

# Synthesis of Acetone-Derived C<sub>6</sub>, C<sub>9</sub>, and C<sub>12</sub> Carbon Scaffolds for Chemical and Fuel Applications

Cameron M. Moore,<sup>[a]</sup> Rhodri W. Jenkins,<sup>[a]</sup> Michael T. Janicke,<sup>[a]</sup> William L. Kubic, Jr.,<sup>[b]</sup> Evgueni Polikarpov,<sup>[c]</sup> Troy A. Semelsberger,<sup>[d]</sup> and Andrew D. Sutton<sup>\*,[a]</sup>

A simple, inexpensive catalyst system (Amberlyst 15 and Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) is described for the upgrading of acetone to a range of chemicals and potential fuels. Stepwise hydrodeoxygenation of the produced ketones can yield branched alcohols, alkenes, and alkanes. An analysis of these products is provided, which demonstrates that this approach can provide a product profile of valuable bioproducts and potential biofuels.

Steady increases in global oil consumption aggravated by declining fossil-fuel reserves necessitate the continued development of technologies to manufacture chemicals and fuels from non-petroleum sources of carbon. As the global population is projected to continue to grow through the end of this century,<sup>[1]</sup> consumption of alternative sources of energy must be adopted to meet rising demand.<sup>[2-4]</sup> Non-food-based biomass represents a vast source of renewable carbon for the synthesis of chemicals and fuels.<sup>[3,5-8]</sup> The U.S. is projected to have the ability to produce over a billion tons of biomass for the bioenergy and bioproducts industry within the next six years alone.<sup>[9]</sup> To effectively utilize this massive resource, however, efficient methodologies for transforming biomass-derived carbon material into useful chemicals and fuels must be developed at a comparable rate. Moreover, one approach to enable future biorefineries to produce fuels for the transportation sector that are cost-competitive with traditional petroleum refineries is to co-produce high-value chemicals from biomass to offset the cost of producing inherently low-value fuels.<sup>[10]</sup> To illustrate this point, in the U.S., 76% of a barrel of oil (by

volume) is used for the production of gasoline, diesel, and jet fuel, and this market is worth \$935 billion annually. In contrast, 16% is used for production of chemicals in a market worth \$812 billion.<sup>[11]</sup> In a commercial biomass-upgrading process in which volumetric output is limited, one strategy would be to pursue small-volume, high-value chemical production in the short term. If fuels could be produced using the same process, this approach would allow the expansion to an almost limitless market upon reaching the upper limit of the chemical market as production volume increases.

Herein, we describe our preliminary efforts toward such an approach for converting bio-derived isopropanol/acetone mixtures to known chemicals and molecules with promising fuel properties for both gasoline and diesel applications. Specifically, we present an inexpensive dual catalyst system for the upgrading of acetone through polyaldol condensations to provide C<sub>6</sub>, C<sub>9</sub>, and C<sub>12</sub> aliphatic ketones, along with C<sub>9</sub>, C<sub>12</sub>, and C<sub>15</sub> aromatic compounds.<sup>[12,13]</sup> Additionally, we demonstrate that the mild conditions for acetone upgrading can be modified to subsequently defunctionalize the aliphatic ketones and readily produce branched alkanes. Along with being known solvents and industrially used chemicals, predicted/measured fuel properties of a selection of these molecules reveal that certain compounds produced herein are candidates as drop-in fuel replacements for spark- and compression-ignition engines.

