Direct upstream integration of biogasoline production into current light straight run naphtha petrorefinery processes

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There is an urgent need to address environmental problems caused by our transportation systems, which include the reduction of associated CO₂ emissions. In the short term, renewable drop-in fuels are ideal, as they allow a direct integration into the existing infrastructure. However, preferably they would perform better than current alternatives (for example, bioethanol) and be synthesized in a more efficient way. Here we demonstrate the production of biogasoline with a direct upstream integration into processes in existing petrorefinery facilities that targets the 10% bio-based carbon in accordance with the current European Union directives (for 2020) for biofuels. To achieve this goal, we show the valorization of (hemi)cellulose pulp into light naphtha using a two-phase (H₂O:organic) catalytic slurry process. A C₅–C₆ alkane stream, enriched with bio-derived carbon and compatible with further downstream petrorefinery operations for (bio)gasoline production, is automatically obtained by utilizing fossil light straight run naphtha as the organic phase. The ease of integration pleads for a joint petro/bio effort to gradually produce bio-enriched gasolines, wherein the chemical compounds of the bio-derived fraction are indistinguishable from those in current high-quality gasoline compositions.

A growing body of literature recognizes the importance of a sustainable production of fuel (additives)^{1–3}, chemicals and materials⁴ from abundant and renewable lignocellulose^{5,6}. Despite lignocellulose's high degree of functionality⁷, its conversion into alkanes can become an important alternative for bio-enrichment or the replacement of fossil-based alkanes⁸. The synthesis of identical molecules from an alternative biomass feedstock, instead of from crude oil, encompasses a promising strategy for the integration of bio-based carbon in the short term⁹. Integration of these technologies in an existing petrorefinery is, perhaps, the most straightforward and efficient way to proceed, but such synergies are currently immature.

In line with rising concerns about fossil-derived CO₂ and climate change, objectives related to the implementation of renewable energy, including biofuels, have been put forward (Supplementary Note 1)¹⁰. The dependency of our current transportation market on diesel (C₁₀–C₂₂), kerosene (C₈–C₁₆) and gasoline (C₅–C₁₂), certainly in the short-to-mid term, will still be high¹¹. Therefore, the European Union for one, has targeted a market share of 10% for biofuels in transportation by 2020¹², with a maximum of 7% from first-generation biomass¹⁰. Introducing renewable diesel as a drop-in fuel, for instance, by Neste Oil, is one example to achieve these objectives. Nevertheless, the consumption of diesel, in contrast to that of gasoline, leads to a higher emission of particulate matter and NO_x (for example, diesel exhaust emission scandals), a problem not solved by biodiesel replacement. Therefore, the importance of light fuels, such as gasoline, whether or not as an energy carrier in a future hybrid engine, will probably increase. Currently, gasoline, which is synthesized by blending different petrorefinery streams (for example, alkylate, isomerate and reformate) and light distillate feedstock, has an annual consumption of approximately 32 vol% of

the global oil market, which corresponds to more than 1,350 (or 4,200 for the total oil market) million metric tonnes yearly¹³.

Blending bio-based ethanol with fossil gasoline is today's most widely used option, and therefore, most objectives are expressed in E values (% ethanol in fuel blends, for instance E10 in several European countries). The implementation of ethanol, synthesized through an already well-developed technology, leads to lower CO₂ emissions and a higher combustion quality because of ethanol's high octane number (the research octane number is 130 (ref. ¹⁴)). Although bioethanol is on the rise, its blending into gasoline also encompasses some drawbacks and limitations: the direct loss of two carbons in form of CO₂ per C₆-hexose during the production of ethanol⁷, a lower energy density compared to that of conventional gasoline (so a lower vehicle distance range)¹⁵ and an ongoing debate about the compatibility with traditional vehicle materials¹⁵. Moreover, the current fermentative ethanol production mainly consumes edible carbohydrate resources (for example, corn and sugarcane). This is a consequence of the complexity of cellulose conversion, which leads to an approximately three times higher investment cost for a second-generation plant in comparison with a first-generation plant¹⁰.

Besides bioethanol, myriads of emerging technologies to transform lignocellulose into alkanes have been reported, which encompass thermochemical and mild catalytic approaches. Gasification^{16,17} and pyrolysis/liquefaction^{18–20} are the most promising thermochemical technologies. These methods generally yield a broad product distribution (namely, an enormous diversity of liquid hydrocarbons as well as gases and solid biochar), which may complicate the introduction in operational petrorefinery facilities because of serious risks (for example, the necessity to modify the traditional petrorefinery at different levels). Moreover, the valorization towards light

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Fig. 1 | Schematic representation of a petrorefinery with upstream integration of the LPCtoN technology. LPCtoN enriches a petrochemical stream (gold) with renewable bio-naphtha (C_5-C_6 (green), and thus chemically identical molecules) before its processing in an existing LSR isomerization unit of the petrorefinery. In line with European Union directives, an integration of 10% bio-derived carbon in transportation fuels by 2020 is the aim. Current bio-enrichment is done by ethanol blending downstream (below right). LSR, light straight run naphtha; HSR, heavy straight run naphtha; FCC, fluid catalytic cracking; LPG, liquid petroleum gas; LPCtoN, liquid phase cellulose-to-naphtha.

biofuels (gasoline) is rather limited, for instance, obtaining mainly heavy fractions from the Fischer–Tropsch synthesis using biomass-derived syngas or from typical liquefaction processes^{20,21}.

