of HDO product at 80 C-mol % yield, corresponding to 93% of the theoretical maximum when accounting for methoxy group loss ([Note S1](#); [Table S3](#)). This yield represents the highest reported for the RCF-HDO process, most likely due to reduced mass transfer

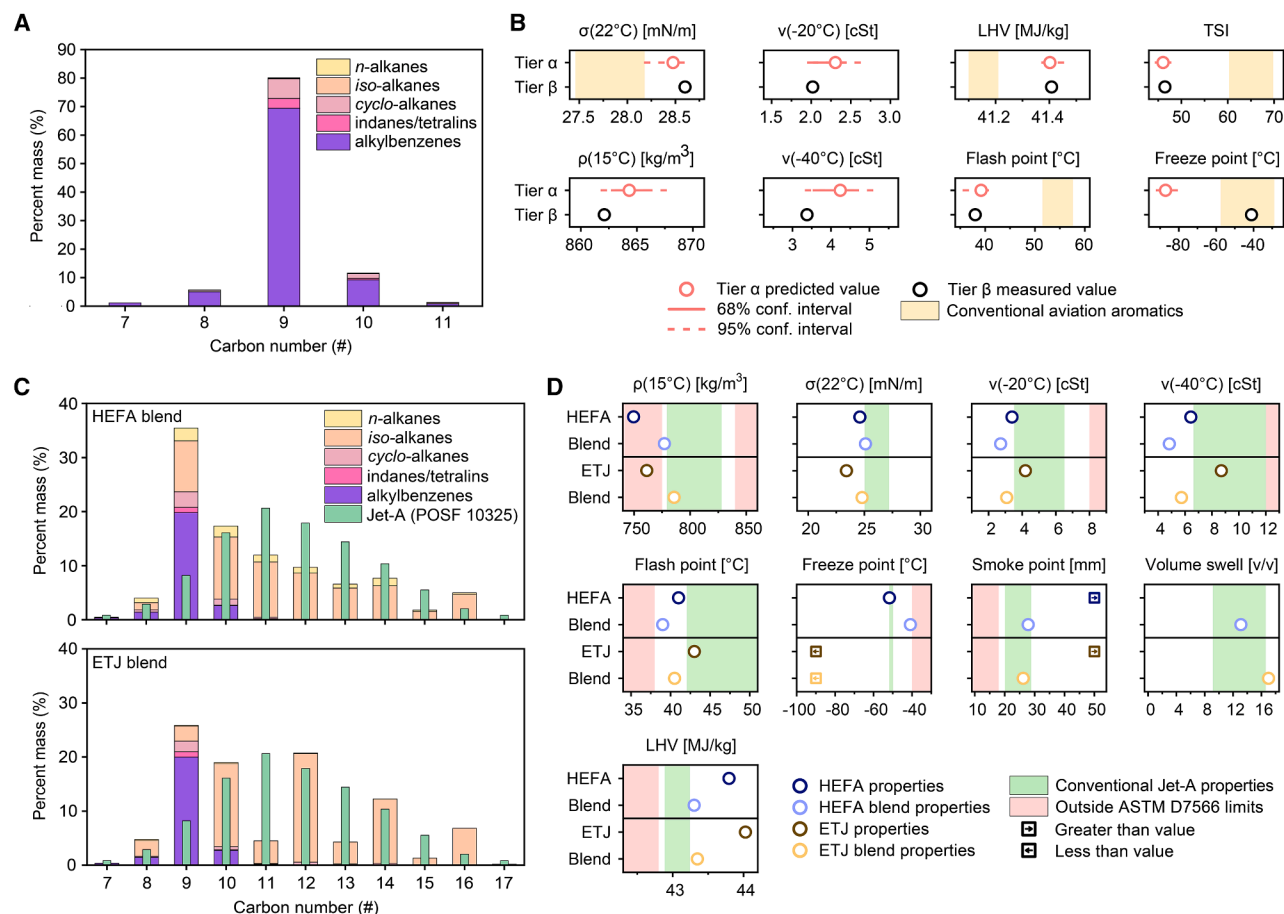


Figure 2. Pre-screening of poplar-derived deoxygenation products

(A) Hydrocarbon composition for distilled SAF-range aromatic products.