Ketones are a versatile class of chemical building blocks that can be renewably produced from biomass.<sup>[14-17]</sup> In particular, methyl ketones have shown promise as bio-derived synthons for the production of chemical/fuel precursors because their carbon chain can be readily extended through aldol condensation.<sup>[17-19]</sup> Acetone, the simplest ketone building block, has been industrially produced for nearly a century by the microbial fermentation of biomass through the acetone-butanol-ethanol (ABE) fermentation process, with the products obtained in roughly a 3:6:1 ratio, respectively. Recently, however, metabolically engineered microorganisms were developed that can produce mixtures of isopropanol and acetone in high titers from carbohydrate inputs using strains that have the potential to be scaled up industrially.<sup>[20]</sup> These isopropanol/acetone mixtures are much more attractive from a techno-economic perspective because 1) the output stream from fermentation contains a larger fraction of isopropanol/acetone, and 2) in situ dehydrogenation of the isopropanol fraction can be performed to provide the system with bio-derived H<sub>2</sub> sufficient for acetone upgrading (Scheme 1). This is an advantage over other processes that incorporate acetone from ABE fermentation, such as furfural-acetone condensation<sup>[21,22]</sup> and acetone alkyla-

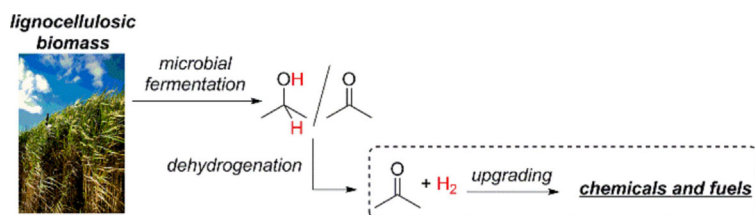
[a] Dr. C. M. Moore, Dr. R. W. Jenkins, Dr. M. T. Janicke, Dr. A. D. Sutton  
Chemistry Division  
Los Alamos National Laboratory  
MS K558, Los Alamos, NM 87544 (USA)  
E-mail: adsutton@lanl.gov

[b] Dr. W. L. Kubic, Jr.  
Applied Engineering and Technology Division  
Los Alamos National Laboratory  
MS E548, Los Alamos, NM 87544 (USA)

[c] Dr. E. Polikarpov  
Applied Materials and Performance  
Pacific Northwest National Laboratory  
Richland, WA 99352 (USA)

[d] Dr. T. A. Semelsberger  
Material Physics Applications Division  
Los Alamos National Laboratory  
MS K793, Los Alamos, NM 87544 (USA)

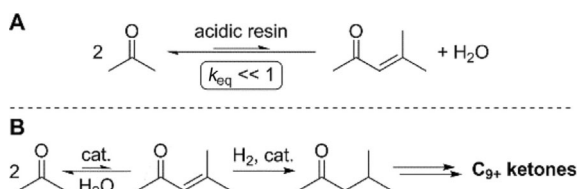
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**Scheme 1.** Strategy for production of chemicals and fuels employing acetone upgrading as a key step.

tion using other bio-derived alcohols<sup>[17,23]</sup> because an isopropanol feed could supplement an H<sub>2</sub> supply required for further processing steps.

We first investigated the conversion of acetone into higher-molecular-weight ketones using a commercially available sulfonic-acid-functionalized polystyrene resin (Amberlyst 15). The initial self-condensation of acetone to afford mesityl oxide was previously reported to be thermodynamically limited if catalyzed by similar ion-exchange resins such as Dowex (Scheme 2 A).<sup>[24]</sup> This constraint can be alleviated in two ways:

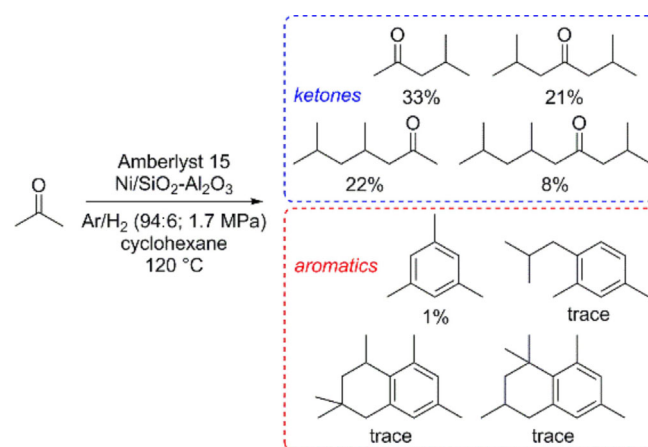


**Scheme 2.** Equilibrium for acetone self-condensation over acidic resins (A) and strategy to promote polyaldol condensations of acetone using catalytic hydrogenation (B).