Here we demonstrate an alternative catalytic approach at lower temperature that converts (hemi)cellulosic pulp into light naphtha in a two-phase catalytic slurry process. The typical C_5-C_6 cut from a petrorefinery is ideal as the organic phase (solvent), in addition to its high stability, and alkanes therein are capable of dissolving substantial amounts of water at elevated temperatures, which improves its extraction ability for intermediate furanics in the chemical process. The integration of such a petrorefinery stream enables its immediate and controlled enrichment with bio-carbon in a single step, validated by ^{14}C -isotope measurements. The hydrogen-rich light naphtha stream is easily fed into a classic petrorefinery hydro-isomerization unit to produce a bio-enriched isomerate with improved octane properties.

Integration in the petrorefinery

Mild catalytic approaches, which require fractionated (and purified) cellulosic substrates, enable the preservation of the native carbon skeleton and thus a high C_5-C_6 product selectivity from the carbohydrate streams^{22–25}. Such a C_5-C_6 alkane cut resembles the so-called light straight run naphtha (LSR) in petrorefineries, which is typically isomerized into branched alkanes to increase the gasoline octane number, from below 70 to above 90, before its blending into gasoline. The need for this light isomerization unit is gaining importance because of the restrictions on sulfur, olefin and aromatic content in gasoline^{13,26}. At the same time, the processed quantity of these light isomerization units is diminishing because heavier crude oils are becoming relatively more important¹³. Therefore, this

contribution proposes the use of larger quantities of light naphtha streams, enriched from a bio-source, in gasoline blends. The strategy, presented in Fig. 1, envisions, in contrast to current state-of-the-art procedures, the direct bio-enrichment of the present LSR streams by converting (ligno)cellulosic feedstock in a biphasic slurry process into light bio-naphtha in the presence of deep hydrodeoxygenation (HDO) catalysts with LSR as the organic phase. In line with traditional petrorefinery operations, the preferred LSR streams undergo hydrotreatment to prevent catalyst deactivation and are thus sulfur free prior to the enrichment^{27,28}. The subsequent hydro-isomerization unit converts the total LSR stream into a high-quality bio-enriched isomerate for gasoline blends. The literature shows that the choice of catalyst (for example, chlorinated alumina, sulfated zirconia or zeolites) in the isomerization unit is crucial, and this is determined by the catalyst lifetime and the tolerance against S-, N- and O-containing compounds and H_2O , as well as the operating process window of the existing facility^{26,29,30}. For instance, Pt-loaded zeolites need to work at higher temperature, which shifts the thermodynamic equilibrium in a negative way (to less-branched isomers), but they have a higher tolerance regarding impurities such as H_2O and oxygenates²⁶, and are therefore preferred here. Optionally, oxygenates (for example, 2,5-dimethyltetrahydrofuran with a research octane number of 82 (ref. 14)) may be removed by distillation prior to isomerization, and then added back into the gasoline blend as valuable substitutes for their superior properties, such as their higher energy density than ethanol¹⁵.

The scalability of the proposed bio-integration in the petrorefinery is motivated by detailed calculations in Supplementary Note 2 and Supplementary Figs. 1 and 2. In general, a petrorefinery plant processes approximately 20 million metric tonnes of crude

Fig. 2 | Direct enrichment of fossil-derived LSR (petroleum ether) with bio-naphtha via the LPCtoN process. Conditions: 2 g Vivapur cellulose, 4.8 g $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, 0.25 g Ru/C; biphasic system (40 ml), H_2O /petroleum ether (75:25), 5 MPa H_2 at room temperature (r.t.); temperature programme from r.t. to 423 K ($\pm 12 \text{ K min}^{-1}$) and from 423 K to 493 K ($\pm 0.5 \text{ K min}^{-1}$); total reaction time of 5 h. Other alkanes (LPCtoN): *n*-butane, 2-methylpentane, 3-methylpentane. Oxygenates: $\text{C}_x\text{H}_y\text{O}_1$ present in the organic phase. MCP, methylcyclopentane.

oil annually¹³, of which 5–15 vol% (depending on the oil feedstock) ends up in LSR³¹. Enrichment of the fossil LSR with, for instance, 10% bio-based carbon from lignocellulose carbohydrate streams therefore requires an annual processing of approximately one million metric tonnes of lignocellulose. This capacity, which is the typically applied feedstock volume in the pulp and paper industry (for example, a large-sized paper-mill), thus indicates its feasibility in terms of logistics, sustainability and so on.