(B) Comparison between properties resulting from Tier α predictions and Tier β measurements for distilled SAF-range aromatic products. Solid bars indicate a 68% confidence interval for the estimated range. Dotted bars indicate a 95% confidence interval for the estimated range.

(C) Hydrocarbon distributions for 25/75 (v/v) blends of lignin-derived aromatics with paraffinic mixtures resulting from HEFA and ETJ.

(D) Properties for the 25/75 fuel blends as compared to neat HEFA- and ETJ-derived SAFs.

σ , surface tension; ρ , density; ν , kinematic viscosity; LHV, lower heating value; TSI, threshold sooting index. Tabulated data are provided in [Data S1](#).

losses during product workup as a result of an increased reaction scale (Figure S4). SIMDIST analysis (Figure 1B) revealed that 49 wt % of the deoxygenated product falls within the optimal volatility range (148°C–189°C) for use in SAFs. While the light (<148°C) and heavy (>189°C) distillation fractions are not ideally suited for aviation fuels, they could be repurposed for gasoline and marine bunker fuel applications, respectively.

Lignin-derived aromatics imbue the requisite characteristics for drop-in SAFs

The deoxygenated product was next distilled between 148°C and 189°C via spinning band distillation to remove volatile and heavy components that negatively impact fuel flash and freezing points, respectively. This process recovered 48 wt % of the initial HDO product mass, closely matching the predicted SIMDIST yield reported in Figure 1B. The distillate composition (Figure 2A) was dominated by C₉ aromatics, primarily propylbenzene. Property predictions (Tier α pre-screening) for the resulting

aromatic distillate were calculated for multiple fuel properties critical to aircraft operability using a previously described hydrocarbon group distribution model (Figure 2B; Table S4).^{27,31,32} These values were then compared to directly measured properties (Tier β pre-screening) (Figure 2B; Table S4) to probe the predictive accuracy of this model for lignin-derived mixtures. Most predicted values aligned well with experimental data, except for the freezing point, which was significantly higher than expected. This discrepancy likely stems from small amounts of unidentified aromatics with elevated freezing points relative to propylbenzene and motivates the need for improved methods to predict freezing points in SAF candidates, particularly for those rich in aromatic components. Despite this, the mixture possessed a freeze point of -41.1°C , meeting the ASTM threshold for Jet A ($< -40^\circ\text{C}$) but falling short of the Jet A-1 threshold ($< -47^\circ\text{C}$).²⁸ The threshold sooting index (TSI) and lower heating value (LHV) of the lignin-derived aromatic mixture showed improved combustion properties relative to the aromatic

fraction in conventional aviation fuel, meaning the aromatic product exhibited higher energy content per unit mass and reduced particulate matter (PM) emissions upon combustion. This reduction in emissions is significant, as PM emissions are carcinogenic and may contribute to radiative forcing via contrail formation.³³

