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BIOFUELS

Bio-enriching gasoline

Combining biofuel synthesis with petrorefinery operations may provide efficiency benefits, but procedures to do so are not yet well-established. Now, researchers describe a two-phase catalytic scheme for production of 10% bio-enriched gasoline by directly using petroleum fractions in the catalytic processing of (hemi)cellulose.

Katalin Barta

The ever-growing use of fossil-derived transportation fuels contributes to the increasing global levels of atmospheric carbon dioxide¹. To mitigate the adverse environmental impact caused by these greenhouse gas (GHG) emissions, and to decrease societal dependence on non-renewable petroleum, several directives have been put forward worldwide to stimulate the use of liquid energy carriers derived from renewable resources^{2–4}. For example, the European Union aims for a 20% reduction in GHG emissions by 2020, largely by ensuring that at least 10% of transportation fuels are bio-based. The United States are aiming to use 36 billion gallons of biofuels, including advanced biofuels, by 2022 (ref. ³).

Bioethanol and biodiesel, typically blended with conventional fuels in various proportions (expressed by E and B values, respectively), represent biofuel alternatives that are already implemented. However, reaching the 10% bioethanol content (as per the EU target) would require engine modification due to incompatibility issues (the ‘blend wall’ that limits the amount of ethanol that is blended with gasoline)⁴. In addition, both bioethanol and biodiesel are primarily first generation — meaning that they are obtained from edible resources such as corn, sugarcane or vegetable oils and thus may represent competition with the food supply^{4,5}. These limitations will require a shift toward the use of non-edible second-generation resources such as cellulose as well as the identification of suitable targets that would serve as alternative liquid energy carriers^{4–6}. However, cellulose is a much more challenging substrate due to its recalcitrance and feasible, scalable catalytic approaches are lacking. In order to reach the 10% biofuel target by 2020, new, robust catalytic solutions are urgently required and these evolving technologies need to be compatible with large-scale production⁴. Now, writing in *Nature Energy*, Michiel Dusselier, Bert Sels and coworkers at Katholieke Universiteit Leuven and the Hungarian Academy of Sciences Centre for

Fig. 1 | Established and emerging strategies for increasing bio-based carbon content in gasoline. a, Bio-ethanol is an established first-generation biofuel, which is typically produced by fermentation and subsequently blended with crude-oil-derived gasoline. **b,** Dusselier, Sels and colleagues achieve 10% bio-enriched fuel from cellulose by using light straight run (LSR) naphtha derived from crude oil directly as the organic phase in the biphasic organic–aqueous catalytic processing of cellulose. Monosaccharides are converted into bio-based alkanes and oxygenates (some examples are shown in the yellow bubble), moving from the aqueous phase to the organic phase. MCP, methylcyclopentane; RON, research octane number

Energy Research describe the production of bio-based gasoline from cellulose and lignocellulose in a manner that not only allows for but explicitly relies on integration into existing petrochemical refinery schemes⁷.

In a conventional refinery, crude oil is separated into several fractions by distillation. One of these fractions is light straight run (LSR) naphtha, a low-boiling fraction that mainly consists of C5–C6 alkanes. Glucose, the monosaccharide making up cellulose that bears a six-carbon-atom skeleton, would also turn into C6 alkanes upon exhaustive hydrodeoxygenation (HDO) at reaction temperatures low enough to maintain the C6 connectivity. In their clever approach, Dusselier, Sels and colleagues use the LSR naphtha cut of petroleum (C5–C6 alkane fraction) itself as part of a biphasic reaction medium in which cellulose is converted to mainly (C6) alkanes, leading to enrichment

of the original alkane mixture with virtually identical, but bio-based, components.

This process is dubbed Liquid Phase Cellulose-to-Naphtha (LPCtoN) technology. Central to the process is a biphasic catalytic system that consists of an aqueous and an organic phase (the naphtha cut itself), both incorporating an appropriate catalytic function designed for the above-mentioned multistep cellulose-to-alkane conversion. The aqueous layer carries a soluble heteropolyacid catalyst ($H_3SiW_{12}O_{40}$) and is responsible for ‘cutting’ the cellulose into smaller monosaccharide units, as well as their further dehydration, mostly to furanics such as 5-hydroxymethylfurfural (5-HMF). These cyclic oxygenated intermediates then partition to the organic phase and undergo full HDO to produce (C6) alkanes via a series of hydrogenation and dehydration events promoted by a bifunctional acid-metal catalyst (polyacid-modified Ru/C).

Applying the LSR cut to serve as the organic phase for the HDO is a remarkable choice by the researchers, since one would expect insufficient solubility of the oxygenated intermediates in the apolar alkane phase. Nevertheless, the elevated temperatures appear to markedly increase the solubility of water in hydrocarbons. The researchers therefore hypothesised and experimentally confirmed that the ability of the alkanes to efficiently extract oxygenated intermediates is also enhanced at the reaction temperature (493 K), ensuring high product yields.

Because the alkane mixtures after LPCtoN treatment consist of molecules originating partly from petrochemicals and partly from renewables with largely overlapping compositions, the extent of bio-enrichment was confirmed by using a ^{14}C isotope-labelling technique. The half-life of the ^{14}C isotope is 5,736 years — and crude oil is much older than that — so this measurement only detects carbon atoms derived from fresh biomass. Overall, an 11–18% bio-based carbon enrichment was measured, depending on process conditions.

The obtained fuel, which is enriched with bio-based naphtha, consists of mainly linear alkanes (n-hexane being the major component; see Fig. 1) and so its research octane number (RON) is not sufficient for use in typical gasoline engines. Therefore, the researchers apply an isomerization step

using Pt/ZSM-5 as the catalyst. This elevates the RON from an average of 50 to 80 and produces the desired bio-enriched fuel that is ready to be blended with other refinery streams to form gasoline.

Notably, the described LPCtoN methodology is compatible with other emerging 'lignin-first' technologies that utilize raw lignocellulose as the starting material, thus enabling the utilization of both the lignin and the (hemi)cellulose fractions of lignocellulose. In most of these technologies, a reductive processing step is performed to obtain aromatic monomers from lignin, while the remaining crude (hemi)cellulose residue is subjected to the LPCtoN process, to give alkane products similar to those obtained with pure cellulose starting materials, albeit with a slightly higher fraction of C5 alkanes due to the hemicellulose present.

In summary, the presented catalytic strategy is elegant as it allows for desired reaction pathways from cellulose to C6 alkanes with minimal C–C bond cleavage, taking advantage of catalyst compartmentalization in a biphasic reaction medium where one of the phases is light naphtha itself. The reaction product is bio-enriched light naphtha, which can be directly integrated into existing infrastructures and therefore would facilitate possible commercialization. The process scheme, including material

balances provided by the researchers, shows promising opportunities for upscaling. However, several aspects require further exploration, such as catalyst stability and recyclability and the effect of small amounts of bio-based oxygenates on further processing units. Moreover, coupling the hydrodeoxygenation step, which uses 80 kg of H_2 per ton of carbohydrate, with emerging renewable H_2 technologies⁸ might be an interesting future direction. Nevertheless, the results presented here are an exciting step toward achieving the ambitious 10% bio-based carbon target for liquid transportation fuels.

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