Direct bio-based carbon enrichment of fossil light naphtha

The liquid phase cellulose-to-naphtha (LPCtoN) technology we have designed comprises a biphasic catalytic system that consists of a reactive aqueous phase with a soluble heteropolyacid, and a reactive organic phase with polyacid-modified ruthenium on carbon, executed in a stirred slurry reactor. Heteropolyacids were chosen because of their high solubility in polar solvents, strong acidity and interaction with carbohydrates, which enable fast hydrolysis and dehydration, high affinity for adsorption on carbon and non-volatile character, which avoid downstream product contamination^{32,33}. For the heterogeneous redox catalyst, smooth metal surfaces of, for instance, Ru are required to facilitate 5-hydroxymethylfurfural (5-HMF) hydrogenation. The hydrophobic carbon support adsorbs part of the heteropolyacid and compartmentalizes this bifunctional acid–metal catalyst in the organic phase, where it selectively executes dehydration/hydrogenation cycles with a minimum carbon–carbon bond dissociation. In this way, the direct conversion of cellulose into light naphtha, in the order of 300 kilograms of cellulose per day per cubic metre of reactive phase, can be achieved at mild temperatures (493 K) under a H_2 atmosphere (5 MPa). Although this value is non-optimized and may probably be improved further, it already surpasses that of more mature bioethanol fermentation processes, which show about 50 kilograms of sugar conversion per day per cubic metre³⁴.

Few liquid-phase cellulose-to-alkane conversions in biphasic catalytic conditions are reported^{22,23}. The chemistry related to these HDO strategies is discussed in Supplementary Note 3 with the reaction paths in Supplementary Fig. 3. Accordingly, we studied cellulose-to-alkane conversions in a fossil naphtha/ H_2O system in the presence of the aforementioned polyacid and modified Ru on carbon catalyst, but used petrol and petroleum ether (instead of the commonly used (do)decane solvent). Petrol, with a boiling point between 363 and 373 K, mainly contains C_7 alkanes (99%), of which 43% are linear, 29% branched and 27% cyclic. Petroleum ether is a lighter fraction with a boiling point between 333 and 353 K, and mainly contains C_6 alkanes (98%), of which 47% are linear, 35% branched and 16% cyclic. Particularly the latter solvent resembles

the C_6 composition of a typical LSR before isomerization³⁵. The use of petroleum ether and petrol as the organic solvents was investigated in the biphasic slurry reactor first using a naphtha/ H_2O (25:75) mixture that contained 7 wt% cellulose in water. Complete cellulose conversion was achieved with a cellulose-to-alkane efficiency of 76 mol% C and 68 mol% C for petroleum ether (Fig. 2) and petrol, respectively (measured in the organic phase). The distribution within the bio-based products is approximately equal for both fractions: 70% *n*-hexane, 10% methylcyclopentane, 9% *n*-pentane, 4% other C_{4-6} alkanes and 7% oxygenates (which consist of tetrahydrofuran, pyran and oxepane-related C_{5-6} structures, as well as C_{5-6} mono-alcohols). Thus, cellulose can be converted in both LSR model solvents, but a significant difference in carbon efficiency was observed.

Solubility is key in the biphasic cellulose-to-alkane process. It is desirable that cellulose hydrolysis and sugar dehydration (for example, to 5-HMF) are carried out in the water phase, whereas further hydrogenation and conversion via dehydration–hydrogenation to alkanes should occur in the organic phase. The catalyst properties play a crucial role in this dual compartmentalization strategy, as discussed in Supplementary Note 4, Supplementary Figs. 4 and 5 and Supplementary Table 1. It is essential that the metal is loaded on a hydrophobic support to keep metal redox activity exclusively in the organic phase, the support is able to adsorb and extract part of the acidity in the organic phase to ensure its bifunctional catalytic property (heteropolyacids and carbon are good partners³⁶) and, in the case of Ru, large particle sizes are used to favour aromatics hydrogenation.

Besides the catalytic properties, the solvent choice is of utmost importance to achieve the highest C efficiency, as we observed. Alkanes are the best choice in terms of stability regarding HDO. The solvent extractability, though, looks insufficient, especially for the early dehydrated intermediates such as 5-HMF. Dumesic et al. were first to demonstrate the usefulness of a biphasic solvent system for hydroxymethylfurfural (HMF) production from fructose^{14,37,38}. The extraction–stabilization trends for the production of HMF are highlighted in a recent review³⁹. To our knowledge, the use of alkanes, explicitly in our interest for the integration, has not been reported, obviously because of the very low extraction capacity of alkanes for HMF at a moderate reaction temperature.