To assess the performance of our aromatic hydrocarbon mixture in aviation fuel applications, we prepared 25 vol % blends of the distilled aromatic product with synthetic paraffinic hydrocarbons from both the HEFA and ETJ pathways (Figure 2C) and measured the resulting physical and combustion properties (Figure 2D). This blend ratio satisfies the ASTM: D7566 minimum density requirement while remaining within the 25 vol % limit for aromatic content in jet fuel. Promisingly, all measured properties for both fuel blends fell within ASTM: D7566 specifications for Jet A.²⁸ The blend utilizing ETJ-derived hydrocarbons showed a significantly decreased freeze point ($< -90^{\circ}\text{C}$) relative to the mixture utilizing HEFA-derived paraffins (-40.9°C), thereby meeting the necessary specification for Jet A-1 after blending. This improvement likely stems from the higher concentration of iso-alkanes in the ETJ paraffinic mixture, which could enhance the solubility of high-freezing-point aromatics at low temperatures. Both blends also demonstrated superior combustion characteristics, exhibiting elevated LHVs (43.3 MJ/kg for both mixtures) and smoke points (26.2–27.8 mm) compared to conventional aviation fuels.^{10,27} Critically, the measured volume swells of the blended fuels showed drastic improvement over conventional paraffinic SAFs, achieving between 13.1 and 17.0 vol % swell for nitrile rubber.³⁴ These results closely match the performance of conventional aviation fuels and may enable the removal of the 50% blend limit imposed on conventional SAFs, advancing the feasibility of a 100% drop-in SAF formulation.

Interdependence of lignin source and deoxygenation product distributions

The chemical structure of lignin varies widely across plant species, within species of undomesticated plants, and in response to environmental factors.^{35–37} These variations pose challenges for biomass upgrading, as most processes are optimized for specific feedstocks. However, owing to the seasonal and geographic variability in biomass availability, there is a critical need for flexible processes capable of utilizing variable lignin sources.^{26,38} For instance, in the US, softwoods and hardwoods each constitute $\sim 50\%$ of forest biomass,³⁹ meaning a process capable of handling both would have double the available feedstock supply. In RCF, lignin structural variation—such as the differences in methoxy/ether content present in syringyl/guaiacyl (S/G) and guaiacyl/p-coumaryl (G/H) lignins—largely dictates product distributions.^{26,40–42} These effects raise a key question: can the RCF-HDO process consistently yield fuels with uniform properties despite differences in lignin composition?

To assess the impact of lignin structure on fuel characteristics, we selected three woody biomasses, pine, poplar, and birch (Table S1), which were chosen for their distinct $\beta\text{-O-4}$ contents and functional group variability.^{26,36,42} Each feedstock underwent RCF under identical conditions to those reported in Figure 1, followed by a detailed characterization of the resulting

oils, including monomer quantification (Figure S5), trimethylsilyl-derivatized GC-FID/MS (Figure S6; Data S2), gel permeation chromatography (Figure S7), and HSQC-NMR (Figures S8 and S9). Each RCF oil was then subjected to continuous HDO over Mo_2C in a $\frac{1}{4}$ -inch OD three-phase downflow reactor, using a similar reaction configuration to that reported in Figure 1. To evaluate the effect of temperature on hydrocarbon distributions, we investigated two second-pass conditions: 375°C (Figure 3A) and 400°C (Figure S10). Note that thermal hydrocracking reactions remained negligible under these conditions, as evinced by the near-identical product yields and distributions across the two utilized temperatures. This suggests that product selectivity was primarily governed by catalytic deoxygenation rather than uncontrolled thermal degradation.

Carbon balances for the 350°C – 375°C dual-pass process ranged between 69 and 75 C-mol % across different feedstocks, with higher yields resulting for softwoods (pine) than for hardwoods (poplar and birch). This difference is attributed to the lower methoxy content of pine lignin than hardwood lignins, which contain S-type units, which results in heightened carbon loss via demethoxylation. This trend is further supported by the lower alkylated propylbenzene concentration in the pine HDO product (8.9 mol %) compared to that from birch (14.9 mol %), where methoxylated aromatics tend to preferentially undergo methyl transfer and C-alkylation over molybdenum-based catalysts.^{16,43,44} This highlights a promising direction, wherein deoxygenation catalysts could be engineered to promote further extents of alkylation (e.g., via the addition of further acidic character), thereby improving carbon yields beyond what is achievable with HDO alone. After accounting for this carbon loss resulting from demethoxylation (Note S1; Table S3), all feedstocks exhibited similar carbon yields between 83% and 84% of the theoretical maximum.

