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(54) Title: CONTINUOUS HYDRODEOXYGENATION OF LIGNIN TO JET-RANGE AROMATIC HYDROCARBONS

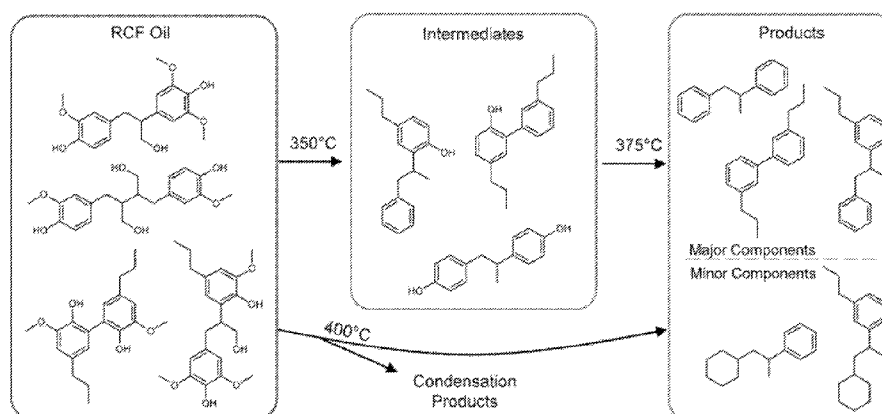


Fig. 1B

(57) Abstract: Described herein are systems and methods for the catalytic deoxygenation of lignin to generate low-oxygen aromatics that may be useful as a sustainable aviation or marine fuel. The provided systems and methods may be performed continuously without the need for a solvent, increasing both efficiency and cost effectiveness.



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CONTINUOUS HYDRODEOXYGENATION OF LIGNIN TO JET-RANGE AROMATIC HYDROCARBONS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from U.S. Provisional Patent Application No. 63/395,067, filed on August 4, 2022, the contents of which are incorporated herein by reference in their entirety.

CONTRACTUAL ORIGIN

[0002] This invention was made with government support under Contract No. DE-AC36-08GO28308 awarded by the Department of Energy. The government has certain rights in the invention.

BACKGROUND

[0003] In 2019, 106 billion gallons of jet fuel were consumed globally and this number is expected to more than double by 2050 as a result of increased travel demand. To mitigate its impact on climate change, the aviation industry has pledged to reduce net CO₂ emissions in half by 2050. To achieve this goal, sustainable aviation fuel (SAF) must be deployed at a massive scale. Today, most commercially available SAF is synthesized via deoxygenation of plant-derived lipid feedstocks to produce iso- and n-alkane hydrocarbon blends, but these feedstocks are not available in the volumes required to meet the projected fuel demand. Notably, cycloalkanes and aromatics together comprise between 30 and 70 wt% of modern aviation fuel or between 32 and 74 billion gallons per year. However, current SAF technologies cannot produce the aromatic or the cycloalkane components at the scale necessary to satisfy the required properties of jet fuel (namely fuel density and elastomer compatibility) to power the existing fleet of aircrafts, which is a constraint that has resulted in a 50% blending wall with conventional fossil fuels. A technology capable of generating aromatics and cycloalkanes from renewable feedstocks is thus essential for the development of a viable 100% drop-in SAF.

[0004] Lignin is the largest source of renewable aromatics available in nature comprising between 15-30% of lignocellulosic biomass. In principle, the 90 million dry-tons of lignin harvested in the United States in 2017 could generate 15 billion gallons of jet-range hydrocarbons based on carbon content. By 2040, this value could increase to 63 billion gallons annually (>50% of current global demand) given projections on future lignin availability. Despite its potential, lignin is currently either re-dispersed in the field or slated to be burned

for low grade heat by the cellulosic ethanol and paper industries because lignin becomes highly recalcitrant when separated from the cellulose fibers in biomass. Alternative lignin extraction methods that rely on reductive catalytic fractionation (RCF), protection group chemistries or flow-through solvolysis minimize re-condensation pathways, but the resulting lignin oils have high oxygen contents ranging between 27-34 wt% which must be reduced to trace levels for use in jet fuel. To this end, significant progress has been made in the development of catalysts capable of hydrodeoxygenation (HDO) of oxygenated aromatics. However, the translation of promising catalysts to viable processing strategies with real lignin feedstocks has been hindered by major challenges, such as the use of expensive noble-metal catalysts, catalyst deactivation coupled with low deoxygenation efficiency when using real feedstocks, excessive hydrogen consumption due to ring hydrogenation and hydrocracking, and low carbon yields due to condensation/coking, hydrocracking to gaseous products, or upgrading of only the monomeric fraction.

SUMMARY

[0005] Described herein are systems and methods for the catalytic deoxygenation of lignin to generate low-oxygen aromatics that may be useful as a sustainable aviation or marine fuel. The provided systems and methods may be performed continuously without the need for a solvent, increasing both efficiency and cost effectiveness.

[0006] In one aspect, provided is a method for generating aromatic compounds from a lignin feed stock by utilizing a two stage process, first at a lower temperature and second at a higher temperature to fully deoxygenate the lignin while avoiding unwanted secondary reactions such as condensation reactions. This method may utilize a single or multiple catalysts, including as an example an Mo₂C-based catalyst. The first, lower temperature may, for example, be selected from the range of 250 °C to 450 °C, 300 °C to 400 °C, 325 °C to 375 °C, 325 °C to 350 °C, or about 350 °C. The second, higher temperature may, for example, be selected from the range of 275 °C to 475 °C, 325 °C to 425 °C, 350 °C to 400 °C, 350 °C to 375 °C, or about 375 °C. The resulting aromatic hydrocarbons may have very low oxygen content, for example, having a mole fraction of oxygen in the resulting compounds of less than or equal to 10%, 5%, 1%, 0.5%, or 0.1%.

[0007] The method may be performed with neat lignin oil, e.g., lignin without the presence of a solvent. The ability to react neat lignin oil could provide various benefits such as a reduction in cost, smaller reactor requirements, etc. However, the described systems and methods also

can be utilized in situations where it is preferable to dissolve the lignin reactant into a solvent, such as an aromatic solvent, for example, toluene.

[0008] In an aspect, provide is a system or reactor for the generation of low-oxygen aromatics comprising: a first reaction zone comprising a first catalyst at a first temperature; a second reaction zone comprising a second catalyst at a second temperature; where in the reactor is capable of performing hydrodeoxygenation of lignin to generate aromatic products. The reactor may be a packed bed reactor or a trickle bed reactor. The reactor may also allow for continuous process flow, either as individual steps (e.g., each step is continuous) or a single continuous process. The reactor may be capable of steady state operation.

[0009] Other catalysts may be useful including supported metal catalysts as the second, higher-temperature catalyst. Additionally, the described process may be altered to generate cycloalkanes rather than aromatic products. This may be accomplished by incorporating a metal-doped Mo₂C-based catalyst or substituting one or both of the catalysts with a catalyst comprising nickel phosphide.

[0010] In an aspect, provided is a catalyst comprising Mo₂C capable of partially or fully deoxygenating lignin, as described by the systems and methods provided herein.

BRIEF DESCRIPTION OF DRAWINGS

[0011] Some embodiments are illustrated in referenced figures of the drawings. It is intended that the embodiments and figures disclosed herein are to be considered illustrative rather than limiting.

[0012] Figure 1 provides an Overview schematic of HDO of RCF lignin oil. Figure 1A provides a summary of the lignin monomers quantified as described herein at all levels of partial conversion. Monomer conversion in single pass or two-pass achieves similar results yielding propylbenzene as a major product. The darker shades represent the major reaction pathway on Mo₂C and the lighter shades are products resulting from side-reactions, including rearrangement of the functional group position and ring alkylation (products noted with an asterisk), which have previously been observed during deoxygenation with molybdenum oxide catalysts. The acronyms are as follows: PS: propylsyringol, PS=: propenylsyringol, PS-OH: dihydrosinapyl alcohol, PG: propylguaiacol, PG=: propenylguaiacol, PG-OH: dihydroconiferyl alcohol, PP: propylphenol, Alk. PG: methyl-propylguaiacol, Alk. PP: methyl-propylphenol, Rearr. PG: methoxy-propylphenol, PB-OMe: propylanisole, PB: propylbenzene,

PCH: propylcyclohexane. Figure 1B shows examples of dimers identified in the feed, intermediates, and products. Dimer conversion is sensitive to temperature with a parallel pathway toward condensation products at higher temperatures.

[0013] Figure 2 illustrates Catalyst-free control experiments to evaluate lignin oil stability. Figure 2A shows mass balance on steady state samples collected during no-catalyst control experiments. The bars show mass fractions of monomers and non-monomers, and the product bars are scaled by the overall mass recovery. The height of the bar is the average value, and the error bars show one standard deviation for 3 steady state samples. The feed bar is included for each experiment to account for slight variability between batches of RCF oil. Figure 2B provides GPC on the feed (“RCF Oil”) and the products from no-catalyst control experiments at different temperatures, with the inset showing the dimer and oligomer portion of the curve to highlight the shift in product distribution with increasing temperature. All samples were prepared to the same concentration of 2 mg/mL and the traces were not normalized or scaled.

[0014] Figure 3 illustrates evaluation of activity and stability of Mo₂C for solvent-free lignin HDO. Figure 3A shows steady state results of monomer distribution and monomer mole balance from HDO experiments flowing neat RCF lignin oil (“Feed”) over a packed bed of 2.88 g Mo₂C (60-100 mesh) in a trickle bed reactor. Steady state results were taken after 2.5 h on stream, combined from several hours, and the water formed during reaction was removed prior to performing mass and mole balance calculations. Each bar is labelled with the reactor temperature and the weighted hourly space velocity (WHSV) calculated as the mass flowrate of lignin oil divided by mass of catalyst. The transient distribution of quantified monomers as a function of time on stream at (Figure 3B) 300°C, (Figure 3C) 325°C, and (Figure 3D) 350°C and 0.1 mL/min lignin oil (WHSV = 2.35 h⁻¹). Figure 3E provides the conversion of oxygen from the monomer fraction for each experiment shown in Figures 3B-3D, plotted as the mole percent of oxygen removed from the monomers at each time on stream. Constant conditions: 900 psi, 2.88 g Mo₂C (60-100 mesh), 90 mL/min H₂, and toluene at 1 mL/min for 30 min during start-up.

[0015] Figure 4 provides optimization of deep deoxygenation of lignin oil for jet-range aromatic production. (Figure 4A) Carbon, oxygen, and hydrogen content in the oil on a mass basis, as determined via total carbon analysis. The weight percent results of total carbon analysis were multiplied by the mass recovery of oil at steady state after removing the aqueous fraction to generate the plot. (Figure 4B) Results of quantitative GCxGC analysis of the final

deoxygenated oils from each of the experiments shown in Figure 4A. (Figure 4C) Simulated distillation generated by the ASTM D2887 method of the fully deoxygenated product from each multi-pass experiment, with a zoomed-in plot on the dimer region. Protocols and conditions described herein. (Figure 4D) Production of fully deoxygenated lignin oil using optimized multi-pass conditions. The Sankey diagram shows the carbon balance on each pass of the optimum multi-pass experiment. The carbon content in the whole oil was determined using total carbon analysis. The monomer carbon content was determined with GC-FID analysis and is plotted as a fraction of the total carbon content. The carbon content was multiplied by the steady state recovery of the oil (by mass) across each pass. Photos show the oil at each stage of the process, with water (bottom phase) formed during the reaction separating from the deoxygenated organics (top phase). Conditions: 2.88 g Mo₂C (60-100 mesh), 0.1 mL/min lignin oil, 90 mL/min H₂, 900 psi, 350°C first pass, 375°C second pass, and toluene at 1 mL/min for 30 min during start-up.

[0016] Figure 5 provides an example process for reductive catalytic fractionation as described herein utilizing poplar as a lignin source.

[0017] Figure 6 provides an example process for hydrodeoxygenation and an example trickle bed reactor.

[0018] Figure 7 illustrates example cycloalkane and aromatic products resulting from the described processes. The color or gray scale can corresponds to the graphs provided in Figures 8, 10A, 10B, 12A and 12B.

[0019] Figure 8 provides feed compositions and monomer/oil ratios for polar, pine and corn stover feedstocks, illustrating a lower monomer to oil ratio for pine.

[0020] Figure 9 provides GPC-UV chromatography for poplar, pine and corn stover feedstocks.

[0021] Figure 10A shows monomer distribution for pine feedstock at different times for 350 °C and 400 °C.

[0022] Figure 10B shows the carbon, hydrogen and oxygen content for pine feedstock.

[0023] Figure 11 illustrates the effect of feedstock ether content on fuel properties, indicating that 66% of products fall within jet fuel range aromatics.

[0024] Figure 12 shows monomer distribution for corn stover feedstock at different times for 350 °C and 400 °C.

[0025] Figure 13 shows the elemental content for poplar, pine and corn stover feedstocks. Nitrogen and sulfur are likely due to proteins and extractives.

DETAILED DESCRIPTION

[0026] The embodiments described herein should not necessarily be construed as limited to addressing any of the particular problems or deficiencies discussed herein. References in the specification to “one embodiment”, “an embodiment”, “an example embodiment”, “some embodiments”, etc., indicate that the embodiment described may include a particular feature, structure, or characteristic, but every embodiment may not necessarily include the particular feature, structure, or characteristic. Moreover, such phrases are not necessarily referring to the same embodiment. Further, when a particular feature, structure, or characteristic is described in connection with an embodiment, it is submitted that it is within the knowledge of one skilled in the art to affect such feature, structure, or characteristic in connection with other embodiments whether or not explicitly described.

[0027] As used herein the term “substantially” is used to indicate that exact values are not necessarily attainable. By way of example, one of ordinary skill in the art will understand that in some chemical reactions 100% conversion of a reactant is possible, yet unlikely. Most of a reactant may be converted to a product and conversion of the reactant may asymptotically approach 100% conversion. So, although from a practical perspective 100% of the reactant is converted, from a technical perspective, a small and sometimes difficult to define amount remains. For this example of a chemical reactant, that amount may be relatively easily defined by the detection limits of the instrument used to test for it. However, in many cases, this amount may not be easily defined, hence the use of the term “substantially”. In some embodiments of the present invention, the term “substantially” is defined as approaching a specific numeric value or target to within 20%, 15%, 10%, 5%, or within 1% of the value or target. In further embodiments of the present invention, the term “substantially” is defined as approaching a specific numeric value or target to within 1%, 0.9%, 0.8%, 0.7%, 0.6%, 0.5%, 0.4%, 0.3%, 0.2%, or 0.1% of the value or target.

[0028] As used herein, the term “about” is used to indicate that exact values are not necessarily attainable. Therefore, the term “about” is used to indicate this uncertainty limit. In some embodiments of the present invention, the term “about” is used to indicate an uncertainty limit

of less than or equal to $\pm 20\%$, $\pm 15\%$, $\pm 10\%$, $\pm 5\%$, or $\pm 1\%$ of a specific numeric value or target. In some embodiments of the present invention, the term “about” is used to indicate an uncertainty limit of less than or equal to $\pm 1\%$, $\pm 0.9\%$, $\pm 0.8\%$, $\pm 0.7\%$, $\pm 0.6\%$, $\pm 0.5\%$, $\pm 0.4\%$, $\pm 0.3\%$, $\pm 0.2\%$, or $\pm 0.1\%$ of a specific numeric value or target.

[0029] As used herein, the term “Mo₂C” or “Mo₂C-based catalyst” refers to a catalyst comprising or consisting essentially of a form of molybdenum carbide. In some embodiments, the catalyst may comprise or consist essentially of Mo₂C or β -Mo₂C, but other forms or phases of molybdenum carbide may also be the primary or a secondary component. Further, Mo₂C-based catalysts may include metal-doped catalyst where a metal, such as a transition metal, is included in the catalyst, for example, Cu, Ni, Pt. Mo₂C based catalysts may also be multidimensional or multilayered.

[0030] The provided discussion and examples have been presented for purposes of illustration and description. The foregoing is not intended to limit the aspects, embodiments, or configurations to the form or forms disclosed herein. In the foregoing Detailed Description for example, various features of the aspects, embodiments, or configurations are grouped together in one or more embodiments, configurations, or aspects for the purpose of streamlining the disclosure. The features of the aspects, embodiments, or configurations, may be combined in alternate aspects, embodiments, or configurations other than those discussed above. This method of disclosure is not to be interpreted as reflecting an intention that the aspects, embodiments, or configurations require more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed embodiment, configuration, or aspect. While certain aspects of conventional technology have been discussed to facilitate disclosure of some embodiments of the present invention, the Applicants in no way disclaim these technical aspects, and it is contemplated that the claimed invention may encompass one or more of the conventional technical aspects discussed herein. Thus, the following claims are hereby incorporated into this Detailed Description, with each claim standing on its own as a separate aspect, embodiment, or configuration.

Example 1 – Continuous hydrodeoxygenation of lignin to jet-range aromatic hydrocarbons

[0031] Described in this example is a solvent-free process for the HDO of poplar RCF lignin oil with near-quantitative carbon yields using earth-abundant molybdenum carbide (Mo₂C)

catalysts. Continuous flow HDO experiments with real lignin feeds under solvent-free conditions were performed in a custom-built three-phase trickle bed reactor. Poplar RCF lignin oil was chosen as an illustrative lignin substrate, with recent studies showing potential for commercial implementation of RCF in a lignin- first biorefinery. The RCF process solvolytically extracts and catalytically depolymerizes lignin from whole biomass to produce an oxygenated aromatic oil consisting of ~50 wt% monomeric species and ~50 wt% carbon-carbon linked dimers and larger oligomers. Accordingly, complete deoxygenation of RCF oil would generate a mixture rich in alkylated arenes ranging between C₉ and C₂₀, which is ideal for jet fuel blending.

Results

[0032] Tracking deoxygenation with Mo₂C-based catalysts. The complexity of lignin oil components and their deoxygenated products necessitates rigorous analytical methods to close mass balances accurately. Accordingly, we identified and quantified partially and fully deoxygenated monomers and dimers during HDO experiments using a feed consisting of 2 wt% RCF oil dissolved in toluene. Unsupported Mo₂C was used as the catalyst due to its ability to directly cleave C–O bonds in model aromatic oxygenate molecules without hydrogenating the aromatic rings. Although Mo₂C has not been studied extensively for the deep deoxygenation of lignin oil, we hypothesized it could provide a route toward hydrogen- efficient deoxygenation with control over aromatic product selectivity. **Fig. 1A** summarizes all the lignin-derived monomers quantified by gas chromatography with flame ionization detection (GC-FID) in this study. This method afforded monomer mole balances of 100% +/- 5% at all levels of partial conversion investigated. We used trimethylsilyl derivatization with GC coupled with mass spectrometry (GC- MS) to identify dimeric compounds at different levels of conversion (**Fig. 1B**). Generally, both monomeric and dimeric species followed similar conversion and selectivity trends to those observed during vapor-phase Mo₂C HDO with model compounds. The first functional groups to undergo deoxygenation are the γ - hydroxyl groups (e.g., dihydroconiferyl alcohol, PG-OH), generating guaiacol and syringol derivatives. Next, deoxygenation of the methoxy group (e.g., propylguaiacol, PG) produces phenolics. Finally, the phenolic groups (e.g., propylphenol, PP) are cleaved to produce alkylbenzenes.

[0033] Evaluating solvent-free lignin oil stability. While 2 wt% RCF oil in toluene was a useful system for the development of analytical methods, toluene only dissolves ~70 wt% of the RCF oil, extracting low molecular weight components preferentially. For this reason, neat RCF oil

was used as the feedstock for all subsequent studies. To study the stability of solvent-free RCF oil under elevated temperatures and determine acceptable operating temperatures for the HDO process, we performed catalyst-free flow experiments using conditions otherwise amenable to HDO chemistry. Reactor temperatures of 325, 350, and 375°C showed lignin oil mass recoveries of 98.7 (± 1.2), 98.5 (± 2.0), and 98.6 (± 2.5) wt%, respectively, whereas at 400°C, the mass recovery was 93.2 (± 0.9) wt% (**Fig. 2A**). PG-OH and PS-OH, which make up 15 wt% of the RCF oil feed, were the most sensitive monomers to temperature, with combined recoveries of 90.0, 87.9, 40.2 and 17.8 wt% at 325°C, 350°C, 375°C and 400°C, respectively. Additionally, a combined 5.6 wt% of rearranged, alkylated, and partially deoxygenated monomeric products were formed during the no-catalyst experiment at 400°C. Changes in the molecular weight distribution of the lignin oil, characterized using gel permeation chromatography (GPC) and GC-MS data of derivatized samples, indicated that increasing the temperature from 325 to 400°C progressively decreased dimer concentrations and promoted the formation of new oligomers via condensation reactions (**Fig. 2B**).

[0034] Mo₂C catalyst activity during HDO of lignin oil. We next evaluated both the activity and stability of the Mo₂C for the continuous HDO of undiluted lignin oil at temperatures below 400°C to reduce deleterious lignin condensation (**Figs. 3A-3E**). To avoid structural changes caused by the exposure of the carbide phase to molecular oxygen, fresh Mo₂C was synthesized *in situ* via the carburization of ammonium molybdate tetrahydrate (AMT) immediately prior to the start of each experiment. At 350°C and a weighted hourly space velocity (WHSV) of 2.35 g_{lignin}/g_{catalyst}/h, a steady state monomer oxygen conversion of 65.8 $\pm$ 0.05 mol% was achieved with major monomeric products of 50.2 mol% PP, 13.8 mol% PB and 11.6 mol% PB-OMe (**Fig. 3A**). Despite achieving stable deoxygenation at these conditions, neither doubling the residence time (WHSV = 1.175 h⁻¹), nor recycling the partially deoxygenated oil over a fresh catalyst bed at 350°C resulted in complete monomer deoxygenation. Higher temperatures were required to activate the aryl-OH bonds, with 375°C and a WHSV=2.35 h⁻¹ achieving 48.5% removal of phenolic groups. **Fig. 3B** and **Fig. 3C** show the effect of temperature on catalyst stability. Transient data collected at 300 and 325°C from 2.5 to 6 h on stream showed steady deactivation profiles with a decrease in monomer oxygen conversion of 58 to 52 mol% for 325°C and 32 to 22 mol% for 300°C. Although temperatures as low as 150°C have been used to deoxygenate anisole and 280°C to achieve near complete deoxygenation of model phenolic mixtures to aromatics at steady state with Mo₂C, our data indicate that temperatures of 350°C and 375°C are needed for stable removal of methoxy and phenolic groups in neat lignin oil,

respectively. These results on activity and stability resemble the performance of MoO₃ during HDO. Although PXRD analysis of the catalyst after reaction does not show bulk oxidation to MoO₃, *in situ* techniques have shown the surface of Mo₂C is oxidized during reaction with oxygenates. This potentially explains why prior work on HDO of oxygen-rich real lignin feeds with Mo₂C did not achieve complete deoxygenation and highlights the difficulty in translating the results of model systems to biomass feedstocks.

[0035] Achieving deep deoxygenation to aromatic hydrocarbons. Together, lignin oil stability (**Figs. 2A-2B**) and catalyst activity (**Figs. 3A-3E**) experiments revealed an important trade-off in lignin oil HDO: low temperatures result in catalyst deactivation but achieve high carbon balances by preserving oligomers, while high temperatures are necessary to maintain catalyst activity and achieve full deoxygenation, but result in the loss of dimers through condensation. We evaluated two routes for generating deeply deoxygenated oil products: i) increasing the temperature and the residence time in a single-pass at 400°C and WHSV = 1.175 h⁻¹ and ii) operating in a two-pass mode wherein an initial HDO run is performed at an intermediate temperature to generate a mixture of partially deoxygenated monomers and oligomers that is more resistant towards subsequent condensation reactions, followed by a second pass at a higher temperature to achieve full deoxygenation. For the two-pass experiments, first-pass products were collected at 325°C, 350°C, or 375°C, each over a fresh catalyst bed. Next, these products were deoxygenated at 375°C in a second run with a fresh catalyst bed. **Fig. 4A** summarizes the carbon, hydrogen, and oxygen content of each oil scaled by the mass recovery from each pass along with the overall carbon recovery. After the first pass at 400°C, 375°C, 350°C, and 325°C, 0.7, 8.0, 11.7, 15.8 wt% oxygen remained, respectively. This was reduced to 1.0, 2.1 and 1.2 wt% for 375-375°C, 350-375°C, and 325-

[0036] 375°C, respectively. The near complete deoxygenation of the products was confirmed with heteronuclear single quantum coherence (HSQC) nuclear magnetic resonance spectroscopy (NMR) and derivatization + GC-MS. The final monomer product distributions were similar in all cases, with propylbenzene selectivity values of ca. 78 mol%. The dimer products were more sensitive to temperature, showing 8.9, 9.5, 11.9, and 14.2 wt% dimer content for first pass temperatures of 400°C, 375°C, 350°C, and 325°C, respectively as determined by quantitative GCxGC analysis (**Fig. 4B**). This trend in dimer recovery was supported by simulated distillation (**Fig 4C**), and additional chromatography techniques.

[0037] Two-pass operation with 350°C followed by 375°C achieved an optimal balance for catalyst stability and jet-range aromatic production. Indeed, 350°C was the optimal temperature to maintain stable catalyst activity at partial deoxygenation in the first pass (total product oxygen content of 11.7%), while higher temperatures of 375°C and 400°C resulted in an elevated loss of aromatic dimers. **Fig. 4D** summarizes the optimal overall process, where we obtained a reduction in total oxygen content from 26.3 mol% to 2.1 mol% (95.7% conversion), with an unprecedented 73.1 C-mol% recovery (86% of theoretical based on removal of methoxy groups) and 87.5% monomer selectivity toward aromatic hydrocarbons. For reference, recent reports have shown yields between 10-30 wt% and 30-50 wt% via one- and two- step processes, respectively, while our process's mass recovery is consistently between 50-60 wt% while achieving higher levels of deoxygenation than those studies discussed. GCxGC quantification determined a final aromatic dimer (C14- C20) content of 11.9 wt.% and aromatic monomer (C9-C12) content of 56 wt%, summing to 67.9 wt% of jet-range aromatics in the final oil.

Discussion, Recommendations and Conclusions

[0038] The provided example demonstrates that lignin stability is a key constraint under typical HDO conditions, and that two-pass HDO, with the first pass used for stabilization via partial conversion and the second pass for deep deoxygenation, is a viable strategy for lignin upgrading with high atom economy. This strategy could be broadly applicable to other lignin feedstocks. Furthermore, HDO reactions with Mo₂C selectively cleaved C-O bonds while leaving the C-C structure of the lignin substrate intact. In addition to minimizing the consumption of hydrogen, this selectivity indicates that the distribution of HDO products could be tuned by modifying the lignin feedstock itself. For example, a lignin substrate with a higher fraction of dimeric components could be utilized to increase the C14-C20 aromatic fraction in the resulting deoxygenated product. Furthermore, the carbon backbone of the dimer and oligomer fraction retains sufficient chemical functionality during reaction to differentiate between types of lignin inter-unit linkages that are synthesized *in planta* (e.g., β -1 vs β -5), providing an analytical opportunity to quantitatively track lignin bond distributions.

[0039] This example motivates the development of catalysts that can achieve stable HDO of real lignin feedstocks at low temperatures. Notably, the behavior of the catalyst under reaction with neat lignin oil was distinctly different than vapor-phase model compound studies reported to date. Furthermore, while the existing literature contains a strong fundamental framework

from which to understand the impact of controlled Mo₂C surface oxidation on model compound reactivity, the parameters that determine extent of catalyst oxidation under reaction conditions with real lignin feeds have not been mapped and are not well understood. Understanding the factors that drive catalyst surface deactivation under reaction conditions with real feedstocks may enable rational catalyst design or reaction engineering solutions to mitigate catalyst deactivation and enable lower operating temperatures. Altogether, performing experiments in a trickle-bed reactor to generate continuous, steady-state HDO data using a real lignin feedstock, along with rigorous analytics to track carbon balances and individual components, was essential to understanding the limitations of this complex system.

[0040] Deoxygenated aromatics resulting from this process could be directly blended with existing commercial SAFs (which mainly consist of iso and n-alkanes), potentially overcoming the existing 50% blend-wall by providing the necessary aromatic components to increase both fuel density and elastomeric compatibility. Alternatively, subsequent hydrogenation, ring-opening, and/or hydrocracking reactions could be implemented to convert a fraction of the lignin-derived aromatics to other paraffinic compounds (including naphthenes and iso/n-alkanes), thereby generating an entirely lignin-derived SAF.

[0041] Finally, we propose potentially blending feedstocks (rather than deoxygenated products) to achieve desired aromatic/aliphatic ratios followed by subsequent deoxygenation over Mo₂C to directly generate a complete drop-in SAF. Ongoing techno-economic analyses and life cycle assessments are geared towards identifying critical areas for further development and integration of our product into a 100% SAF blend.

Materials and Methods

[0042] Generation of RCF lignin oil. 60 g of poplar (milled and sieved to <2 mm), 12 g of 5 wt% ruthenium on carbon (Sigma-Aldrich®) and 400 mL methanol (ACS reagent grade, Macron Fine Chemicals) were loaded into a 1 L batch reactor (Parr instrument company®, Series 4525HP). The reactor was sealed, flushed 3 times and pressurized to 30 bar with H₂ (UHP, Airgas®). During reaction, the mixture was stirred at 700 rpm with an overhead impeller. The temperature was monitored using an internal thermocouple and the furnace, stir rate, and cooling water were controlled with a Parr® instrument controller (series 4848). The temperature was ramped from 25°C to 225°C for 1.5 h, then held at 225°C for 3 h before rapidly cooling to 25°C via cooling water. Catalyst loading, hydrogen pressure, and reaction time were

optimized to achieve complete conversion of ether bonds, ensuring no additional monomers were produced during HDO to enable monomer mole closure.

[0043] After reaction, the lignin fraction was isolated by vacuum filtration through a 4 μm ceramic filter. The solids were rinsed twice with methanol and the solvent was removed under vacuum. The resulting oil was purified to remove any sugars or acids that were extracted from the biomass during RCF with a dichloromethane (DCM)/water extraction, starting with 30 mL DCM (Laboratory-plus grade, Honeywell®) and 30 mL water (Milli-Q®) and subsequently rinsing the aqueous phase twice with 15 mL DCM. The DCM was removed from the organic phase under vacuum, with a preliminary removal at 100 torr by rotary evaporation followed by a secondary 0.1 mTorr evacuation on a Schlenk line with magnetic stirring at 250 rpm. Overall, this process obtained ~9 g of purified RCF lignin oil from a single 60 g poplar RCF experiment.

[0044] Catalyst synthesis. AMT (ACS reagent grade, Sigma-Aldrich®) was sieved between 60-100 mesh and an appropriate amount to achieve the desired quantity of Mo₂C was loaded into the trickle-bed reactor (see loading procedure). The reactor was then heated from 25°C to 700 °C over 3.5 h and held at 700°C for 3 h. Hydrogen gas was flowed at 55 mL/min for the duration of the synthesis, and methane (UHP, Airgas) was flowed at 15 mL/min for the first 6 h, enabling a 0.5 h scavenging step with pure hydrogen gas at 700°C. The reactor was then cooled and left sealed under hydrogen gas flow prior to reaction.

[0045] Trickle bed reactor design. Reactions were performed in a custom trickle-bed reactor. A 21" long, 1/4" OD Hastelloy reactor tube was heated in a vertically-mounted, insulated, single-zone, split furnace (Applied Test Systems® Series 3210) with steel blocks (machined to fill void space in the furnace) to ensure adequate heat transfer and maintain isothermal operation. A K-type thermocouple slotted to contact the outside of the reactor tube was used to measure temperature while another thermocouple at the middle of the furnace and contacting the outside of the steel blocks was used to regulate temperature with a PID temperature controller (Digi-sense® TC9500). Gas flow rates were controlled using mass flow controllers (Brooks® SLA5850S1BAB1B2A1) and liquid was pumped using a Teledyne® ISCO syringe pump (Model 500D). Liquid was fed into the top of the reactor through a 1/16" OD 316 stainless steel tube which extended to the start of the heating zone. Gas was fed into the top of the reactor via 1/4" 316 stainless steel tubing and flowed co-currently with liquid in the down-flow direction through the packed catalyst bed. Liquid samples were collected at room temperature in a gas/liquid separator (Jerguson Gage & Valve Co.®). Gas flowed out of the

top of the gas/liquid separator and through a diaphragm back- pressure regulator (Equilibar® H3P1SNN8-NSBP1500T100G20KK), which maintained the overall system pressure. A nitrogen back-fill line enabled system pressure maintenance during sampling through a needle valve (Swagelok®).

[0046] Reactor packing procedure. A quartz wool (Technical Glass Products Inc.®) plug was placed in the bottom of the reactor tube, followed by 9.75” of quartz chips (fused silicon dioxide (granular), Sigma-Aldrich®), filling from the bottom of the reactor to the center of the heating zone of the furnace. A quartz wool plug, followed by the catalyst bed, followed by another quartz wool plug were then loaded. For neat lignin oil experiments, the bed comprised pure catalyst only. For 2 wt% lignin oil in toluene experiments, the catalyst was diluted to 1 g using 120 grit silicon carbide powder ($\geq 98.0\%$, Alfa Aesar®). Finally, quartz chips were added up to 1” below the level of the drip tube at the top of the reactor.

