

Upgrading Lignocellulosic Products to Drop-In Biofuels via Dehydrogenative Cross-Coupling and Hydrodeoxygenation Sequence

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Life-cycle analysis (LCA) allows the scientific community to identify the sources of greenhouse gas (GHG) emissions of novel routes to produce renewable fuels. Herein, we integrate LCA into our investigations of a new route to produce drop-in diesel/jet fuel by combining furfural, obtained from the catalytic dehydration of lignocellulosic pentose sugars, with alcohols that can be derived from a variety of bio- or petroleum-based feedstocks. As a key innovation, we developed recyclable transition-metal-free hydrotalcite catalysts to promote the dehydrogenative cross-coupling reaction of furfural and alcohols to give high molecular weight adducts via a transfer hydrogenation–aldol condensation pathway. Subsequent hydrodeoxygenation of adducts over Pt/NbOPO₄ yields alkanes. Implemented in a Brazilian sugarcane biorefinery such a process could result in a 53–79% reduction in life-cycle GHG emissions relative to conventional petroleum fuels and provide a sustainable source of low carbon diesel/jet fuel.

The transportation sector is responsible for 13% of global greenhouse gas (GHG) emissions, and 95% transportation energy demand is met by petroleum.^[1] Concerns regarding climate change and security of supply have prompted countries around the world to adopt policies that encourage growth of renewable fuels and research into development of new low-carbon fuels. However, early investments in biofuel production have relied on resource-intensive crops and led to fuels such as ethanol and routes involving furans have gained promi-

nence.^[2] Although these studies hold great promise for creating drop-in fuel alternatives, there are several major gaps that limit the practical applicability of these technologies. For example, some discoveries involve biodiesel that are incompatible with the existing fuel infrastructure and also subject to blend wall (maximum allowable fraction of biodiesel blended into petroleum diesel) limitations. The thermochemical catalytic conversion of sugars into diesel range fuels has gained credibility over the past decade and routes involving furans have gained prominence.^[2] While these studies hold great promise for creating drop-in fuel alternatives, there are several major gaps that limit the practical applicability of these technologies. For example, some discoveries involve utilization of stoichiometric quantities of reagents such as NaOH or homogeneous organo-catalysts while some others have limited substrate scope for nucleophiles.^[2a,b,d] Perhaps the biggest research gap is the lack of integration between developing fuel technologies and an understanding of the impact that these technologies can have on net GHG emissions. Such an understanding can help not only researchers to develop strategies that reduce GHG emissions but also policy makers to enact regulations in an informed fashion.

The limitations of previous fuel pathways and our interest in catalytically upgrading fermentation products to biofuels^[3] prompted us to explore an alternate strategy utilizing the cross-coupling reaction of furan building blocks with alcohols and integrating life-cycle assessment (LCA) at an early stage to quantify the impact of our technology in reducing “well-to-wheel” GHG emissions relative to petroleum. In our scheme, we assumed that furans could be sourced from lignocellulosic biomass using existing technologies,^[4] whereas the alcohols could be produced from renewable sources through several routes such as traditional fermentation, enzymatic biocatalysis, or chemical catalytic schemes.^[3,5] Our key innovation lies in the chemical process, and we demonstrate the utility of the dehydrogenation–aldol sequence between alcohols and furfural to produce furan adducts over recyclable hydrotalcite (HT), which to the best of our knowledge has not been reported elsewhere.^[6] Furancarbinols are produced as by-products and these can be reoxidized to furfural and reused in the reaction scheme (Figure 1).^[7] On the other hand, the furan adducts can be hydrodeoxygenated over a suitable catalyst such as heterogeneous bifunctional platinum on niobium phosphate (Pt/NbOPO₄) to yield hydrocarbons (C₇–C₂₀) that can be used as blendstocks for jet and diesel fuels (Scheme 1). Practical ap-