Notably, use of high temperature ($>500 \text{ K}$) shows a different solvation behaviour. The thermodynamics of the water–alkane mutual solubility at such circumstances have been reported^{40–43}. Under our reaction conditions, namely, up to 493 K, the biphasic alkane–water solvent system behaves like a three-phase system in which the gas composition is in equilibrium with two liquid phases, one water rich

Fig. 3 | Influence of the alkane solvent on the biphasic LPCtoN technology. **a**, Representation of the LPCtoN efficiency using different linear alkanes as the solvent, ranging from *n*-heptane (C₇, octane number 0) to *n*-hexadecane (C₁₆). **b**, Cumulative representation of the individual product yields as well as the total yield as a function of wt% H₂O in the alkane solvent. The wt% H₂O in each alkane solvent is estimated via the mutual solubility data of normal alkanes and H₂O at 493 K. The shorter the alkane solvents, the higher the amount of H₂O (on a weight basis) in the alkane solvent^{41–43}. **c**, LPCtoN reaction scheme that highlights the intermediates with no pronounced preference for the H₂O or organic phase. The polarity, determined by means of ChemDraw Ultra 12.0 software, is presented by log *P*, which is the concentration (*C*) of molecule *X* in octanol in relation to the concentration of molecule *X* in H₂O. A low log *P* corresponds to a high polarity, whereas a high log *P* corresponds to a low polarity. Conditions: 2 g Vivapur cellulose, 4.8 g H₄SiW₁₂O₄₀, 0.25 g Ru/C; biphasic system (40 ml), H₂O/alkane (75:25), 5 MPa H₂ at r.t.; temperature programme from r.t. to 423 K (±12 K min^{−1}) and from 423 K to 493 K (±0.5 K min^{−1}); total reaction time of 5 h. DHMF, dihydroxymethylfurfural; DMTHF, dimethyltetrahydrofuran, DMF, dimethylfuran.

and the other alkane rich phase. The compositions of each phase can be estimated using the reported mutual solubility data of water and alkanes^{40–43}. The solubility of alkanes in water, although higher at a higher temperature and higher for shorter carbon chain lengths, remains very low, namely, in the order of 1–1,000 ppm. Any solvent effect in the water phase from such low solute molarities on catalysis (in terms of partition, pH or H₂ solubility) can probably be discarded. However, the solubility of water in alkanes at an elevated temperature is surprisingly high, reaching values up to around 50% mole fraction at 513 K. As this mole fraction only differs slightly with the carbon number of the alkane, short alkanes at a high temperature contain higher weight amounts of water than long alkanes. We hypothesize, therefore, that the extraction of intermediate oxygenates (needed for their further conversion into alkanes in the LSR phase) likewise becomes sufficiently high in the aqueous alkane phase at the elevated temperature and is especially favourable for the shorter-chain alkanes.

To substantiate this hypothesis, we performed the biphasic cellulose-to-alkane catalytic system using alkane solvents with a varying carbon number (Fig. 3a) (and skeleton (Supplementary Table 2)). The results show a substantial increase in C yield with decreasing carbon number of the alkane solvent, ranging from 52 mol% C (for *n*-hexadecane) to 81 mol% C (for *n*-heptane). This trend correlates well with the aforementioned calculated water solubility (Fig. 3b). In fact, one can also assume a higher polarity of the short alkane solvents as they allow a higher uptake of water per volume. Estimations of the partition coefficient of the alkanes in water–octanol (as log *P* (Supplementary Fig. 6)) subscribe the polarity differences with the carbon chain length. The polarity values (as log *P*) of the reaction

intermediates involved in the cellulose-to-alkane conversion are illustrated in Fig. 3c.

Taken together, short alkanes lead to a relatively polar organic phase, which in turn favours the solvent interaction with water and the intermediates (for example, HMF). C₅–C₆-containing light naphtha streams are therefore ideally suited for the anticipated cellulose-to-alkane conversion and afford high C yields.

Towards a targeted bio-enrichment

The LPCtoN technology is highly flexible in terms of bio-enrichment of the produced LSR fraction. Two process parameters can be adapted to target a specified enrichment: the ratio of the organic to water phase, and the loading of cellulose.

First, we note that the amount of water strongly affects the maximum alkane yield, and this value depends on the choice of the organic phase. This is illustrated, for instance, for *n*-heptane and *n*-hexadecane in Fig. 4a (and Supplementary Fig. 7). The results show that the use of *n*-heptane leads to an 81% maximum C yield at a 75:25 water-to-alkane volume ratio, and the same exercise with *n*-hexadecane gives a 68% maximum C yield at a 50:50 volume ratio. Remarkably, the absolute mass of water present in the alkane solvent, which is estimated from mutual solubility data^{41–43}, is equal for *n*-heptane and *n*-hexadecane at their maximum LPCtoN yield (Supplementary Fig. 8). The plot demonstrates that, even after optimizing the water-to-alkane ratio for each solvent, light alkanes remain the preferred organic solvent for the LPCtoN technology. As a reference, an experiment without the additional organic phase produces only a 41% alkanes C yield.