[0047] Feed preparation. Neat lignin oil was used directly after the procedure outlined above for generating RCF oil, combining the oil generated from 5-10 batch reactions to generate 45-90 g of feed oil. Recycled lignin oil was prepared by combining the samples from a previous experiment(s) after removing enough sample for analysis. The water fraction phase-separated from the partially deoxygenated lignin oil and was removed with a pipette. Diluted 2 wt% lignin oil in toluene was prepared by adding 2 wt% lignin oil, 0.2 wt% decane ($\geq 99.0\%$, Sigma-Aldrich®), and 97.8 wt% toluene (≥ 99.8 , VWR Chemicals® BDH) to a large glass container. It was then shaken vigorously, sonicated for 20 minutes, and left overnight to equilibrate. To remove the suspended undissolved lignin oil and prevent clogging, the cloudy lignin oil in toluene was centrifuged at 8,000 rpm for 5 minutes. The resulting liquid was decanted and used for reaction.

[0048] Running a reaction. After catalyst synthesis, the reactor was cooled to room temperature at atmospheric pressure under flowing hydrogen at 55 mL/min. The steel heat transfer blocks were placed in the furnace and the reactor was slowly pressurized by nitrogen back-fill to the reaction pressure of 900 psi. The hydrogen flowrate was set to 30 mL/min for reagents dissolved in toluene or 90 mL/min for neat lignin oil. The reactor was leak checked and heated. For reagents dissolved in toluene, the feed was flowed at 2 mL/min during heating to pre- wet the catalyst bed, and the flowrate was reduced to the reaction flowrate once the furnace reached temperature. The liquid collector was drained when the furnace reached 200°C, and samples were taken when the furnace reached 250°C and 300°C. Samples were taken every 40 min for

the duration of the experiment. For neat lignin oil experiments, the reactor was heated to reaction temperature while flowing pure toluene at 1 mL/min. Once the reactor reached temperature, the liquid feed was switched to neat lignin oil flowing at 0.1 or 0.05 mL/min. Samples were taken every 30 or 60 min.

[0049] Sample work-up and analysis. Each sample was collected into a pre-weighed vial, allowing for sample mass measurement post-experiment. To prepare neat lignin oil samples for gas chromatography with flame ionization detection (GC-FID) analysis, 30 μ L of oil was dissolved in 2 mL of acetone containing 2 mg/mL of 1,3,5-tri-tert-butylbenzene ($\geq 98.0\%$, TCI®), measuring the weight of oil and acetone solution to improve accuracy. Samples from experiments with reagent dissolved in toluene were weighed and injected on GC-FID with no additional work-up procedure, using the contained decane internal standard. To prepare samples for NMR analysis, 100 mg of oil was dissolved in 500 μ L acetone- d_6 (≥ 99 atom% D, Acros Organics®).

[0050] Quantification of monomers with GC-FID. An Agilent Technologies® 7693 autosampler injected a 1 μ L volume of each prepared sample into an Agilent® 7890A GC system. The GC method utilized a split ratio of 10:1, an inlet temperature of 280°C and a ramp rate of 10°C/min from 50°C to 280°C followed by a 10-minute hold at 280°C for a total run time of 29 min. The GC was outfitted with a 30 m x 250 μ m x 0.25 μ m Agilent Technologies® HP-5MS column and a flame ionization detector (FID) was used to quantify the products.

[0051] The GC-FID was calibrated with methylcyclohexane ($\geq 99.0\%$, TCI®), toluene ($\geq 99.8\%$, VWR Chemicals® BDH), propylcyclohexane ($\geq 98.0\%$, TCI), propylbenzene ($\geq 99.0\%$, Sigma-Aldrich®), 4-propyltoluene ($\geq 99.0\%$, TCI®), p-propylanisole ($\geq 99.0\%$, Sigma-Aldrich®), 4-propylphenol ($\geq 99.0\%$, Sigma-Aldrich®), 2-methoxy-4-propylphenol (propylguaiacol) ($\geq 99.0\%$, Sigma-Aldrich®), isoeugenol ($\geq 98.0\%$, Sigma-Aldrich®), 4-allyl-2, 6-dimethoxyphenol ($\geq 95.0\%$, Sigma-Aldrich®) and dihydroconiferyl alcohol (synthesized in-house). Relative response factors (RFs) were generated for each of these compounds relative to decane (for experiments performed in toluene with decane as an internal standard) and 1,3,5-tri-tert-butylbenzene (for neat lignin oil experiments). Additionally, decane was calibrated with a relative response factor to 1,3,5-tri-tert-butylbenzene to enable accurate quantification of decane in the lignin oil in toluene feeds. RFs were calculated by fitting the line of relative mass fraction vs area ratio of the compound of interest to the standard. Adjustment factors were used to generate approximate RFs for products that were not available commercially. For each

sample, the peak areas corresponding to known products were integrated. The ratio of compound peak area and standard peak area was calculated and multiplied by the RF and mass fraction of standard to obtain the mass fraction of compound. The mass fractions were then used for subsequent calculations of mole balance, conversion, yield, etc.

[0052] Gas chromatography and mass spectrometry (GC-MS). Analysis was performed using an Agilent Technologies® 7820A GC System outfitted with an HP-5MS Ultra Inert 30 m x 250 µm x 0.25 µm column and an Agilent® 5977B single quadrupole MS detector. Monomeric compounds in the feed and product were identified by injecting identical samples on a GC-FID and a GC-MS using the same column and method. The products were identified using the fragmentation patterns in GC-MS and matched with the same retention time observed in GC-FID.

[0053] Dimers were analyzed using derivatization followed by GC- MS, similar to our previously published method. Solvent-free lignin oil samples were dissolved in tetrahydrofuran (HPLC Grade, VWR Chemicals® BDH) (THF) at a concentration of 10 mg/mL. The derivatization reaction was performed by combining 600 µL of 10 mg/mL lignin oil solution, 50 µL of pyridine and 100 µL of silylating agent [N,O- Bis(trimethylsilyl)-trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMS) (Sigma-Aldrich®)], then heating for 20 min at 50°C. BSTFA reacts readily with water, so it was ordered in 1 mL ampules and used immediately after opening.

[0054] For analysis, 1 µL samples were manually injected into the GC- MS. The method utilized a split ratio of 10:1, a split flow of 12 mL/min, and an inlet temperature of 280°C. The oven was programmed to ramp from 150°C to 300°C at a rate of 5°C/min and held at 300°C for 18 min for a total run time of 49 min. GC- MS spectra were analyzed by comparing with published dimer structures and by predicting structures that may be present and comparing them with unknown MS spectra.

[0055] Gel permeation chromatography (GPC). Gel permeation chromatography was performed following a procedure similar to our previously published methods. Solvent-free oil samples were prepared for gel permeation chromatography by dissolution in THF at a concentration of 2 mg/mL (HPLC Grade, VWR Chemicals® BDH) and filtration using a 0.2 µm PTFE syringe filter. 20 µL of each sample was injected using a Hewlett Packard 1100 series autosampler. THF was used as the carrier solvent at a flowrate of 0.3 mL/min. Three 5 µm PLgel Agilent GPC columns (10⁴ Å, 10³ Å, and 50 Å) were arranged in series in order of

decreasing pore size. The columns were maintained at a constant temperature of 26°C, and the system ran at a pressure of approximately 30 bar (a function of the flowrate, column choice, and temperature). A UV diode array detector at a wavelength of 280 nm with a reference wavelength of 360 nm and a 4 nm slit was used to analyze eluents.

[0056] NMR spectroscopy. NMR spectra were acquired on a Bruker® Advance Neo 400 MHz equipped with a 5 mm broad band observe (BBFO) SmartProbe, and spectral processing used Bruker's TopSpin® 4.0.8 (Windows) software. The central solvent peaks (acetone-*d*₆) were used as the internal references ($\delta\text{C}/\delta\text{H}$: 29.84/2.05 ppm). Standard Bruker® implementations of the traditional suite of 1D and 2D [gradient-selected and ¹H- detected; for example, ¹H–¹³C HSQC] NMR experiments were used for structural elucidation and assignment authentication for monomers and oligomers. Processing used typical matched Gaussian apodization in F2 (LB = –0.1; GB = 0.001) and squared cosine-bell apodization in F1.

[0057] Quantitative GCxGC TOF-FID Analysis. Detailed characterization of deoxygenated hydrocarbon products was conducted by comprehensive two-dimensional gas chromatography with simultaneous time-of-flight mass spectrometry and flame ionization detection (GCxGC TOF- FID). Samples were prepared for analysis by dilution (1:10 gravimetrically in acetone). Analysis was conducted using a LECO Pegasus® 4D system (LECO Corp®) equipped with a liquid nitrogen cooled thermal modulator and post column flow splitter. The primary column was a Rtx-17sil, 20 m x 180 μm x 0.18 μm and the secondary column was a ZB-5HT, 1.0 m x 180 μm x 0.18 μm . The method utilized a 1.0 μL injection, split ratio 100:1, and injector temperature of 300°C. The primary oven held at 35°C for 5 minutes prior to 3°C/min ramp to 125°C, 10°C/min ramp to 350°C, and hold for 1 min. The secondary oven was 40°C offset from primary and the modulator was 15°C offset from secondary. The modulator period was set to 8 seconds, with 1 s hot pulse and 3 s cold pulse from the start of run to 800 s, followed by 2 s hot pulse and 2 s cold pulse to end of the run. The transfer line to the mass spectrometer and FID were held at 350°C. The TOF mass range was m/z 29-600, with an acquisition rate of 200 spectra/s, and solvent delay of 70s. The FID flows were set at 40 mL/min H₂, Air flow of 300 mL/min and N₂ flow of 25 mL/min. Compounds were identified using library matching and utilization of retention time regions in 2D chromatograms using LECO ChromaTof® Software. The FID signal was calibrated using a series of representative compounds to establish linearity and accuracy. All linear calibrations resulted in $R^2 \geq 0.995$. Compounds were quantified from their theoretical response factors calculated via effective carbon numbers.

[0058] Qualitative GCxGC FID/MS analysis. Qualitative characterization of deoxygenated products was done using two- dimensional gas chromatography with coupled flame ionization detection and mass spectrometry (GCxGC FID/MS). This analysis was conducted using an Agilent® 7890A GC with an Agilent 5975C Inert XL MSD. The system was equipped with a chiller-cooled (PolyScience® P10N4A101B) thermal modulator (Zoex ZX10711). Samples were injected neat post- reaction. Data analysis was completed using the software package Canvas™ v4.

[0059] The primary column used was a Rxi-5HT, 30 m x 0.25 mm x 0.25 µm while the secondary column used was a BPX50, 2 m x 0.15 mm x 0.25 µm. The method utilized a split ratio of 50:1, a 5 µL injection, and an injector temperature of 350°C. The primary oven was held at 45°C for 1 minute followed by a ramp to 300°C at 3°C/min. This temperature was then held for 5 minutes. The secondary column was offset from the primary by 25°C while the thermal modulator thermal modulator was offset from the secondary by 5°C. The modulator used a 16 second period with a 375 ms hot jet duration. The transfer line to the MS was held at 250°C. The mass range was set to 40-550 m/z, with an acquisition rate of 50 spectra/s and no solvent delay. The FID detector was held at 300°C with an H₂ flow of 30 mL/min, an air flow of 400 mL/min.

[0060] Total carbon, hydrogen, and oxygen (CHO) analysis method. Total carbon and hydrogen were determined by combustion using a LECO® Series CHN628 elemental analyzer (LECO® Corp). Oxygen content was calculated by difference.

[0061] Simulated distillation. Due to limited sample volume, distillation temperatures were determined by simulated distillation rather than physical distillation (i.e., ASTM D86). Boiling range distributions of deoxygenated oils were measured by simulated distillation following ASTM method D2887-19. An Agilent® 7890A GC equipped with cool-on- column inlet and FID was used. Method settings were used as found in ASTM D2887 Table 1 for an open tubular column (option 7). The column used was an MXT-1HT, 10 m x 530 µm x 2.65 µm (Restek Corp®). Samples were diluted 1:10 by volume in carbon disulfide for analysis. An injection volume of 0.1 µL was injected onto the analytical column. Boiling point calibrations were made using prepared standards purchased from Sigma-Aldrich® (Part # 500658) and accuracy was verified with standard reference gasoil as described in D2887. Data analysis was conducted using Separation Systems SimDis Expert® 9.

[0062] Mass balance on neat lignin HDO experiment. To calculate a mass balance, a single-pass neat lignin oil experiment was performed in which a steady-state sample was accumulated for 3 hours. The ~18 mL sample was collected into a pre-weighed flask. The total sample was weighed, then a pipette was used to remove the aqueous phase. The remaining organic phase was weighed and characterized. The mass flowrate of the lignin oil feed was measured in triplicate by weighing the oil collected for 4 minutes at the experimental flowrate directly at the outlet of the ISCO pump. The mass flowrate was multiplied by the steady-state collection time to obtain the feed mass. The feed mass and steady-state oil mass were multiplied by the carbon mass percent of each sample to obtain the carbon mass recovery.

[0063] Solids compositional analysis procedure. Compositional analysis of the poplar samples was performed based on NREL's published guidelines. The poplar used was a reference material from Idaho National Laboratory, (Source: Morrow County, Oregon, Harvested: 2013, Hybrid Clone: *Populus deltoides* x *Populus nigra*, clone OP-367). Samples were first extracted with a high pressure and temperature flow through aqueous rinse followed by an ethanol rinse. The biomass was then treated with 72 wt% sulfuric acid for 1 h at 30°C with mixing. The slurry was then diluted with water to 4 wt% sulfuric acid and heated in an autoclave for 1 h at 121°C. Klason lignin content was determined gravimetrically by filtering the acid insoluble residue out of the acidified aqueous slurry. The Klason lignin was combusted to determine the ash content in the biomass. The acid soluble lignin was quantified by UV/Vis spectroscopy (Thermo Scientific Nanodrop® 8000 spectrophotometer). Lignin absorbance measurements were performed at 240 nm and quantified with an extinction coefficient of 2.5. The sugar content was determined by high performance liquid chromatography (HPLC, Agilent® 1100 HPLC) using a refractive index detector (RI) kept at 55°C. A Shodex® Sugar SP0810 column equipped with a guard column was used for analysis at 85°C with a flow rate of 0.6 mL/min of HPLC grade water as the mobile phase.

[0064] Catalyst characterization with powder X-ray diffraction. Powder X-ray diffraction (PXRD) was performed on a Bruker® D8 diffractometer using Cu K α radiation, a step size of 0.02°, and a step time of 0.2 s.

Example 2 – Comparison of Poplar, Pine and Corn Stover Feedstocks

[0065] Comparison of various lignin feedstocks is provided in **Figs. 8-12**. **Fig. 7** provides example monomers corresponding to jet-range cycloalkanes and aromatics that can be generated by the methods provided herein.

[0066] The described invention can be further understood by the following non-limiting examples:

[0067] Example 1. A method comprising:

providing a reactant comprising lignin and hydrogen;

partially deoxygenating the reactant in the presence of a first catalyst at a first temperature, thereby generating an intermediate;

deoxygenating the intermediate in the presence of a second catalyst at a second temperature, thereby generating a product comprising aromatic hydrocarbons.

[0068] Example 2. The method of example 1, wherein the second temperature is greater than the first temperature.

[0069] Example 3. The method of example 1 or 2, wherein the reactant comprises greater than 50% lignin oil.

[0070] Example 4. The method of any of examples 1-3, wherein the reactant comprises greater than 99% lignin oil.

[0071] Example 5. The method of any of examples 1-4, wherein the reactant *does not* comprise a solvent.

[0072] Example 6. The method of any of examples 1-5, wherein the first temperature is selected from the range of 250 °C to 450 °C.

[0073] Example 7. The method of any of examples 1-6, wherein the second temperature is selected from the range of 275 °C to 475 °C.

[0074] Example 8. The method of any of examples 1-7, wherein the first catalyst, the second catalyst or both comprise Mo₂C.

[0075] Example 9. The method of any of examples 1-8, wherein the first catalyst and the second catalyst are the same.

[0076] Example 10. The method of any examples 1-9, wherein the steps of partially deoxygenating and deoxygenating are each performed continuously.

[0077] Example 11. The method of examples 1-10, wherein the steps of partially deoxygenating and deoxygenating are part of a continuous process.

[0078] Example 12. The method of any of examples 1-11, wherein the product is sustainable aviation or marine fuel.

[0079] Example 13. The method of any of examples 1-12, wherein the product comprises an oxygen mole fraction less than or equal to 5%.

[0080] Example 14. A reactor comprising:

a first reaction zone comprising a first catalyst at a first temperature;

a second reaction zone comprising a second catalyst at a second temperature;

where in the reactor is capable of performing hydrodeoxygenation of lignin to generate aromatic products.

[0081] Example 15. The reactor of example 14, wherein the second temperature is greater than the first temperature.

[0082] Example 16. The reactor of example 14 or 15, wherein the reactor is a trickle bed reactor.

[0083] Example 17. The reactor of any of examples 14-16, wherein the first catalyst, the second catalyst or both comprise Mo_2C .

[0084] Example 18. The reactor of any of examples 14-17, wherein the reactor is capable generating aromatic products with continuous flow.

[0085] Example 19. A catalyst comprising Mo_2C , wherein the catalyst is capable of converting lignin to aromatic compounds at a yield greater than or equal to 80%.

[0086] The terms and expressions which have been employed herein are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments, exemplary embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims. The specific embodiments provided herein are examples of useful embodiments of the present invention and it will be apparent to one skilled in the art that the present invention may be carried out using a large

number of variations of the devices, device components, methods steps set forth in the present description. As will be obvious to one of skill in the art, methods and devices useful for the present methods can include a large number of optional composition and processing elements and steps.

[0087] As used herein and in the appended claims, the singular forms "a", "an", and "the" include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to "a cell" includes a plurality of such cells and equivalents thereof known to those skilled in the art. As well, the terms "a" (or "an"), "one or more" and "at least one" can be used interchangeably herein. It is also to be noted that the terms "comprising", "including", and "having" can be used interchangeably. The expression "of any of claims XX-YY" (wherein XX and YY refer to claim numbers) is intended to provide a multiple dependent claim in the alternative form, and in some embodiments is interchangeable with the expression "as in any one of claims XX-YY."

[0088] When a group of substituents is disclosed herein, it is understood that all individual members of that group and all subgroups, are disclosed separately. When a Markush group or other grouping is used herein, all individual members of the group and all combinations and subcombinations possible of the group are intended to be individually included in the disclosure. For example, when a device is set forth disclosing a range of materials, device components, and/or device configurations, the description is intended to include specific reference of each combination and/or variation corresponding to the disclosed range.

[0089] Every formulation or combination of components described or exemplified herein can be used to practice the invention, unless otherwise stated.

[0090] Whenever a range is given in the specification, for example, a density range, a number range, a temperature range, a time range, or a composition or concentration range, all intermediate ranges and subranges, as well as all individual values included in the ranges given are intended to be included in the disclosure. It will be understood that any subranges or individual values in a range or subrange that are included in the description herein can be excluded from the claims herein.

[0091] All patents and publications mentioned in the specification are indicative of the levels of skill of those skilled in the art to which the invention pertains. References cited herein are incorporated by reference herein in their entirety to indicate the state of the art as of their

publication or filing date and it is intended that this information can be employed herein, if needed, to exclude specific embodiments that are in the prior art. For example, when composition of matter is claimed, it should be understood that compounds known and available in the art prior to Applicant's invention, including compounds for which an enabling disclosure is provided in the references cited herein, are not intended to be included in the composition of matter claims herein.

[0092] As used herein, "comprising" is synonymous with "including," "containing," or "characterized by," and is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. As used herein, "consisting of" excludes any element, step, or ingredient not specified in the claim element. As used herein, "consisting essentially of" does not exclude materials or steps that do not materially affect the basic and novel characteristics of the claim. In each instance herein any of the terms "comprising", "consisting essentially of" and "consisting of" may be replaced with either of the other two terms. The invention illustratively described herein suitably may be practiced in the absence of any element or elements, limitation or limitations which is not specifically disclosed herein.

[0093] All art-known functional equivalents, of any such materials and methods are intended to be included in this invention. The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

CLAIMS

What is claimed is:

1. A method comprising:

providing a reactant comprising lignin and hydrogen;

partially deoxygenating the reactant in the presence of a first catalyst at a first temperature, thereby generating an intermediate;

deoxygenating the intermediate in the presence of a second catalyst at a second temperature, thereby generating a product comprising aromatic hydrocarbons.
2. The method of claim 1, wherein the second temperature is greater than the first temperature.
3. The method of claim 1, wherein the reactant comprises greater than 50% lignin oil.
4. The method of claim 1, wherein the reactant comprises greater than 99% lignin oil.
5. The method of claim 1, wherein the reactant **does not** comprise a solvent.
6. The method of claim 1, wherein the first temperature is selected from the range of 250 °C to 450 °C.
7. The method of claim 1, wherein the second temperature is selected from the range of 275 °C to 475 °C.
8. The method claim 1, wherein the first catalyst, the second catalyst or both comprise Mo₂C.
9. The method of claim 1, wherein the first catalyst and the second catalyst are the same.
10. The method of claim 1, wherein the steps of partially deoxygenating and deoxygenating are each performed continuously.
11. The method claim 1, wherein the steps of partially deoxygenating and deoxygenating are part of a continuous process.
12. The method of any claim 1, wherein the product is sustainable aviation or marine fuel.

13. The method of claim 1, wherein the product comprises an oxygen mole fraction less than or equal to 5%.
14. A reactor comprising:
 - a first reaction zone comprising a first catalyst at a first temperature;
 - a second reaction zone comprising a second catalyst at a second temperature;
 - wherein the reactor is capable of performing hydrodeoxygenation of lignin to generate aromatic products.
15. The reactor of claim 14, wherein the second temperature is greater than the first temperature.
16. The reactor of claim 14, wherein the reactor is a trickle bed reactor.
17. The reactor of claim 14, wherein the first catalyst, the second catalyst or both comprise Mo_2C .
18. The reactor of claim 14, wherein the reactor is capable generating aromatic products with continuous flow.
19. A catalyst comprising Mo_2C , wherein the catalyst is capable of converting lignin to aromatic compounds at a yield greater than or equal to 80%.