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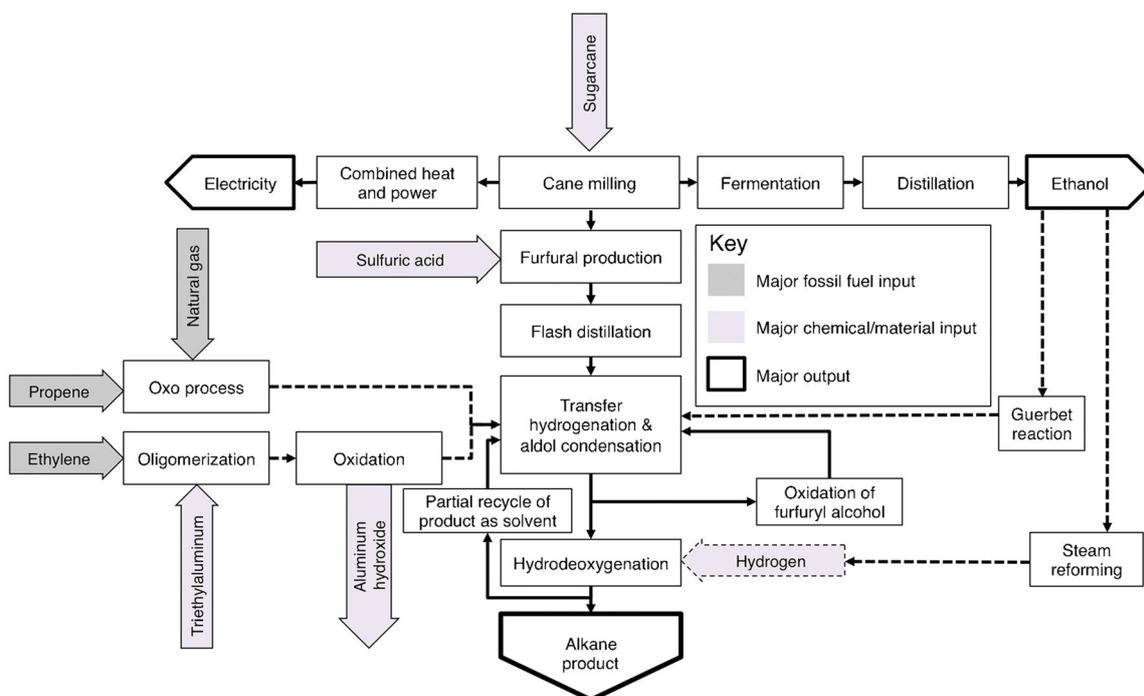
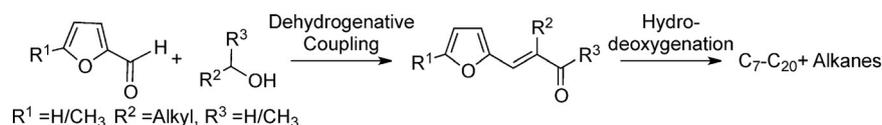


Figure 1. Process flow diagram for the conversion of sugarcane to ethanol and alkanes, generating electricity as a co-product. Three possible sources for alcohol are indicated by dashed lines: petroleum-based butanol, higher alcohols, or bioalcohols produced through Guerbet reaction.



Fermentative and non-fermentative routes: 1-propanol, 1-butanol, 3-methyl-1-butanol, 1-pentanol, 1-hexanol, 1-phenylethanol, 1-octanol, 2-propanol

Chemical treatment of sugars: 1,6-hexanediol (illustrative example)

Chemical hydrolysis of FAME: 1-tetradecanol (illustrative example)

Scheme 1. Synthetic strategy to upgrade lignocellulosic furfural to high value biofuels.

proaches to biofuel production could utilize raw materials and intermediates from various sources and each of these routes has a strong impact on overall GHG emissions. To understand this aspect further, we use a combination of process synthesis and LCA to model a Brazilian biorefinery. Using our experimental results and existing literature, we analyze the tradeoffs associated with different sources of hydrogen and higher alcohols and determine the GHG intensity of various pathways. This allows us to examine the feasibility of our technology for producing diesel fuels for complying with regulations set in parts of United States as well as in Europe by the Renewable Energy Directive and its fallout in various member states.

