The hydrodeoxygenation of bioderived furans into alkanes

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The conversion of biomass into fuels and chemical feedstocks is one part of a drive to reduce the world's dependence on crude oil. For transportation fuels in particular, wholesale replacement of a fuel is logistically problematic, not least because of the infrastructure that is already in place. Here, we describe the catalytic defunctionalization of a series of biomass-derived molecules to provide linear alkanes suitable for use as transportation fuels. These biomass-derived molecules contain a variety of functional groups, including olefins, furan rings and carbonyl groups. We describe the removal of these in either a stepwise process or a one-pot process using common reagents and catalysts under mild reaction conditions to provide *n*-alkanes in good yields and with high selectivities. Our general synthetic approach is applicable to a range of precursors with different carbon content (chain length). This allows the selective generation of linear alkanes with carbon chain lengths between eight and sixteen carbons.

he world's major oil fields have been in production decline for decades¹⁻⁵. The use of heavy oil, shale oil and oil sands is ramping up, but at an insufficient rate to compensate for the production losses in the oil fields. Fossil fuel consumption is also projected to increase further, with potentially catastrophic consequences for global ecosystems^{6,7}. Sustainable and renewable alternatives to petroleum are therefore critically needed to fill future gaps in the supply of transportation fuels and chemical feedstocks⁸.

The conversion of crude oil into fuels and synthetic feedstocks has been investigated for more than a century, resulting in an enormous body of knowledge and an understanding of the processes required to effect these transformations. In contrast, however, there is only limited scientific and engineering knowhow on how to catalytically convert biomass-derived molecules into hydrocarbons for fuels and chemical feedstocks. The conversion of fossil fuel-derived molecules into useful petrochemicals, polymers and so on represents an issue of chemical 'underfunctionalization'⁹. Research and development in the field of catalysis has traditionally been aimed at introducing necessary functionality into these molecules via processes such as hydroformylation, amination, oxidation, among others. However, biomass-derived molecules such as carbohydrates pose the opposite problem of being overfunctionalized by virtue of having an abundance of oxygen atoms.

To access species such as high-energy-density hydrocarbons from these bioavailable sources, efficient dehydration, hydrogenation and hydrogenolysis reactions are required. By necessity, such conversions will have to be catalytic in nature, but this area represents a complete paradigm shift from traditional catalysis science, which has focused on the development of chemo-, regioand enantioselective catalysts and processes. In contrast, the efficient production of transportation fuels from non-food-derived biomass requires the opposite approach: the development of promiscuous, non-selective catalysts capable of dehydrating, hydrogenating and deoxygenating a wide variety of functionalities (including hydroxyl, olefinic and ketonic groups), in as few steps as possible to perform reactions in non-traditional media (that is, water or water mixtures) under acidic conditions. This significantly increases the overall difficulty in effecting what may be viewed, by some, as trivial reactions. The robustness of existing catalysts traditionally applied to fossilderived source upgrading would indeed be put to severe test under the constraints listed above. Although this scenario presents some daunting challenges, it also presents some great opportunities to redefine and advance some areas of modern catalysis science.

Carbohydrates are an attractive carbon source for use as transportation fuel synthons¹⁰. Glucose and xylose, as the main building blocks of ligno-cellulosic biomass, are the most abundant monosaccharides on the planet and their use as a fuel precursor represents a worthwhile target if cost-effective (hemi-)cellulose depolymerizations and chemical transformations of the resulting monomers or their dehydrated derivatives such as methylfurfural (FF) or 5-hydroxy-methyl-furfural (HMF) can be developed. In addition to the overfunctionalization problem alluded to above, the carbon chain lengths of these molecules, once hydrodeoxygenated, are in general too short for transportation fuel purposes (that is, they have low boiling points and lack sufficient specific energy density for this purpose). However, the furan aldehydes derived from hexoses and pentoses offer pathways for the desired chain extensions via aldol condensation chemistry (see below)¹¹. Moreover, lignocellulose and corn stover have been directly converted into furans for fuels and chemical applications¹². Coupling these aldehydes with other biomass-derived carbon units using aldol condensation chemistry is thus an attractive route towards fuel precursors of sufficient energy density.