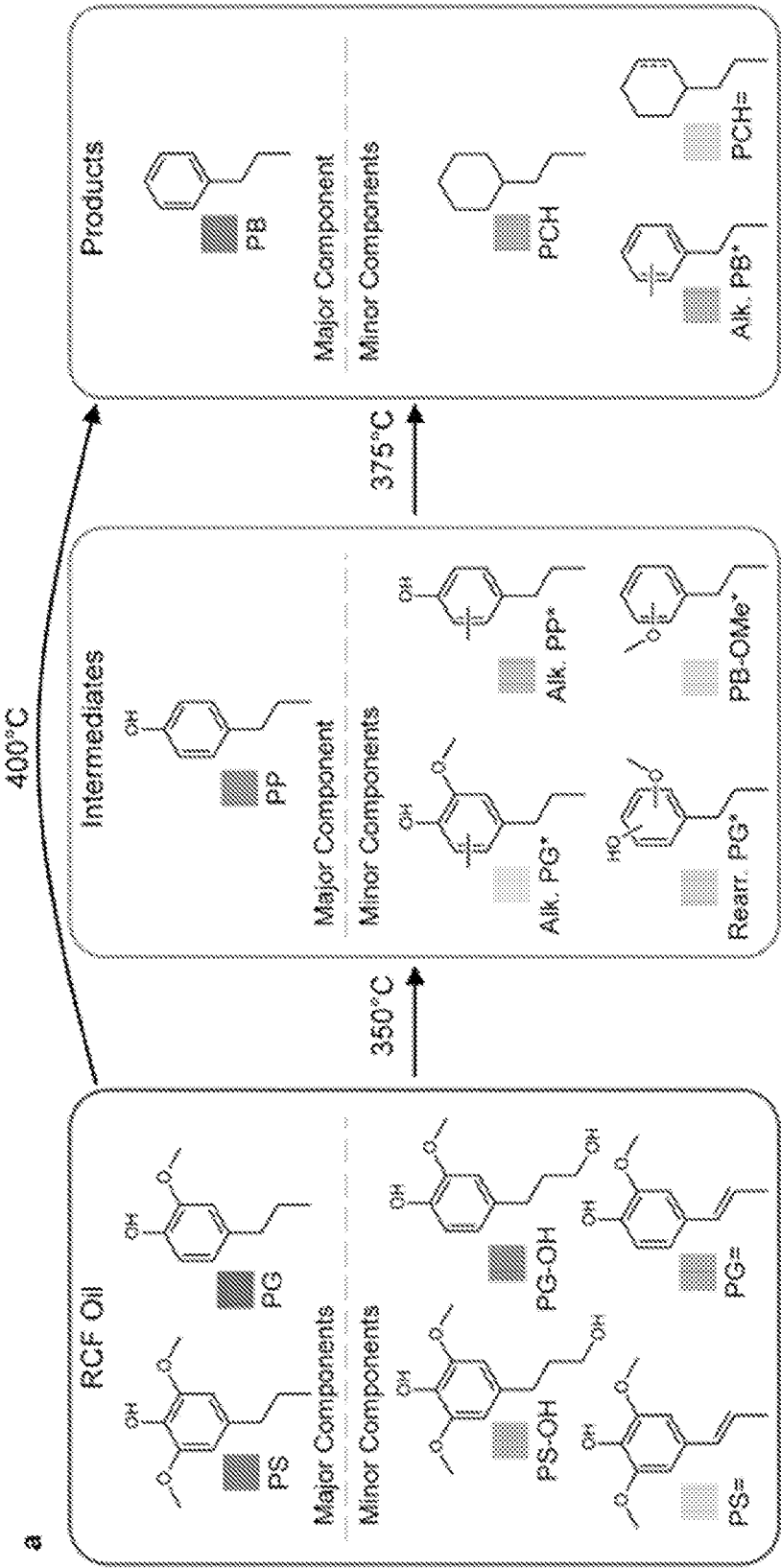


Fig. 1A

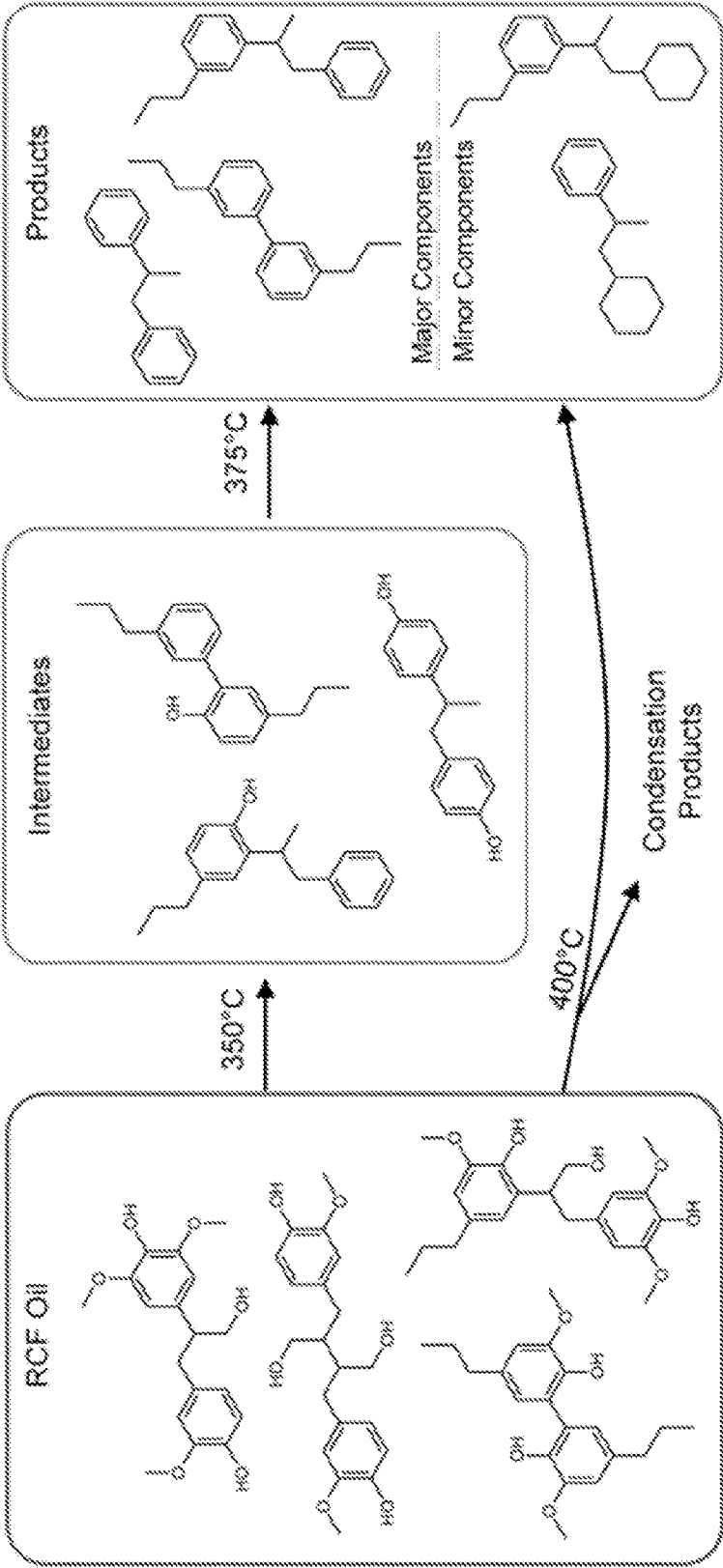


Fig. 1B

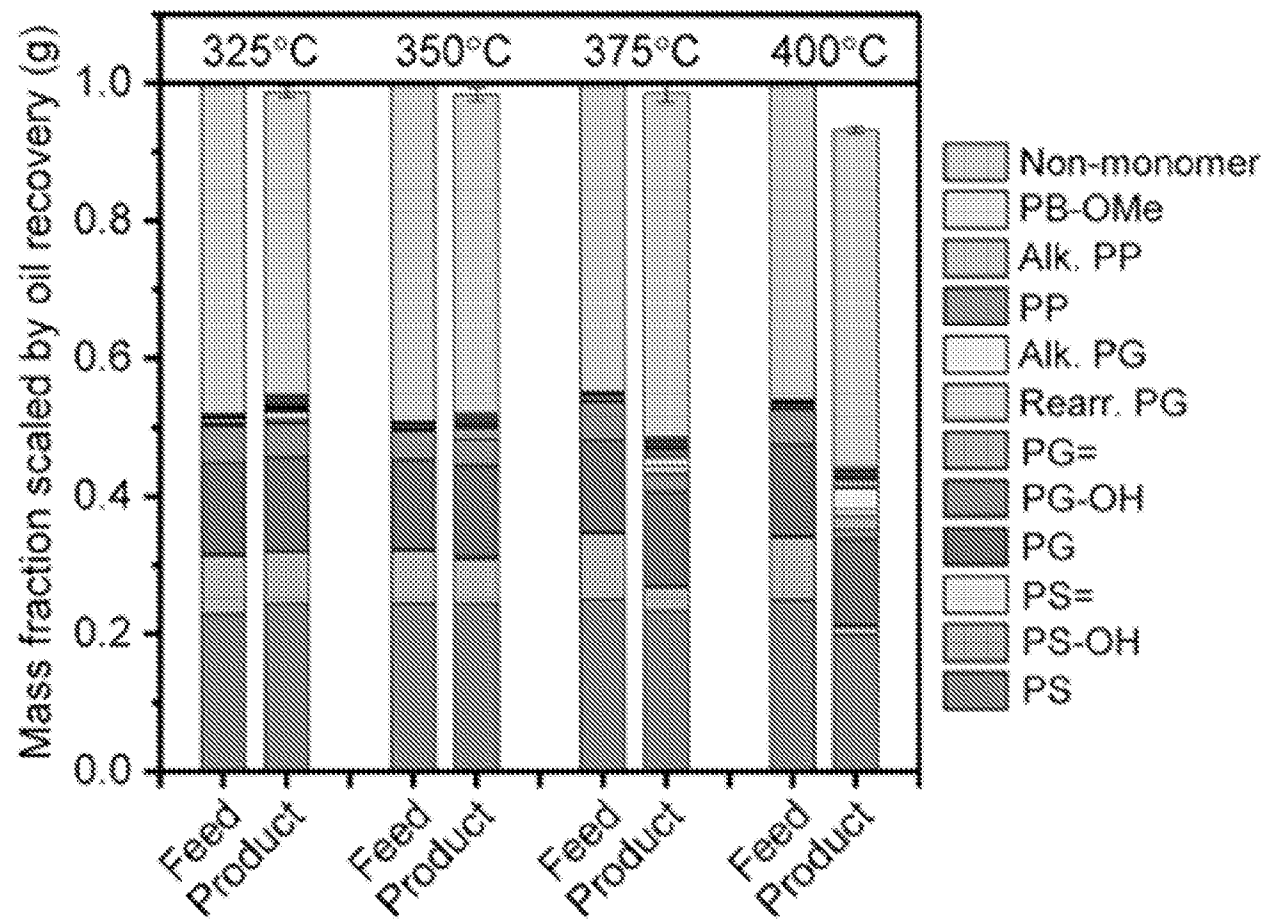


Fig. 2A

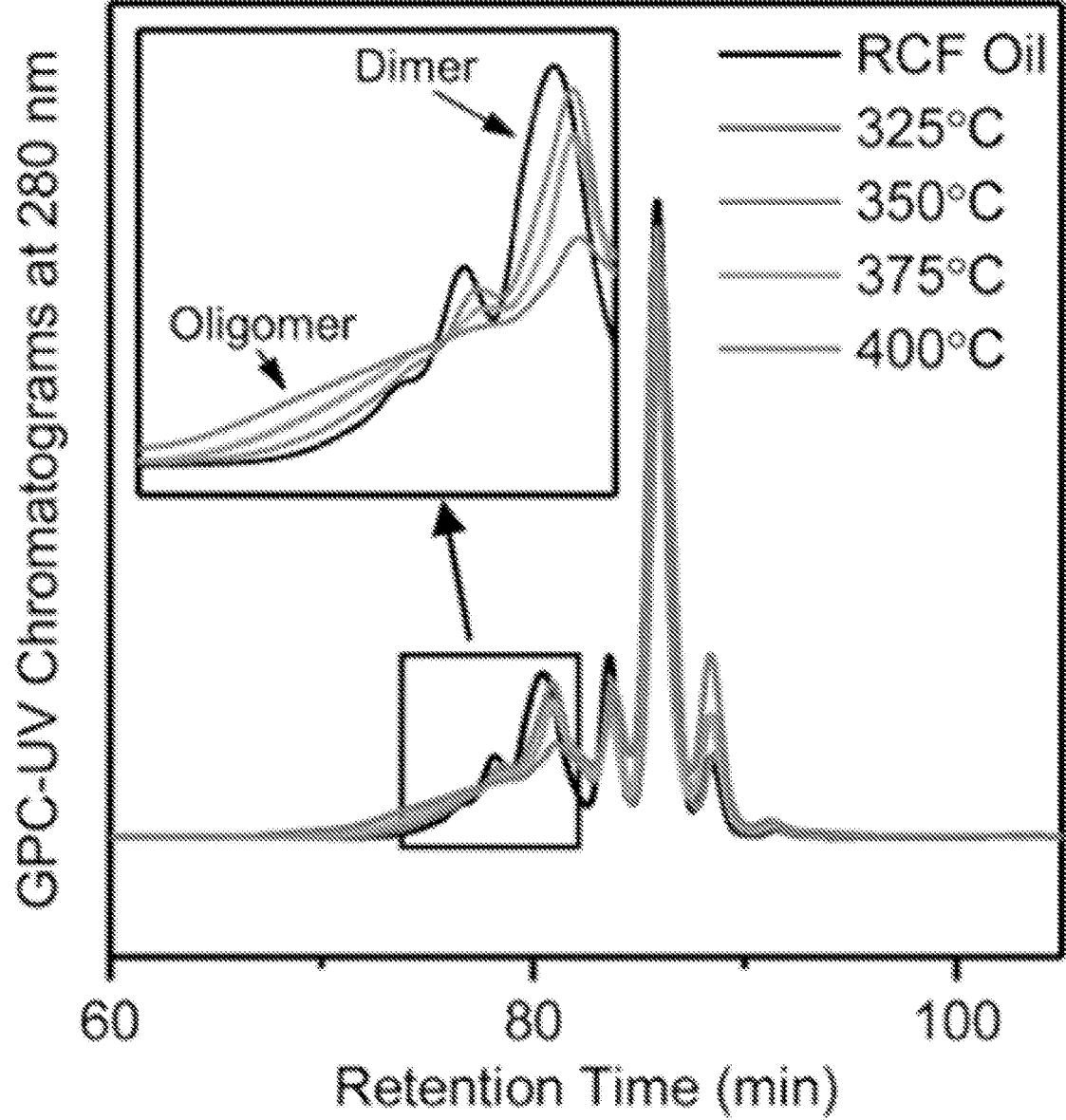


Fig. 2B

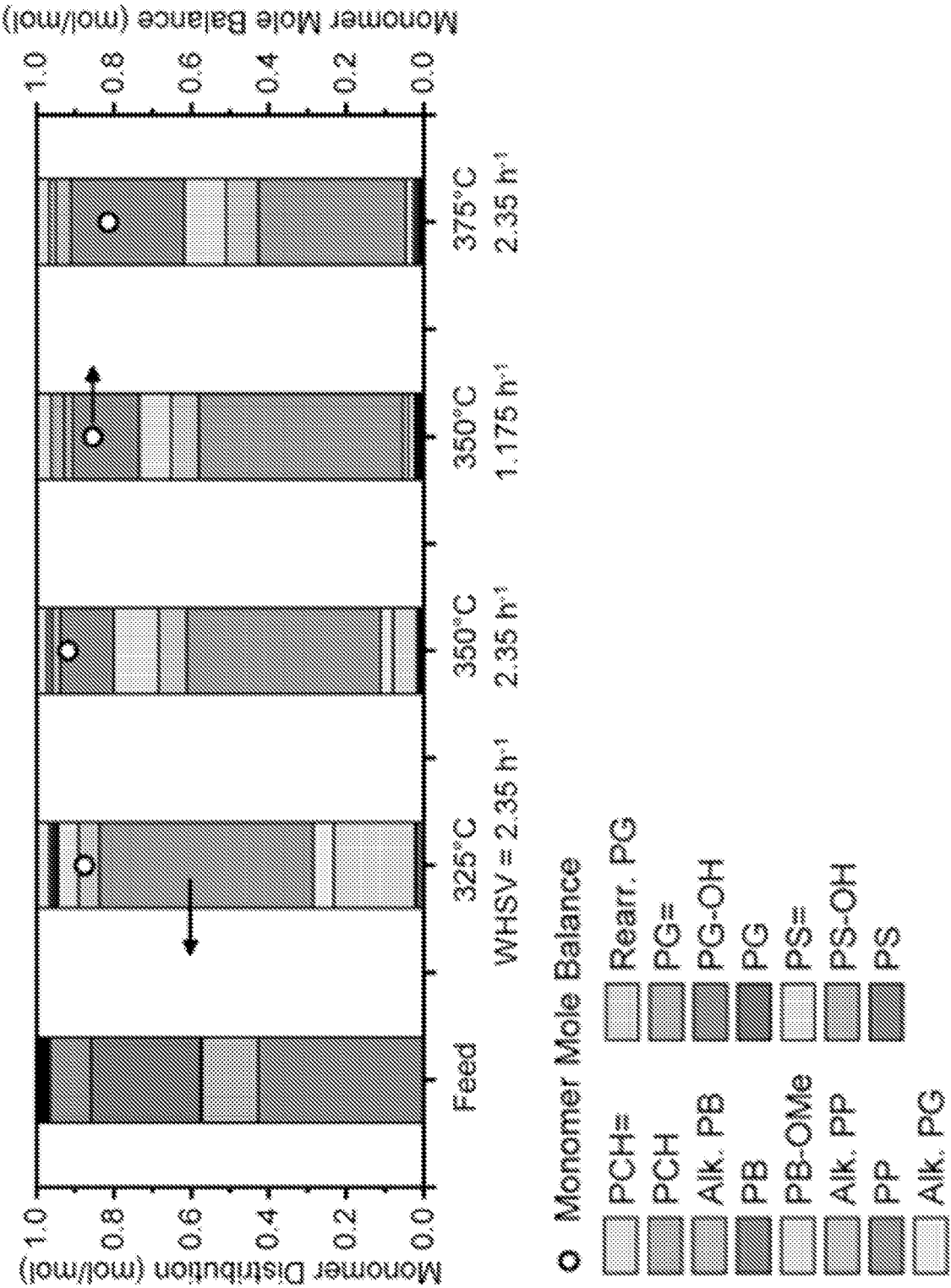


Fig. 3A

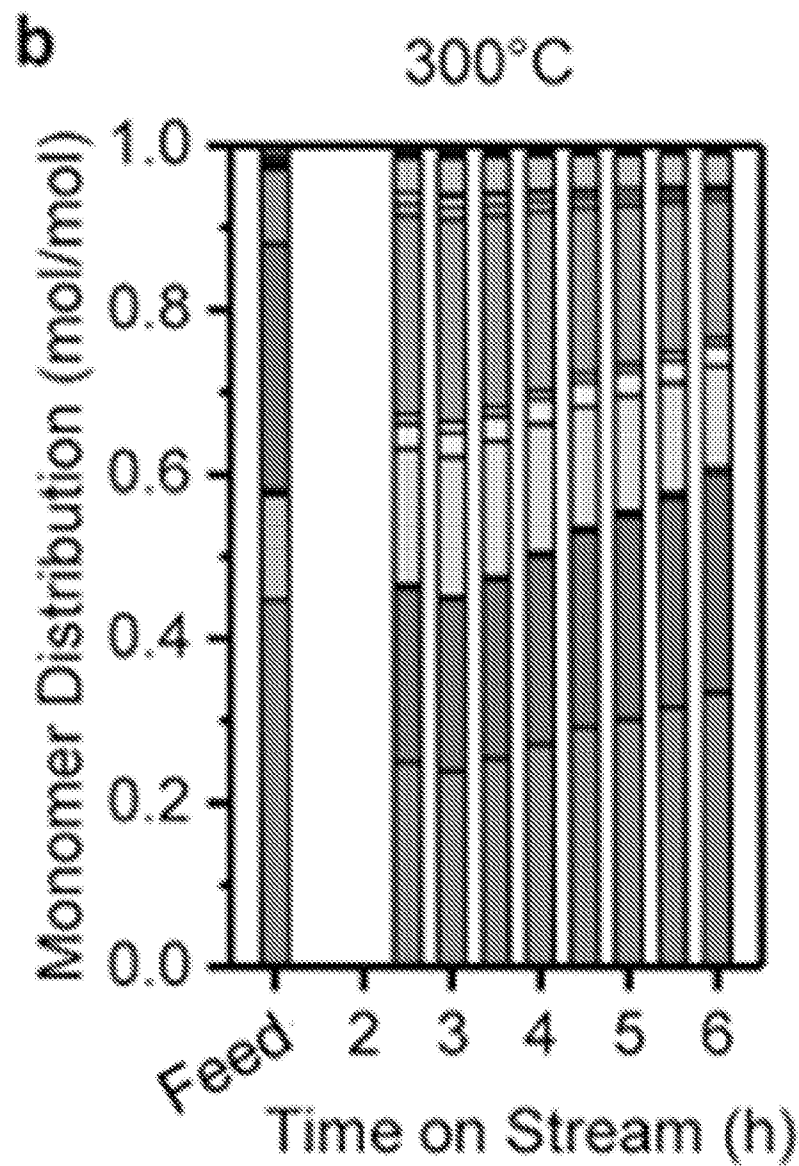


Fig. 3B

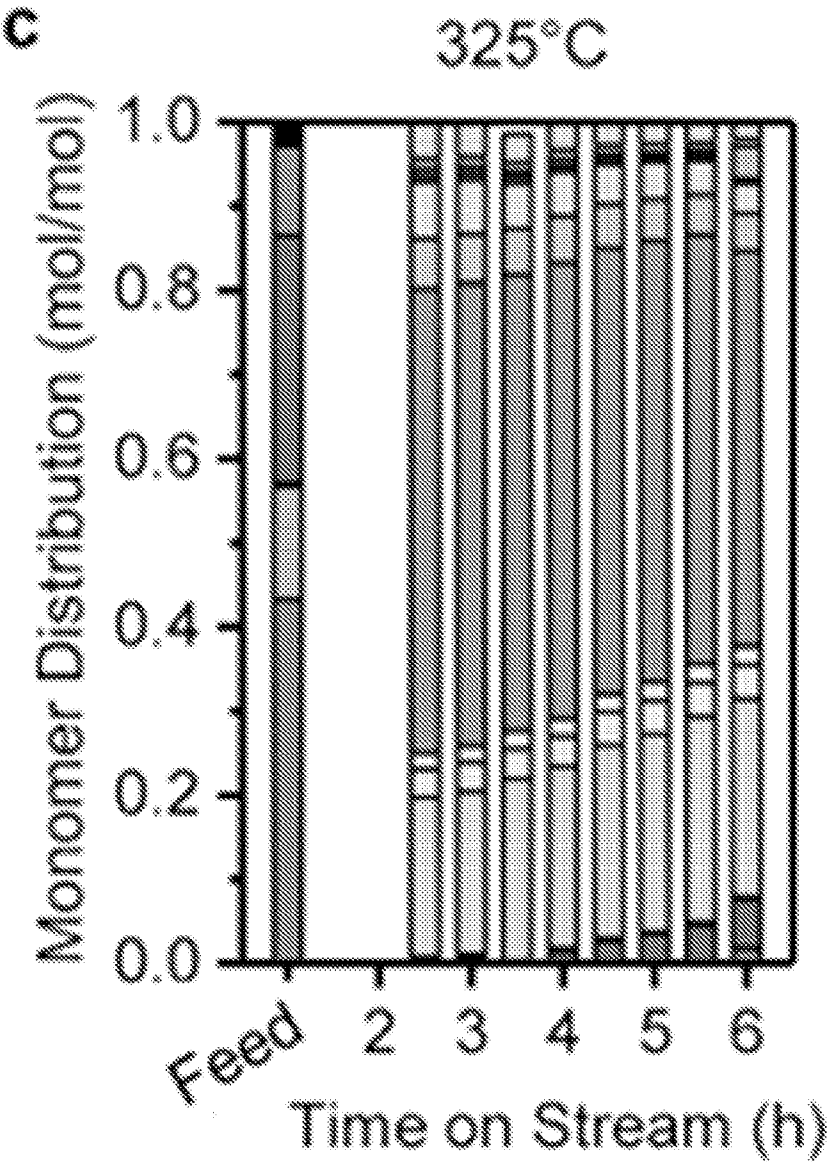


Fig. 3C

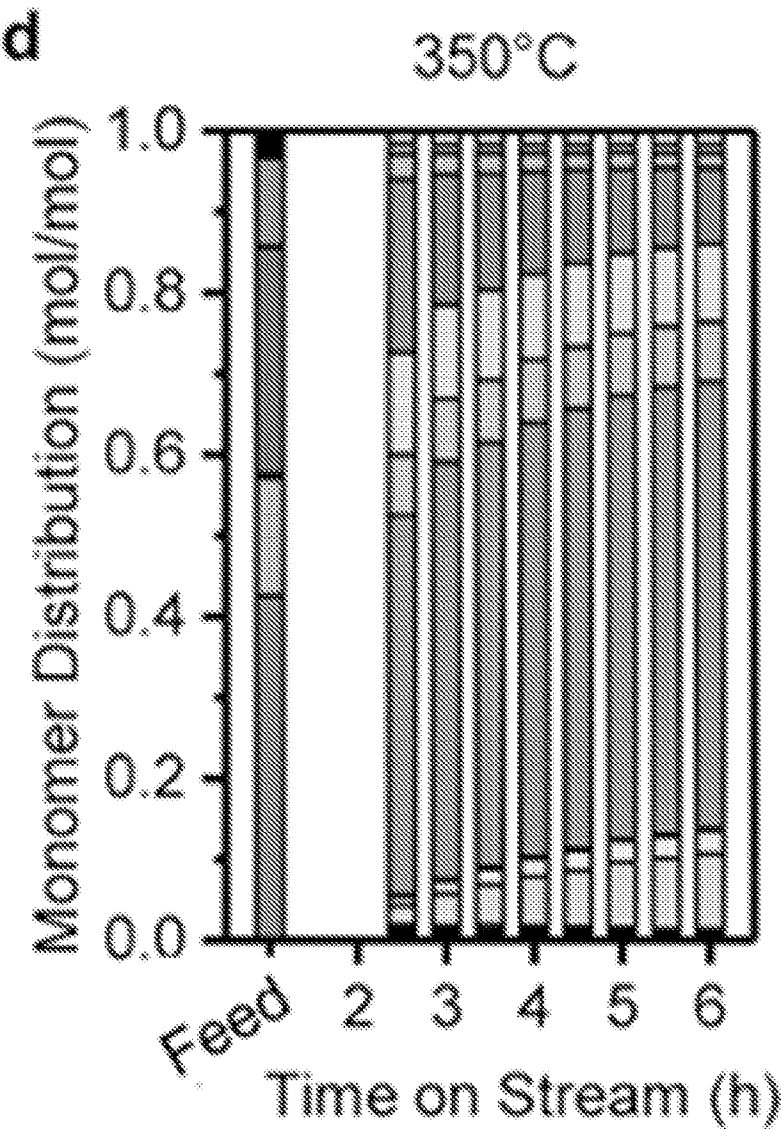


Fig. 3D

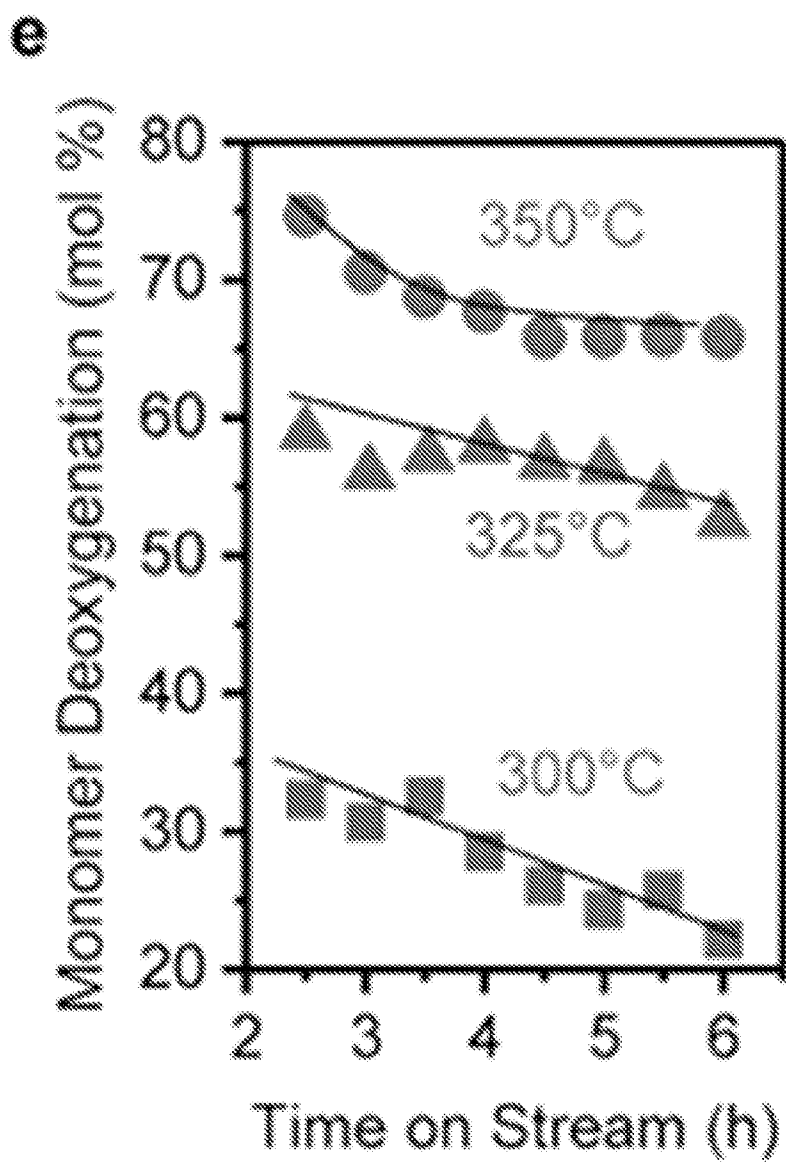


Fig. 3E

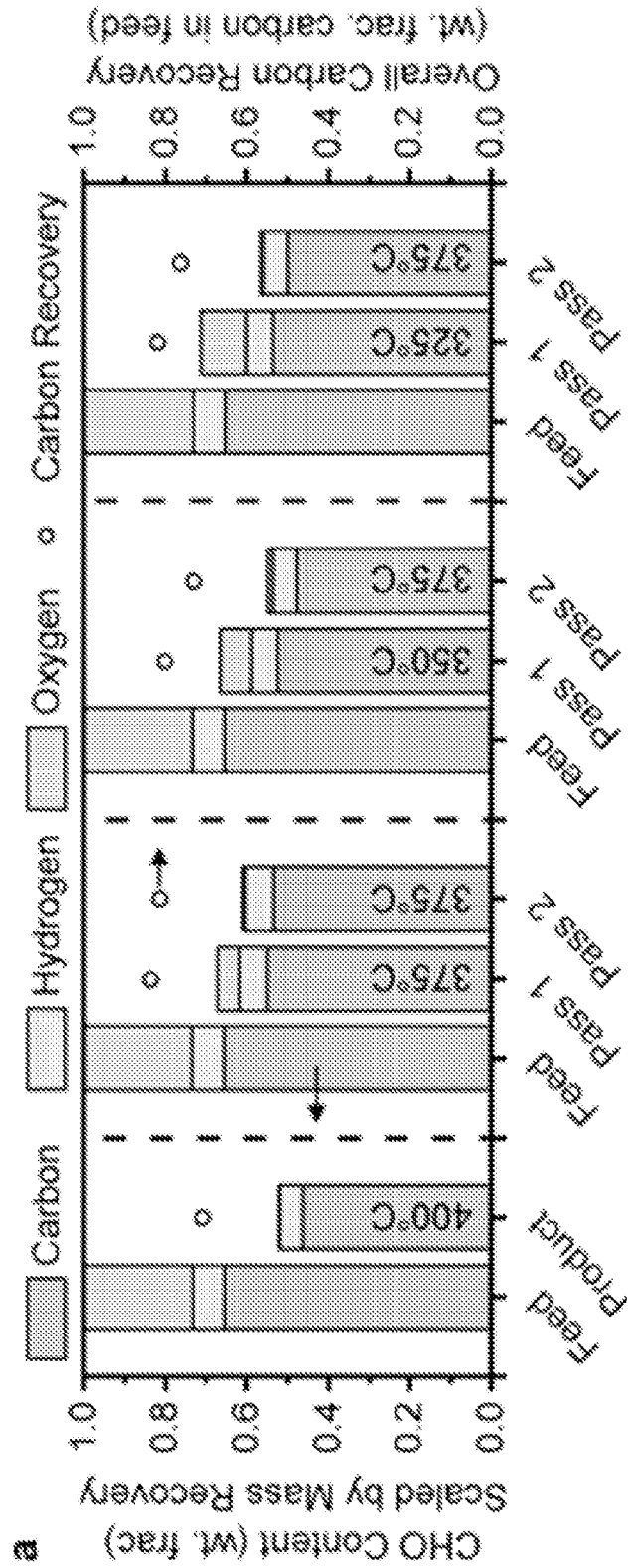


Fig. 4A

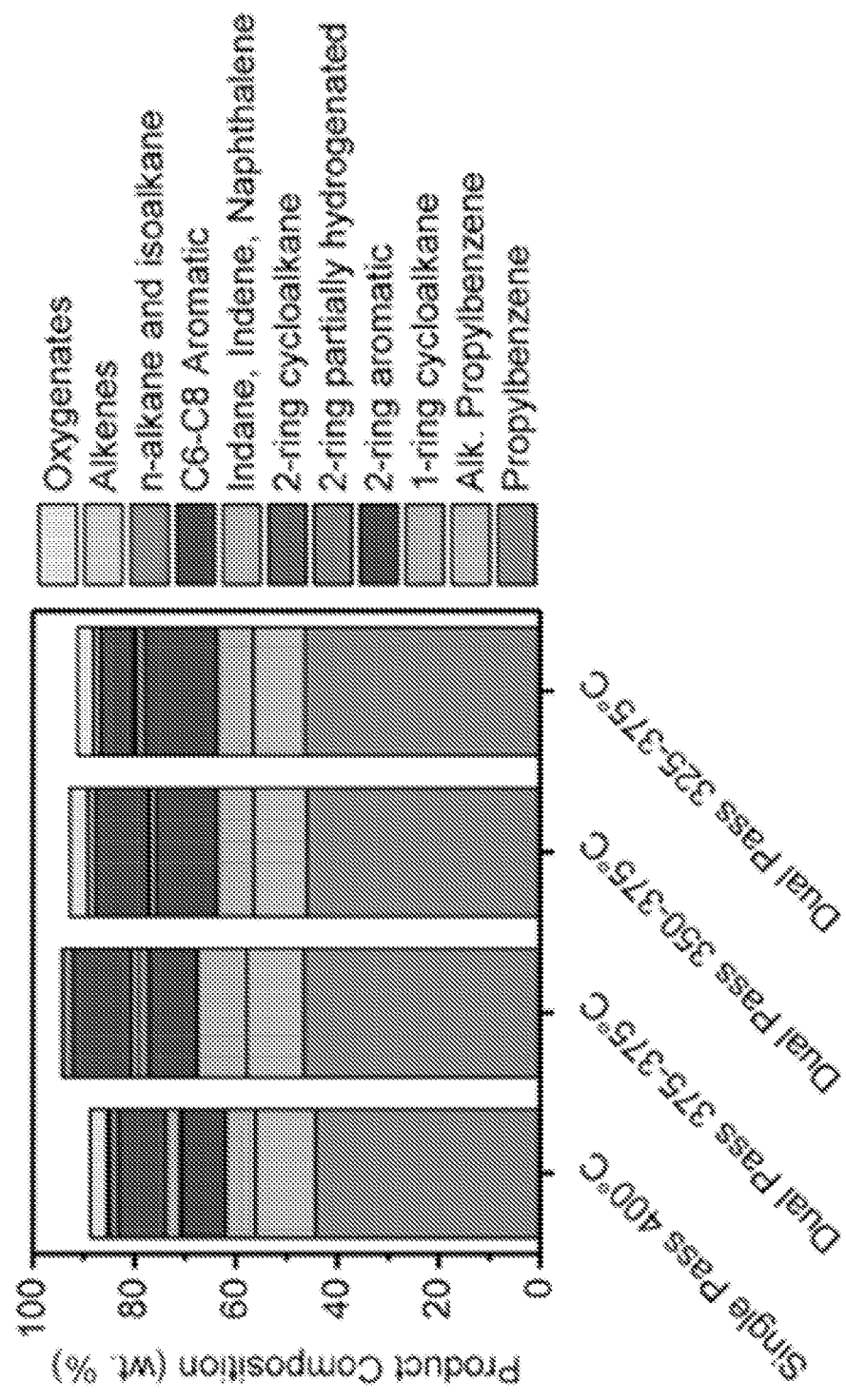


Fig. 4B

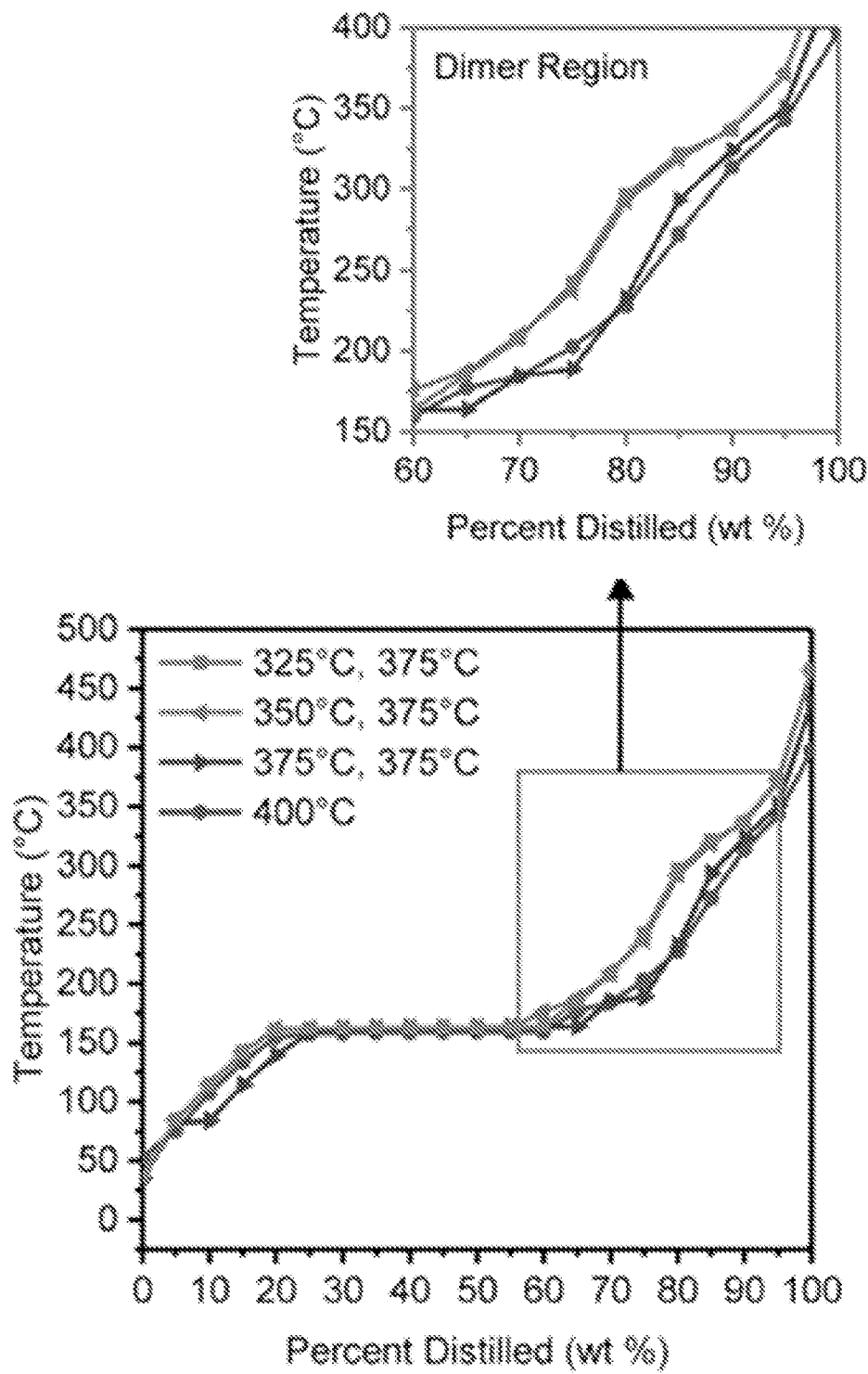


Fig. 4C

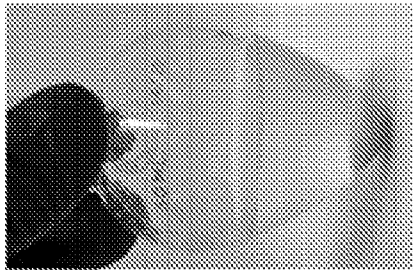
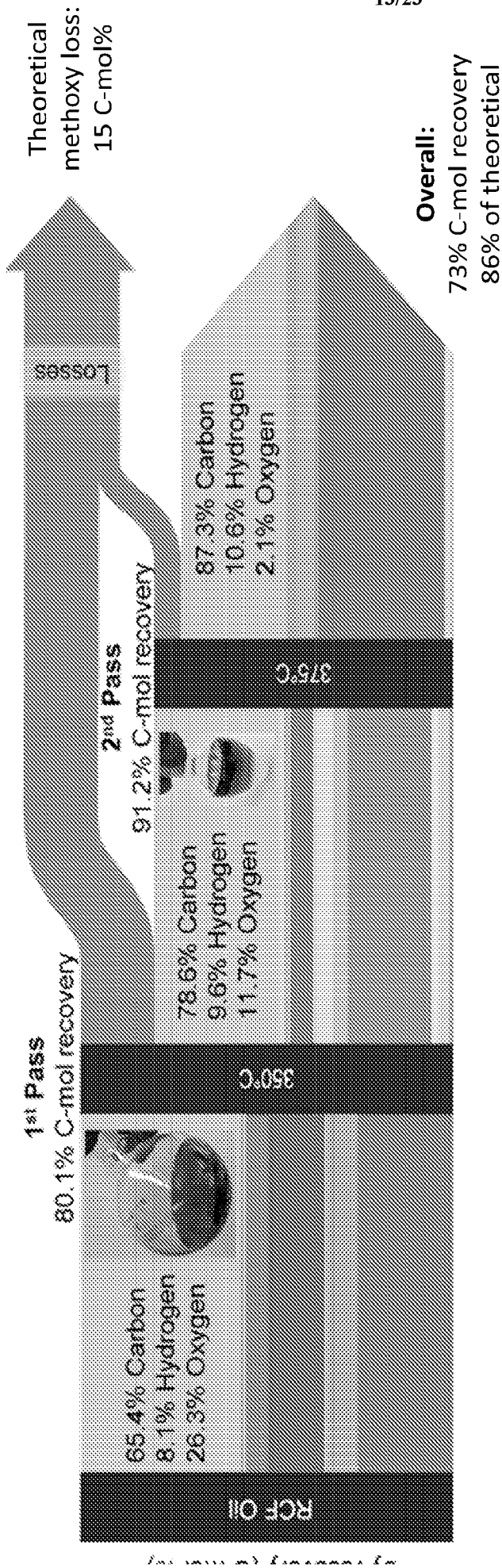


Fig. 4D
REPLACEMENT SHEET

PS=	PG=	PP	PB	PCH=	Non-monomer
PS-OH	PG-OH	Alk. PG	PB-OMe	PCH	
PS	PG	Rearr. PG	Alk. PP	Alk. PB	