We began our optimization studies for the coupling of furfural (1) with 1-butanol (2) by screening first-row transition metal catalysts in conjunction with substoichiometric amounts of potassium carbonate as base (Table 1). Iron(II) salts remained inactive for the desired dehydrogenative coupling reaction to yield the furan adduct 3 (Table 1, entry 1). Copper(II) acetate was active but also promoted the Tishchenko type reaction, giving

ester 4 along with the desired compound 3 in low selectivity (Table 1, entry 2). On the other hand, Ni(dppe)Cl₂ (dppe = ethylenebis(diphenylphosphine)) was considerably more active under homogenous reaction conditions and almost exclusively gave the furan adduct 3 (Table 1, entry 3). Control experiments performed either without nickel catalyst or without potassium carbonate

Table 1. Optimization of olefination of furfural using 1-butanol.

Entry ^[a]	Catalyst	Base	3/4 ^[b]	Yield ^[c]
1	Fe(BF ₄)·6H ₂ O	K ₂ CO ₃	–	–
2	Cu(OAc) ₂	K ₂ CO ₃	3:1	10
3	Ni(dppe)Cl ₂	K ₂ CO ₃	> 99:1	75
4	–	K ₂ CO ₃	–	–
5	Ni(dppe)Cl ₂	–	–	–
6	–	HT ^[d]	> 99:1	55
7	–	HT ^[e]	> 99:1	82

[a] Reaction conditions: 1-butanol (1 mmol), 2-furfural (2 mmol), metal catalyst (5 mol%), base (30 mol%), 145 °C, toluene (1 mL), 20 h. [b] Selectivity determined by GC analysis of the crude sample; yield determined by calibrated internal standard (*n*-dodecane) on GC-FID. [c] Yield in parenthesis include corresponding alcohol of 3. [d] HT = Mg₆Al₂(OH)₁₆CO₃·4H₂O, 0.4 g, HT was calcined at 500 °C for 4 h prior to use, 150 °C, 7 h. [e] 20 h.

did not provide aldehyde **3** but instead furnished the undesirable furan dibutyl acetal in both cases (Table 1, entry 4 and 5). These results show that both the metal and the base play an important role in the reaction, which is suggestive of a transition metal-catalyzed hydrogen-borrowing-type mechanism.^[8]

Based on an earlier report wherein heterogeneous potassium phosphate was shown to be active in the transfer hydrogenation of aromatic aldehydes and ketones,^[9] we envisaged that a recyclable heterogeneous base would allow us to implement our reaction both under batch or continuous flow conditions. Thus, we used a calcined HT catalyst for condensing **1** with **2**. This metal-free reaction provided **3** in 55 and 82% yield and in excellent selectivity after 7 and 20 h, respectively (Table 1, entries 6 and 7).

In subsequent studies, we evaluated the substrate scope for the dehydrogenative cross-coupling reaction by employing various bioalcohols (1-butanol, 1-propanol, 1-pentanol, 3-methyl-1-butanol, 1-hexanol, 2-phenylethanol, 1-octanol, 2-propanol, 1,6-hexanediol, 1-tetradecanol) and lignocellulosic furfural as outlined in Table 2. In general, the dehydrogenative cross-coupling of 2-furfural and 5-methyl furfural with primary and secondary alcohols produced from (i) fermentative and non-fermentative pathways of sugars,^[3,5] (ii) chemical deoxygenation of sugars,^[10] and (iii) alcohols derived from long chain fatty alcohols in the presence of HT showed selectivities >99% even at high conversions. Furthermore, the catalyst itself showed high activity after three cycles (>90% yield, >99:1 selectivity). Aldehyde **3** was formed as a mixture of *E*- and *Z*-isomers along with the trace amounts of the corresponding primary alcohols. The high selectivity of the cross-condensation product for the heterogeneous reaction suggests that in the presence of HT the reaction proceeds via a hydride transfer from butanol to furfural, consistent with the Meerwein–Ponndorf–Verley reaction, followed by an aldol condensation of the resulting butyraldehyde with a second molecule of furfural.^[11]