Fig. 4 | Influence of process variables and lignocellulose processing on the LPCtoN efficiency. a, The light naphtha yield for different H₂O:alkane solvent ratios. **b**, Bio-carbon enrichment in petrol as well as the cellulose-to-alkane efficiency (at the same catalyst loading) for different cellulose loadings (wt% in H₂O). **c**, Schematic representation of RCF of woody resources (here, birch sawdust) as the fractionation tool for the production of lignin-derived phenolics and a carbohydrate-enriched pulp (that is, a substrate for LPCtoN). Conditions for RCF: 2 g birch sawdust, 0.2 g Ni-Al₂O₃ catalyst pellets, 40 ml methanol, 3 MPa H₂ at r.t.; temperature programme: from r.t. to 523 K (±10 K min⁻¹); total reaction time of 3 h. Conditions for LPCtoN: 2 g carbohydrate pulp (mixture of pulps obtained after two identical RCF reactions on 2 g birch sawdust) for **c** or 2 g Vivapur cellulose for **a**; 4.8 g H₂SiW₁₂O₄₀, 0.25 g Ru/C; biphasic system (40 ml), H₂O/alkane (75:25 for **c**), 5 MPa H₂ at r.t.; temperature programme: r.t. to 423 K (±12 K min⁻¹) and from 423 K to 493 K (±0.5 K min⁻¹); total reaction time of 5 h. Other alkanes: *n*-butane, 2-methylpentane, 3-methylpentane. Oxygenates: C_xH_yO₁ present in the organic phase.

Not only is the yield of the C₅–C₆ alkanes in *n*-heptane higher, but also the bio-enrichment increases because less organic solvent volume was used for the same amount of converted cellulose. For instance, the enrichment in *n*-hexadecane is 4%, whereas it is 10% in *n*-heptane in the solvent conditions of their respective highest alkane C yields. Similar enrichment levels were obtained with petrol (Fig. 4b), a model LSR organic solvent. Higher bio-carbon enrichment up to 16% can be achieved in petrol without significantly affecting the cellulose-to-alkane efficiency (around 75 mol% C) by lowering the petrol volume from 25 to 12.5%. The highest bio-enrichment (20%) was achieved with the same solvent ratio using a cellulose loading of 9 wt%, which corresponds to a productivity level of 360 kilograms of cellulose per day per cubic meter of reactive phase, at a somewhat lower alkane C yield (55%). A further increase in cellulose loading (>10 wt%) does not result in a higher bio-carbon enrichment due to a too low HDO efficiency. The negative impact of a higher cellulose loading in water is further corroborated by additional experiments, discussed in Supplementary Note 5 and Supplementary Table 3, which indicates enhanced degradation reactions when the water-soluble species (such as 5-HMF) are concentrated.

Although petroleum ether is the most reliable solvent mixture to mimic real LSR, the study in petroleum ether is complicated due to the coinciding alkane composition with the products formed. So far in petrol, the yield of bio-based alkanes was determined by neglecting the fossil naphtha alkanes from the solvent in the integrated gas chromatography–flame ionization detector (GC–FID) signals of the

final alkane product mixture, but this methodology is unreliable for petroleum ether. Therefore, isotope ¹⁴C measurements were used to monitor the carbon origin. This low abundance isotope is less stable than ¹²C and ¹³C, and the moment a living organism dies, its ¹⁴C level decreases faster in accordance with the half-life time (5,730 years); this explains the presence of ¹⁴C isotopes in the biomass (for example, only several years old) and its absence in crude oil (millions of years old). The results of the ¹⁴C isotope measurements are summarized in Table 1, and confirm the aforementioned bio-enrichment of the naphtha streams in petroleum ether (Table 1, entry 1) and petrol (entry 2).

Conversion of real cellulosic biomass

A smooth integration of the biorefining process in current petro-refinery schemes demands a complete valorization of every component of a lignocellulosic feedstock⁴⁴. More specifically, a viable scheme should include valorization of lignin, the largest renewable source of aromatics^{5,45}. Recently, the advent of lignin-first biomass fractionation was highlighted⁴⁶, either through a depolymerization–stabilization⁴⁷ strategy or by preservation of the original ether linkages to generate a separate delignified pulp and a useful lignin oil⁴⁸. To demonstrate the cellulose-to-alkane conversion with real feedstock, birch wood was processed by reductive catalytic fractionation (RCF) to provide impure (hemi)cellulose pulp. RCF was conducted here with a Ni–Al₂O₃ pellet catalyst under a H₂ atmosphere at 523 K using methanol⁴⁹. After 3 h, a delignification degree of 84% was obtained, which provided a solid carbohydrate pulp

Table 1 | Biomass-derived content, based on GC analysis and liquid scintillation counter (LSC) ^{14}C determination, of three selected LPCtoN samples