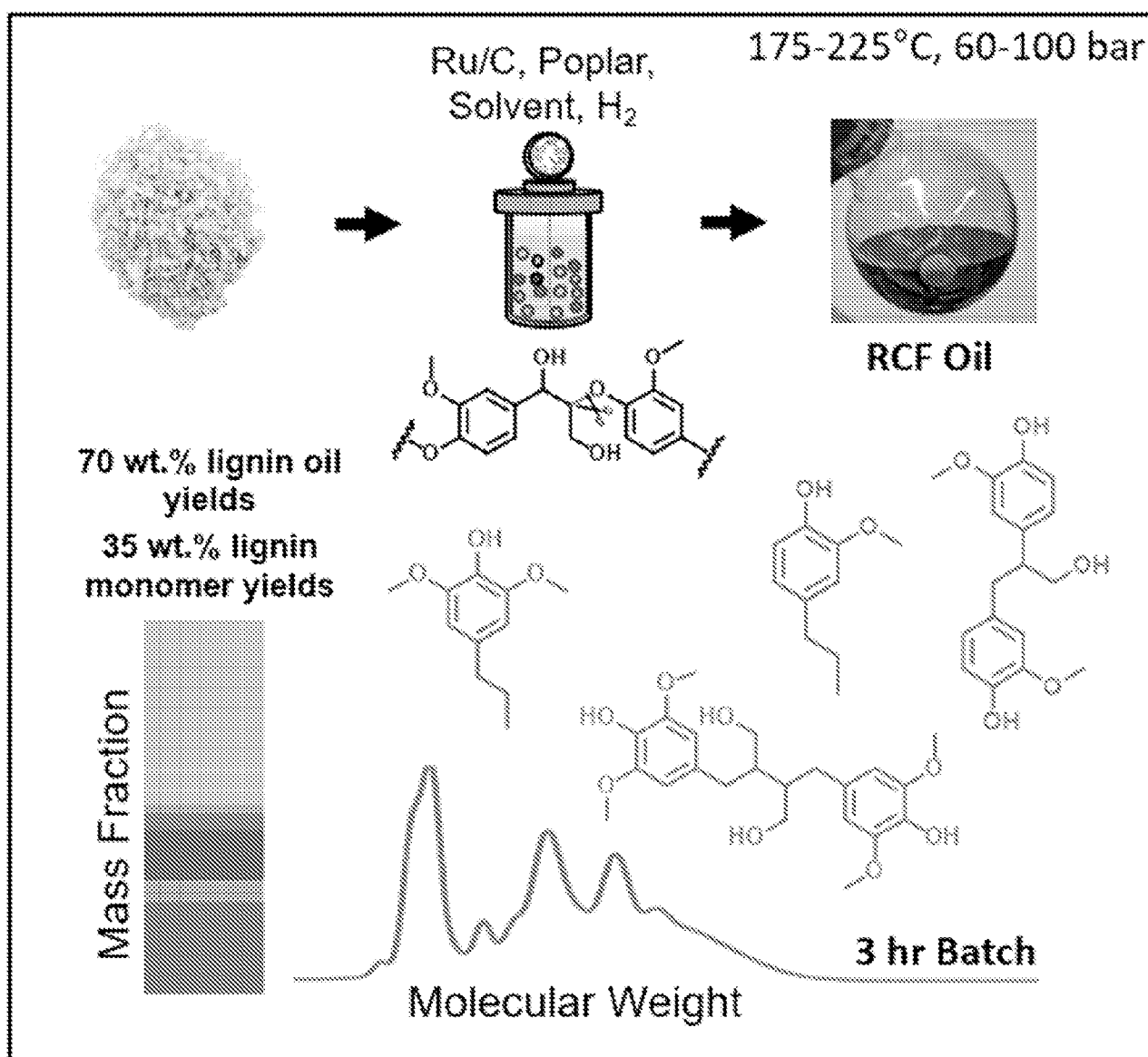


Fig. 5

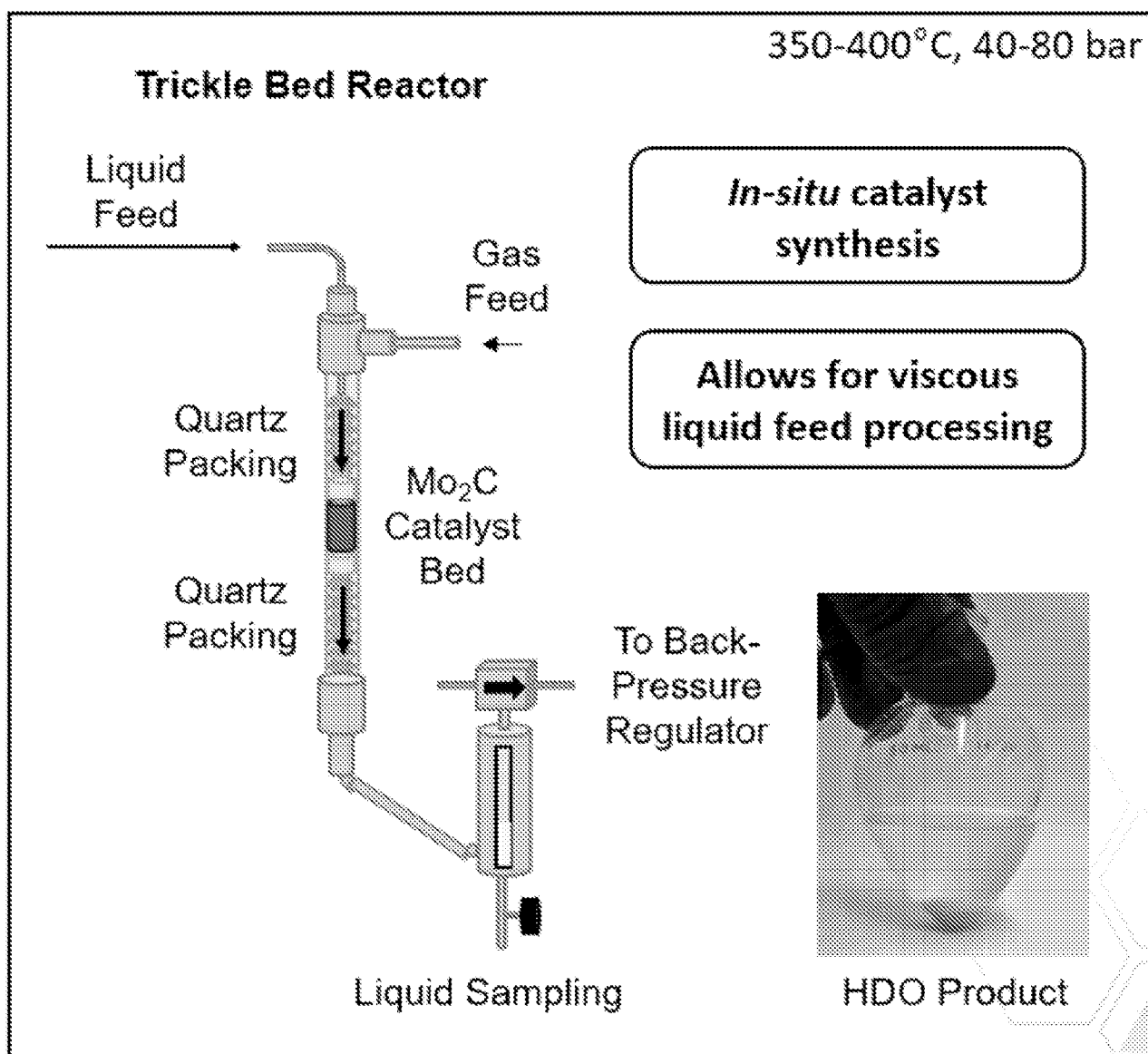


Fig. 6

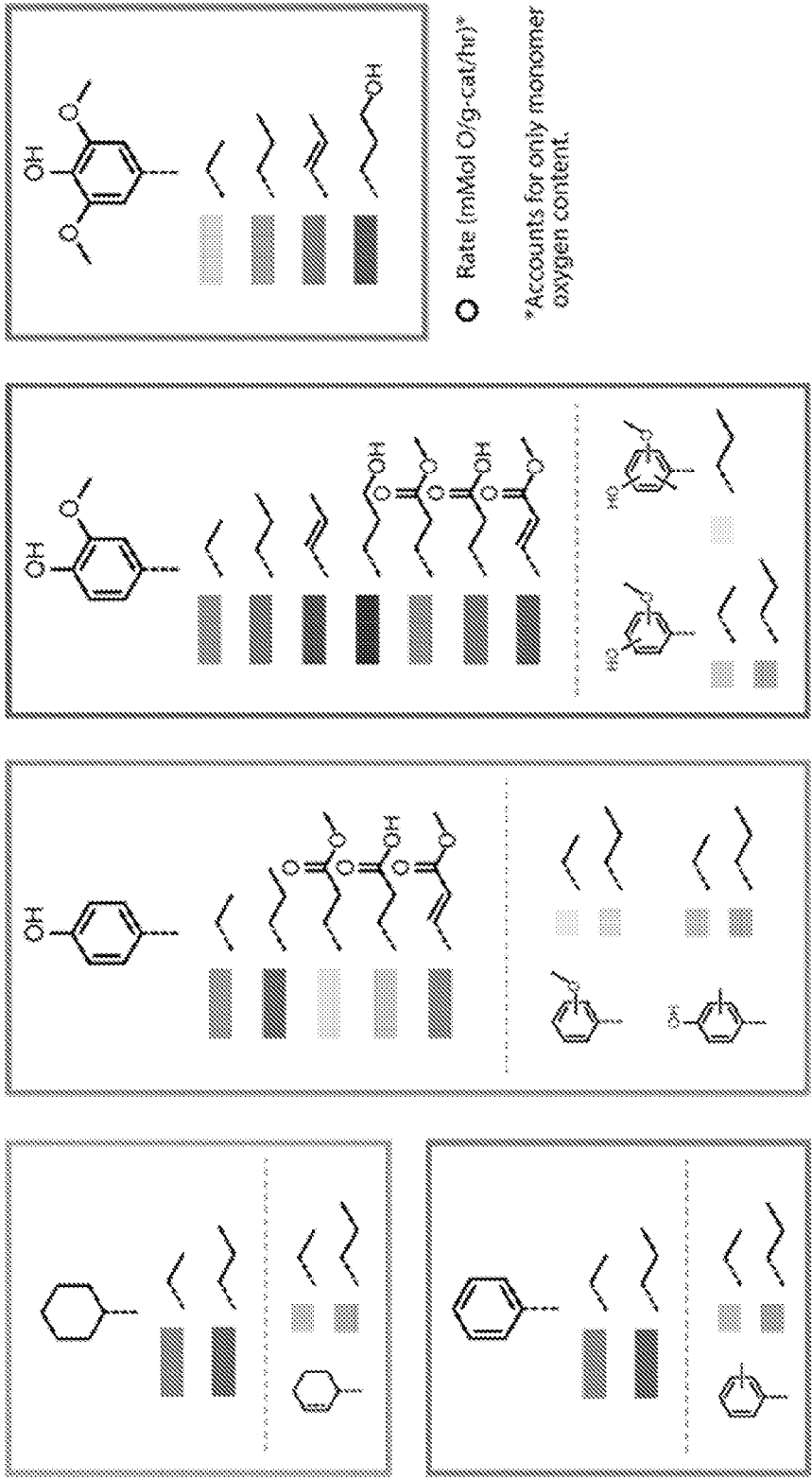


Fig. 7

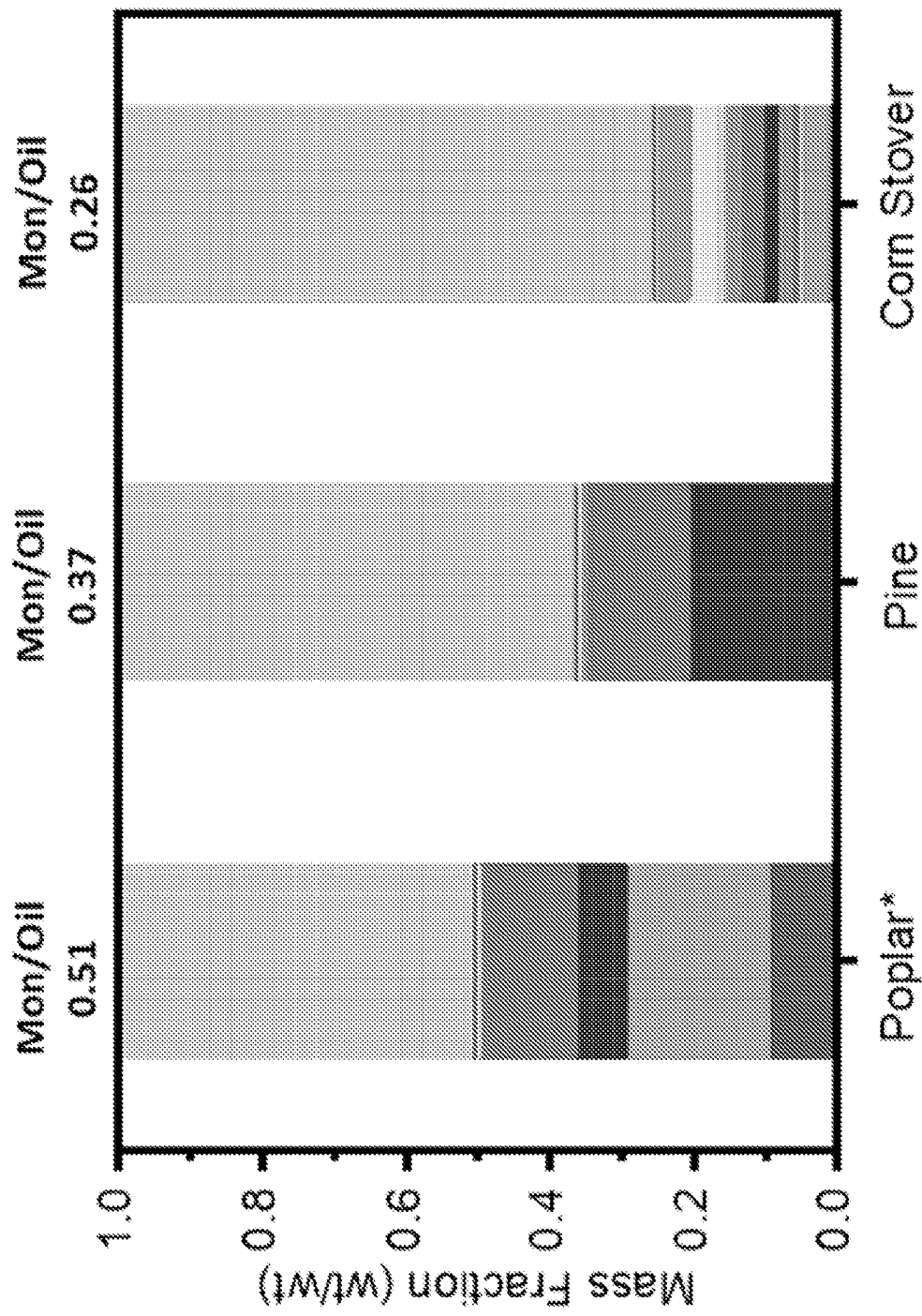


Fig. 8

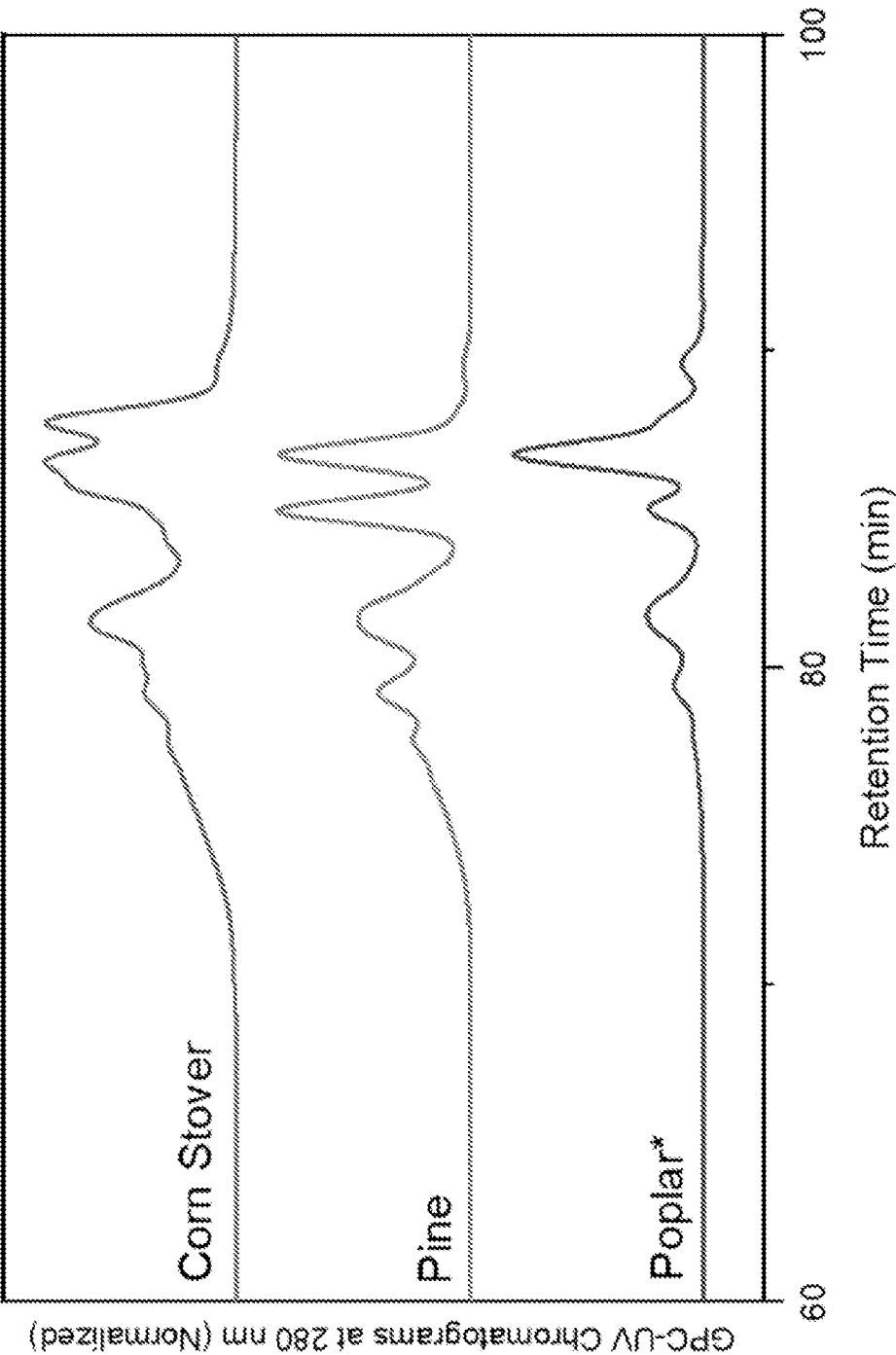


Fig. 9

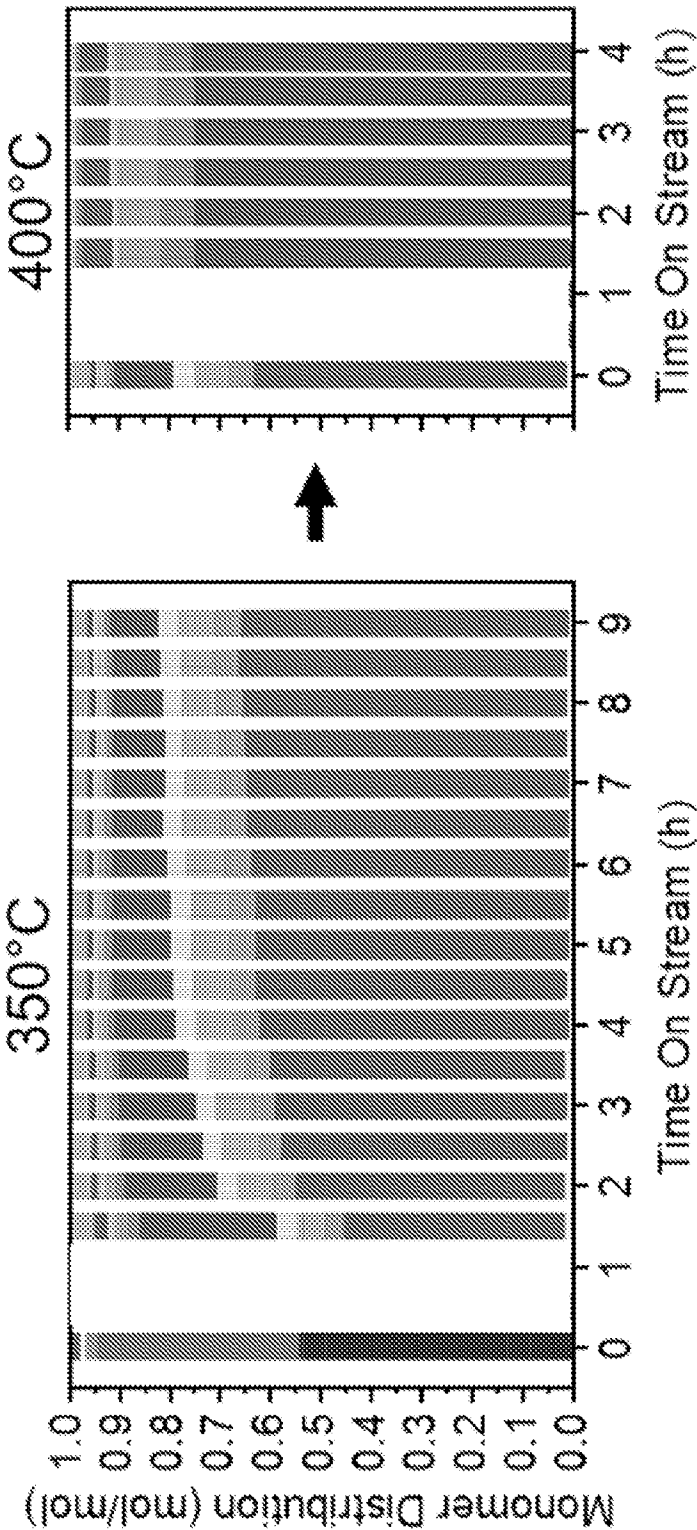


Fig. 10A

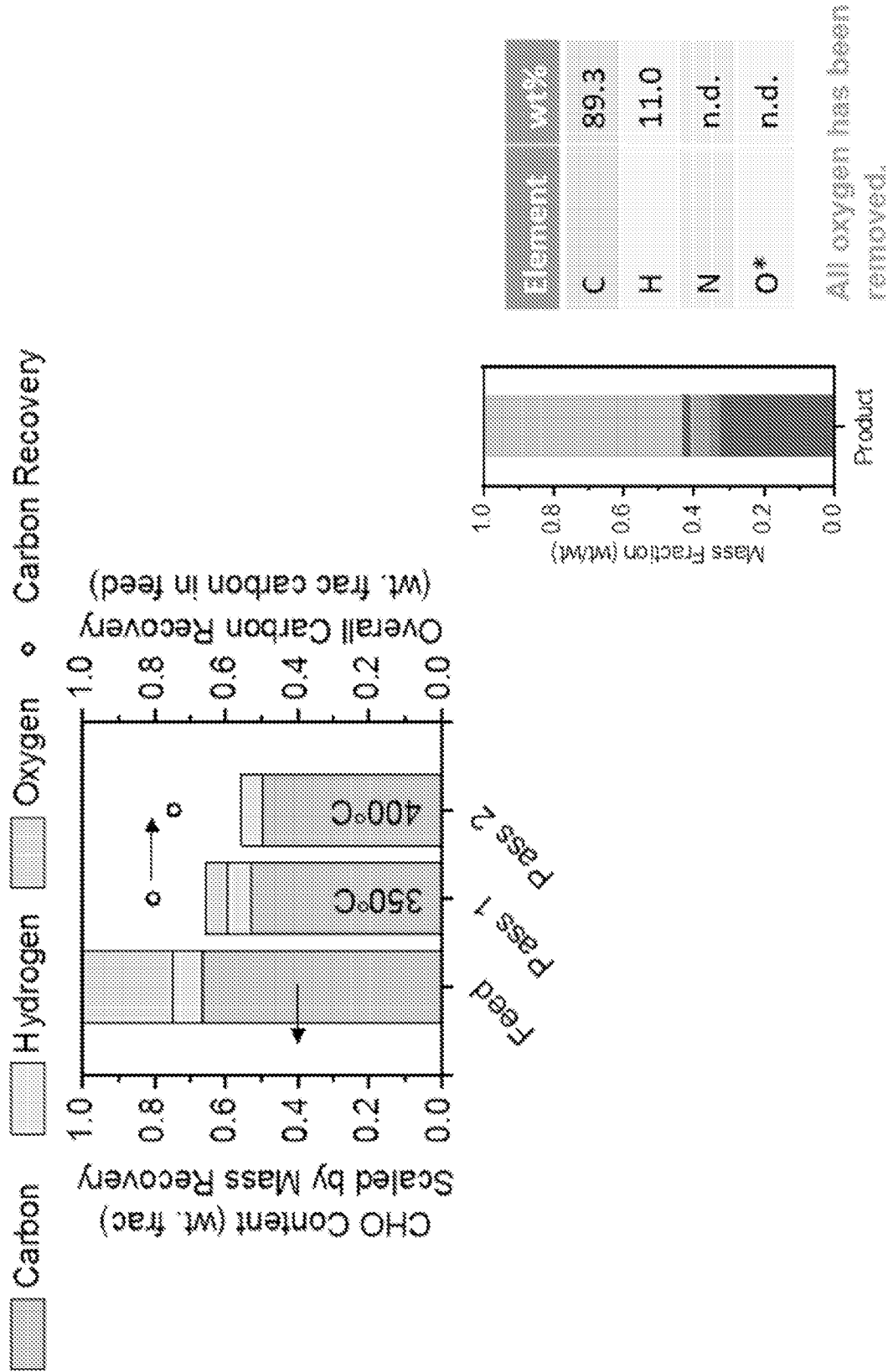


Fig. 10B

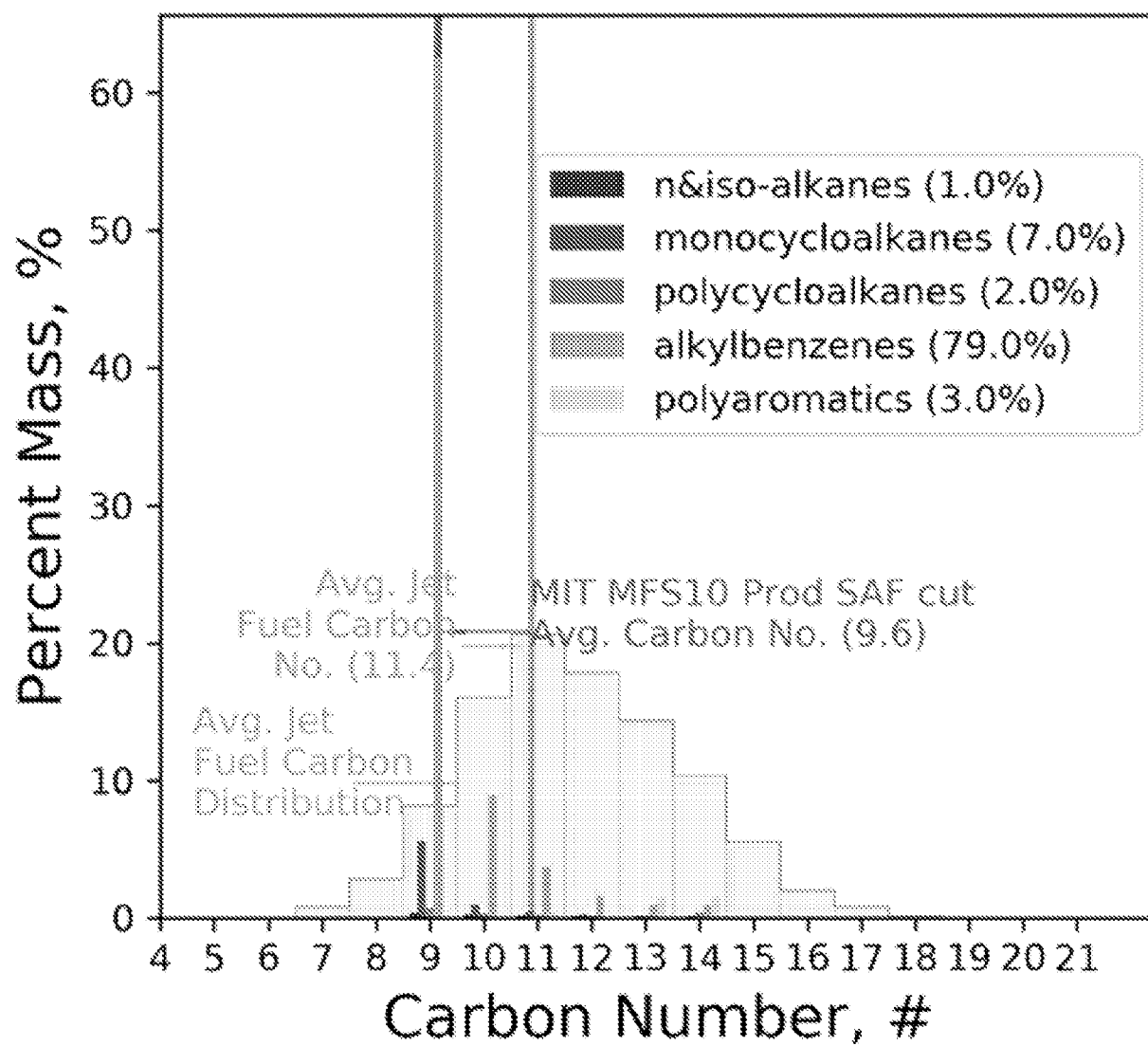


Fig. 11

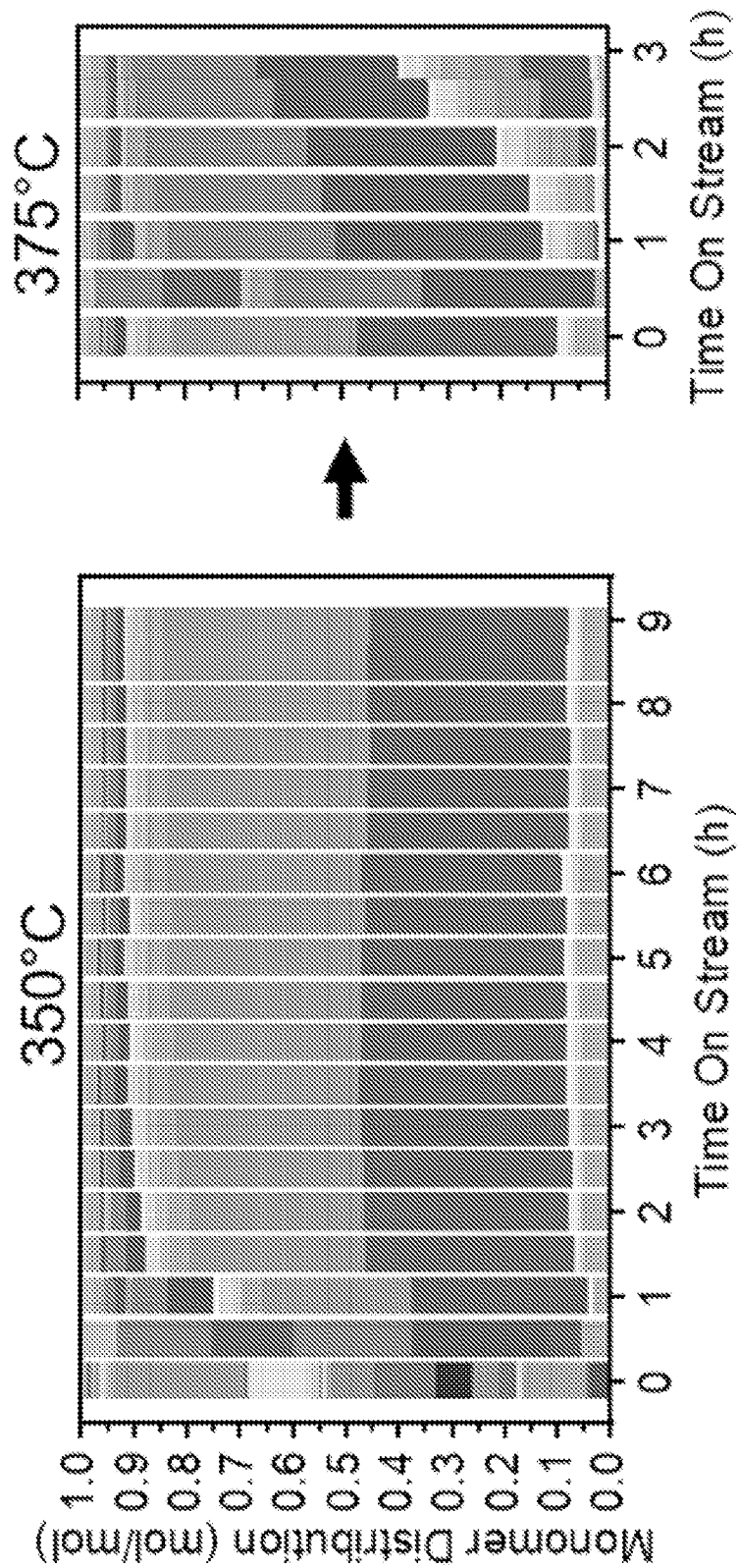


Fig. 12

		RCF Oil	
Element	Poplar	Pine	Corn Stover
O	25.7 wt%	25.1 wt%	26.1 wt%
N	0.2 wt%	0.2 wt%	1.0 wt%
S	<10 ppm	<10 ppm	39 ppm
Si	23 ppm	<10 ppm	<10 ppm
K	43 ppm	29 ppm	71 ppm
Ca	52 ppm	54 ppm	71 ppm

Fig. 13



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UNITED STATES DEPARTMENT OF COMMERCE
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Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY. DOCKET NO	TOT CLAIMS	IND CLAIMS
63/395,067	08/04/2022		150	NREL PROV/22-94		

CONFIRMATION NO. 5743

FILING RECEIPT

23712
Alliance for Sustainable Energy, LLC
15013 Denver West Parkway
RSF-056
GOLDEN, CO 80401-3305



Date Mailed: 08/16/2022

Receipt is acknowledged of this provisional patent application. It will not be examined for patentability and will become abandoned not later than twelve months after its filing date. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF FIRST INVENTOR, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection.