Hydrodeoxygenation is the final step in our process scheme; toward this end, the hydrodeoxygenation of furanyl aldehydes **3a**, **3h**, and **3k** were examined to convert these substrates to alkanes that are components of jet or diesel fuels. A bifunctional Pt/NbOPO₄ catalyst has been shown to deoxygenate sorbitol to alkanes via aqueous-phase dehydration–hydrogenation reactions.^[12] Recyclability of catalyst is important from a process perspective; after verifying the recyclability of Pt/NbOPO₄ (see the Supporting Information), we used this catalyst for the hydrodeoxygenation of furanyl aldehydes **3a**, **3h**, and **3k** under a hydrogen atmosphere at elevated pressure and temperature. This gave us a mixture of cyclic and acyclic alkanes consisting of C₈–C₁₉ carbons in 75–78% overall yield (Scheme 2). We expect this fuel mixture to be compatible with existing infrastructure vehicles without requiring any modifications.

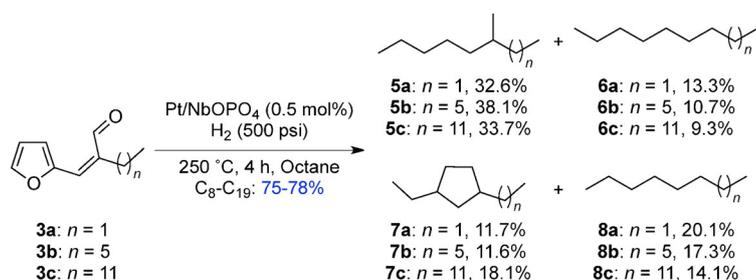
Although the fuels produced using our strategy are compatible with the current diesel vehicle fleet, they need to meet a variety of regulatory criteria to qualify for renewable fuel credits, including limits on life-cycle GHG emissions. We model our process as an annex of a Brazilian sugarcane biorefinery that produces ethanol and diesel-range alkanes by utilizing cane sugar and the hemicellulose fraction of bagasse as indi-

Table 2. Scope for olefination reaction of furfural and bioalcohols.

Entry	Product	Yield [%]
1		82
2		48
3		64
4		80
5		49
6		76
7		95
8		99
9		51
10		66 ^[b]
11		99

[a] Reaction conditions: Alcohol (1 mmol), furfural (2 mmol), HT (0.4 g), 150 °C, toluene (1 mL), 20 h, selectivity determined by GC analysis of the crude sample. Combined yield of *E*- and *Z*-olefin plus minor quantities of the corresponding primary alcohol of **3** determined by calibrated internal standard (*n*-dodecane) on GC-FID. [b] furfural (4.3 mmol), 120 °C yield in parenthesis includes cyclized product (see supporting information).

cated in Figure 1 (see the Supporting Information for additional details). By utilizing cellulose for heat and power instead of conversion to ethanol, our scheme avoids the use of costly enzymes. Furfural, a precursor to diesel-range alkanes in our scheme, can be produced from pentose sugars found in the hemicellulose fraction of bagasse via sulfuric acid-catalyzed dehydration.^[4] The ethanol produced in this facility from cane sugar can be sold entirely as fuel, in which case higher alcohols