Recently, Dumesic and co-workers reported a hydroxide-based method (that relies on sodium hydroxide in non-catalytic quantities) to promote aldol reactions for the elongation of furan aldehydes using ketones. This approach indeed promotes carbon chain extensions, but does so in a non-selective manner as a result of self- and cross-condensation chemistries under the conditions studied¹³. The resulting deoxygenation of these molecules (carried out in the same reaction vessel) provided a complex mixture of molecules ranging from C_1 to C_{15} in chain length

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Figure 1 | **Organocatalysed routes to chain extended furfurals.** A range of different extended FFs can be prepared by varying the components of the aldol reaction to give derivatives with between eight and sixteen carbon atoms. In this case, by altering the stoichiometry using acetone, we can generate C₉ (A and B) or C₁₅ (C) precursor molecules.

under high H_2 pressures and high temperatures. Intrigued by this report, we recently investigated the use of water-soluble and inexpensive organocatalysts for selective chain extension chemistries of FF and HMF. Organocatalysts can eliminate the need for large quantities of caustic base or flammable organic solvents, and in some cases their reactions can be run solventless^{14,15}. These classes of catalyst also potentially lend themselves to support on solid matrixes, making the separation of products and reuse of catalyst potentially more viable.

This general organocatalysed aldol approach has provided us with access to a range of isolable furfuraldehyde-based derivatives with between eight and sixteen carbon atoms. The details of this work have been described elsewhere^{11,14,15}. Examples of C₉ and C₁₅ fragments derived from the organocatalysed aldol reaction between acetone and either HMF or methylfurfural (FF) are shown in Fig. 1 (ref. 11). It should be noted that acetone itself is also available from renewable biomass through fermentation or via the sequence EtOH \rightarrow HOAc \rightarrow acetone (the last step being a catalytic ketonization)¹⁶.

Results

Compounds accessible by organocatalysed aldol routes still need to be defunctionalized to alkanes to provide utility as 'drop-in' fuel replacements. This is the subject of the work described in detail in the following. From our perspective, achieving the synthesis of hydrocarbons requires three key chemical transformations to be effected on these classes of molecules: ring opening of furans, hydrogenation of olefins, and hydrodeoxygenation (HDO) of ketones. The order in which these are carried out proved to be crucial to the efficacy of our approach.

Initial hydrogenation and divergent reaction pathway. A significant proportion of our efforts focused on the study of C₉ compounds, and, within this class, two particular systems were studied. As shown in Fig. 1, one is derived from the aldol condensation between FF (R=H) and acetone A, and the other is derived from the corresponding reaction between HMF (R=OH) and acetone B. Removal of the exocylic double bond within these classes of molecules proved to be a key first step for the subsequent HDO chemistry to be successful, as it prevents fragmentation of the substrate by retro-aldol reaction in the aqueous reaction medium. This can be accomplished using several approaches and we initially used stoichiometric reagents such as Mg/MeOH (see Supplementary Information). However, a report from Ram and Spicer indicated that such exocylic unsaturation could also be removed using catalytic transfer hydrogenolysis with ammonium formate in acetic acid¹⁷. This approach also proved applicable to A and B and we further simplified the method by replacing ammonium formate with H₂ gas. This enabled us to readily remove the exocyclic saturation by, for example, heating A to 65 °C in the presence of palladium (0.16 mol%), under 1 atm



Figure 2 | Removal of exocyclic unsaturation. The key first step in this conversion is removal of the carbon-carbon double bond to give species 1 and 2. This can be achieved in a variety of ways, but using a palladium catalyst with H_2 gas with gentle heating proved to be the most successful approach.

of H_2 in a 50% aqueous acetic acid solution to give 1 (Fig. 2). The same approach can be applied to **B** to give 2 in excellent isolated yield.