Entry	Substrate	Substrate loading in water (wt%)	Fossil solvent	Naphtha:H ₂ O	Biomass-derived content (wt%)		Detailed information
					GC	LSC (^{14}C)	
1	Vivapur cellulose	7	Petroleum ether	25:75	10.7	12.1	Figure 2
2	Vivapur cellulose	6	Petrol	12.5:87.5	15.6	18.0	Figure 4b
3 ^a	Lignin-first carbohydrate pulp	7	Petrol	25:75	6.6	11.8	Figure 4c

^aCarbohydrate pulp, obtained after a RCF of a second-generation biomass (here, birch sawdust), is mainly composed of C₆ sugars, but also C₅ sugars, residual lignin and other impurities (Supplementary Fig. 9). This substrate composition (before LPCtoN) results, in contrast to pure cellulose as the substrate, in a larger biomass-derived content difference between the GC and LSC analysis, probably through the presence of additional soluble bio-organics.

with 83% C₅ and 93% C₆ sugar retention. Subsequently, the carbohydrate pulp was converted into alkanes, as described above, with petrol as the organic solvent (Fig. 4c and additional experiments in Supplementary Notes 6 and 7, Supplementary Figs. 9 and 10 and Supplementary Tables 4 and 5). The (hemi)cellulose-to-alkane efficiency of this reaction amounted to a 56 mol% C yield, which corresponds to a bio-based carbon enrichment of 7%. Additional analysis of the bio-enriched LSR with ^1H -NMR and ^{13}C -NMR spectroscopy (Supplementary Fig. 11) confirmed the presence of mainly (fossil and bio-derived) alkanes and only minor amounts of sugar-derived oxygenates. Phenolics, which are detrimental when present in gasoline, and aromatics in general were not found using NMR analysis of the obtained raw bio-naphtha. Given that the content of these molecules needs to be as low as possible for gasoline applications, the selective removal of lignin during RCF highlights the value of this fractionation step before LPCtoN. Besides, the presence of hemicellulose in the carbohydrate pulp did not hamper the HDO process, and resulted in more *n*-pentane formation, which is also present in typical fossil LSR (C₅–C₆) streams. The fibrous structure of the pulp after RCF, visualized by scanning electron microscopy (SEM) (Supplementary Fig. 12), and the high cellulose content substantially improve the cellulose-to-hexane efficiency (46 mol% C), in line with previous insights that reported the beneficial effect of large cellulose particle sizes and/or fibres⁵⁰. The bio-carbon enrichment from this lignin-first carbohydrate pulp was confirmed via ^{14}C isotope measurement (Table 1, entry 3). A successful integration of real lignocellulosic feedstock was thus realized, which yields valuable product streams for the chemical industry, namely, phenolics from lignin and bio-naphtha from the (hemi)cellulose pulp produced in only two catalytic steps. Although the valorization of sugar (streams) is well established in the current chemical industry (for example, bio-ethanol and paper), valorization of lignin towards phenolics is lacking at an industrial level. Today, lignin of a biorefinery, which is typically condensed/degraded, is burned for energy recuperation or used in low-value applications such as fillers. Nevertheless, recently developed lignin-first strategies are a stimulant to investigate new routes towards phenolics from native lignin with potentially high added value⁴⁶. These phenolics can be immediately integrated in the current industrial market of phenolic resins. Moreover, different lignin-derived applications, that is, bulk chemicals, such as phenol⁵¹ or new types of bisphenol polymers^{52,53}, are reported at the academic level.

Isomerization of bio-based carbon-enriched LSR

As already mentioned, petroleum ether used here resembles the C₆ part of LSR. In petrorefineries, LSR, obtained after the atmospheric distillation of crude oil, is typically hydrotreated (for example, for S removal) and isomerized to obtain a highly branched C₅–C₆ fraction. In addition, supplementary units can be integrated before and/or after a typical naphtha isomerization, for instance a benzene satu-

ration unit to decrease the aromatic content or de-isopentanizer/isohexanizer to recover low-octane molecules for multiple isomerization runs. In the end, an upgraded C₅–C₆ fraction suitable for gasoline is obtained.

The bio-enrichment of LSR with 10% bio-based carbon (denoted as LSR(10%) (Figs. 2 and 5)), following our technology, results in an alkane composition of approximately 50% *n*-hexane, and this fraction thus features a low octane number. Therefore, and in line with the activity in current petrorefineries, the fraction requires a hydro-isomerization upgrade. Isomerization is here performed in the presence of a Pt-loaded ZSM-5 zeolite, because oxygenates (<1% in LSR(10%)) and H₂O (0.5 × 10^{−3} mole fraction (estimation at room temperature based on literature⁴¹)) are reported to poison typical isomerization catalysts, such as Pt on chlorinated alumina or sulfated zirconia^{26,29,30}. Noticeably, the equimolar ratio of hydrogen to alkane of the bio-enriched naphtha stream is in line with the operating standard conditions of isomerization units (Supplementary Note 8)²⁶. Despite the impurities, identical hydro-isomerization results were obtained with LSR as well as with LSR(10%), as demonstrated in the time-on-stream profiles of Fig. 5 (the difference between the circles and squares; the full composition of the LSR isomerization (ISO(10%)) is given in Supplementary Fig. 13). The influence of individual sugar-derived oxygenates on *n*-hexane isomerization is visualized in more detail in Supplementary Figs. 14–16, which indicates that most important LPCtoN impurities, that is C₆ mono-alcohols and dimethyltetrahydrofuran, have the lowest impact on isomerization deactivation. Although long-term stability may be different, there is still the practical option to remove the valuable oxygenates (and water) by distillation and use them in the gasoline blend afterwards; this will certainly further stabilize the isomerization catalysis.