Scheme 2. Hydrodeoxygenation reaction of furanyl adducts **3a**, **3b**, and **3c**. Reaction conditions: Furanyl aldehyde (1 mmol), Pt/NbOPO₄ (0.5 mol%), H₂ (500 psi; 1 psi = 68948·10³ Pa), 250 °C, octane (8 mL), 4 h, internal standard (dodecane). Yield of C₈–C₁₉ paraffins were determined using the response factor of alkanes for the GC-flame ionization detector (FID) analysis of the crude sample.

must be purchased for use in the transfer hydrogenation reactions. However, the Guerbet reaction can be used for upgrading ethanol produced on site to a mixture of butanol, hexanol, octanol, 2-ethylbutanol, and 2-ethylhexanol;^[13] these alcohols can then be used for the dehydrogenative condensation reactions with furfural, thus giving adducts with carbon numbers suitable for hydrogenation into diesel-range compounds. To optimize the process energetics, we wanted to eliminate the solvent separation step that would be needed following the hydrogen-transfer reaction if toluene were to be used. Hence, we envisioned a scheme in which a part of the paraffin products produced in the final hydrogenation step could be recycled as solvents (see Figure 1). To demonstrate the efficacy of this scheme, we conducted the reaction using nonane and tridecane as proxies for paraffin solvents and showed that the high selectivity (> 99%) to condensation product **3** was retained (see the Supporting Information).

Petroleum feedstocks provide another option for providing the C₄₊ alcohols; this can increase the net fuel yield per hectare of sugarcane cultivated while also reducing the capital investment deployed per MJ of energy produced. Two processes that give alcohols that can be used for diesel synthesis using our strategy are: (i) Ziegler–Alfol process, which involves oligomerization of ethylene using triethylaluminum (TEA) followed by oxidation to give mixtures of C₄–C₁₀ alcohols;^[14] and (ii) oxo process, which can be used to convert propylene and natural gas into butanol.^[15] In both scenarios, the final diesel product is only partially renewable and we account for fossil carbon emissions accordingly. In both the petroleum- and bio-derived alcohol cases, our model biorefinery produces a combination of diesel-range alkanes and fuel ethanol. All cases require hydrogen for hydrodeoxygenation, which we assume can be produced through steam-reforming of either natural gas or a portion of the ethanol produced on site. Producing hydrogen from ethanol results in less fuel ethanol available for sale, but reduces the GHG intensity of the remaining fuel products. We calculated the resulting GHG emissions in terms of the reductions achieved relative to conventional petroleum gasoline and diesel (see the Supporting Information).

We find that, when the higher alcohols derived from the Guerbet reaction of ethanol are employed and hydrogen is fossil-derived, the fuel products achieve a 69% reduction in

life-cycle GHG intensity relative to their petroleum counterparts, excluding indirect land use change (iLUC; see Figure 2). If hydrogen is produced on site, the GHG intensity reduction reaches 79%. In this biorefinery configuration, diesel-range alkanes make up 60–66% of total fuel output per km traveled in a standard sedan (fuel economy equivalent to 3.6 MJ of gasoline or ethanol per km traveled and 3.3 MJ of diesel per km traveled; see the Supporting Information), and ethanol comprises the remaining 34–40%. In total, the biorefinery produces 700–800 km-equivalents per metric ton of sugarcane. These fuel outputs fit within the advanced biofuel definition set by the European Union (EU) as set in the Fuel-Quality Directive, which calls for a 35% GHG intensity reduction,

increasing to 60% reduction by 2018.^[16] The less stringent requirements for the US Renewable Fuel Standard 2 (RFS2) and California Low Carbon Fuel Standard for advanced biofuels naturally make this fuel acceptable.^[17]

The Ziegler–Alfol and oxo process options considered here result in 53–60% and 59–67% emission reductions, respectively, with the low end representing the fossil-derived hydrogen and ethanol-derived hydrogen producing the greatest reductions. Both petroleum-based alcohol options produce approximately 30% more fuel per metric ton of sugarcane processed (900–1000 km-equivalents per metric ton of sugarcane, compared to 700–800 km-equivalents for the Guerbet option), and diesel-range alkanes comprise a smaller fraction of fuel output at approximately 50% of the total km-equivalent output. For each case, we explore the sensitivity of the results to changes