Aviation fuel standards require an oxygen content below 0.5 wt %, necessitating rigorous verification of deoxygenation efficiency across feedstocks. Karl-Fischer titration confirmed <0.25 wt % water in all products (Table S5), while $^1\text{H-NMR}$ spectroscopy (Figure S11) detected methoxy content below 0.1 wt % (with methoxy-related signals appearing between 3.6 and 4.3 ppm) (Table S6). Additionally, $^{31}\text{P-NMR}$ spectroscopy after derivatization with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (Figure S12; Table S7) confirmed ≤ 0.1 wt % hydroxyl content for all measured samples.^{45–47} It should be noted that these measurements were generally at or near their detection limits but nonetheless confirm that all deoxygenated products meet the SAF oxygen threshold of <0.5 wt %.¹⁶

The deoxygenated products from Figures 3 and S10 were also analyzed via SIMDIST to estimate their jet-range hydrocarbon contents as well as examine overall product volatility trends relative to those for conventional Jet A and the maximum allowed temperatures per ASTM: D7566 (Figure 3B).⁴⁸ Distillation profiles varied significantly across biomass sources, where pine-derived blendstocks contained a higher fraction of heavy components than those from hardwoods, consistent with the higher molar mass distributions of the original RCF oils and minimal C–C bond cleavage occurring during HDO. In contrast, poplar-derived blendstocks contained a greater fraction of light components, likely due to the deoxygenation of p-hydroxybenzoate, an