While attempting to achieve milder conditions for the removal of exocyclic unsaturation in **B**, divergent reaction pathways were observed that are dependent on the rate of furan hydrogenation versus furan ring-opening (Fig. 3). Using solvents that promote higher H_2 solubility and faster reaction kinetics (for example, THF or MeOH; see Supplementary Information), complete hydrogenation of 2 occurs to give compound 3.

The other pathway occurs under acidic conditions where the solubility of H_2 is lower. For example, the use of dilute aqueous acetic acid solution allows acid-promoted ring-opening to occur faster than furan hydrogenation, resulting in 2,5,8-nonanetrione 4 as the sole product. We can completely avoid the formation of 3 from B by preparing 2 *in situ* and then heating the acidic solution in air (thereby releasing H_2 and preventing further reduction) to form 4 in one pot in excellent yield (Fig. 3). Product 2 can be readily isolated and dissolved in acidic solutions and heated to generate 4, allowing for a one-pot or stepwise synthesis of the polyketone. As a point of note, A and B can both act as precursors for the formation of triketone 4 due to the facile hydrogenolysis of the hydroxymethyl group in B to a methyl group under the acidic conditions and temperatures required for ring-opening.

The formation of 4 from 2 provides a facile route to generate hydrocarbons (see below) from aldol condensation products without having to potentially resort to the more forcing conditions required to ring-open a tetrahydrofuran^{18,19}. The tendency to fully hydrogenate species such as **A** or **B** is well recognized¹³ but, in the case of these particular biomass-derived constructs, we have observed that exerting selective control over hydrogenation of the exocyclic unsaturation first, followed by furan ring-opening, rather than attempting to ring-open a saturated tetrahydrofuran fragment, provides a milder route to generate hydrocarbons. Thus the formation of species such as **3** should be (and can be) avoided.

Hydrogeoxygenation (HDO) reaction and alkane production. To facilitate subsequent oxygen atom removal and perform the desired HDO chemistry, we envisioned that a Lewis or Brønsted acid could aid in the removal of the C=O bonds in 4 via iterative reduction and dehydration, and the resulting unsaturation could then be reduced with H_2 and a suitable hydrogenation catalyst. Initial forays in this regard revealed that conversion into the corresponding *n*-alkane was achieved upon the addition of La(OTf)₃ to a mixture of Pd/C, acetic acid and the polyketone, and heating this mixture at 200 °C under H_2 pressures up to 3.45 MPa for 12 h (see Methods). Tetrahydrofuran species such as 3 proved to be completely unreactive under any HDO conditions that could

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Figure 3 | Divergent pathway leads to different products. Full

hydrogenation of the furan ring to form **3** proved to be a dead end for the synthesis of alkanes under mild conditions. However, if the ring is opened to a polyketone (**4**) before this can happen, this provides a significantly lower energy route to generate alkanes (**5**) selectively in excellent yield.

convert polyketones into hydrocarbons (Fig. 3) emphasizing the importance of avoiding the formation of such species.

At pressures less than 0.69 MPa, the HDO chemistry appeared to be sluggish and gave rise to mixtures of intermediate (that is, partially deoxygenated) products. As the H₂ pressure was increased above 1.03 MPa, the reaction proceeded rapidly to provide a single alkane product. Similarly, at temperatures less than 180 $^{\circ}$ C, HDO did not proceed at any of the pressure tested (up to 2.76 MPa).

The method described above for accessing polyketones and the subsequent HDO reaction appears to be general for a variety of aldol products containing different carbon chain lengths (Fig. 4). This provides a facile general route to *n*-alkanes with *n*-nonane, *n*-dodecane and *n*-pentadecane being readily isolated in 87%, 76% and 65% isolated yields, respectively (based on the corresponding

polyketone). All alkane products were authenticated by gas chromatography mass spectrometry (GC–MS) and comparison of their ¹³C and ¹H NMR spectra to those of pure authentic reference samples.