Please verify the accuracy of the data presented on this receipt. If an error is noted on this Filing Receipt, please submit a written request for a corrected Filing Receipt identifying the requested changes, preferably by including a properly marked-up ADS showing the changes with strike-through for deletions and underlining for additions. If you received a "Notice to File Missing Parts" or other Notice requiring a response for this application, please submit any request for correction to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections provided that the request is grantable.

Inventor(s)

Gregg Tyler BECKHAM, Golden, CO;
Michael L. STONE, Cambridge, MA;
Yuriy ROMÁN, Cambridge, MA;
Matthew S. WEBBER, Cambridge, MA;

Applicant(s)

Alliance for Sustainable Energy, LLC, Golden, CO;
Massachusetts Institute of Technology, Cambridge, MA

Power of Attorney:

Neal Vickery--73035

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

Applicant may provide or rescind an authorization for access using Form PTO/SB/39 or Form PTO/SB/69 as appropriate.

If Required, Foreign Filing License Granted: 08/15/2022

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 63/395,067**

Projected Publication Date: None, application is not eligible for pre-grant publication

Non-Publication Request: No

Early Publication Request: No

**** SMALL ENTITY ****

Title

CONTINUOUS HYDRODEOXYGENATION OF LIGNIN TO JET-RANGE AROMATIC
HYDROCARBONS

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

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Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at <http://www.uspto.gov/web/offices/pac/doc/general/index.html>.

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DOCUMENT MADE AVAILABLE UNDER THE PATENT COOPERATION TREATY (PCT)

International application number:	PCT/US2023/029488
International filing date:	04 August 2023 (04.08.2023)
Document type:	Certified copy of priority document
Document details:	Country/Office: US
	Number: 63/395,067
	Filing date: 04 August 2022 (04.08.2022)
Date of receipt at the International Bureau:	24 August 2023 (24.08.2023)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a),(b) or (b-bis)

1276912

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

August 23, 2023

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APPLICATION NUMBER: 63/395,067

FILING DATE: August 04, 2022

RELATED PCT APPLICATION NUMBER: PCT/US23/29488

THE COUNTRY CODE AND NUMBER OF YOUR PRIORITY APPLICATION, TO BE USED FOR FILING ABROAD UNDER THE PARIS CONVENTION, IS US63/395,067



Certified by

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Performing the Functions and Duties of the
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DocCode - SCORE

SCORE Placeholder Sheet for IFW Content

Application Number: 63395067

Document Date: 08/04/2022

The presence of this form in the IFW record indicates that the following document type was received in electronic format on the date identified above. This content is stored in the SCORE database.

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Application Data Sheet 37 CFR 1.76		Attorney Docket Number	NREL PROV/22-94
		Application Number	
Title of Invention	CONTINUOUS HYDRODEOXYGENATION OF LIGNIN TO JET-RANGE AROMATIC HYDROCARBONS		
The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76. This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.			

Secrecy Order 37 CFR 5.2:

☐	Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)
--------------------------	---

Inventor Information:

Inventor	1				Remove	
Legal Name						
Prefix	Given Name	Middle Name	Family Name	Suffix		
	Gregg	Tyler	BECKHAM			
Residence Information (Select One) • US Residency Non US Residency Active US Military Service						
City	Golden	State/Province	CO	Country of Residence	US	
Mailing Address of Inventor:						
Address 1		c/o National Renewable Energy Laboratory				
Address 2		15013 Denver West Parkway				
City	Golden	State/Province	CO			
Postal Code	80401	Country i	US			
Inventor	2				Remove	
Legal Name						
Prefix	Given Name	Middle Name	Family Name	Suffix		
	Michael	L.	STONE			
Residence Information (Select One) • US Residency Non US Residency Active US Military Service						
City	Cambridge	State/Province	MA	Country of Residence	US	
Mailing Address of Inventor:						
Address 1		c/o MIT Technology Licensing Office, Room NE18-501				
Address 2		255 Main Street				
City	Cambridge	State/Province	MA			
Postal Code	02142-1493	Country i	US			
Inventor	3				Remove	
Legal Name						
Prefix	Given Name	Middle Name	Family Name	Suffix		
	Yuri		ROMÁN			
Residence Information (Select One) • US Residency Non US Residency Active US Military Service						

Application Data Sheet 37 CFR 1.76		Attorney Docket Number	NREL PROV/22-94
		Application Number	
Title of Invention	CONTINUOUS HYDRODEOXYGENATION OF LIGNIN TO JET-RANGE AROMATIC HYDROCARBONS		

City	Cambridge	State/Province	MA	Country of Residence ⁱ	US
------	-----------	----------------	----	-----------------------------------	----

Mailing Address of Inventor:

Address 1	c/o MIT Technology Licensing Office, Room NE18-501				
Address 2	255 Main Street				
City	Cambridge	State/Province	MA		
Postal Code	02142-1493	Country ⁱ	US		
Inventor	4				Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Matthew	S.	WEBBER	

Residence Information (Select One) ☒ US Residency ☐ Non US Residency ☐ Active US Military Service

City	Cambridge	State/Province	MA	Country of Residence ⁱ	US
------	-----------	----------------	----	-----------------------------------	----

Mailing Address of Inventor:

Address 1	c/o MIT Technology Licensing Office, Room NE18-501				
Address 2	255 Main Street				
City	Cambridge	State/Province	MA		
Postal Code	02142-1493	Country ⁱ	US		

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button.

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ An Address is being provided for the correspondence Information of this application.

Customer Number	23712		
Email Address	ipdocketing@nrel.gov	Add Email	Remove Email
Email Address	Nancy.Ronzzone@nrel.gov	Add Email	Remove Email
Email Address	Neal.Vickery@nrel.gov		Remove Email

Application Information:

Title of the Invention	CONTINUOUS HYDRODEOXYGENATION OF LIGNIN TO JET-RANGE AROMATIC HYDROCARBONS		
Attorney Docket Number	NREL PROV/22-94	Small Entity Status Claimed ☒	
Application Type	Provisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	13	Suggested Figure for Publication (if any)	

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Application Data Sheet 37 CFR 1.76		Attorney Docket Number	NREL PROV/22-94
		Application Number	
Title of Invention	CONTINUOUS HYDRODEOXYGENATION OF LIGNIN TO JET-RANGE AROMATIC HYDROCARBONS		

Filing By Reference:

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not be** the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

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Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32). Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	☒ Customer Number	☐ US Patent Practitioner	☐ Limited Recognition (37 CFR 11.9)
Customer Number	23712		

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, 365(c), or 386(c) or indicate National Stage entry from a PCT application. Providing benefit claim information in the Application Data Sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.

When referring to the current application, please leave the "Application Number" field blank.

Prior Application Status		Remove	
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the Add button.			Add

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Application Data Sheet 37 CFR 1.76		Attorney Docket Number	NREL PROV/22-94
		Application Number	
Title of Invention	CONTINUOUS HYDRODEOXYGENATION OF LIGNIN TO JET-RANGE AROMATIC HYDROCARBONS		

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55. When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)ⁱ the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(i)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Application Number	Country ⁱ	Filing Date (YYYY-MM-DD)	Access Code ⁱ (if applicable)	Remove

Additional Foreign Priority Data may be generated within this form by selecting the **Add** button.

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013. NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

Application Data Sheet 37 CFR 1.76		Attorney Docket Number	NREL PROV/22-94
		Application Number	
Title of Invention	CONTINUOUS HYDRODEOXYGENATION OF LIGNIN TO JET-RANGE AROMATIC HYDROCARBONS		

Authorization or Opt-Out of Authorization to Permit Access:

When this Application Data Sheet is properly signed and filed with the application, applicant has provided written authority to permit a participating foreign intellectual property (IP) office access to the instant application-as-filed (see paragraph A in subsection 1 below) and the European Patent Office (EPO) access to any search results from the instant application (see paragraph B in subsection 1 below).

Should applicant choose not to provide an authorization identified in subsection 1 below, applicant **must opt-out** of the authorization by checking the corresponding box A or B or both in subsection 2 below.

NOTE: This section of the Application Data Sheet is **ONLY** reviewed and processed with the **INITIAL** filing of an application. After the initial filing of an application, an Application Data Sheet cannot be used to provide or rescind authorization for access by a foreign IP office(s). Instead, Form PTO/SB/39 or PTO/SB/69 must be used as appropriate.

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A. Priority Document Exchange (PDX) - Unless box A in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the State Intellectual Property Office of the People's Republic of China (SIPO), the World Intellectual Property Organization (WIPO), and any other foreign intellectual property office participating with the USPTO in a bilateral or multilateral priority document exchange agreement in which a foreign application claiming priority to the instant patent application is filed, access to: (1) the instant patent application-as-filed and its related bibliographic data, (2) any foreign or domestic application to which priority or benefit is claimed by the instant application and its related bibliographic data, and (3) the date of filing of this Authorization. See 37 CFR 1.14(h)(1).

B. Search Results from U.S. Application to EPO - Unless box B in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the EPO access to the bibliographic data and search results from the instant patent application when a European patent application claiming priority to the instant patent application is filed. See 37 CFR 1.14(h)(2).

The applicant is reminded that the EPO's Rule 141(1) EPC (European Patent Convention) requires applicants to submit a copy of search results from the instant application without delay in a European patent application that claims priority to the instant application.

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

☐ A. Applicant **DOES NOT** authorize the USPTO to permit a participating foreign IP office access to the instant application-as-filed. If this box is checked, the USPTO will not be providing a participating foreign IP office with any documents and information identified in subsection 1A above.

☐ B. Applicant **DOES NOT** authorize the USPTO to transmit to the EPO any search results from the instant patent application. If this box is checked, the USPTO will not be providing the EPO with search results from the instant application.

NOTE: Once the application has published or is otherwise publicly available, the USPTO may provide access to the application in accordance with 37 CFR 1.14.

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Application Data Sheet 37 CFR 1.76		Attorney Docket Number	NREL PROV/22-94
		Application Number	
Title of Invention	CONTINUOUS HYDRODEOXYGENATION OF LIGNIN TO JET-RANGE AROMATIC HYDROCARBONS		

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant	1	Remove
If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.		
Clear		
☒ Assignee	Legal Representative under 35 U.S.C. 117	Joint Inventor
Person to whom the inventor is obligated to assign.		Person who shows sufficient proprietary interest
If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:		
Name of the Deceased or Legally Incapacitated Inventor:		
If the Applicant is an Organization check here. ☒		
Organization Name	Alliance for Sustainable Energy, LLC	
Mailing Address Information For Applicant:		
Address 1	c/o National Renewable Energy Laboratory	
Address 2	15013 Denver West Parkway	
City	Golden	State/Province
Country	US	Postal Code
Phone Number	303-384-7571	Fax Number
Email Address	ipdocketing@nrel.gov	
Additional Applicant Data may be generated within this form by selecting the Add button. Add		

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	NREL PROV/22-94
	Application Number	
Title of Invention CONTINUOUS HYDRODEOXYGENATION OF LIGNIN TO JET-RANGE AROMATIC HYDROCARBONS		

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CONTINUOUS HYDRODEOXYGENATION OF LIGNIN TO JET-RANGE AROMATIC HYDROCARBONS

CONTRACTUAL ORIGIN

[0001] This invention was made with government support under Contract No. DE-AC36-08GO28308 awarded by the Department of Energy. The government has certain rights in the invention.

BACKGROUND

[0002] In 2019, 106 billion gallons of jet fuel were consumed globally and this number is expected to more than double by 2050 as a result of increased travel demand. To mitigate its impact on climate change, the aviation industry has pledged to reduce net CO₂ emissions in half by 2050. To achieve this goal, sustainable aviation fuel (SAF) must be deployed at a massive scale. Today, most commercially available SAF is synthesized via deoxygenation of plant-derived lipid feedstocks to produce iso- and n-alkane hydrocarbon blends, but these feedstocks are not available in the volumes required to meet the projected fuel demand. Notably, cycloalkanes and aromatics together comprise between 30 and 70 wt% of modern aviation fuel or between 32 and 74 billion gallons per year. However, current SAF technologies cannot produce the aromatic or the cycloalkane components at the scale necessary to satisfy the required properties of jet fuel (namely fuel density and elastomer compatibility) to power the existing fleet of aircrafts, which is a constraint that has resulted in a 50% blending wall with conventional fossil fuels. A technology capable of generating aromatics and cycloalkanes from renewable feedstocks is thus essential for the development of a viable 100% drop-in SAF.

[0003] Lignin is the largest source of renewable aromatics available in nature comprising between 15-30% of lignocellulosic biomass. In principle, the 90 million dry-tons of lignin harvested in the United States in 2017 could generate 15 billion gallons of jet-range hydrocarbons based on carbon content. By 2040, this value could increase to 63 billion gallons annually (>50% of current global demand) given projections on future lignin availability. Despite its potential, lignin is currently either re-dispersed in the field or slated to be burned for low grade heat by the cellulosic ethanol and paper industries because lignin becomes highly recalcitrant when separated from the cellulose fibers in biomass. Alternative lignin extraction methods that rely on reductive catalytic

fractionation (RCF), protection group chemistries or flow-through solvolysis minimize re-condensation pathways, but the resulting lignin oils have high oxygen contents ranging between 27-34 wt% which must be reduced to trace levels for use in jet fuel. To this end, significant progress has been made in the development of catalysts capable of hydrodeoxygenation (HDO) of oxygenated aromatics. However, the translation of promising catalysts to viable processing strategies with real lignin feedstocks has been hindered by major challenges, such as the use of expensive noble-metal catalysts, catalyst deactivation coupled with low deoxygenation efficiency when using real feedstocks, excessive hydrogen consumption due to ring hydrogenation and hydrocracking, and low carbon yields due to condensation/coking, hydrocracking to gaseous products, or upgrading of only the monomeric fraction.

SUMMARY

[0004] Described herein are systems and methods for the catalytic deoxygenation of lignin to generate low-oxygen aromatics that may be useful as a sustainable aviation or marine fuel. The provided systems and methods may be performed continuously without the need for a solvent, increasing both efficiency and cost effectiveness.

[0005] In one aspect, provided is a method for generating aromatic compounds from a lignin feed stock by utilizing a two stage process, first at a lower temperature and second at a higher temperature to fully deoxygenate the lignin while avoiding unwanted secondary reactions such as condensation reactions. This method may utilize a single or multiple catalysts, including as an example an Mo₂C-based catalyst. The first, lower temperature may, for example, be selected from the range of 250 °C to 450 °C, 300 °C to 400 °C, 325 °C to 375 °C, 325 °C to 350 °C, or about 350 °C. The second, higher temperature may, for example, be selected from the range of 275°C to 475°C, 325 °C to 425 °C, 350 °C to 400 °C, 350 °C to 375 °C, or about 375 °C. The resulting aromatic hydrocarbons may have very low oxygen content, for example, having a mole fraction of oxygen in the resulting compounds of less than or equal to 10%, 5%, 1%, 0.5%, or 0.1%.

[0006] The method may be performed with neat lignin oil, e.g., lignin without the presence of a solvent. The ability to react neat lignin oil could provide various benefits such as a reduction in cost, smaller reactor requirements, etc. However, the described systems and methods also can be utilized in situations where it is preferable to dissolve the lignin reactant into a solvent, such as an aromatic solvent, for example, toluene.

[0007] In an aspect, provide is a system or reactor for the generation of low-oxygen aromatics comprising: a first reaction zone comprising a first catalyst at a first temperature; a second reaction zone comprising a second catalyst at a second temperature; where in the reactor is capable of performing hydrodeoxygenation of lignin to generate aromatic products. The reactor may be a packed bed reactor or a trickle bed reactor. The reactor may also allow for continuous process flow, either as individual steps (e.g., each step is continuous) or a single continuous process. The reactor may be capable of steady state operation.

[0008] Other catalysts may be useful including supported metal catalysts as the second, higher-temperature catalyst. Additionally, the described process may be altered to generate cycloalkanes rather than aromatic products. This may be accomplished by incorporating a metal-doped Mo₂C-based catalyst or substituting one or both of the catalysts with a catalyst comprising nickel phosphide.

[0009] In an aspect, provided is a catalyst comprising Mo₂C capable of partially or fully deoxygenating lignin, as described by the systems and methods provided herein.

BRIEF DESCRIPTION OF DRAWINGS

[0010] Some embodiments are illustrated in referenced figures of the drawings. It is intended that the embodiments and figures disclosed herein are to be considered illustrative rather than limiting.

[0011] Figure 1 provides an Overview schematic of HDO of RCF lignin oil. Figure 1A provides a summary of the lignin monomers quantified as described herein at all levels of partial conversion. Monomer conversion in single pass or two-pass achieves similar results yielding propylbenzene as a major product. The darker shades represent the major reaction pathway on Mo₂C and the lighter shades are products resulting from side-reactions, including rearrangement of the functional group position and ring alkylation (products noted with an asterisk), which have previously been observed during deoxygenation with molybdenum oxide catalysts. The acronyms are as follows: PS: propylsyringol, PS=: propenylsyringol, PS-OH: dihydrosinapyl alcohol, PG: propylguaiacol, PG=: propenylguaiacol, PG-OH: dihydroconiferyl alcohol, PP: propylphenol, Alk. PG: methyl-propylguaiacol, Alk. PP: methyl-propylphenol, Rearr. PG: methoxy-propylphenol, PB-OMe: propylanisole, PB: propylbenzene, PCH: propylcyclohexane. Figure 1B shows examples of dimers

identified in the feed, intermediates, and products. Dimer conversion is sensitive to temperature with a parallel pathway toward condensation products at higher temperatures.

[0012] Figure 2 illustrates Catalyst-free control experiments to evaluate lignin oil stability. Figure 2A shows mass balance on steady state samples collected during no-catalyst control experiments. The bars show mass fractions of monomers and non-monomers, and the product bars are scaled by the overall mass recovery. The height of the bar is the average value, and the error bars show one standard deviation for 3 steady state samples. The feed bar is included for each experiment to account for slight variability between batches of RCF oil. Figure 2B provides GPC on the feed (“RCF Oil”) and the products from no-catalyst control experiments at different temperatures, with the inset showing the dimer and oligomer portion of the curve to highlight the shift in product distribution with increasing temperature. All samples were prepared to the same concentration of 2 mg/mL and the traces were not normalized or scaled.

[0013] Figure 3 illustrates evaluation of activity and stability of Mo₂C for solvent-free lignin HDO. Figure 3A shows steady state results of monomer distribution and monomer mole balance from HDO experiments flowing neat RCF lignin oil (“Feed”) over a packed bed of 2.88 g Mo₂C (60-100 mesh) in a trickle bed reactor. Steady state results were taken after 2.5 h on stream, combined from several hours, and the water formed during reaction was removed prior to performing mass and mole balance calculations. Each bar is labelled with the reactor temperature and the weighted hourly space velocity (WHSV) calculated as the mass flowrate of lignin oil divided by mass of catalyst. The transient distribution of quantified monomers as a function of time on stream at (Figure 3B) 300°C, (Figure 3C) 325°C, and (Figure 3D) 350°C and 0.1 mL/min lignin oil (WHSV = 2.35 h⁻¹). Figure 3E provides the conversion of oxygen from the monomer fraction for each experiment shown in Figures 3B-3D, plotted as the mole percent of oxygen removed from the monomers at each time on stream. Constant conditions: 900 psi, 2.88 g Mo₂C (60-100 mesh), 90 mL/min H₂, and toluene at 1 mL/min for 30 min during start-up.

[0014] Figure 4 provides optimization of deep deoxygenation of lignin oil for jet-range aromatic production. (Figure 4A) Carbon, oxygen, and hydrogen content in the oil on a mass basis, as determined via total carbon analysis. The weight percent results of total carbon analysis were multiplied by the mass recovery of oil at steady state after removing the aqueous fraction to generate the plot. (Figure 4B) Results of quantitative GCxGC analysis of the final deoxygenated

oils from each of the experiments shown in Figure 4A. (Figure 4C) Simulated distillation generated by the ASTM D2887 method of the fully deoxygenated product from each multi-pass experiment, with a zoomed-in plot on the dimer region. Protocols and conditions described herein. (Figure 4D) Production of fully deoxygenated lignin oil using optimized multi-pass conditions. The Sankey diagram shows the carbon balance on each pass of the optimum multi-pass experiment. The carbon content in the whole oil was determined using total carbon analysis. The monomer carbon content was determined with GC-FID analysis and is plotted as a fraction of the total carbon content. The carbon content was multiplied by the steady state recovery of the oil (by mass) across each pass. Photos show the oil at each stage of the process, with water (bottom phase) formed during the reaction separating from the deoxygenated organics (top phase). Conditions: 2.88 g Mo2C (60-100 mesh), 0.1 mL/min lignin oil, 90 mL/min H₂, 900 psi, 350°C first pass, 375°C second pass, and toluene at 1 mL/min for 30 min during start-up.

DETAILED DESCRIPTION

[0015] The embodiments described herein should not necessarily be construed as limited to addressing any of the particular problems or deficiencies discussed herein. References in the specification to “one embodiment”, “an embodiment”, “an example embodiment”, “some embodiments”, etc., indicate that the embodiment described may include a particular feature, structure, or characteristic, but every embodiment may not necessarily include the particular feature, structure, or characteristic. Moreover, such phrases are not necessarily referring to the same embodiment. Further, when a particular feature, structure, or characteristic is described in connection with an embodiment, it is submitted that it is within the knowledge of one skilled in the art to affect such feature, structure, or characteristic in connection with other embodiments whether or not explicitly described.

[0016] As used herein the term “substantially” is used to indicate that exact values are not necessarily attainable. By way of example, one of ordinary skill in the art will understand that in some chemical reactions 100% conversion of a reactant is possible, yet unlikely. Most of a reactant may be converted to a product and conversion of the reactant may asymptotically approach 100% conversion. So, although from a practical perspective 100% of the reactant is converted, from a technical perspective, a small and sometimes difficult to define amount remains. For this example of a chemical reactant, that amount may be relatively easily defined by the detection limits of the

instrument used to test for it. However, in many cases, this amount may not be easily defined, hence the use of the term “substantially”. In some embodiments of the present invention, the term “substantially” is defined as approaching a specific numeric value or target to within 20%, 15%, 10%, 5%, or within 1% of the value or target. In further embodiments of the present invention, the term “substantially” is defined as approaching a specific numeric value or target to within 1%, 0.9%, 0.8%, 0.7%, 0.6%, 0.5%, 0.4%, 0.3%, 0.2%, or 0.1% of the value or target.

[0017] As used herein, the term “about” is used to indicate that exact values are not necessarily attainable. Therefore, the term “about” is used to indicate this uncertainty limit. In some embodiments of the present invention, the term “about” is used to indicate an uncertainty limit of less than or equal to $\pm 20\%$, $\pm 15\%$, $\pm 10\%$, $\pm 5\%$, or $\pm 1\%$ of a specific numeric value or target. In some embodiments of the present invention, the term “about” is used to indicate an uncertainty limit of less than or equal to $\pm 1\%$, $\pm 0.9\%$, $\pm 0.8\%$, $\pm 0.7\%$, $\pm 0.6\%$, $\pm 0.5\%$, $\pm 0.4\%$, $\pm 0.3\%$, $\pm 0.2\%$, or $\pm 0.1\%$ of a specific numeric value or target.

[0018] As used herein, the term “Mo₂C” or “Mo₂C-based catalyst” refers to a catalyst comprising or consisting essentially of a form of molybdenum carbide. In some embodiments, the catalyst may comprise or consist essentially of Mo₂C or β -Mo₂C, but other forms or phases of molybdenum carbide may also be the primary or a secondary component. Further, Mo₂C-based catalysts may include metal-doped catalyst where a metal, such as a transition metal, is included in the catalyst, for example, Cu, Ni, Pt. Mo₂C based catalysts may also be multidimensional or multilayered.

[0019] The provided discussion and examples have been presented for purposes of illustration and description. The foregoing is not intended to limit the aspects, embodiments, or configurations to the form or forms disclosed herein. In the foregoing Detailed Description for example, various features of the aspects, embodiments, or configurations are grouped together in one or more embodiments, configurations, or aspects for the purpose of streamlining the disclosure. The features of the aspects, embodiments, or configurations, may be combined in alternate aspects, embodiments, or configurations other than those discussed above. This method of disclosure is not to be interpreted as reflecting an intention that the aspects, embodiments, or configurations require more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed embodiment, configuration, or aspect. While certain aspects of conventional technology have been discussed to

facilitate disclosure of some embodiments of the present invention, the Applicants in no way disclaim these technical aspects, and it is contemplated that the claimed invention may encompass one or more of the conventional technical aspects discussed herein. Thus, the following claims are hereby incorporated into this Detailed Description, with each claim standing on its own as a separate aspect, embodiment, or configuration.

Example 1 – Continuous hydrodeoxygenation of lignin to jet-range aromatic hydrocarbons

[0020] Described in this example is a solvent-free process for the HDO of poplar RCF lignin oil with near-quantitative carbon yields using earth-abundant molybdenum carbide (Mo₂C) catalysts. Continuous flow HDO experiments with real lignin feeds under solvent-free conditions were performed in a custom-built three-phase trickle bed reactor. Poplar RCF lignin oil was chosen as an illustrative lignin substrate, with recent studies showing potential for commercial implementation of RCF in a lignin- first biorefinery. The RCF process solvolytically extracts and catalytically depolymerizes lignin from whole biomass to produce an oxygenated aromatic oil consisting of ~50 wt% monomeric species and ~50 wt% carbon-carbon linked dimers and larger oligomers. Accordingly, complete deoxygenation of RCF oil would generate a mixture rich in alkylated arenes ranging between C₉ and C₂₀, which is ideal for jet fuel blending.

Results

[0021] Tracking deoxygenation with Mo₂C-based catalysts. The complexity of lignin oil components and their deoxygenated products necessitates rigorous analytical methods to close mass balances accurately. Accordingly, we identified and quantified partially and fully deoxygenated monomers and dimers during HDO experiments using a feed consisting of 2 wt% RCF oil dissolved in toluene. Unsupported Mo₂C was used as the catalyst due to its ability to directly cleave C–O bonds in model aromatic oxygenate molecules without hydrogenating the aromatic rings. Although Mo₂C has not been studied extensively for the deep deoxygenation of lignin oil, we hypothesized it could provide a route toward hydrogen- efficient deoxygenation with control over aromatic product selectivity. **Fig. 1A** summarizes all the lignin-derived monomers quantified by gas chromatography with flame ionization detection (GC-FID) in this study. This method afforded monomer mole balances of 100% +/- 5% at all levels of partial conversion investigated. We used trimethylsilyl derivatization with GC coupled with mass spectrometry (GC-

MS) to identify dimeric compounds at different levels of conversion (**Fig. 1B**). Generally, both monomeric and dimeric species followed similar conversion and selectivity trends to those observed during vapor-phase Mo₂C HDO with model compounds. The first functional groups to undergo deoxygenation are the γ - hydroxyl groups (e.g., dihydroconiferyl alcohol, PG-OH), generating guaiacol and syringol derivatives. Next, deoxygenation of the methoxy group (e.g., propylguaiacol, PG) produces phenolics. Finally, the phenolic groups (e.g., propylphenol, PP) are cleaved to produce alkylbenzenes.

[0022] Evaluating solvent-free lignin oil stability. While 2 wt% RCF oil in toluene was a useful system for the development of analytical methods, toluene only dissolves ~70 wt% of the RCF oil, extracting low molecular weight components preferentially. For this reason, neat RCF oil was used as the feedstock for all subsequent studies. To study the stability of solvent-free RCF oil under elevated temperatures and determine acceptable operating temperatures for the HDO process, we performed catalyst-free flow experiments using conditions otherwise amenable to HDO chemistry. Reactor temperatures of 325, 350, and 375°C showed lignin oil mass recoveries of 98.7 (± 1.2), 98.5 (± 2.0), and 98.6 (± 2.5) wt%, respectively, whereas at 400°C, the mass recovery was 93.2 (± 0.9) wt% (**Fig. 2A**). PG-OH and PS- OH, which make up 15 wt% of the RCF oil feed, were the most sensitive monomers to temperature, with combined recoveries of 90.0, 87.9, 40.2 and 17.8 wt% at 325°C, 350°C, 375°C and 400°C, respectively. Additionally, a combined 5.6 wt% of rearranged, alkylated, and partially deoxygenated monomeric products were formed during the no-catalyst experiment at 400°C. Changes in the molecular weight distribution of the lignin oil, characterized using gel permeation chromatography (GPC) and GC-MS data of derivatized samples, indicated that increasing the temperature from 325 to 400°C progressively decreased dimer concentrations and promoted the formation of new oligomers via condensation reactions (**Fig. 2B**).

[0023] Mo₂C catalyst activity during HDO of lignin oil. We next evaluated both the activity and stability of the Mo₂C for the continuous HDO of undiluted lignin oil at temperatures below 400°C to reduce deleterious lignin condensation (**Figs. 3A-3E**). To avoid structural changes caused by the exposure of the carbide phase to molecular oxygen, fresh Mo₂C was synthesized *in situ* via the carburization of ammonium molybdate tetrahydrate (AMT) immediately prior to the start of each experiment. At 350°C and a weighted hourly space velocity (WHSV) of 2.35 g_{lignin}/g_{catalyst}/h,

a steady state monomer oxygen conversion of 65.8 +/- 0.05 mol% was achieved with major monomeric products of 50.2 mol% PP, 13.8 mol% PB and 11.6 mol% PB-OMe (**Fig. 3A**). Despite achieving stable deoxygenation at these conditions, neither doubling the residence time (WHSV = 1.175 h⁻¹), nor recycling the partially deoxygenated oil over a fresh catalyst bed at 350°C resulted in complete monomer deoxygenation. Higher temperatures were required to activate the aryl-OH bonds, with 375°C and a WHSV=2.35 h⁻¹ achieving 48.5% removal of phenolic groups. **Fig. 3B** and **Fig. 3C** show the effect of temperature on catalyst stability. Transient data collected at 300 and 325°C from 2.5 to 6 h on stream showed steady deactivation profiles with a decrease in monomer oxygen conversion of 58 to 52 mol% for 325°C and 32 to 22 mol% for 300°C. Although temperatures as low as 150°C have been used to deoxygenate anisole and 280°C to achieve near complete deoxygenation of model phenolic mixtures to aromatics at steady state with Mo₂C, our data indicate that temperatures of 350°C and 375°C are needed for stable removal of methoxy and phenolic groups in neat lignin oil, respectively. These results on activity and stability resemble the performance of MoO₃ during HDO. Although PXRD analysis of the catalyst after reaction does not show bulk oxidation to MoO₃, *in situ* techniques have shown the surface of Mo₂C is oxidized during reaction with oxygenates. This potentially explains why prior work on HDO of oxygen-rich real lignin feeds with Mo₂C did not achieve complete deoxygenation and highlights the difficulty in translating the results of model systems to biomass feedstocks.

[0024] Achieving deep deoxygenation to aromatic hydrocarbons. Together, lignin oil stability (**Figs. 2A-2B**) and catalyst activity (**Figs. 3A-3E**) experiments revealed an important trade-off in lignin oil HDO: low temperatures result in catalyst deactivation but achieve high carbon balances by preserving oligomers, while high temperatures are necessary to maintain catalyst activity and achieve full deoxygenation, but result in the loss of dimers through condensation. We evaluated two routes for generating deeply deoxygenated oil products: i) increasing the temperature and the residence time in a single-pass at 400°C and WHSV = 1.175 h⁻¹ and ii) operating in a two-pass mode wherein an initial HDO run is performed at an intermediate temperature to generate a mixture of partially deoxygenated monomers and oligomers that is more resistant towards subsequent condensation reactions, followed by a second pass at a higher temperature to achieve full deoxygenation. For the two-pass experiments, first-pass products were collected at 325°C, 350°C, or 375°C, each over a fresh catalyst bed. Next, these products were deoxygenated at 375°C

in a second run with a fresh catalyst bed. **Fig. 4A** summarizes the carbon, hydrogen, and oxygen content of each oil scaled by the mass recovery from each pass along with the overall carbon recovery. After the first pass at 400°C, 375°C, 350°C, and 325°C, 0.7, 8.0, 11.7, 15.8 wt% oxygen remained, respectively. This was reduced to 1.0, 2.1 and 1.2 wt% for 375-375°C, 350-375°C, and 325-

[0025] 375°C, respectively. The near complete deoxygenation of the products was confirmed with heteronuclear single quantum coherence (HSQC) nuclear magnetic resonance spectroscopy (NMR) and derivatization + GC-MS. The final monomer product distributions were similar in all cases, with propylbenzene selectivity values of ca. 78 mol%. The dimer products were more sensitive to temperature, showing 8.9, 9.5, 11.9, and 14.2 wt% dimer content for first pass temperatures of 400°C, 375°C, 350°C, and 325°C, respectively as determined by quantitative GCxGC analysis (**Fig. 4B**). This trend in dimer recovery was supported by simulated distillation (**Fig 4C**), and additional chromatography techniques.

[0026] Two-pass operation with 350°C followed by 375°C achieved an optimal balance for catalyst stability and jet-range aromatic production. Indeed, 350°C was the optimal temperature to maintain stable catalyst activity at partial deoxygenation in the first pass (total product oxygen content of 11.7%), while higher temperatures of 375°C and 400°C resulted in an elevated loss of aromatic dimers. **Fig. 4D** summarizes the optimal overall process, where we obtained a reduction in total oxygen content from 26.3 mol% to 2.1 mol% (95.7% conversion), with an unprecedented 73.1 C-mol% recovery (86% of theoretical based on removal of methoxy groups) and 87.5% monomer selectivity toward aromatic hydrocarbons. For reference, recent reports have shown yields between 10-30 wt% and 30-50 wt% via one- and two- step processes, respectively, while our process's mass recovery is consistently between 50-60 wt% while achieving higher levels of deoxygenation than those studies discussed. GCxGC quantification determined a final aromatic dimer (C14- C20) content of 11.9 wt.% and aromatic monomer (C9-C12) content of 56 wt%, summing to 67.9 wt% of jet-range aromatics in the final oil.