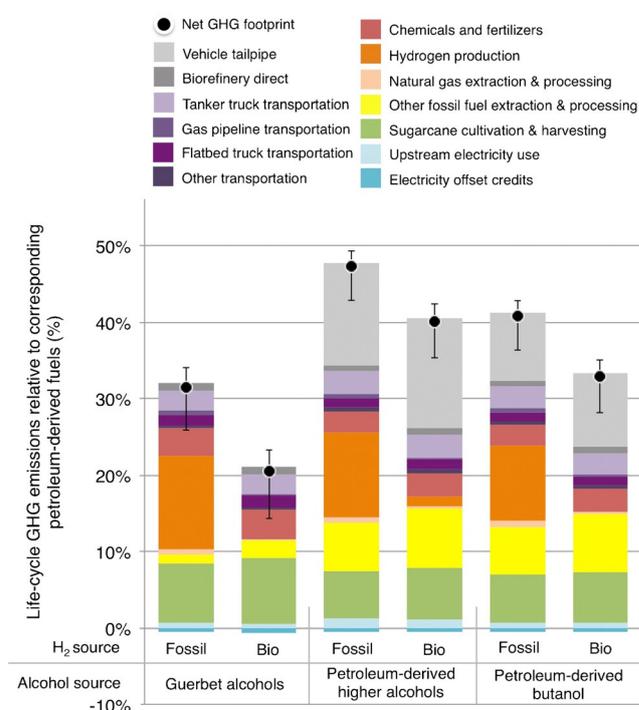


Figure 2. Life-cycle GHG emission results for three production pathways, differentiated by alcohol and hydrogen sources, normalized relative to the reduction in GHG emissions compared to conventional petroleum fuels.

in heat/power demand and production, as well as the Brazilian power mix offset by net electricity exports (see Figure 2). See the Supporting Information for additional details.

In all three cases, the impact of using fossil fuel-derived hydrogen is significant and producing hydrogen from sugarcane-derived ethanol substantially reduces the net GHG impact and makes the partially petroleum-based fuels acceptable as biofuels under EU regulations up to 2018 if iLUC is excluded. However, regulations in the US such as the RFS2 petroleum feedstocks provide another option for providing the C_{4+} alcohols, which can increase the net fuel yield per hectare of sugarcane cultivated while also reducing the capital investment deployed per MJ of energy produced. Two processes that give alcohols that can be used for diesel synthesis using our strategy are: (i) Ziegler–Alfol process, which involves oligomerization of ethylene using TEA followed by oxidation to give mixtures of C_4 – C_{10} alcohols;^[14] and (ii) oxo process, which can be used to convert propylene and natural gas into butanol.^[15] In both scenarios, the final diesel product is only partially renewable and we account for fossil carbon emissions accordingly. In both the petroleum-derived and bio-derived alcohol cases, our model biorefinery produces a combination of diesel-range alkanes and fuel ethanol. All cases require hydrogen for hydrodeoxygenation, which we assume can be produced through steam reforming of either natural gas or a portion of the ethanol produced on site. Producing hydrogen from ethanol results in less fuel ethanol available for sale, but reduces the GHG intensity of the remaining fuel products. We calculate the resulting GHG emissions in terms of the reductions achieved relative to conventional petroleum gasoline and diesel (see the Supporting Information).

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The Ziegler–Alfol and Oxo process options considered here result in 53–60% and 59–67% emissions reductions, respectively, with the low end representing the fossil-derived hydrogen and ethanol-derived hydrogen producing the greatest reductions. Both petroleum-based alcohol options produce approximately 30% more fuel per metric ton of sugarcane processed (900–1000 km-equivalents/metric ton cane, compared to 700–800 km-equivalents for the Guerbet option), and diesel-range alkanes comprise a smaller fraction of fuel output at ap-

proximately 50% of the total km-equivalent output. For each case, we explore the sensitivity of the results to changes in heat/power demand and production, as well as the Brazilian power mix offset by net electricity exports (see Figure 2). See the Supporting Information for additional details.