In the case of 4 (prepared from A), the HDO chemistry to form n-nonane was followed by H₂ uptake measurements (see Supplementary Information for these experimental details). These studies revealed that 6 equiv. H₂ are consumed in the reaction to form n-nonane. This observation accounts for the reduction of the C=O bonds and the unsaturation following dehydration of the resulting –OH groups leading to the formation of 3 equiv. H₂O. GC/GC–MS analysis of this reaction also affirmed that no triketone remained, and quantitative GC analysis of the reaction solutions using calibrated standards of n-nonane indicated that the alkane is produced in \geq 90% yield. The remaining mass balance is attributed to coking and the formation of small amounts of CO₂, as observed in the headspace of the reaction vessel by micro-GC against an authentic CO₂ gas sample.

In a further refinement of this approach, we assumed that $La(OTf)_3$ could be simply acting as a source of triflic acid (TfOH) in solution. Thus, the dissolution of polyketones 4 or 10 in 1 M aqueous TfOH in the presence of palladium under the same conditions of temperature and H₂ pressure permits the production of the corresponding *n*-alkane without the necessity for a lanthanide metal. Similarly, performing the reaction with 1 M HCl in the absence of a Lewis acid yields similar results but at higher palladium catalyst loadings (16 mol%). This general Lewis acid-free approach can also be applied to other polyketones to afford the corresponding *n*-alkanes.

Owing to the commonality of substrate functionalities and reagents used to effect exocyclic double-bond removal, furan ringopening, followed by HDO of the resultant polyketones, it became evident that isolation of each intermediate on the way to hydrocarbons may not be required. We therefore demonstrated that the formation of 4 can readily be achieved in a single vessel without the need for isolation of 2. Having achieved the formation of polyketones without the need for the isolation of intermediates, we believed that further process refinement could achieve complete conversion into n-alkanes, directly from the initial aldol constructs in a single vessel.

One-pot synthesis of alkane from bioderived precursor. The solubility of the aldol condensation products (A, B, C and D) is limited in water alone, and the higher temperatures required for HDO result in increased substrate decomposition and charring,



Figure 4 | Conversion of carbon chain extended furans into polyketones and *n*-alkanes. This general synthetic approach to use palladium, H₂ and acid to generate alkanes is applicable to a range of aldol products, all of which share the same furan, alkene and carbonyl functional groups. This allows us to isolate a range of different linear alkanes.

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Figure 5 | One-pot synthesis of *n***-nonane.** Isolation of the intermediates is not necessary, and we can successfully produce alkanes from the aldol products by control of the reaction conditions.

thus limiting the use of 1 M HOTf or 1 M HCl as a solvent for all steps. However, the solubility of these compounds in acetic acid solutions (10% by volume, up to glacial acetic acid) is excellent and allows for a one-pot sequential synthesis of n-nonane. The initial hydrogenation and ring-opening steps of A or B can be achieved in 3 h by heating at 100 °C, under 0.34 MPa H₂, in the presence of 1.6 mol% palladium in glacial acetic acid. Formation of 4 is confirmed by NMR spectroscopy carried out on an aliquot of the reaction mixture. Upon complete conversion to 4, La(OTf)3 can then be added, and the reaction mixture repressurized to 2.07 MPa H₂ and heated at 200 °C for 12 h to yield the n-alkane in 74% isolated yield (Fig. 5). It should be noted that when performing this reaction at sufficient scale, phase separation of *n*-nonane is observed. $La(OTf)_3$ can also be added at the initial hydrogenation/ring-opening stage as this does not impinge upon the initial hydrogenation or ring-opening sequences.