Discussion, Recommendations and Conclusions

[0027] The provided example demonstrates that lignin stability is a key constraint under typical HDO conditions, and that two-pass HDO, with the first pass used for stabilization via partial conversion and the second pass for deep deoxygenation, is a viable strategy for lignin upgrading

with high atom economy. This strategy could be broadly applicable to other lignin feedstocks. Furthermore, HDO reactions with Mo₂C selectively cleaved C-O bonds while leaving the C-C structure of the lignin substrate intact. In addition to minimizing the consumption of hydrogen, this selectivity indicates that the distribution of HDO products could be tuned by modifying the lignin feedstock itself. For example, a lignin substrate with a higher fraction of dimeric components could be utilized to increase the C₁₄-C₂₀ aromatic fraction in the resulting deoxygenated product. Furthermore, the carbon backbone of the dimer and oligomer fraction retains sufficient chemical functionality during reaction to differentiate between types of lignin inter-unit linkages that are synthesized *in planta* (e.g., β -1 vs β -5), providing an analytical opportunity to quantitatively track lignin bond distributions.

[0028] This example motivates the development of catalysts that can achieve stable HDO of real lignin feedstocks at low temperatures. Notably, the behavior of the catalyst under reaction with neat lignin oil was distinctly different than vapor-phase model compound studies reported to date. Furthermore, while the existing literature contains a strong fundamental framework from which to understand the impact of controlled Mo₂C surface oxidation on model compound reactivity, the parameters that determine extent of catalyst oxidation under reaction conditions with real lignin feeds have not been mapped and are not well understood. Understanding the factors that drive catalyst surface deactivation under reaction conditions with real feedstocks may enable rational catalyst design or reaction engineering solutions to mitigate catalyst deactivation and enable lower operating temperatures. Altogether, performing experiments in a trickle-bed reactor to generate continuous, steady-state HDO data using a real lignin feedstock, along with rigorous analytics to track carbon balances and individual components, was essential to understanding the limitations of this complex system.

[0029] Deoxygenated aromatics resulting from this process could be directly blended with existing commercial SAFs (which mainly consist of iso and n-alkanes), potentially overcoming the existing 50% blend-wall by providing the necessary aromatic components to increase both fuel density and elastomeric compatibility. Alternatively, subsequent hydrogenation, ring-opening, and/or hydrocracking reactions could be implemented to convert a fraction of the lignin-derived aromatics to other paraffinic compounds (including naphthenes and iso/n-alkanes), thereby generating an entirely lignin-derived SAF.

[0030] Finally, we propose potentially blending feedstocks (rather than deoxygenated products) to achieve desired aromatic/aliphatic ratios followed by subsequent deoxygenation over Mo₂C to directly generate a complete drop-in SAF. Ongoing techno-economic analyses and life cycle assessments are geared towards identifying critical areas for further development and integration of our product into a 100% SAF blend.

Materials and Methods

[0031] Generation of RCF lignin oil. 60 g of poplar (milled and sieved to <2 mm), 12 g of 5 wt% ruthenium on carbon (Sigma-Aldrich®) and 400 mL methanol (ACS reagent grade, Macron Fine Chemicals) were loaded into a 1 L batch reactor (Parr instrument company®, Series 4525HP). The reactor was sealed, flushed 3 times and pressurized to 30 bar with H₂ (UHP, Airgas®). During reaction, the mixture was stirred at 700 rpm with an overhead impeller. The temperature was monitored using an internal thermocouple and the furnace, stir rate, and cooling water were controlled with a Parr® instrument controller (series 4848). The temperature was ramped from 25°C to 225°C for 1.5 h, then held at 225°C for 3 h before rapidly cooling to 25°C via cooling water. Catalyst loading, hydrogen pressure, and reaction time were optimized to achieve complete conversion of ether bonds, ensuring no additional monomers were produced during HDO to enable monomer mole closure.

[0032] After reaction, the lignin fraction was isolated by vacuum filtration through a 4 µm ceramic filter. The solids were rinsed twice with methanol and the solvent was removed under vacuum. The resulting oil was purified to remove any sugars or acids that were extracted from the biomass during RCF with a dichloromethane (DCM)/water extraction, starting with 30 mL DCM (Laboratory-plus grade, Honeywell®) and 30 mL water (Milli-Q®) and subsequently rinsing the aqueous phase twice with 15 mL DCM. The DCM was removed from the organic phase under vacuum, with a preliminary removal at 100 torr by rotary evaporation followed by a secondary 0.1 mTorr evacuation on a Schlenk line with magnetic stirring at 250 rpm. Overall, this process obtained ~9 g of purified RCF lignin oil from a single 60 g poplar RCF experiment.

[0033] Catalyst synthesis. AMT (ACS reagent grade, Sigma-Aldrich®) was sieved between 60-100 mesh and an appropriate amount to achieve the desired quantity of Mo₂C was loaded into the trickle-bed reactor (see loading procedure). The reactor was then heated from 25°C to 700 °C over

3.5 h and held at 700°C for 3 h. Hydrogen gas was flowed at 55 mL/min for the duration of the synthesis, and methane (UHP, Airgas) was flowed at 15 mL/min for the first 6 h, enabling a 0.5 h scavenging step with pure hydrogen gas at 700°C. The reactor was then cooled and left sealed under hydrogen gas flow prior to reaction.

[0034] Trickle bed reactor design. Reactions were performed in a custom trickle-bed reactor. A 21" long, 1/4" OD Hastelloy reactor tube was heated in a vertically-mounted, insulated, single-zone, split furnace (Applied Test Systems® Series 3210) with steel blocks (machined to fill void space in the furnace) to ensure adequate heat transfer and maintain isothermal operation. A K-type thermocouple slotted to contact the outside of the reactor tube was used to measure temperature while another thermocouple at the middle of the furnace and contacting the outside of the steel blocks was used to regulate temperature with a PID temperature controller (Digi-sense® TC9500). Gas flow rates were controlled using mass flow controllers (Brooks® SLA5850S1BAB1B2A1) and liquid was pumped using a Teledyne® ISCO syringe pump (Model 500D). Liquid was fed into the top of the reactor through a 1/16" OD 316 stainless steel tube which extended to the start of the heating zone. Gas was fed into the top of the reactor via 1/4" 316 stainless steel tubing and flowed co-currently with liquid in the down-flow direction through the packed catalyst bed. Liquid samples were collected at room temperature in a gas/liquid separator (Jerguson Gage & Valve Co.®). Gas flowed out of the top of the gas/liquid separator and through a diaphragm back-pressure regulator (Equilibar® H3P1SNN8-NSBP1500T100G20KK), which maintained the overall system pressure. A nitrogen back-fill line enabled system pressure maintenance during sampling through a needle valve (Swagelok®).

[0035] Reactor packing procedure. A quartz wool (Technical Glass Products Inc.®) plug was placed in the bottom of the reactor tube, followed by 9.75" of quartz chips (fused silicon dioxide (granular), Sigma-Aldrich®), filling from the bottom of the reactor to the center of the heating zone of the furnace. A quartz wool plug, followed by the catalyst bed, followed by another quartz wool plug were then loaded. For neat lignin oil experiments, the bed comprised pure catalyst only. For 2 wt% lignin oil in toluene experiments, the catalyst was diluted to 1 g using 120 grit silicon carbide powder ($\geq 98.0\%$, Alfa Aesar®). Finally, quartz chips were added up to 1" below the level of the drip tube at the top of the reactor.

[0036] Feed preparation. Neat lignin oil was used directly after the procedure outlined above for generating RCF oil, combining the oil generated from 5-10 batch reactions to generate 45-90 g of feed oil. Recycled lignin oil was prepared by combining the samples from a previous experiment(s) after removing enough sample for analysis. The water fraction phase-separated from the partially deoxygenated lignin oil and was removed with a pipette. Diluted 2 wt% lignin oil in toluene was prepared by adding 2 wt% lignin oil, 0.2 wt% decane ($\geq 99.0\%$, Sigma- Aldrich®), and 97.8 wt% toluene (≥ 99.8 , VWR Chemicals® BDH) to a large glass container. It was then shaken vigorously, sonicated for 20 minutes, and left overnight to equilibrate. To remove the suspended undissolved lignin oil and prevent clogging, the cloudy lignin oil in toluene was centrifuged at 8,000 rpm for 5 minutes. The resulting liquid was decanted and used for reaction.

[0037] Running a reaction. After catalyst synthesis, the reactor was cooled to room temperature at atmospheric pressure under flowing hydrogen at 55 mL/min. The steel heat transfer blocks were placed in the furnace and the reactor was slowly pressurized by nitrogen back-fill to the reaction pressure of 900 psi. The hydrogen flowrate was set to 30 mL/min for reagents dissolved in toluene or 90 mL/min for neat lignin oil. The reactor was leak checked and heated. For reagents dissolved in toluene, the feed was flowed at 2 mL/min during heating to pre- wet the catalyst bed, and the flowrate was reduced to the reaction flowrate once the furnace reached temperature. The liquid collector was drained when the furnace reached 200°C, and samples were taken when the furnace reached 250°C and 300°C. Samples were taken every 40 min for the duration of the experiment. For neat lignin oil experiments, the reactor was heated to reaction temperature while flowing pure toluene at 1 mL/min. Once the reactor reached temperature, the liquid feed was switched to neat lignin oil flowing at 0.1 or 0.05 mL/min. Samples were taken every 30 or 60 min.

[0038] Sample work-up and analysis. Each sample was collected into a pre-weighed vial, allowing for sample mass measurement post-experiment. To prepare neat lignin oil samples for gas chromatography with flame ionization detection (GC-FID) analysis, 30 μ L of oil was dissolved in 2 mL of acetone containing 2 mg/mL of 1,3,5-tri-tert-butylbenzene ($\geq 98.0\%$, TCI®), measuring the weight of oil and acetone solution to improve accuracy. Samples from experiments with reagent dissolved in toluene were weighed and injected on GC-FID with no additional work-up procedure, using the contained decane internal standard. To prepare samples for NMR analysis, 100 mg of oil was dissolved in 500 μ L acetone-d₆ (≥ 99 atom% D, Acros Organics®).

[0039] Quantification of monomers with GC-FID. An Agilent Technologies® 7693 autosampler injected a 1 µL volume of each prepared sample into an Agilent® 7890A GC system. The GC method utilized a split ratio of 10:1, an inlet temperature of 280°C and a ramp rate of 10°C/min from 50°C to 280°C followed by a 10-minute hold at 280°C for a total run time of 29 min. The GC was outfitted with a 30 m x 250 µm x 0.25 µm Agilent Technologies® HP-5MS column and a flame ionization detector (FID) was used to quantify the products.

[0040] The GC-FID was calibrated with methylcyclohexane (≥99.0%, TCI)®, toluene (≥99.8%, VWR Chemicals® BDH), propylcyclohexane (≥98.0%, TCI), propylbenzene (≥99.0%, Sigma-Aldrich®), 4-propyltoluene (≥99.0%, TCI®), p- propylanisole (≥99.0%, Sigma-Aldrich®), 4-propylphenol (≥99.0%, Sigma-Aldrich®), 2-methoxy-4-propylphenol (propylguaiacol) (≥99.0%, Sigma-Aldrich®), isoeugenol (≥98.0%, Sigma-Aldrich®), 4-allyl-2, 6-dimethoxyphenol (≥95.0%, Sigma-Aldrich®) and dihydroconiferyl alcohol (synthesized in-house). Relative response factors (RFs) were generated for each of these compounds relative to decane (for experiments performed in toluene with decane as an internal standard) and 1,3,5-tri-tert-butylbenzene (for neat lignin oil experiments). Additionally, decane was calibrated with a relative response factor to 1,3,5-tri-tert-butylbenzene to enable accurate quantification of decane in the lignin oil in toluene feeds. RFs were calculated by fitting the line of relative mass fraction vs area ratio of the compound of interest to the standard. Adjustment factors were used to generate approximate RFs for products that were not available commercially. For each sample, the peak areas corresponding to known products were integrated. The ratio of compound peak area and standard peak area was calculated and multiplied by the RF and mass fraction of standard to obtain the mass fraction of compound. The mass fractions were then used for subsequent calculations of mole balance, conversion, yield, etc.

[0041] Gas chromatography and mass spectrometry (GC-MS). Analysis was performed using an Agilent Technologies® 7820A GC System outfitted with an HP-5MS Ultra Inert 30 m x 250 µm x 0.25 µm column and an Agilent® 5977B single quadrupole MS detector. Monomeric compounds in the feed and product were identified by injecting identical samples on a GC-FID and a GC-MS using the same column and method. The products were identified using the fragmentation patterns in GC-MS and matched with the same retention time observed in GC-FID.

[0042] Dimers were analyzed using derivatization followed by GC- MS, similar to our previously published method. Solvent-free lignin oil samples were dissolved in tetrahydrofuran (HPLC

Grade, VWR Chemicals® BDH) (THF) at a concentration of 10 mg/mL. The derivatization reaction was performed by combining 600 μ L of 10 mg/mL lignin oil solution, 50 μ L of pyridine and 100 μ L of silylating agent [N,O- Bis(trimethylsilyl)-trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMS) (Sigma-Aldrich®)], then heating for 20 min at 50°C. BSTFA reacts readily with water, so it was ordered in 1 mL ampules and used immediately after opening.

[0043] For analysis, 1 μ L samples were manually injected into the GC- MS. The method utilized a split ratio of 10:1, a split flow of 12 mL/min, and an inlet temperature of 280°C. The oven was programmed to ramp from 150°C to 300°C at a rate of 5°C/min and held at 300°C for 18 min for a total run time of 49 min. GC- MS spectra were analyzed by comparing with published dimer structures and by predicting structures that may be present and comparing them with unknown MS spectra.

[0044] Gel permeation chromatography (GPC). Gel permeation chromatography was performed following a procedure similar to our previously published methods. Solvent-free oil samples were prepared for gel permeation chromatography by dissolution in THF at a concentration of 2 mg/mL (HPLC Grade, VWR Chemicals® BDH) and filtration using a 0.2 μ m PTFE syringe filter. 20 μ L of each sample was injected using a Hewlett Packard 1100 series autosampler. THF was used as the carrier solvent at a flowrate of 0.3 mL/min. Three 5 μ m PLgel Agilent GPC columns (10⁴ Å, 10³ Å, and 50 Å) were arranged in series in order of decreasing pore size. The columns were maintained at a constant temperature of 26°C, and the system ran at a pressure of approximately 30 bar (a function of the flowrate, column choice, and temperature). A UV diode array detector at a wavelength of 280 nm with a reference wavelength of 360 nm and a 4 nm slit was used to analyze eluents.

[0045] NMR spectroscopy. NMR spectra were acquired on a Bruker® Advance Neo 400 MHz equipped with a 5 mm broad band observe (BBFO) SmartProbe, and spectral processing used Bruker's TopSpin® 4.0.8 (Windows) software. The central solvent peaks (acetone-*d*6) were used as the internal references (δ C/ δ H: 29.84/2.05 ppm). Standard Bruker® implementations of the traditional suite of 1D and 2D [gradient-selected and ¹H- detected; for example, ¹H–¹³C HSQC] NMR experiments were used for structural elucidation and assignment authentication for monomers and oligomers. Processing used typical matched Gaussian apodization in F2 (LB = –0.1; GB = 0.001) and squared cosine-bell apodization in F1.

[0046] Quantitative GCxGC TOF-FID Analysis. Detailed characterization of deoxygenated hydrocarbon products was conducted by comprehensive two-dimensional gas chromatography with simultaneous time-of-flight mass spectrometry and flame ionization detection (GCxGC TOF-FID). Samples were prepared for analysis by dilution (1:10 gravimetrically in acetone). Analysis was conducted using a LECO Pegasus® 4D system (LECO Corp®) equipped with a liquid nitrogen cooled thermal modulator and post column flow splitter. The primary column was a Rtx-17sil, 20 m x 180 µm x 0.18 µm and the secondary column was a ZB-5HT, 1.0 m x 180 µm x 0.18 µm. The method utilized a 1.0 µL injection, split ratio 100:1, and injector temperature of 300°C. The primary oven held at 35°C for 5 minutes prior to 3°C/min ramp to 125°C, 10°C/min ramp to 350°C, and hold for 1 min. The secondary oven was 40°C offset from primary and the modulator was 15°C offset from secondary. The modulator period was set to 8 seconds, with 1 s hot pulse and 3 s cold pulse from the start of run to 800 s, followed by 2 s hot pulse and 2 s cold pulse to end of the run. The transfer line to the mass spectrometer and FID were held at 350°C. The TOF mass range was m/z 29-600, with an acquisition rate of 200 spectra/s, and solvent delay of 70s. The FID flows were set at 40 mL/min H₂, Air flow of 300 mL/min and N₂ flow of 25 mL/min. Compounds were identified using library matching and utilization of retention time regions in 2D chromatograms using LECO ChromaTof® Software. The FID signal was calibrated using a series of representative compounds to establish linearity and accuracy. All linear calibrations resulted in $R^2 \geq 0.995$. Compounds were quantified from their theoretical response factors calculated via effective carbon numbers.

[0047] Qualitative GCxGC FID/MS analysis. Qualitative characterization of deoxygenated products was done using two- dimensional gas chromatography with coupled flame ionization detection and mass spectrometry (GCxGC FID/MS). This analysis was conducted using an Agilent® 7890A GC with an Agilent 5975C Inert XL MSD. The system was equipped with a chiller-cooled (PolyScience® P10N4A101B) thermal modulator (Zoex ZX10711). Samples were injected neat post- reaction. Data analysis was completed using the software package Canvas™ v4.

[0048] The primary column used was a Rxi-5HT, 30 m x 0.25 mm x 0.25 µm while the secondary column used was a BPX50, 2 m x 0.15 mm x 0.25 µm. The method utilized a split ratio of 50:1, a 5 µL injection, and an injector temperature of 350°C. The primary oven was held at 45°C for 1

minute followed by a ramp to 300°C at 3°C/min. This temperature was then held for 5 minutes. The secondary column was offset from the primary by 25°C while the thermal modulator thermal modulator was offset from the secondary by 5°C. The modulator used a 16 second period with a 375 ms hot jet duration. The transfer line to the MS was held at 250°C. The mass range was set to 40-550 m/z, with an acquisition rate of 50 spectra/s and no solvent delay. The FID detector was held at 300°C with an H₂ flow of 30 mL/min, an air flow of 400 mL/min.

[0049] Total carbon, hydrogen, and oxygen (CHO) analysis method. Total carbon and hydrogen were determined by combustion using a LECO® Series CHN628 elemental analyzer (LECO® Corp). Oxygen content was calculated by difference.

[0050] Simulated distillation. Due to limited sample volume, distillation temperatures were determined by simulated distillation rather than physical distillation (i.e., ASTM D86). Boiling range distributions of deoxygenated oils were measured by simulated distillation following ASTM method D2887-19. An Agilent® 7890A GC equipped with cool-on- column inlet and FID was used. Method settings were used as found in ASTM D2887 Table 1 for an open tubular column (option 7). The column used was an MXT-1HT, 10 m x 530 µm x 2.65 µm (Restek Corp®). Samples were diluted 1:10 by volume in carbon disulfide for analysis. An injection volume of 0.1 µL was injected onto the analytical column. Boiling point calibrations were made using prepared standards purchased from Sigma-Aldrich® (Part # 500658) and accuracy was verified with standard reference gasoil as described in D2887. Data analysis was conducted using Separation Systems SimDis Expert® 9.

[0051] Mass balance on neat lignin HDO experiment. To calculate a mass balance, a single-pass neat lignin oil experiment was performed in which a steady-state sample was accumulated for 3 hours. The ~18 mL sample was collected into a pre-weighed flask. The total sample was weighed, then a pipette was used to remove the aqueous phase. The remaining organic phase was weighed and characterized. The mass flowrate of the lignin oil feed was measured in triplicate by weighing the oil collected for 4 minutes at the experimental flowrate directly at the outlet of the ISCO pump. The mass flowrate was multiplied by the steady-state collection time to obtain the feed mass. The feed mass and steady-state oil mass were multiplied by the carbon mass percent of each sample to obtain the carbon mass recovery.

[0052] Solids compositional analysis procedure. Compositional analysis of the poplar samples was performed based on NREL's published guidelines. The poplar used was a reference material from Idaho National Laboratory, (Source: Morrow County, Oregon, Harvested: 2013, Hybrid Clone: *Populus deltoides* x *Populus nigra*, clone OP-367). Samples were first extracted with a high pressure and temperature flow through aqueous rinse followed by an ethanol rinse. The biomass was then treated with 72 wt% sulfuric acid for 1 h at 30°C with mixing. The slurry was then diluted with water to 4 wt% sulfuric acid and heated in an autoclave for 1 h at 121°C. Klason lignin content was determined gravimetrically by filtering the acid insoluble residue out of the acidified aqueous slurry. The Klason lignin was combusted to determine the ash content in the biomass. The acid soluble lignin was quantified by UV/Vis spectroscopy (Thermo Scientific Nanodrop® 8000 spectrophotometer). Lignin absorbance measurements were performed at 240 nm and quantified with an extinction coefficient of 2.5. The sugar content was determined by high performance liquid chromatography (HPLC, Agilent® 1100 HPLC) using a refractive index detector (RI) kept at 55°C. A Shodex® Sugar SP0810 column equipped with a guard column was used for analysis at 85°C with a flow rate of 0.6 mL/min of HPLC grade water as the mobile phase.

[0053] Catalyst characterization with powder X-ray diffraction. Powder X-ray diffraction (PXRD) was performed on a Bruker® D8 diffractometer using Cu K α radiation, a step size of 0.02°, and a step time of 0.2 s.

[0054] The terms and expressions which have been employed herein are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments, exemplary embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims. The specific embodiments provided herein are examples of useful embodiments of the present invention and it will be apparent to one skilled in the art that the present invention may be carried out using a large number of variations of the devices, device components, methods steps set forth in the present description. As will be obvious to one of skill

in the art, methods and devices useful for the present methods can include a large number of optional composition and processing elements and steps.

[0055] As used herein and in the appended claims, the singular forms "a", "an", and "the" include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to "a cell" includes a plurality of such cells and equivalents thereof known to those skilled in the art. As well, the terms "a" (or "an"), "one or more" and "at least one" can be used interchangeably herein. It is also to be noted that the terms "comprising", "including", and "having" can be used interchangeably. The expression "of any of claims XX-YY" (wherein XX and YY refer to claim numbers) is intended to provide a multiple dependent claim in the alternative form, and in some embodiments is interchangeable with the expression "as in any one of claims XX-YY."

[0056] When a group of substituents is disclosed herein, it is understood that all individual members of that group and all subgroups, are disclosed separately. When a Markush group or other grouping is used herein, all individual members of the group and all combinations and subcombinations possible of the group are intended to be individually included in the disclosure. For example, when a device is set forth disclosing a range of materials, device components, and/or device configurations, the description is intended to include specific reference of each combination and/or variation corresponding to the disclosed range.

[0057] Every formulation or combination of components described or exemplified herein can be used to practice the invention, unless otherwise stated.

[0058] Whenever a range is given in the specification, for example, a density range, a number range, a temperature range, a time range, or a composition or concentration range, all intermediate ranges and subranges, as well as all individual values included in the ranges given are intended to be included in the disclosure. It will be understood that any subranges or individual values in a range or subrange that are included in the description herein can be excluded from the claims herein.

[0059] All patents and publications mentioned in the specification are indicative of the levels of skill of those skilled in the art to which the invention pertains. References cited herein are incorporated by reference herein in their entirety to indicate the state of the art as of their publication or filing date and it is intended that this information can be employed herein, if needed,

to exclude specific embodiments that are in the prior art. For example, when composition of matter is claimed, it should be understood that compounds known and available in the art prior to Applicant's invention, including compounds for which an enabling disclosure is provided in the references cited herein, are not intended to be included in the composition of matter claims herein.

[0060] As used herein, "comprising" is synonymous with "including," "containing," or "characterized by," and is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. As used herein, "consisting of" excludes any element, step, or ingredient not specified in the claim element. As used herein, "consisting essentially of" does not exclude materials or steps that do not materially affect the basic and novel characteristics of the claim. In each instance herein any of the terms "comprising", "consisting essentially of" and "consisting of" may be replaced with either of the other two terms. The invention illustratively described herein suitably may be practiced in the absence of any element or elements, limitation or limitations which is not specifically disclosed herein.

[0061] All art-known functional equivalents, of any such materials and methods are intended to be included in this invention. The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

CLAIMS

What is claimed is:

1. A method comprising:

providing a reactant comprising lignin and hydrogen;

partially deoxygenating the reactant in the presence of a first catalyst at a first temperature, thereby generating an intermediate;

deoxygenating the intermediate in the presence of a second catalyst at a second temperature, thereby generating a product comprising aromatic hydrocarbons.
2. The method of claim 1, wherein the second temperature is greater than the first temperature.
3. The method of claim 1 or 2, wherein the reactant comprises greater than 50% lignin oil.
4. The method of any of claims 1-3, wherein the reactant comprises greater than 99% lignin oil.
5. The method of any of claims 1-4, wherein the reactant *does not* comprise a solvent.
6. The method of any of claims 1-5, wherein the first temperature is selected from the range of 250 °C to 450 °C.
7. The method of any of claims 1-6, wherein the second temperature is selected from the range of 275 °C to 475 °C.
8. The method of any of claims 1-7, wherein the first catalyst, the second catalyst or both comprise Mo₂C.
9. The method of any of claims 1-8, wherein the first catalyst and the second catalyst are the same.
10. The method of any claims 1-9, wherein the steps of partially deoxygenating and deoxygenating are each performed continuously.

11. The method of claims 1-10, wherein the steps of partially deoxygenating and deoxygenating are part of a continuous process.
12. The method of any of claims 1-11, wherein the product is sustainable aviation or marine fuel.
13. The method of any of claims 1-12, wherein the product comprises an oxygen mole fraction less than or equal to 5%.
14. A reactor comprising:
a first reaction zone comprising a first catalyst at a first temperature;
a second reaction zone comprising a second catalyst at a second temperature;
wherein the reactor is capable of performing hydrodeoxygenation of lignin to generate aromatic products.
15. The reactor of claim 14, wherein the second temperature is greater than the first temperature.
16. The reactor of claim 14 or 15, wherein the reactor is a trickle bed reactor.
17. The reactor of any of claims 14-16, wherein the first catalyst, the second catalyst or both comprise Mo_2C .
18. The reactor of any of claims 14-17, wherein the reactor is capable generating aromatic products with continuous flow.
19. A catalyst comprising Mo_2C , wherein the catalyst is capable of converting lignin to aromatic compounds at a yield greater than or equal to 80%.

ABSTRACT

Described herein are systems and methods for the catalytic deoxygenation of lignin to generate low-oxygen aromatics that may be useful as a sustainable aviation or marine fuel. The provided systems and methods may be performed continuously without the need for a solvent, increasing both efficiency and cost effectiveness.