A complete material carbon balance (Supplementary Figs. 17 and 18) in combination with a process-flow diagram (Supplementary Fig. 19) from the second-generation biomass via RCF, LPCtoN and a classic isomerization towards the phenolics (85 mol% C of the original lignin) and a bio-enriched light naphtha isomerate (50 mol% C of original sugars) is extensively discussed in Supplementary Note 9 and Supplementary Tables 6–8. After isomerization, the obtained stream is blended with other petrorefinery streams until, finally, gasoline is obtained. Blending levels of the isomerate can reach up to 50% (refs ^{31,54}), which achieves at least the target of 3% advanced biofuels from second-generation biomass. Moreover, the integration of 10% biofuels in the current transportation market seems to be feasible, certainly when LPCtoN is performed with a high cellulose loading at a water to LSR volume ratio of 87.5:12.5 (Fig. 4b, Supplementary Note 2 and Supplementary Figs. 1 and 2). Besides, there is the opportunity to combine multiple biogasoline strategies, for instance bio-ethanol with bio-based carbon-enriched LSR, which may possibly enable higher amounts than 10%.

Fig. 5 | Schematic representation of the downstream integration in the isomerization unit. Hydro-isomerization of LSR and LSR(10%). LSR(10%) is obtained through a typical LPCtoN process with petroleum ether as the organic solvent (Fig. 2). Hydro-isomerization converts a mixture of mainly *n*-hexane into a mixture of mainly branched C_6 alkanes (as in the pie charts). Moreover, hydro-isomerization of LSR(10%) gives almost identical time-on-stream results to hydro-isomerization of original LSR (petroleum ether), shown in the graph. Conditions for hydro-isomerization: continuous-flow gas-phase quadri-reactor, 300 mg Pt-ZSM-5 (Si/Al = 11.5 and loading of 0.5 wt% Pt), total flow LSR = 1.56 ml h⁻¹, total flow H₂ = 90 ml min⁻¹, weight hourly space velocity = 0.84 h⁻¹ and $T = 533$ K. The dotted line represents the part of *n*-hexane in a (non-cyclic) C_6 -alkane mixture at thermodynamic equilibrium ($T = 533$ K). ISO, isomerate.

Conclusion

This work presents the direct upstream integration of bio-derived naphtha into a classic petrorefinery. An efficient two-step conversion, starting from woody resources, is demonstrated to produce a soluble multifunctional lignin oil and a solid (hemi)cellulose pulp, a feedstock readily processed into naphtha. Central to the process design is a LPCtoN conversion, which combines two immiscible solvents (organic/water), each having their own catalyst with a specific activity (either acidic sites or redox capability). By using LSR as the organic phase in the biphasic catalytic system, it becomes enriched with mostly identical hydrocarbon molecules of renewable origin, which are identified by means of ¹⁴C measurement. This allows downstream refining (hydro-isomerization and blending with gasoline) to be operated as per usual, which renders downstream separation and purification redundant, with no restrictions as to the final properties or applications. Using fossil C₅–C₆ alkanes as the organic solvent thus immediately incorporates renewable carbon into the relevant petrorefinery streams. Moreover, this route presents an elegant strategy to achieve renewability targets expressed in short-term regulation, such as the imminent 10% bio-based carbon in EU biofuels (by 2020).

Methods

Synthesis of polyacid-modified Ru/C catalyst. To obtain the polyacid-modified Ru/C, commercial ruthenium on carbon (5 wt%) was modified in a 100 ml batch reactor (Parr Instrument Co.). Ru/C (1.0 g), tungstosilicic acid hydrate (0.25 g) and water (40 ml) were loaded into the reactor. After flushing with N₂, the reactor was pressurized with a H₂ pressure of 5 MPa at room temperature. The modification was conducted with a stirring rate of 700 revolutions per minute (r.p.m.) and a temperature programme, starting at room temperature to 483 K (± 10 K min⁻¹) and kept for 1 h at 483 K. Finally, the synthesized catalyst was filtered, washed with water until the pH of the effluent was neutral and then dried to a constant weight.