We performed several control experiments to rule out the possibility of stainless steel (SS-316) playing a role in the catalysis²⁰. As described, the polyketones can be prepared in glass vessels. To investigate the role of SS-316 in the subsequent HDO steps, we had several of our reaction vessels and fittings coated with Dursan by Silcotek, which provides increased resistance to strong acids. The use of these vessels led to results identical to those in the untreated vessel. Although a small portion of the reactors still had exposed stainless-steel surfaces (pressure gauges, pressure relief devices and so on), this suggested that SS-316 was not playing a role in the catalysis. To further examine this, we also performed control experiments to probe the background catalytic activity of the SS-316 vessels by heating samples of 4 or 10 at 200 °C under 1.38 MPa H₂ for 14-24 h in the presence of glacial acetic acid, 1 M HCl or 1 M HOTf, but in the absence of palladium and/or Lewis acid (see Supplementary Information for experimental details). In all cases studied, conversion of the polyketone into the corresponding alkane was not observed, thus ruling out any significant contribution to HDO chemistry by SS-316 under the conditions applied. However, other acid-based reactivity was observed. For example, 4 dehydrated in the presence of 1 M HOTf acid to ring-close to the exocyclic hydrogenated analogue of A, which is a reaction pathway we have previously observed in glass vessels in the absence of SS-316²¹. Other side reactions resulting from reaction of these acids with 4 and 10 are observed, but alkanes are not produced unless the appropriate combination of hydrogenation catalyst and/or lanthanide containing Lewis acid is present in the vessel.

Discussion

The selective conversion of biomass-derived furans into linear alkanes under mild conditions represents a significant advance towards the production of fuels from non-food-based biomass sources. These conversions can be carried out sequentially in a 'one-pot' approach without isolation of the intermediates. A variety of linear alkanes can be produced selectively in good to excellent yields from bioderived constructs provided by organoaldol chemistry. This provides a powerful synthetic and general approach for the production of higher linear alkanes C_nH_{2n+2} with $n \ge 9$ for

fuel applications. The very general methodology has been refined further to simply use palladium in aqueous acids to generate linear alkanes in excellent yield under conditions similar to those that have previously been shown to allow for recycling of palladium and application in industrial processes^{22,23}.

The key distinguishing feature of our approach is accessing the intermediacy of furans and their ability to undergo hydrolytic ring-opening to polyketones. This subtle modification has significant consequences in terms of minimizing the energy input required to transform these molecules to linear alkanes. Although it is well documented that hydrocarbons can be produced non-selectively from tetrahydrofuran intermediates, much greater forcing conditions are required than we have described (300 °C, 5.5 MPa H₂)¹³.

In conclusion, we have demonstrated the feasibility of alkane production using relatively mild conditions, and we are currently developing this chemistry further through catalyst lifetime and recycle studies with specific application towards scale-up.

Methods

General experimental. Compounds **A**, **B**, **C** and **D** were synthesized as described previously¹¹. Deuterated solvents were purchased from Cambridge Isotope Laboratories. All chemicals and reagent grade solvents were obtained from Acros and used as received. ¹H and ¹³C NMR spectra were obtained at room temperature on a Bruker AV400 MHz spectrometer, with chemical shifts (δ) referenced to the residual solvent signal (¹H and ¹³C). GC–MS analysis was carried out using a Hewlett-Packard 6890 GC system equipped with a Hewlett-Packard 5973 mass selective detector. Illustrative examples of the conversion of **A** and **B** to *n*-nonane are described in the following. Additional experimental procedures, including H₂ uptake measurements involved in the conversion of **3** into *n*-nonane and the synthesis of *n*-dodecane and *n*-pentadecane, are provided in the Supplementary Information.