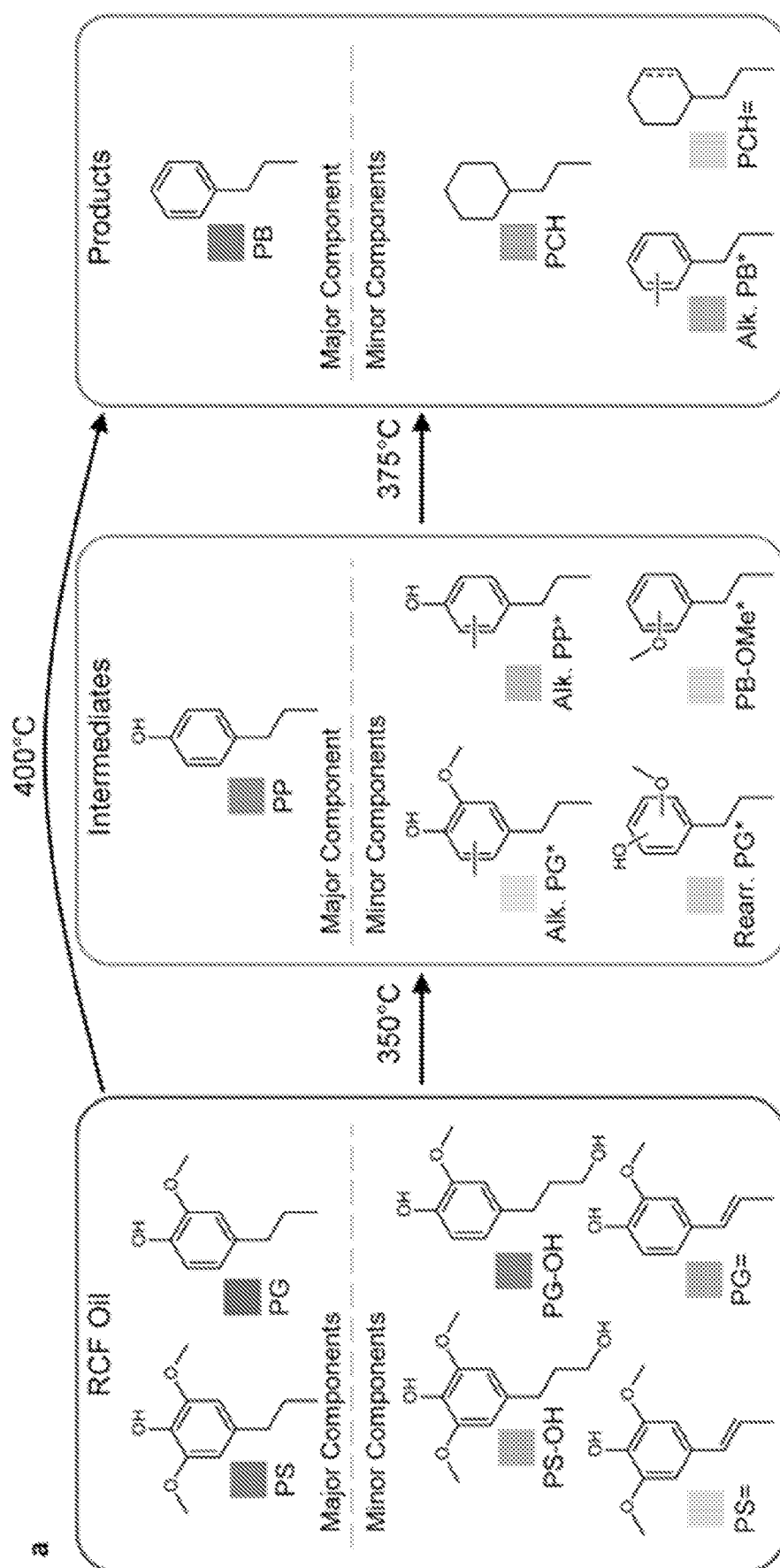


Fig. 1A

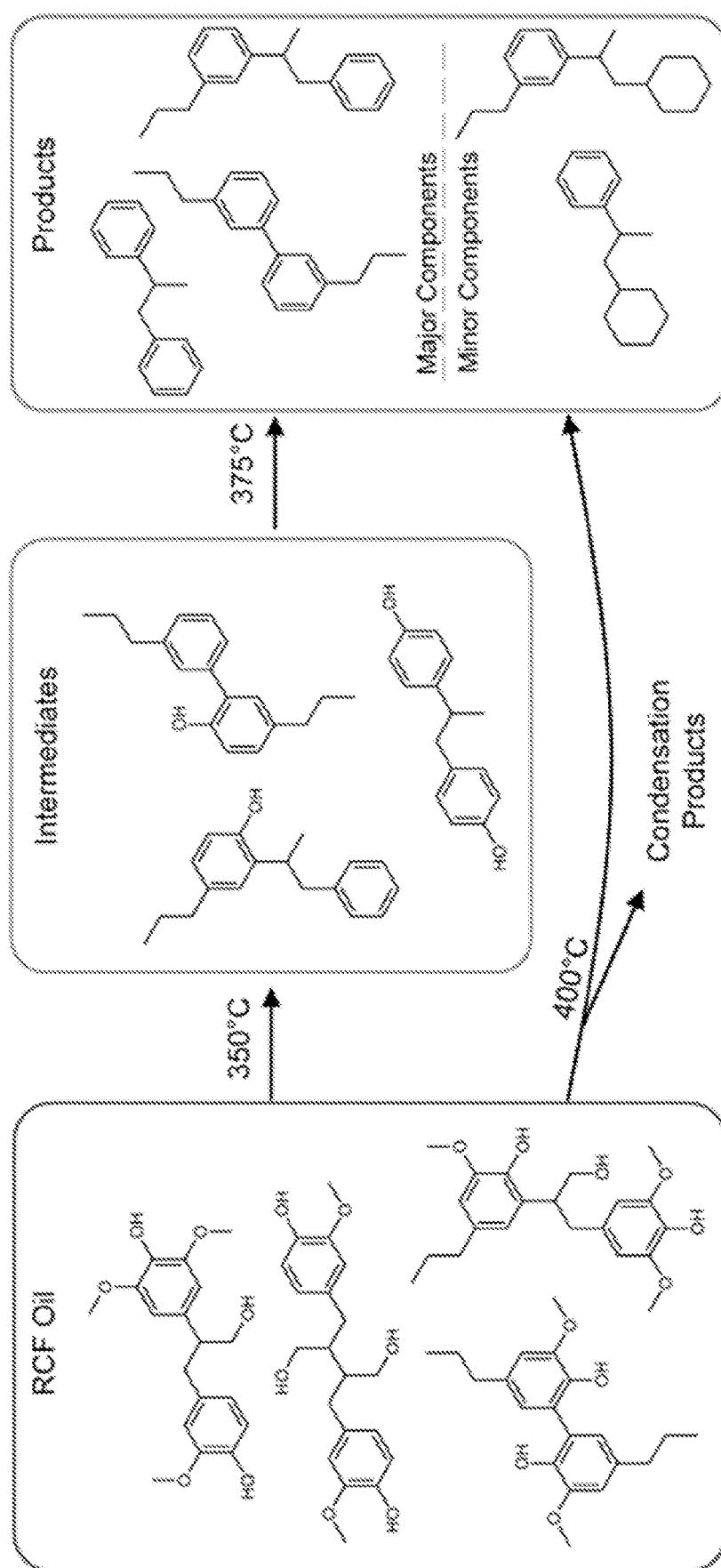


Fig. 1B

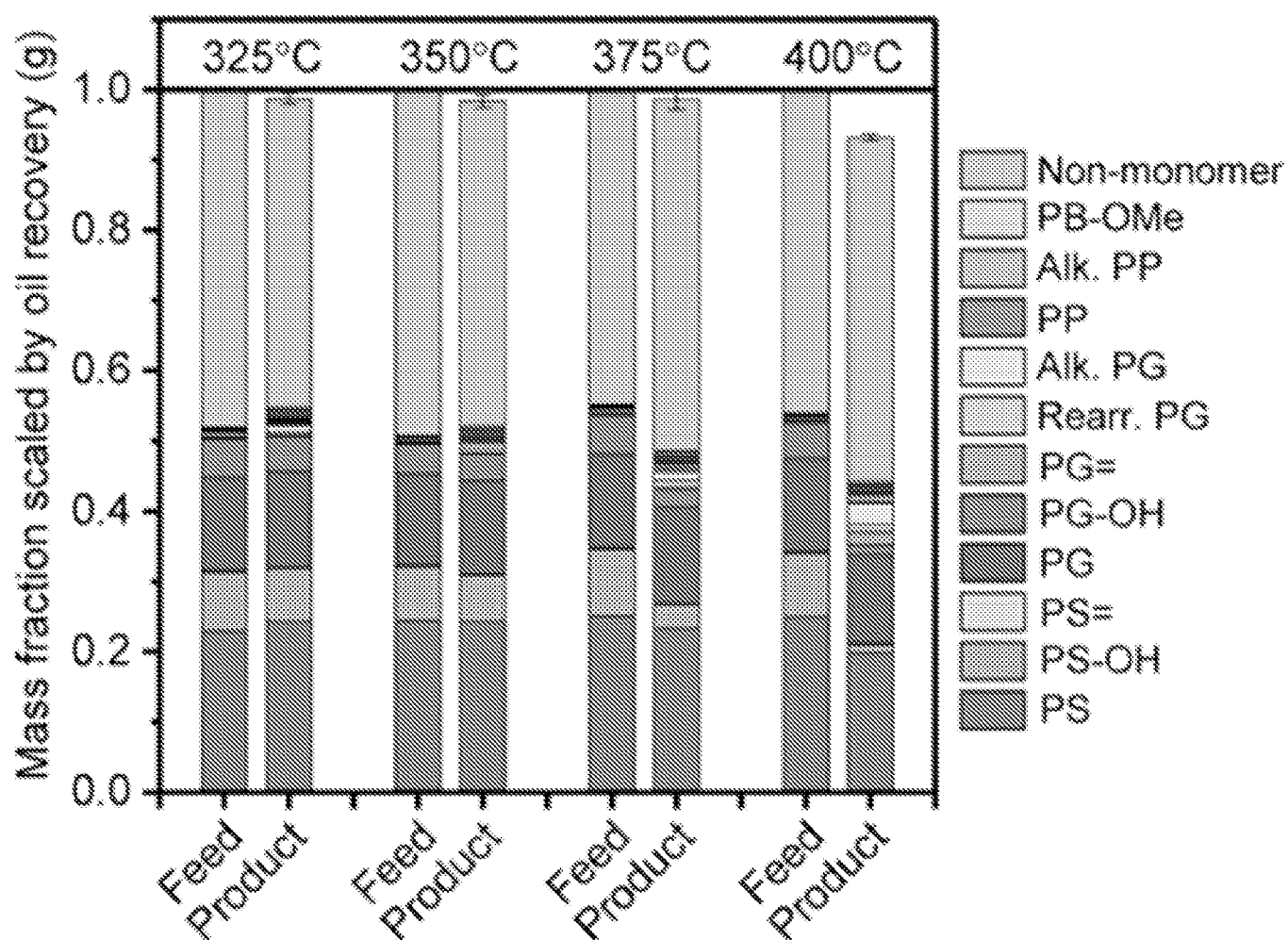


Fig. 2A

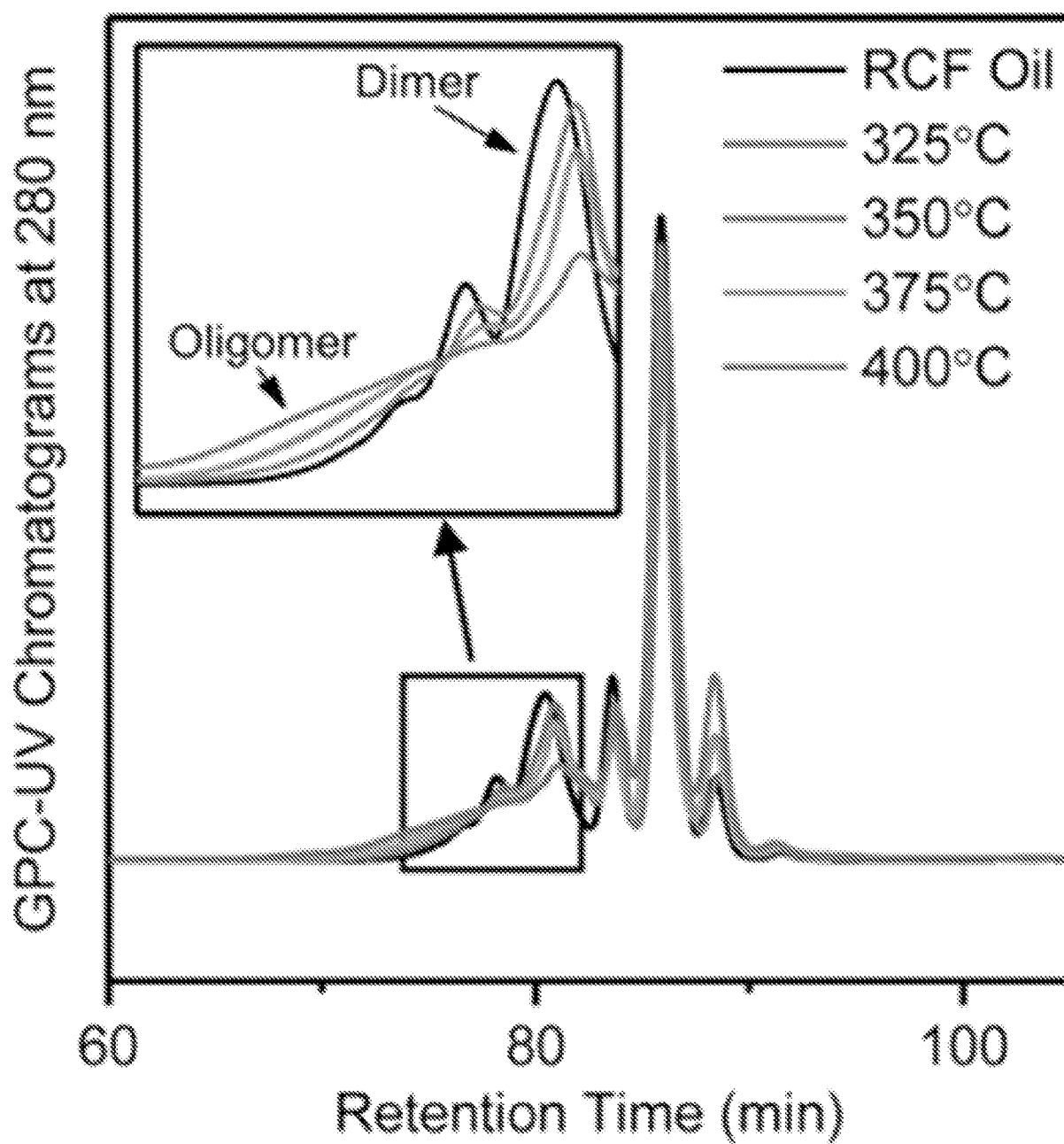


Fig. 2B

Fig. 3A

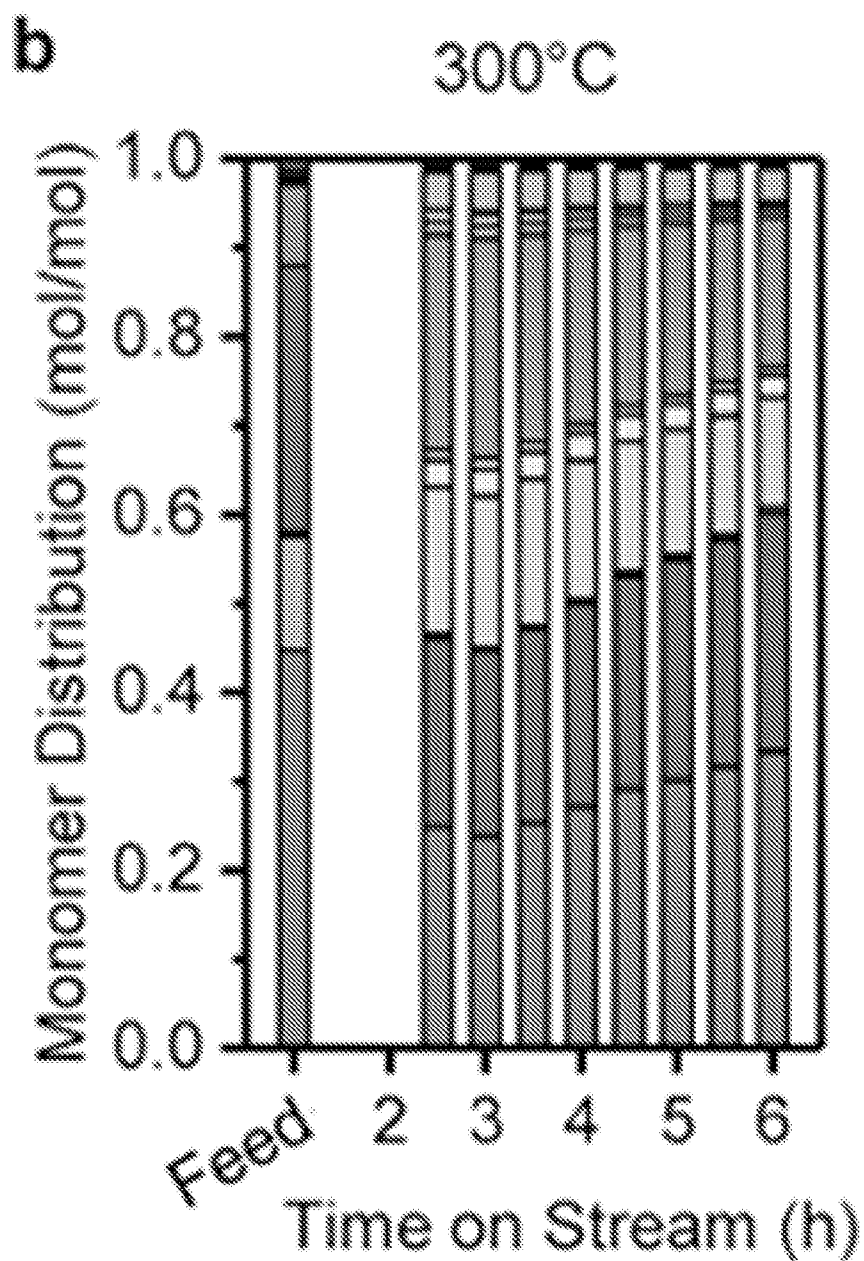


Fig. 3B

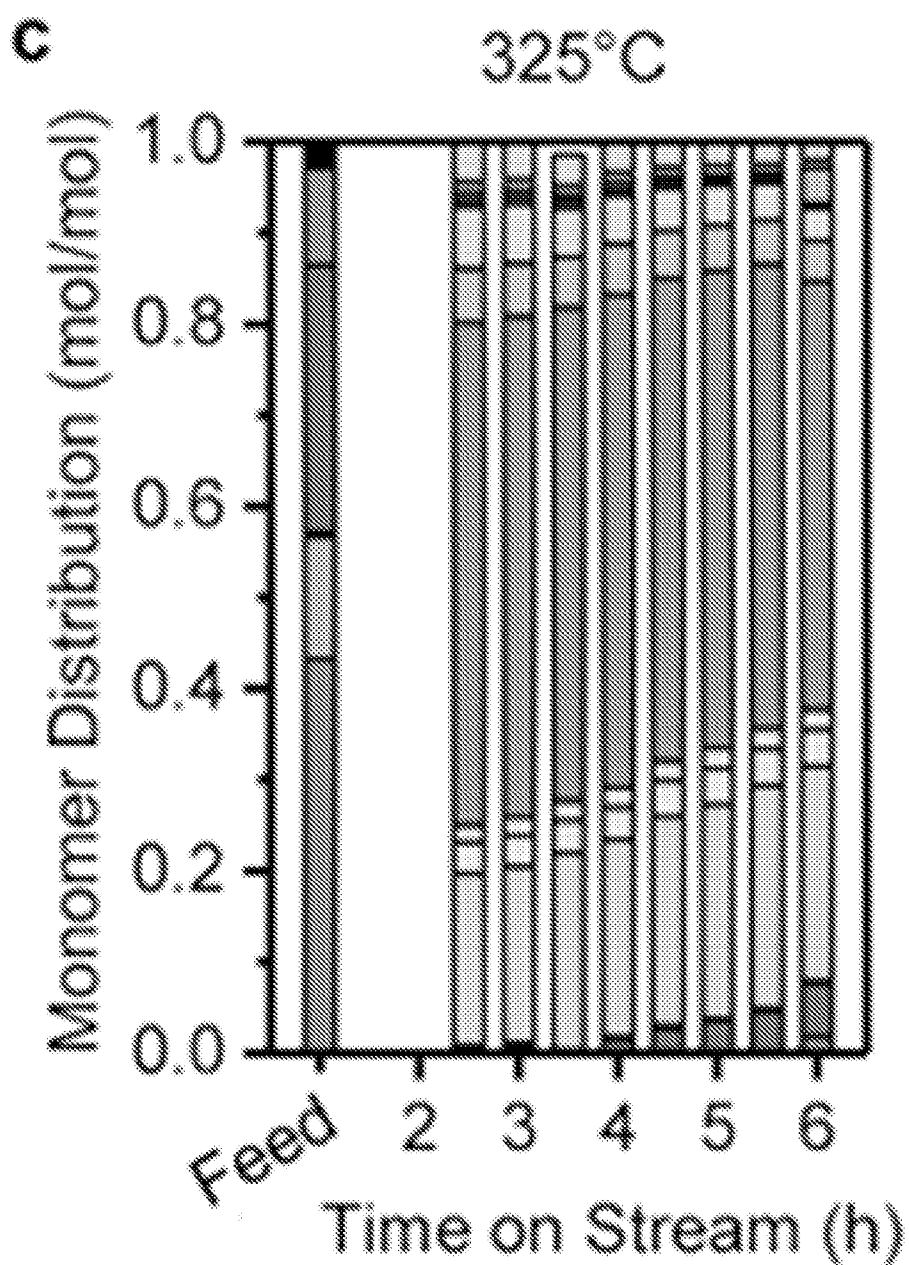


Fig. 3C

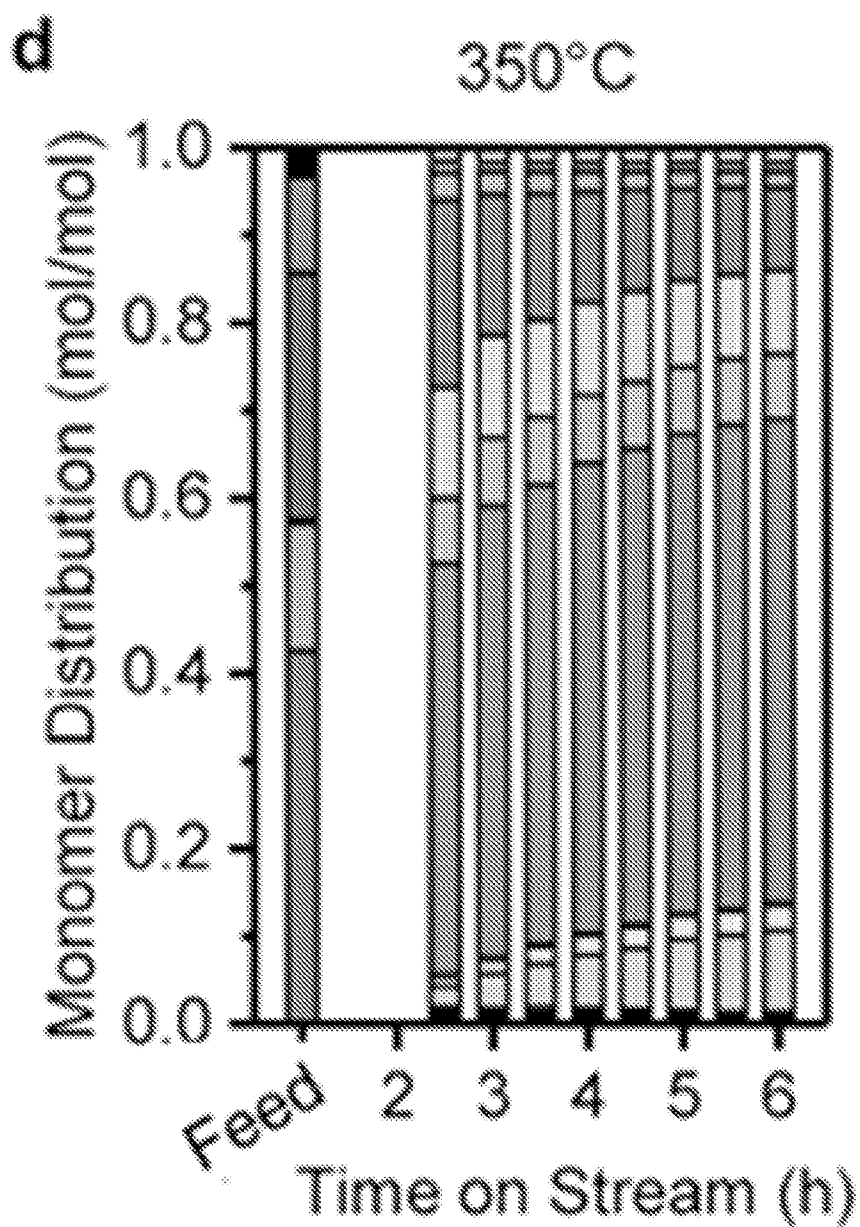


Fig. 3D

e

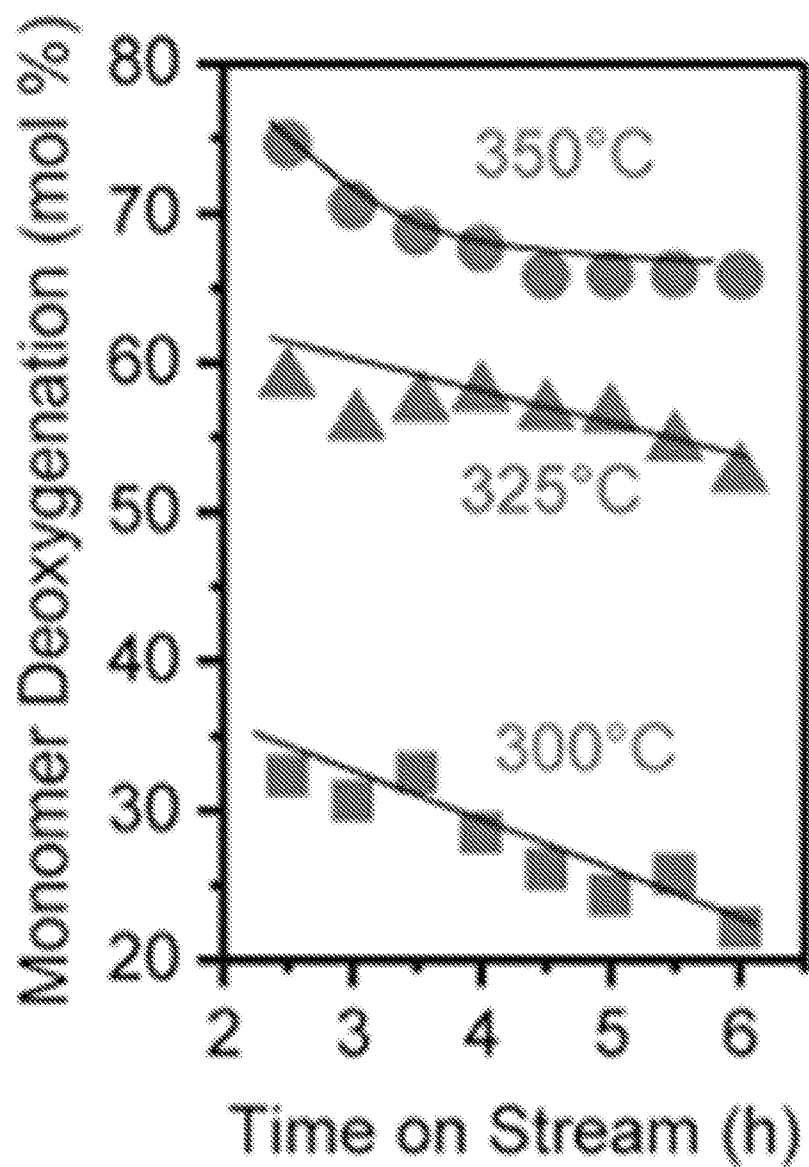


Fig. 3E

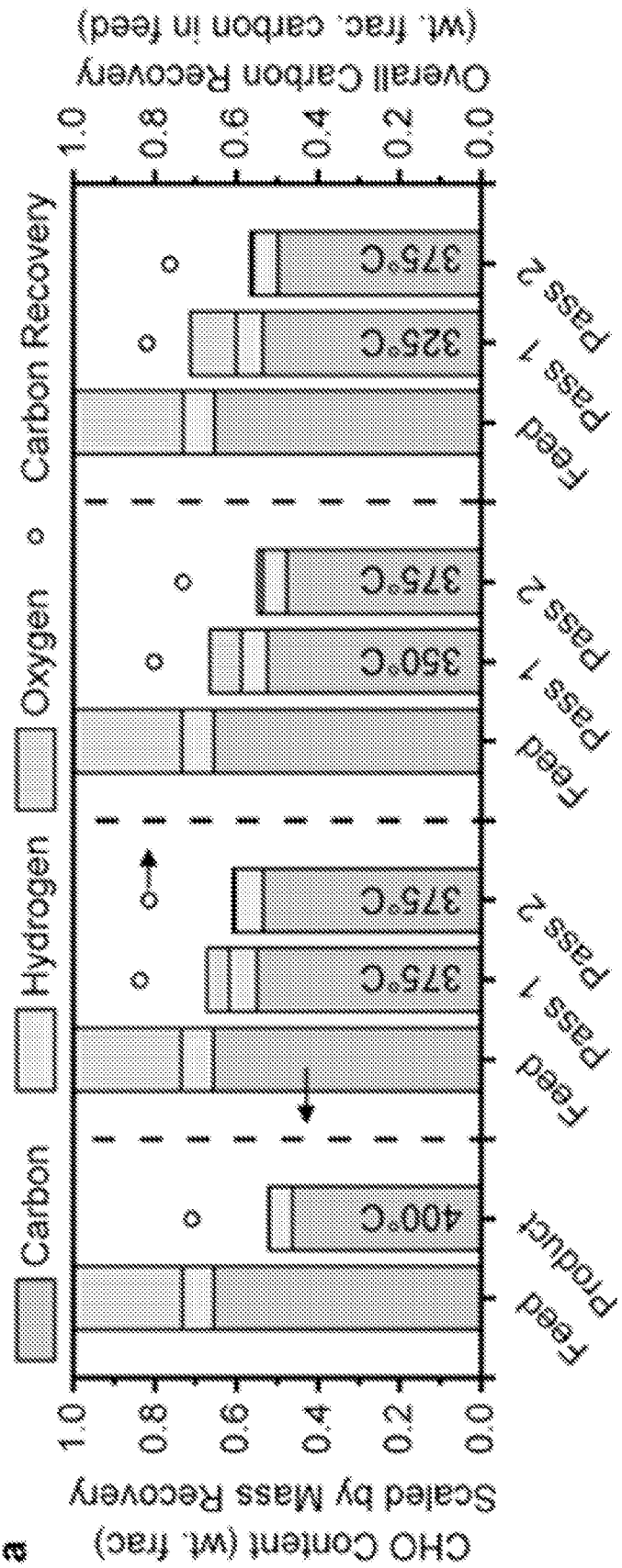


Fig. 4A

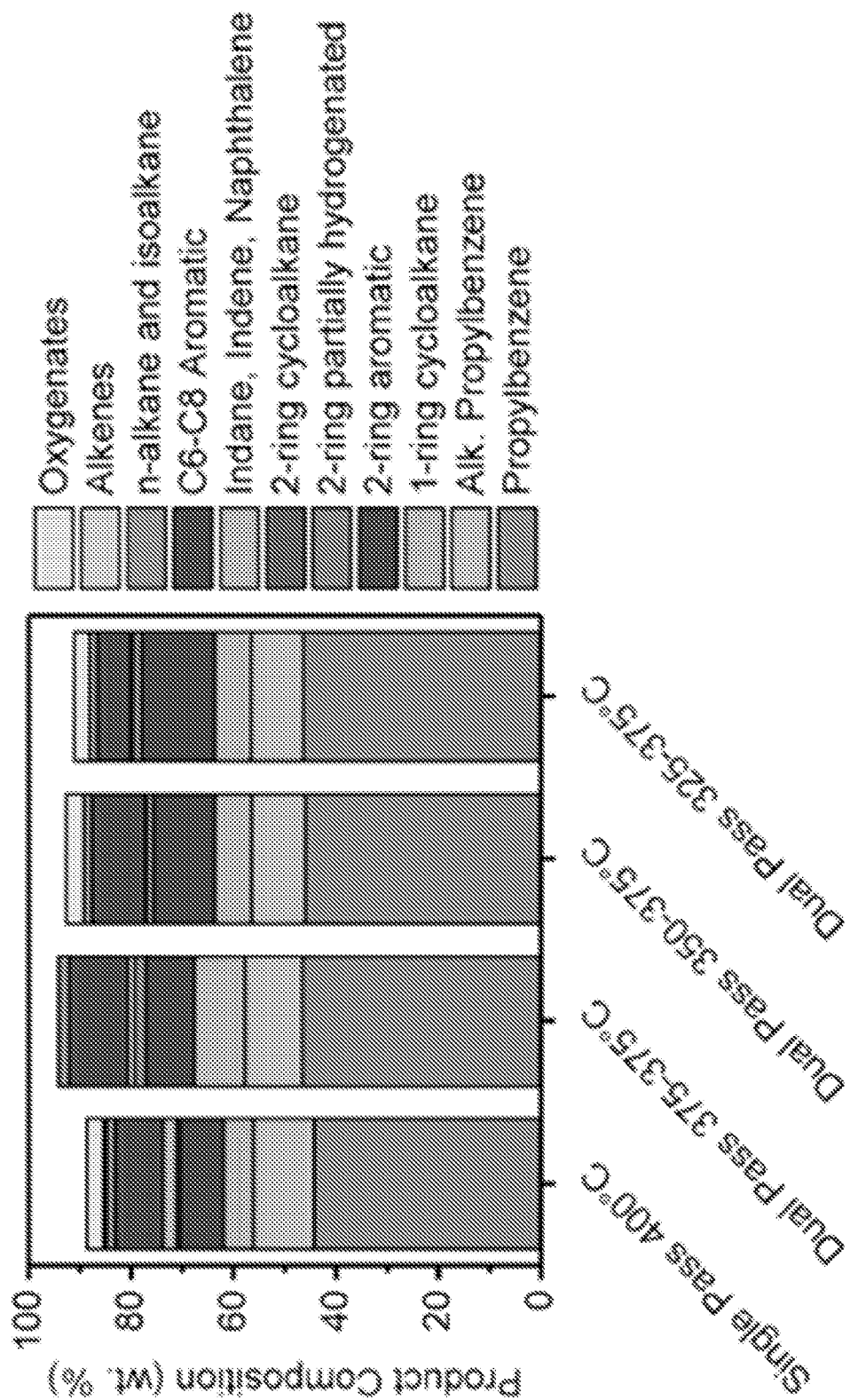


Fig. 4B

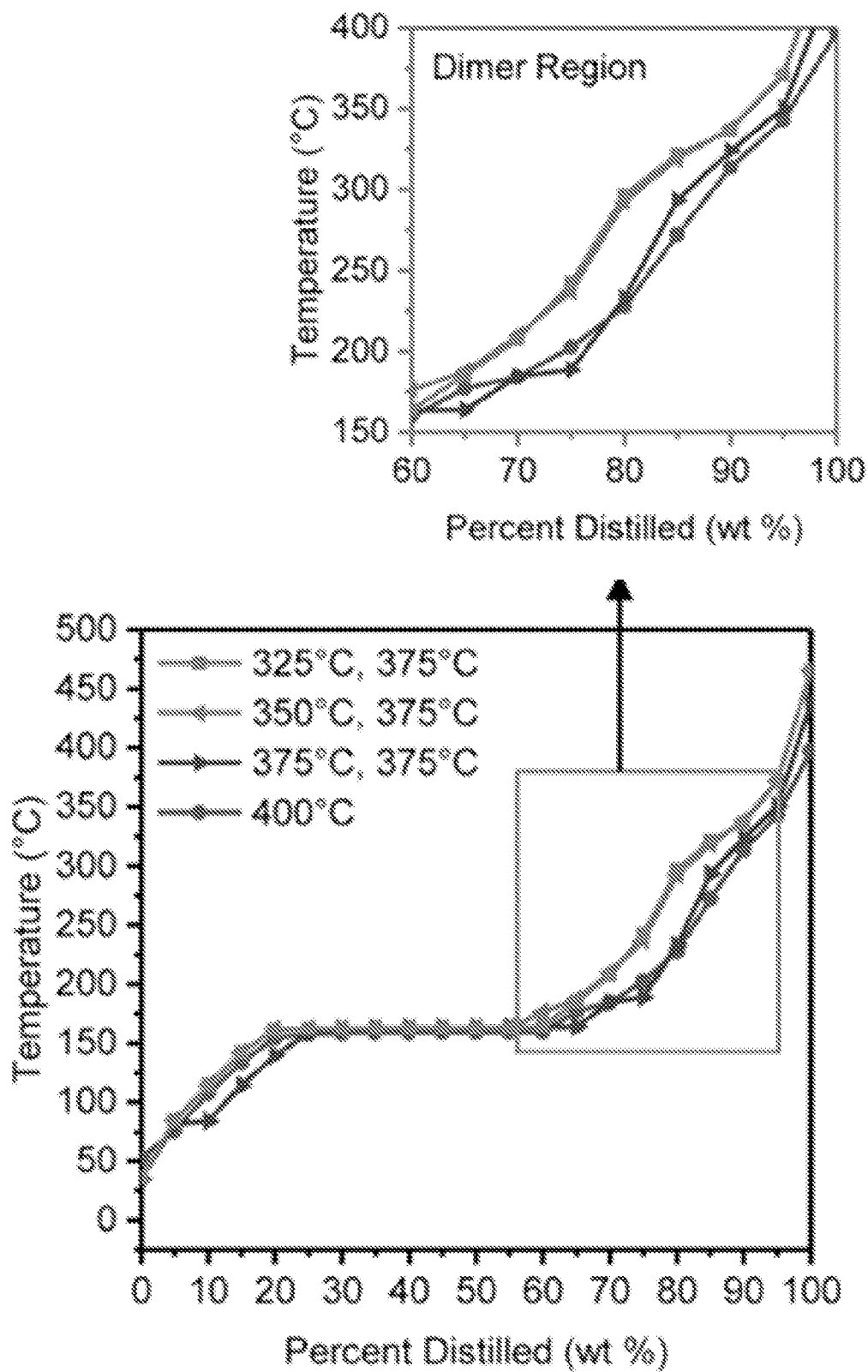


Fig. 4C

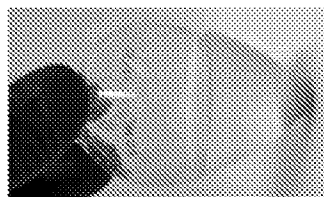


Fig. 4D

Electronic Acknowledgement Receipt

EFS ID:	46342283
Application Number:	63395067
International Application Number:	
Confirmation Number:	5743
Title of Invention:	CONTINUOUS HYDRODEOXYGENATION OF LIGNIN TO JET-RANGE AROMATIC HYDROCARBONS
First Named Inventor/Applicant Name:	Gregg Tyler BECKHAM
Customer Number:	23712
Filer:	Neal Stuart Vickery/Nancy Ronzone
Filer Authorized By:	Neal Stuart Vickery
Attorney Docket Number:	NREL PROV/22-94
Receipt Date:	04-AUG-2022
Filing Date:	
Time Stamp:	13:38:13
Application Type:	Provisional

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	\$ 150
RAM confirmation Number	E202284D38381345
Deposit Account	
Authorized User	

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

File Listing:					
Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Application Data Sheet	PROV22-94_ADS_Signed_4Aug2022.pdf	1256551	no	9
			5333e8b9d32d65d116bf4f64b009e25c9f479a78		
Warnings:					
Information:					
2		PROV22-94_Specification_FINAL_4Aug2022.pdf	227685	yes	24
			fbe90e57a38e47bbd87f57d8b2f191366aec655		
	Multipart Description/PDF files in .zip description				
	Document Description		Start	End	
	Specification		1	21	
	Claims		22	23	
	Abstract		24	24	
Warnings:					
Information:					
3	Drawings-other than black and white line drawings	PROV22-94_Figures_FINAL_4Aug2022.pdf	2301036	no	13
			0cc3d7605f30f1ddd7cad325bd42dc7f29a01521		
Warnings:					
Information:					
4	Fee Worksheet (SB06)	fee-info.pdf	37681	no	2
			a7eb16126f66cee4839cf91d4f9daf5b910b0068		
Warnings:					
Information:					
Total Files Size (in bytes):			3822953		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference NREL PCT22-94		FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, item 5 below.	
International application No. PCT/US 23/29488	International filing date (day/month/year) 04 August 2023 (04.08.2023)	(Earliest) Priority Date (day/month/year) 04 August 2022 (04.08.2022)	
Applicant ALLIANCE FOR SUSTAINABLE ENERGY, LLC			

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 4 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of:



the international application in the language in which it was filed.



a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6bis(a)).

c. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☐ **Certain claims were found unsearchable** (see Box No. II).