LPCtoN. Hydrodeoxygenation of Vivapur cellulose (2.0 g) or (delignified) wood sawdust (between 1.0 g and 3.4 g) was carried out in a 100 ml batch reactor (Parr Instrument Co.). In addition to the substrate, a biphasic system of water:alkane ($x:40 - x$ ml, with $x < 40$), tungstosilicic acid hydrate (4.8 g) and polyacid-modified Ru/C (0.25 g), was loaded into the reactor. After flushing with N₂, the reactor was pressurized with a H₂ pressure of 5 MPa at room temperature. Subsequently,

a stirring rate of 700 r.p.m. was installed. A temperature programme from room temperature to 423 K (± 12 K min⁻¹) and further to 493 K (± 0.5 K min⁻¹) was followed. After a reaction of 5 h, the reactor was cooled, depressurized and opened for sampling and analysis. GC analysis of the organic liquid phase was performed on a Hewlett Packard 5890 GC equipped with an HP 7673 autosampler, a 60 m HP-1 column and a FID. GC analysis of the gaseous phase was performed on an Interscience Trace GC with He, equipped with Haysep Q and RTX-1 columns with a FID and thermal conductivity detector.

RCE. A typical RCE was carried out in a 100 ml batch reactor (Parr Instrument Co.). The reactor was loaded with birch sawdust (2.0 g *Betula pendula*, 0.25–0.50 mm), Ni–Al₂O₃ catalyst (0.2 g, 21% Ni) and methanol (40 ml). After flushing with N₂, the reactor was pressurized with a H₂ pressure of 3 MPa at room temperature. Subsequently, a stirring rate of 750 r.p.m. was installed. A temperature programme from room temperature to 523 K (± 10 K min⁻¹) and kept for 3 h at 523 K was followed. After the reaction, extraction with different solvents and filtration gave a lignin oil and carbohydrate pulp. Both streams were analysed and the carbohydrate pulp was further converted in the LPCtoN process.

Hydro-isomerization. The catalytic hydro-isomerization of bio-based carbon-enriched (10%) LSR was carried out in a downstream continuous-flow quadri-reactor that contained four parallel alloy 600 reactor tubes of 3 mm internal diameter. The reactor was loaded with 300 mg of Pt-ZSM-5 catalyst (Si/Al = 11.5, loading of 0.5 wt% Pt, 0.25–0.5 mm fraction) and placed in the middle part of the reactor between quartz to limit the contact time. The catalyst was synthesized via incipient wetness impregnation with tetraamineplatinum(II) chloride monohydrate and activated before reaction in three steps: (1) oxidation with an O₂ flow (20 ml min⁻¹ per reactor) at 623 K for 2 h, (2) flushing with a N₂ flow (20 ml min⁻¹ per reactor) at 673 K for 15 min and (3) reduction with a H₂ flow (20 ml min⁻¹ per reactor) at 673 K for 2 h. LSR was introduced into the system using a Perfusor Space pump (Braun) at a rate of 1.56 ml h⁻¹ (total flow) and diluted with H₂ as the carrier gas (total flow = 90 ml min⁻¹), which corresponds to a weight hourly space velocity of 0.84 h⁻¹. The reaction was conducted at 533 K and atmospheric pressure. Products were analysed with an online GC (CP-Poraplot Q-HT column) with FID.

SEM. Images were recorded by using a JEOL JSM-6010 JV microscope after coating the samples with gold using a JEOL JSC-1300 sputter.

NMR spectroscopy. In addition to GC, analysis of the organic phase after LPCtoN reaction was carried out by ¹H NMR and H-decoupled ¹³C NMR spectroscopy on a Bruker Avance 400 MHz spectrometer. Chloroform-*d* was used as the NMR solvent.

¹⁴C determination. Samples (1.0–1.5 g) were mixed with 12 ml of 2,5-diphenyloxazole (4 g l⁻¹) and dimethyl 1,4-bis-2-(4-methyl-5-phenyloxazolyl)

benzene (0.35 g l⁻¹) dissolved in a toluene scintillation cocktail. Their radiocarbon content was determined on a Tri-Carb 4810TR LSC at the 0–156 keV count region with a 300 min count time. For the calculation of the biomass carbon content, a ¹⁴C content of 13.56/0.93 disintegrations per minute per gram C was regarded as the 100% biomass carbon content.

Data availability

Supplementary Information gives additional and supporting data. Further data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

M.D., B.F.S. and A.D. conceived the LPCtoN integration. Most experimental work (catalyst preparation, SEM, LPCtoN reactions and GC analysis) was performed by A.D.,

assisted by E.P. Experimental work with the RCF was performed by T.R. and S.V.d.B. The hydro-isomerization experimental work was performed by A.D. and T.E., assisted by N.V.O. The ^{14}C determination was performed by T.S. and T.I.K. Data analysis and writing was done by A.D. supported with the critical input of M.D. and B.F.S.

Competing interests

M.D. and B.F.S. have a pending patent (WO2015172208A1) on the LPCtoN technology. The other authors declare no competing interests.

Additional information

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