Conversion of A into 2,5,8-nonanetrione 4. A (563 mg, 3.75 mmol) was dissolved in a 50% vol/vol solution of acetic acid in H_2O (15 ml) and Pd/C added (13 mg of 5 wt% Pd/C, 0.006 mmol Pd, 0.16 mol% Pd relative to substrate). The solution was added to a round-bottom flask, placed under an atmosphere of H_2 (balloon), and heated at 65 °C for 2 h to yield a near-colourless solution of 1 in quantitative yield, as confirmed by GC–MS and NMR on an aliquot. The flask was then equipped with a condenser, opened to the air, and heated at 100 °C for 3 h to yield a pale yellow solution. On cooling, the solution was filtered to remove the Pd/C and the aqueous layer was neutralized with NaHCO₃, extracted with dichloromethane (3×5 ml), dried over Na₂SO₄, filtered and solvent removed *in vacuo* to yield 3 (0.589 mg, 92% yield). ¹H NMR (400 MHz, CDCl₃) δ 2.92–2.44 (m, 8H), 2.42–1.97 (m, 6 H). ¹³C NMR (101 MHz, CDCl₃) δ 207.99, 207.30, 36.99, 36.09, 29.87.

Conversion of B into 2,5,8-nonanetrione 4. B (830 mg, 5.00 mmol) was dissolved in a 50% vol/vol solution of acetic acid in $\rm H_2O$ (15 ml) and Pd/C added (83 mg of 10 wt% Pd/C, 0.08 mmol Pd, 1.6 mol% Pd relative to substrate). The solution was added to a round-bottom flask and put under an atmosphere of $\rm H_2$ using a balloon and heated at 65 °C for 1 h to yield a pale yellow solution of 2. The flask was then equipped with a condenser, opened to the air and heated at 100 °C for 3 h to yield a colourless solution. On cooling, the solution was filtered to remove the Pd/C, the aqueous layer was neutralized with NaHCO₃ and extracted with dichloromethane (3 × 5 ml), dried over MgSO₄, filtered and solvent removed *in vacuo* to yield 3 (817 mg, 96% yield). ¹H NMR (400 MHz, CDCl₃) δ 2.92–2.44 (m, 8H), 2.42–1.97 (m, 6 H). ¹³C NMR (101 MHz, CDCl₃) δ 207.99, 207.30, 36.99, 36.09, 29.87.

Synthesis of *n*-nonane 5. To a 25.00 ml volumetric flask, 851 mg (5 mmol) of 4 was dissolved in glacial acetic acid together with dimethyl sulfone (DMS) (235.3 mg, 2.5 mmol) as an internal standard for GC–MS to yield an orange solution. The solution was sonicated for 5 min and then loaded in the autoclave reactor with Pd/C (170 mg of 5 wt% Pd/C, 0.08 mmol Pd; that is, 1.6 mol% Pd relative to substrate) and La(OTf)₃ (426 mg, 0.727 mmol) and sealed. The reactor was pressurized with H₂ to 3.45 MPa and vented three times to remove any residual oxygen atmosphere. The reactor was pressurized to 3.45 MPa one final time and heated to the desired reaction temperature (200 °C). After 16 h the reactor was cooled to room temperature and the H₂ pressure released. The sole reaction product was identified as *n*-nonane (90% yield) with no 4 remaining, as confirmed by GC–MS. ¹H NMR (400 MHz, CDCl₃) δ 1.29 (m, 14H), 0.88 (s, 6 H). ¹³C NMR (101 MHz, CDCl₃) δ 32.14, 29.73, 29.57, 22.81, 14.23.

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Author contributions

A.D.S. made the initial discovery. A.D.S., M.S., L.A.S. and J.C.G. conceived and designed the experiments. A.D.S. and F.D.W. performed the experiments. R.W. and L.A.S. contributed materials. A.D.S. and J.C.G. co-wrote the paper. All authors discussed the results and provided input for the manuscript.

Additional information

Supplementary information and chemical compound information are available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to A.D.S. and J.C.G.

Competing financial interests

The authors declare no competing financial interests.