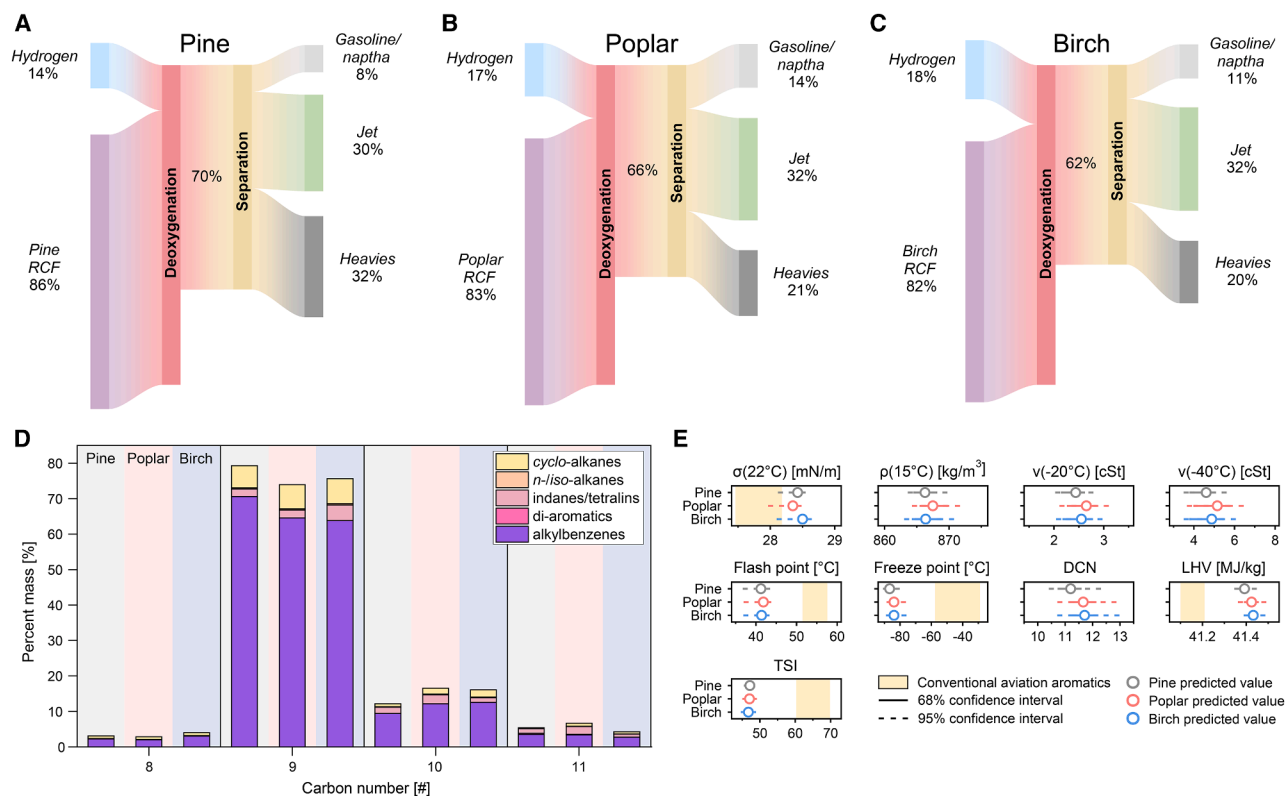


Figure 4. Enthalpy balances (lower heating value basis) and Tier α characterization for dual-pass HDO (350°C–375°C) on varying biomass sources

(A–C) Pine (A), poplar (B), and birch (C) HDO enthalpy balances.

(D) Carbon product distributions for jet-range cuts of lignin-derived HDO products.

(E) Tier α property predictions for jet-range cuts of lignin-derived HDO products. Solid bars indicate a 68% confidence interval for the estimated range. Dotted bars indicate a 95% confidence interval for the estimated range.

σ , surface tension; ρ , density; ν , kinematic viscosity; LHV, lower heating value; TSI, threshold sooting index; DCN, derived cetane number. Tabulated data are provided in [Data S1](#).

Optimal distillation cuts were identified with jet-range selectivities, as shown in [Figure 3C](#). Jet-range molecules were defined as those with boiling points between 148°C and 189°C, as was determined previously due to flash and freeze point considerations ([Figure 1B](#)). Based on this criterion, the jet-range product selectivities were as follows: pine (40%–43%) < poplar (47%–48%) < birch (50%–52%). Pine exhibited the lowest jet-range selectivity due to the higher molar mass of the initial RCF oil, in part driven by the higher dimer and oligomer contents in the RCF feed, as well as the presence of diterpenoid derivatives (dehydroabietic acid), which produce deoxygenated molecules too heavy for SAF.³⁶ Despite its heightened monomer content ([Figure S5](#)), poplar yielded slightly lower jet-range selectivities than birch, likely because p-hydroxybenzoate-derived monomers produce compounds that are too volatile for use in aviation fuels. Among the three substrates, birch was the most favorable for maximizing selectivity to jet-range aromatic hydrocarbons. However, this trend contrasted with carbon retention trends observed in HDO ([Figure 3A](#)), thereby motivating the analysis of process enthalpy flows to further evaluate the impact of RCF oil monomer content on overall jet-range hydrocarbon yield.

Consistent enthalpic yields and fuel properties result for aromatic distillates

We evaluated the overall enthalpy balances of the RCF-HDO process for each feedstock on an LHV basis ([Figures 4A–4C](#); [Table S8](#)), as the LHV directly reflects the combustion energy content of liquid fuels.²⁰ The energy balances across the deoxygenation process ranged from 62% to 70%, with pine retaining the highest enthalpy fraction (70%), followed by poplar (66%) and birch (62%), mainly due to the higher carbon retention during HDO for lignins with lower methoxy contents. In contrast, hardwood lignins required greater hydrogen input due to higher demethoxylation demands. However, their elevated syringyl-to-guaiacyl ratios also increase methane/methanol formation during demethoxylation relative to other feedstocks, potentially enabling hydrogen self-sufficiency via steam methane reforming and water-gas shifting, with surplus hydrogen available for upstream RCF operations ([Note S2](#); [Tables S9](#) and [S10](#)). Energy losses resulting during HDO stem from gas formation during demethoxylation,^{16,51} mass transfer losses, and reaction exotherms, much of which can be recovered through heat integration and byproduct utilization in a commercial setting.