3. ☒ **Unity of invention is lacking** (see Box No. III).

4. With regard to the **title**,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the **drawings**,

a. the figure of the **drawings** to be published with the abstract is Figure No. 1B



as suggested by the applicant.



as selected by this Authority, because the applicant failed to suggest a figure.



as selected by this Authority, because this figure better characterizes the invention.

b. ☐ none of the figures is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 23/29488

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see extra sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-13

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 23/29488

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. B01J 23/28, B01J 27/22, B01J 23/16, B01J 23/24, C10G 3/00 (2023.01)
ADD. B01J 37/02 (2023.01)

CPC - INV. B01J 23/28, B01J 27/22, B01J 23/16, B01J 23/24, C10G 3/44

ADD. B01J 37/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010/0137663 A1 (CHEN ET AL.) 3 June 2010 (03.06.2010) - entire document especially para [0007], [0016], [0020], [0021] and abstract	1-7, 10-13
X	US 2018/0119022 A1 (ALLIANCE FOR SUSTAINABLE ENERGY, LLC) 3 May 2018 (03.05.2018) - entire document especially para [0064], [0079], [0007], [0017] and abstract	1, 8-9
A	WO 2022/027138 A1 (NULIFE GREENTECH INC.) 10 February 2022 (10.02.2022) - entire document	1-13
A	US 10,266,852 B2 (ALLIANCE FOR SUSTAINABLE ENERGY, LLC et al.) 23 April 2019 (23.04.2019) - entire document	1-13
A	US 9,085,505 B2 (DALIAN INSTITUTE OF CHEMICAL PHYSICS, CHINESE ACADEMY OF SCIENCES) 21 July 2015 (21.07.2015) - entire document	1-13

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

3 October 2023 (03.10.2023)

Date of mailing of the international search report

JAN 26 2024

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Kari Rodriguez

Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 23/29488

Box IV (Lack of unity of invention)

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: Claims 1-13 are directed towards a method comprising: providing a reactant comprising lignin and hydrogen; partially deoxygenating the reactant in the presence of a first catalyst at a first temperature, thereby generating an intermediate; deoxygenating the intermediate in the presence of a second catalyst at a second temperature, thereby generating a product comprising aromatic hydrocarbons.

Group II: Claims 14-19 directed towards a reactor comprising: a first reaction zone comprising a first catalyst at a first temperature; a second reaction zone comprising a second catalyst at a second temperature; where in the reactor is capable of performing hydrodeoxygenation of lignin to generate aromatic products.

The inventions listed as Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Group I requires a method comprising: providing a reactant comprising lignin and hydrogen; partially deoxygenating the reactant in the presence of a first catalyst at a first temperature, thereby generating an intermediate; deoxygenating the intermediate in the presence of a second catalyst at a second temperature, thereby generating a product comprising aromatic hydrocarbons, not required by Group II.

Group II requires a reactor comprising: a first reaction zone comprising; a second reaction zone; where in the reactor is capable of performing hydrodeoxygenation of lignin to generate aromatic products, not required by Group I.

Shared Technical Features:

Group I-II share the common technical features of a reactant comprising lignin, a first catalyst at a first temperature, a second catalyst at a second temperature, and deoxygenation of lignin to generate aromatic products. However, these shared technical features do not represent a contribution over prior art because the shared technical features are anticipated by US 2010/0137663 A1 to Chen et al. (hereinafter "Chen"). Chen teaches a reactant comprising lignin (Abstract, The process includes reacting lignin with a hydrogenation catalyst under a hydrogen atmosphere), a first catalyst at a first temperature (Abstract, The process includes reacting lignin with a hydrogenation catalyst under a hydrogen atmosphere to convert acidic oxygenate compounds; para [0007], The present invention for recovering chemicals from lignin includes a combining lignin with a hydrogenation catalyst to form a mixture under a hydrogen atmosphere. The mixture is reacted at hydrolysis process conditions to form an intermediate product stream having reduced oxygen content; para [0016], The hydrolysis reaction conditions include heating the reactor to a temperature between 100 degrees C and 450 degrees C); a second catalyst at a second temperature (Abstract, The process includes...The oxygenate compounds are reacted in a dehydrogenation and deoxygenation process to remove the oxygen and convert the cyclic hydrocarbons back to aromatic compounds; para [0007], The present invention for recovering chemicals from lignin includes...The intermediate product stream is contacted with a dehydrogenation and deoxygenation catalyst...generating a product stream comprising aromatic compounds; para [0020], The dehydrogenation and deoxygenation reactions remove the oxygen...The reaction conditions include...a temperature between 400 degrees C and 900 degrees C), and deoxygenation of lignin to generate aromatic products (Abstract, The process includes...The oxygenate compounds are reacted in a dehydrogenation and deoxygenation process to remove the oxygen and convert the cyclic hydrocarbons back to aromatic compounds; para [0007], The present invention for recovering chemicals from lignin includes...generating a product stream comprising aromatic compounds).

As the shared technical features were known in the art at the time of the invention, they cannot be considered special technical features that would otherwise unify the groups. Therefore, Groups I-II lack unity under PCT Rule 13.

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

PCT

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43bis.1)

To: NEAL VICKERY
C/O NATIONAL RENEWABLE ENERGY
LABORATORY
15013 DENVER WEST PARKWAY
GOLDEN, CO 80401

Date of mailing
(day/month/year)

JAN 26 2024

Applicant's or agent's file reference
NREL PCT22-94

FOR FURTHER ACTION

See paragraph 2 below

International application No.

PCT/US 23/29488

International filing date (day/month/year)

04 August 2023 (04.08.2023)

Priority date (day/month/year)

04 August 2022 (04.08.2022)

International Patent Classification (IPC) or both national classification and IPC

IPC - INV. B01J 23/28, B01J 27/22, B01J 23/16, B01J 23/24, C10G 3/00 (2023.01)

ADD. B01J 37/02 (2023.01)

CPC - INV. B01J 23/28, B01J 27/22, B01J 23/16, B01J 23/24, C10G 3/44

ADD. B01J 37/02

Applicant **ALLIANCE FOR SUSTAINABLE ENERGY, LLC**

I. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☒ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. FURTHER ACTION

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA/US
Mail Stop PCT, Attn: ISA/US
Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-8300

Date of completion of this opinion

3 October 2023 (03.10.2023)

Authorized officer

Kari Rodriguez

PCT Help Desk

Telephone No. 571-272-4300

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.

PCT/US 23/29488

Box No. I Basis of this opinion

1. With regard to the **language**, this opinion has been established on the basis of:
 - ☒ the international application in the language in which it was filed.
 - ☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).
2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43*bis*.1(b)).
3. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing:
 - a. ☐ forming part of the international application as filed.
 - b. ☐ furnished subsequent to the international filing date for the purposes of international search (Rule 13ter.1(a)),
☐ accompanied by a statement to the effect that the sequence listing does not go beyond the disclosure in the international application as filed.
4. ☐ With regard to any nucleotide and/or amino acid sequence disclosed in the international application, this opinion has been established to the extent that a meaningful opinion could be formed without a WIPO Standard ST.26 compliant sequence listing.
5. Additional comments:

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.

PCT/US 23/29488

Box No. IV Lack of unity of invention

1. ☒ In response to the invitation (Form PCT/ISA/206) to pay additional fees the applicant has, within the applicable time limit:
- ☐ paid additional fees.
 - ☐ paid additional fees under protest and, where applicable, the protest fee.
 - ☐ paid additional fees under protest but the applicable protest fee was not paid.
 - ☒ not paid additional fees.

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose not to invite the applicant to pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rule 13.1, 13.2 and 13.3 is

☐ complied with.

☒ not complied with for the following reasons:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: Claims 1-13 are directed towards a method comprising: providing a reactant comprising lignin and hydrogen; partially deoxygenating the reactant in the presence of a first catalyst at a first temperature, thereby generating an intermediate; deoxygenating the intermediate in the presence of a second catalyst at a second temperature, thereby generating a product comprising aromatic hydrocarbons.

Group II: Claims 14-19 directed towards a reactor comprising: a first reaction zone comprising a first catalyst at a first temperature; a second reaction zone comprising a second catalyst at a second temperature; where in the reactor is capable of performing hydrodeoxygenation of lignin to generate aromatic products.

The inventions listed as Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Group I requires a method comprising: providing a reactant comprising lignin and hydrogen; partially deoxygenating the reactant in the presence of a first catalyst at a first temperature, thereby generating an intermediate; deoxygenating the intermediate in the presence of a second catalyst at a second temperature, thereby generating a product comprising aromatic hydrocarbons, not required by Group II.

Group II requires a reactor comprising: a first reaction zone comprising; a second reaction zone; where in the reactor is capable of performing hydrodeoxygenation of lignin to generate aromatic products, not required by Group I.

Shared Technical Features:

Group I-II share the common technical features of a reactant comprising lignin, a first catalyst at a first temperature, a second catalyst at a second temperature, and deoxygenation of lignin to generate aromatic products. However, these shared technical features do not represent a contribution over prior art because the shared technical features are anticipated by US 2010/0137663 A1 to Chen et al. (hereinafter "Chen"). Chen teaches a reactant comprising lignin (Abstract, The process includes reacting lignin with a hydrogenation catalyst under a hydrogen atmosphere), a first catalyst at a first temperature (Abstract, The process includes reacting lignin with a hydrogenation catalyst under a hydrogen atmosphere to convert acidic oxygenate compounds; para [0007], The present invention for recovering chemicals from lignin includes a combining lignin with a hydrogenation catalyst to form a mixture under a hydrogen atmosphere. The mixture is reacted at hydrolysis process conditions to form an intermediate product stream having reduced oxygen content; para [0016], The hydrolysis reaction conditions include heating the reactor to a temperature between 100 degrees C and 450 degrees C); a second catalyst at a second temperature (Abstract, The process includes...The oxygenate compounds are reacted in a dehydrogenation and deoxygenation process to remove the oxygen and convert the cyclic hydrocarbons back to aromatic compounds; para [0007], The present invention for recovering chemicals from lignin includes...The intermediate product stream is contacted with a dehydrogenation and deoxygenation catalyst...generating a product stream comprising aromatic compounds; para [0020], The dehydrogenation and deoxygenation reactions remove the oxygen...The reaction conditions include...a temperature between 400 degrees C and 900 degrees C), and deoxygenation of lignin to generate aromatic products (Abstract, The process includes...The oxygenate compounds are reacted in a dehydrogenation and deoxygenation process to remove the oxygen and convert the cyclic hydrocarbons back to aromatic compounds; para [0007], The present invention for recovering chemicals from lignin includes...generating a product stream comprising aromatic compounds).

--see supplemental box--

4. Consequently, this opinion has been established in respect of the following parts of the international application:

☐ all parts.

☒ the parts relating to claims Nos. 1-13

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.

PCT/US 23/29488

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	3-4, 8-9, 12-13	YES
	Claims	1-2, 5-7, 10-11	NO
Inventive step (IS)	Claims	None	YES
	Claims	1-13	NO
Industrial applicability (IA)	Claims	1-13	YES
	Claims	None	NO

2. Citations and explanations:

Claims 1-2, 5-7 and 10-11 lack novelty under PCT Article 33(2) as being anticipated by US 2010/0137663 A1 to Chen et al. (hereinafter "Chen").

Regarding claim 1, Chen teaches a method (Abstract, A process for the conversion of lignin to chemical precursors is presented) comprising: providing a reactant comprising lignin and hydrogen (Abstract, The process includes reacting lignin with a hydrogenation catalyst under a hydrogen atmosphere); partially deoxygenating the reactant in the presence of a first catalyst at a first temperature, thereby generating an intermediate (Abstract, The process includes reacting lignin with a hydrogenation catalyst under a hydrogen atmosphere to convert acidic oxygenate compounds; para [0007], The present invention for recovering chemicals from lignin includes a combining lignin with a hydrogenation catalyst to form a mixture under a hydrogen atmosphere. The mixture is reacted at hydrolysis process conditions to form an intermediate product stream having reduced oxygen content; para [0016], The hydrolysis reaction conditions include heating the reactor to a temperature between 100 degrees C and 450 degrees C); deoxygenating the intermediate in the presence of a second catalyst at a second temperature, thereby generating a product comprising aromatic hydrocarbons (Abstract, The process includes...The oxygenate compounds are reacted in a dehydrogenation and deoxygenation process to remove the oxygen and convert the cyclic hydrocarbons back to aromatic compounds; para [0007], The present invention for recovering chemicals from lignin includes...The intermediate product stream is contacted with a dehydrogenation and deoxygenation catalyst...generating a product stream comprising aromatic compounds; para [0020], The dehydrogenation and deoxygenation reactions remove the oxygen...The reaction conditions include...a temperature between 400 degrees C and 900 degrees C).

Regarding claim 2, Chen teaches the method of claim 1, wherein the second temperature is greater than the first temperature (para [0016], The hydrolysis reaction conditions include heating the reactor to a temperature between 100 degrees C and 450 degrees C; para [0020], The dehydrogenation and deoxygenation reactions remove the oxygen...The reaction conditions include...a temperature between 400 degrees C and 900 degrees C).

Regarding claim 5, Chen teaches the method of claim 1, wherein the reactant does not comprise a solvent (Abstract, The process includes reacting lignin with a hydrogenation catalyst under a hydrogen atmosphere to convert acidic oxygenate compounds. Hence, the reactant comprises lignin and hydrogen without the presence of a solvent.).

Regarding claim 6, Chen teaches the method of claim 1, wherein the first temperature is selected from the range of 250 degrees C to 450 degrees C (para [0016], The hydrolysis reaction conditions include heating the reactor to a temperature between 100 degrees C and 450 degrees C).

Regarding claim 7, Chen teaches the method of claim 1, wherein the second temperature is selected from the range of 275 degrees C to 475 degrees C (para [0020], The dehydrogenation and deoxygenation reactions remove the oxygen...The reaction conditions include...a temperature between 400 degrees C and 900 degrees C).

Regarding claim 10, Chen teaches the method of claim 1, wherein the steps of partially deoxygenating and deoxygenating are each performed continuously (para [0021], it is believed that the hydrogenation process reduces the need for a significant addition of a strong base to the lignin solution by hydrogenating the more acidic oxygenates, such as phenolic compounds, in addition to depolymerizing the lignin, thereby creating an intermediate stream. The process is then continued with a second step where the intermediate stream is processed using a dehydrogenation and deoxygenation catalyst at dehydrogenation and deoxygenation conditions, thereby generating a hydrocarbon stream comprising aromatics).

Regarding claim 11, Chen teaches the method claim 1, wherein the steps of partially deoxygenating and deoxygenating are part of a continuous process (para [0021], it is believed that the hydrogenation process reduces the need for a significant addition of a strong base to the lignin solution by hydrogenating the more acidic oxygenates, such as phenolic compounds, in addition to depolymerizing the lignin, thereby creating an intermediate stream. The process is then continued with a second step where the intermediate stream is processed using a dehydrogenation and deoxygenation catalyst at dehydrogenation and deoxygenation conditions, thereby generating a hydrocarbon stream comprising aromatics.).

Claims 1 and 8-9 lack inventive step under PCT Article 33(3) as being obvious over US 2018/0119022 A1 to Alliance for Sustainable Energy, LLC (hereinafter "Alliance").

--see supplemental box--

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.

PCT/US 23/29488

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.

Continuation of:

Box IV (Lack of unity of invention)

As the shared technical features were known in the art at the time of the invention, they cannot be considered special technical features that would otherwise unify the groups. Therefore, Groups I-II lack unity under PCT Rule 13.

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.

Continuation of:

Box V.2 (Citations and explanations)

Regarding claim 1, Alliance teaches a method (Abstract, An aspect of the present disclosure is a method that includes contacting an oxygenated compound and hydrogen with a solid catalyst) comprising: providing a reactant comprising lignin and hydrogen (Abstract, An aspect of the present disclosure is a method that includes contacting an oxygenated compound and hydrogen with a solid catalyst); partially deoxygenating the reactant in the presence of a first catalyst at a first temperature, thereby generating an intermediate (Abstract, An aspect of the present disclosure is a method that includes contacting an oxygenated compound and hydrogen with a solid catalyst...and the contacting converts at least a portion of the oxygenated compound to a deoxygenated compound; para [0064], the catalyst positioned within the upgrading unit 140 may include at least one solid catalyst...In some embodiments of the present disclosure, the catalyst (not shown) positioned within the upgrading unit 140 may include at least one solid catalyst such as a metal carbide. Examples of a metal carbide include molybdenum carbide and tungsten carbide; Abstract, ...where the solid catalyst includes a metal carbide...the metal carbide may include at least one of Mo₂C; para [0079], Mo₂C appeared to deactivate faster in the presence of acetic acid as compared to guaiacol, suggesting that some carbohydrate-derived intermediates may play a greater role in catalyst deactivation than lignin-derived intermediates; para [0007], An aspect of the present disclosure is a method that includes heating a first mixture...compound, where the heating is performed at a first temperature up to about 400 degrees C., the first mixture is substantially in a liquid phase while at the first temperature, and the heating produces a second mixture comprising metal carbide nanoparticles); deoxygenating the intermediate in the presence of a second catalyst at a second temperature (Abstract, An aspect of the present disclosure is a method that includes contacting an oxygenated compound and hydrogen with a solid catalyst...and the contacting converts at least a portion of the oxygenated compound to a deoxygenated compound; para [0007], In some embodiments of the present disclosure, the method may further include, after the heating, cooling the second mixture to a second temperature that is between 20 degrees C. and less than the first temperature to form a cooled second mixture. In some embodiments of the present disclosure, the method may further include, after the cooling, separating the metal carbide nanoparticles from the cooled second mixture; para [0064], the catalyst positioned within the upgrading unit 140 may include at least one solid catalyst...In some embodiments of the present disclosure, the catalyst (not shown) positioned within the upgrading unit 140 may include at least one solid catalyst such as a metal carbide. Examples of a metal carbide include molybdenum carbide and tungsten carbide. Hence, the catalyst may comprise two distinct catalysts, the first comprising molybdenum carbide and the second comprising tungsten carbide, at two distinct temperatures, the second temperature being at 20 degrees C.), thereby generating a product comprising aromatic hydrocarbons (para [0017], Fig. 9 illustrates experimental results for the deoxygenation of pine pyrolysis vapors with hydrogen over a fixed-bed of a metal carbide (Mo₂C)...The aromatics from Mo₂C consist of benzene and alkyl benzenes), but does not teach a specific example or embodiment including each aforementioned step in a single method. Based on the teachings of Alliance, it would have been obvious to one of skill in the art to include a single example or embodiment including each aforementioned step in a single method by routine experimentation.

Regarding claim 8, Alliance the method claim 1, wherein the first catalyst, the second catalyst or both comprise Mo₂C (Abstract, ...where the solid catalyst includes a metal carbide...the metal carbide may include at least one of Mo₂C).

Regarding claim 9, Alliance teaches the method of claim 1, wherein the first catalyst and the second catalyst are the same (para [0064], the catalyst positioned within the upgrading may include at least one solid catalyst such as a metal carbide; Abstract, the metal carbide may include at least one of Mo₂C. Hence, there may be more than one catalyst, each comprising Mo₂C).

Claims 3-4 and 12-13 lack inventive step under PCT Article 33(3) as being obvious over Chen.

Regarding claim 3, Chen teaches the method of claim 1, wherein the reactant comprises lignin (Abstract, The process includes reacting lignin with a hydrogenation catalyst under a hydrogen atmosphere) but does not specifically teach wherein the reactant comprises greater than 50% lignin oil. It would have been obvious to one of skill in the art to include 50% lignin oil as the lignin in the reactant to optimize the deoxygenation of the lignin.

Regarding claim 4, Chen teaches the method of claim 1, wherein the reactant comprises lignin (Abstract, The process includes reacting lignin with a hydrogenation catalyst under a hydrogen atmosphere), but does not specifically teach wherein the reactant comprises greater than 99% lignin oil. It would have been obvious to one of skill in the art to include 99% lignin oil as the lignin in the reactant to optimize the deoxygenation of the lignin.

Regarding claim 12, Chen teaches the method of any claim 1, wherein the product is sustainable aviation or marine fuel (para [0020], The product stream has benzenes, toluenes, and other alkyl-benzenes that can be separated for use as precursors to other processes, including the formation of fuel feed stocks; para [0010], The lignin comprises useful aromatic ring compounds, such that when the lignin is broken down, the aromatic ring compounds can be recovered and used as precursors to fuels), but does not specifically teach wherein the fuel is sustainable aviation or marine fuel. It would have been obvious to one of skill in the art to use the fuel as sustainable aviation or marine fuel to optimize the utilization of the produced aromatic hydrocarbons.

Regarding claim 13, Chen teaches the method of claim 1, but does not specifically teach wherein the product comprises an oxygen mole fraction less than or equal to 5%. It would have been obvious to one of skill in the art to adjust the method to produce a product comprising an oxygen mole fraction less than or equal to 5% to improve the quality of the product.

Claims 1-13 have industrial applicability as defined by PCT Article 33(4) because the subject matter can be made or used in industry.

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING SUBMISSION,
OBTENTION OR TRANSMITTAL
OF PRIORITY DOCUMENT
(PCT Administrative Instructions, Section 411)

To:

VICKERY, Neal
c/o National Renewable Energy Laboratory
15013 Denver West Parkway
Golden, Colorado 80401
ÉTATS-UNIS D'AMÉRIQUE

Date of mailing (<i>day/month/year</i>) 07 September 2023 (07.09.2023)	
Applicant's or agent's file reference NREL PCT22-94	IMPORTANT NOTIFICATION
International application No. PCT/US2023/029488	International filing date (<i>day/month/year</i>) 04 August 2023 (04.08.2023)
International publication date (<i>day/month/year</i>) Not yet published	Priority date (<i>day/month/year</i>) 04 August 2022 (04.08.2022)
Applicant ALLIANCE FOR SUSTAINABLE ENERGY, LLC et al	

The applicant is hereby notified of the date of receipt (or of obtaining by the International Bureau) of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to the date of receipt, **the priority document concerned was submitted or transmitted to or obtained by the International Bureau in compliance with Rule 17.1(a), (b) or (b-bis)**. This Form replaces any previously issued notification concerning submission, transmittal or obtaining of priority documents.

Priority datePriority application No.Country or regional Office
or PCT receiving OfficeDate of receipt
of priority document

04 August 2022 (04.08.2022)

63/395,067

US

24 August 2023 (24.08.2023)

The letters "NR" denote a priority document which, on the date of mailing of this Form, had not yet been received or obtained by the International Bureau in compliance with Rule 17.1(a), (b) or (b-bis). Where the applicant has failed to either submit, request to prepare and transmit, or to request the International Bureau to obtain the priority document within the applicable time limit under that Rule, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

An asterisk "*" next to a date of receipt, denotes a priority document submitted or transmitted to or obtained by the International Bureau but not in compliance with Rule 17.1(a), (b) or (b-bis) (the priority document was received after the time limit prescribed in Rule 17.1(a); the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b) or the request to the International Bureau to obtain the priority document was made after the applicable time limit under Rule 17.1(b-bis)). Even though the priority document was not furnished in compliance with Rule 17.1(a), (b) or (b-bis), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as the priority document, Rule 17.1(c) provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

Fiona Dohertye-mail pct.team4@wipo.int

Telephone No. +41 22 338 74 04

From the INTERNATIONAL BUREAU

PCT

SECOND AND SUPPLEMENTARY NOTICE
INFORMING THE APPLICANT OF THE
COMMUNICATION OF THE INTERNATIONAL
APPLICATION (TO DESIGNATED OFFICES
WHICH APPLY THE 30 MONTH TIME
LIMIT UNDER ARTICLE 22(1))

(PCT Rule 47.1(c))

To:

VICKERY, Neal
c/o National Renewable Energy Laboratory
15013 Denver West Parkway
Golden, Colorado 80401
ÉTATS-UNIS D'AMÉRIQUE

Date of mailing (day/month/year)

05 December 2024 (05.12.2024)

Applicant's or agent's file reference

NREL PCT22-94

IMPORTANT NOTICE

International application No.

PCT/US2023/029488

International filing date (day/month/year)

04 August 2023 (04.08.2023)

Priority date (day/month/year)

04 August 2022 (04.08.2022)

Applicant

ALLIANCE FOR SUSTAINABLE ENERGY, LLC et al

1. **ATTENTION:** For any designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002 (30 months from the priority date), **does not apply**, please see Form PCT/IB/308(First Notice) issued previously.
2. Notice is hereby given that the following designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002, **does apply**, has/have requested that the communication of the international application, as provided for in Article 20, be effected under Rule 93bis.1. The International Bureau has effected that communication on the date indicated below:
08 February 2024 (08.02.2024)

EP

In accordance with Rule 47.1(c-bis)(i), those Offices will accept the present notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

3. The following designated Offices, for which the time limit under Article 22(1), as in force from 1 April 2002, **does apply**, have not requested, as at the time of mailing of the present notice, that the communication of the international application be effected under Rule 93bis.1 :

AE, AG, AL, AM, AO, AP, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EA, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OA, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW

In accordance with Rule 47.1(c-bis)(ii), those Offices accept the present notice as conclusive evidence that the Contracting State for which that Office acts as a designated Office does not require the furnishing, under Article 22, by the applicant of a copy of the international application.

4. TIME LIMITS for entry into the national phase

For the designated or elected Office(s) listed above, the applicable time limit for entering the national phase will, **subject to what is said in the following paragraph**, be **30 MONTHS** from the priority date.

In practice, **time limits other than the 30-month time limit** will continue to apply, for various periods of time, in respect of certain of the designated or elected Office(s) listed above. For **regular updates on the applicable time limits** (30 or 31 months, or other time limit), Office by Office, refer to the *PCT Gazette*, the *PCT Newsletter* and the *PCT Applicant's Guide*, National Chapters, all available from WIPO's Internet site, at <http://www.wipo.int/pct/en/guide/index.html>.

It is the applicant's **sole responsibility** to monitor all these time limits.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

Fiona Dohertye-mail pct.team4@wipo.int

Telephone No. +41 22 338 74 04

From the INTERNATIONAL BUREAU

PCT

FIRST NOTICE INFORMING THE APPLICANT OF
THE COMMUNICATION OF THE INTERNATIONAL
APPLICATION (TO DESIGNATED OFFICES WHICH
DO NOT APPLY THE 30 MONTH TIME LIMIT
UNDER ARTICLE 22(1))

(PCT Rule 47.1(c))

To:

VICKERY, Neal
c/o National Renewable Energy Laboratory
15013 Denver West Parkway
Golden, Colorado 80401
ÉTATS-UNIS D'AMÉRIQUE

Date of mailing (day/month/year) 07 March 2024 (07.03.2024)		IMPORTANT NOTICE
Applicant's or agent's file reference NREL PCT22-94		
International application No. PCT/US2023/029488	International filing date (day/month/year) 04 August 2023 (04.08.2023)	Priority date (day/month/year) 04 August 2022 (04.08.2022)
Applicant ALLIANCE FOR SUSTAINABLE ENERGY, LLC et al		

- ATTENTION:** For any designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002 (30 months from the priority date), **does apply**, please see Form PCT/IB/308(Second and Supplementary Notice) (to be issued promptly after the expiration of 28 months from the priority date).
- Notice is hereby given that the following designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002, **does not apply**, has/have requested that the communication of the international application, as provided for in Article 20, be effected under Rule 93bis.1. The International Bureau has effected that communication on the date indicated below:
08 February 2024 (08.02.2024)

None

In accordance with Rule 47.1(c-bis)(i), those Offices will accept the present notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

- The following designated Offices, for which the time limit under Article 22(1), as in force from 1 April 2002, **does not apply**, have not requested, as at the time of mailing of the present notice, that the communication of the international application be effected under Rule 93bis.1:

LU, TZ

In accordance with Rule 47.1(c-bis)(ii), those Offices accept the present notice as conclusive evidence that the Contracting State for which that Office acts as a designated Office does not require the furnishing, under Article 22, by the applicant of a copy of the international application.

4. TIME LIMITS for entry into the national phase

For the designated Office(s) listed above, and unless a demand for international preliminary examination has been filed before the expiration of **19 months** from the priority date (see Article 39(1)), the applicable time limit for entering the national phase will, **subject to what is said in the following paragraph**, be **20 MONTHS** from the priority date.

In practice, **time limits other than the 20-month time limit** will continue to apply, for various periods of time, in respect of certain of the designated Offices listed above. For **regular updates on the applicable time limits** (20 or 21 months, or other time limit), Office by Office, refer to the *PCT Gazette*, the *PCT Newsletter* and the *PCT Applicant's Guide*, National Chapters, all available from WIPO's Internet site, at <http://www.wipo.int/pct/en/guide/index.html>.

It is the applicant's **sole responsibility** to monitor all these time limits.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Fiona Doherty e-mail pct.team4@wipo.int Telephone No. +41 22 338 74 04
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NREL: PCT/22-94
August 4, 2023
Beckham, G. et al.

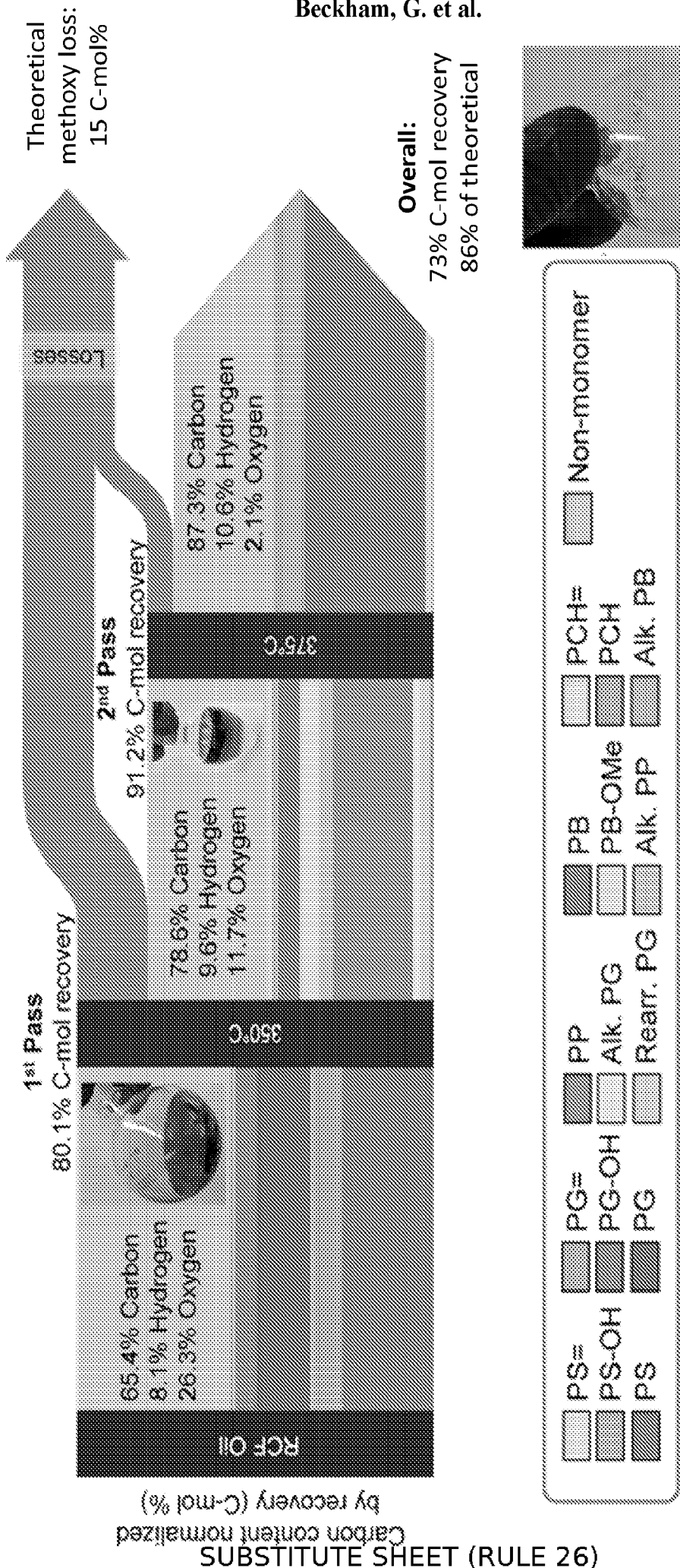


Fig. 4D
REPLACEMENT SHEET