In all three cases, the impact of using fossil fuel-derived hydrogen is significant, and producing hydrogen from sugarcane-derived ethanol substantially reduces the net GHG impact and makes the partially petroleum-based fuels acceptable as biofuels under EU regulations up to 2018 if iLUC is excluded. However, regulations in the US such as RFS2 do not classify fuels produced through co-processing biomass with petroleum-based feedstocks as “biomass-based diesel” for which vegetable oil-based fatty acid methyl esters qualify. Rather, such fuels are classified as “other advanced biofuels” alongside sugarcane ethanol, thereby reducing the incentive to produce these drop-in fuels. Such distinctions under the current regulatory environment in which a pathway with substantial petroleum demand for agricultural inputs, harvesting, and transportation gets favorable treatment over a pathway that has the potential of using a lower-input feedstock and consuming a comparable quantity of petroleum for co-processing appear arbitrary and highlight the need for stronger integration between technology development and policy formulation.

In summary, our protocol involving a sequential transfer hydrogenation reaction between lignocellulose-derived furfurals and alcohols from renewable or petroleum sources over commercially available hydrotalcite followed by a hydrodeoxygenation reaction catalyzed by platinum on niobium phosphate provide alkanes that could serve as drop-in diesel. The study also provides a unique method of utilizing sugars and lignocellulosic biomass to produce a drop-in diesel fuel stream. We show that this scheme has the potential to operate as part of a Brazilian sugarcane refinery complex by utilizing a fraction of bagasse alongside higher alcohols to yield a value-added diesel stream, assuming that experimental results are indicative of commercial-scale performance. Our preliminary modeling suggests this pathway can achieve net reductions in GHG emissions of 53–79% relative to petroleum-derived fuels, with opportunities for further GHG reductions through low-input feedstock selection and renewable sources of hydrogen. Further detailed energy and cost modeling is necessary to refine these estimates, but the sensitivity analysis shows that the carbon intensity of each fuel is unlikely to be substantially higher than these initial results. Our work also highlights some of the anomalies in regulatory environment and demonstrates the need for early-stage engagement between biomass conversion research and LCA to guide scientific research and regulatory policies.

Experimental Section

Representative procedure for the dehydrogenative cross-coupling reaction: In a 12 mL Q-tube containing a stir bar, calcined hydrotalcite (0.4 g) was charged. To the reaction mixture, butanol (0.074 g, 1 mmol), 2-furfural (0.192 g, 2 mmol), internal standard (dodecane, known amount), and toluene (1 mL) were sequentially added. The

Q-tube was sealed, and the reaction mixture was stirred for 20 h at 150 °C in a preheated metal block. The reaction mixture was cooled to room temperature, diluted with tetrahydrofuran, and the GC analysis of the reaction mixture was carried out.

Representative procedure for the hydrodeoxygenation reaction: The hydrodeoxygenation reactions were performed in a 4560 Mini Parr reactor. To a solution of aldol adduct **3a** (0.5 mmol, 0.103 g) in octane (8 mL) was added 2 wt% Pt/NbOPO₄ (0.5 mol%, 0.024 g) and internal standard (undecane/dodecane, known amount) in a 25 mL Parr reactor. The reactor was then sealed, and the dissolved gases in the solution were purged (pressurize/depressurize) using nitrogen at 500 psi (3 times) while stirring. The purging was repeated with hydrogen at 500 psi (3 times) before the reactor was charged with hydrogen (500 psi). Then the reactor was heated to 250 °C and stirred for 4 h at the same temperature. The reactor was cooled to ambient temperature and depressurized. Aliquots were drawn from the reactor, and GC analysis of the reaction mixture was carried out.

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