Both hardwood feeds showed near-identical enthalpy retention toward jet-range hydrocarbons (32%), with birch compensating for lower carbon balances during HDO through increased selectivity toward jet-range hydrocarbons. In contrast, pine retained slightly less enthalpy in the jet-range fraction (30%) due to a higher concentration of heavy products, though this reduction may be offset by the higher lignin content of gymnosperms compared to hardwoods.⁴

In addition to volatility, we examined the influence biomass source plays on distillate composition and resulting SAF blend characteristics. To assess these effects, we conducted Tier α fuel pre-screening on the jet-range products from each feedstock (Figures 4D and 4E; Table S4).^{27,31,32} The resulting jet-range carbon distributions were remarkably similar, with C₉ alkylbenzenes comprising between 63% and 71% of the resulting aromatic blendstock composition. However, there were subtle differences across the jet-range mixtures, such as the lower C₁₀ hydrocarbon content in pine compared to poplar and birch. Despite these variations, property predictions indicated that these minor compositional differences would not significantly impact fuel performance, indicating that RCF-HDO could be applied to mixed woody feedstock streams, such as forestry residues.⁵² This flexibility could allow biorefineries to handle seasonal and annual feedstock fluctuations efficiently without extensive storage or throughput changes.⁵³ Furthermore, feedstock flexibility may also help to enable more sustainable feedstock generation practices, such as crop rotation or double cropping, supporting soil health and biological variability.^{54–56}

In conclusion, sequential RCF-HDO offers a robust approach for the generation of aromatic SAF blendstocks, showing adaptability across diverse woody biomasses while achieving hydrocarbon yields up to 93% of the theoretical limit. After distillation, these mixtures exhibit near-identical hydrocarbon distributions and properties, supporting their use in processing mixed feedstock streams, such as forestry residues. Furthermore, these aromatic blendstocks meet the necessary specifications for drop-in SAFs when blended with existing paraffinic mixtures, including both HEFA- and ETJ-derived fuels. Overall, the RCF-HDO process successfully valorizes lignin—an abundant yet underutilized renewable carbon source—offering a pathway to surpass the 50% petroleum blend limit mandated for all currently approved SAF pathways. In turn, this enables fully drop-in SAFs that integrate seamlessly with existing aviation infrastructure.

METHODS

Details regarding the methods can be found in the [supplemental methods](#).

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Yuriy Román-Leshkov (yroman@mit.edu).

Materials availability

Materials are available upon request. There are restrictions to the availability of oils generated in this study due to lab production capacity.

Data and code availability

- All data are available in either the main text or [supplemental information](#).
- No new code was utilized in conducting this study.
- Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

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AUTHOR CONTRIBUTIONS

Conceptualization, M.S.W., D.G.B., M.L.S., G.T.B., and Y.R.-L.; methodology, M.S.W., Z.Y., D.C.B., D.G.B., and M.L.S.; investigation, M.S.W., Z.Y., D.C.B., J.R.B., J.W., X.W., Q.S.N., and L.C.M.; visualization, M.S.W.; writing – original draft, M.S.W.; writing – review & editing, Z.Y., D.C.B., D.G.B., J.R.B., J.W., M.L.S., X.W., Q.S.N., L.C.M., J.S.H., G.T.B., and Y.R.-L.; supervision, J.S.H., G.T.B., and Y.R.-L.; funding acquisition, G.T.B. and Y.R.-L.

DECLARATION OF INTERESTS

M.S.W., M.L.S., G.T.B., and Y.R.-L. are inventors on a patent application that covers the HDO chemistry to deoxygenate lignin components.

SUPPLEMENTAL INFORMATION

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