By using reactive distillation to remove water from the equilibrium, or by driving the reaction through catalytic hydrogenation of the C=C alkene bond of mesityl oxide to afford methyl isobutyl ketone (MIBK; Scheme 2 B). The latter approach is employed industrially to produce MIBK from petroleum-derived acetone using Pd-impregnated acidic resins under low H<sub>2</sub> partial pressures.<sup>[25]</sup>

Our attempts focused on the latter approach, and we sought to develop a catalyst system using readily available, inexpensive catalysts to target the production of C<sub>6+</sub> ketones that might serve as drop-in fuel replacements for gasoline and diesel. Initial attempts to form MIBK using Pd/C as the hydrogenation catalyst were hampered by acetone volatilization at moderate temperatures, thus minimizing catalyst-substrate contact time and resulting in low conversions. Upon increasing the H<sub>2</sub> pressure to minimize this effect, the yield of condensation products was again inhibited, but in this case by acetone reduction to isopropanol, leading to the ultimate formation of diisopropyl ether as the sole product. To circumvent unwanted C=O bond hydrogenation and thus provide the desired acetone condensation products, we hypothesized that replacement of Pd with Ni would lead to less aggressive hydrogenation reactivity. We therefore selected Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> as a hydrogenation catalyst given that this material is readily available

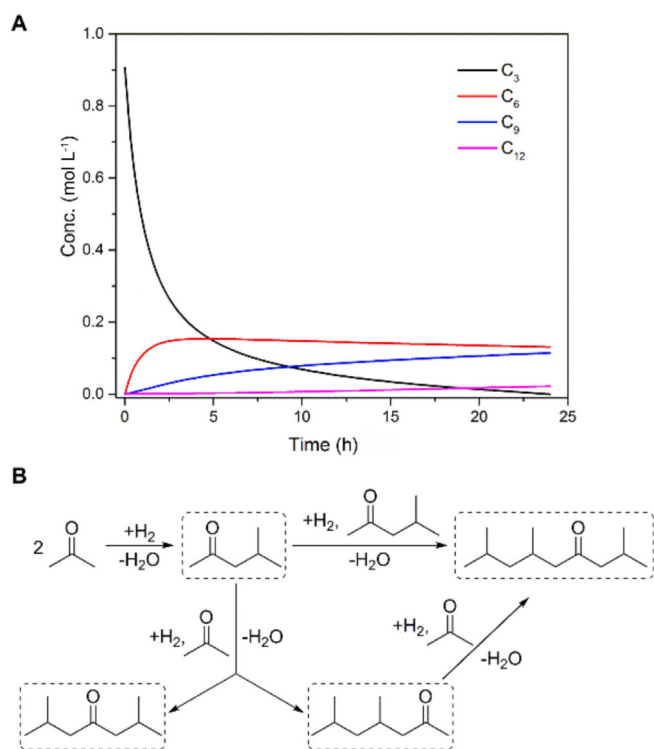
through commercial sources. Reaction of acetone with H<sub>2</sub> (0.3 MPa) in the presence of Amberlyst 15 and Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (85 °C, cyclohexane) successfully provided a mixture of C<sub>6</sub> and C<sub>9</sub> aliphatic ketones without any of the previously observed side reactions. Acetone conversion, however, was low (ca. 50%), and we hypothesized that this could be improved by increasing the reaction temperature and pressure. To maintain a low partial pressure of H<sub>2</sub> (to avoid competing C=O bond hydrogenation), we employed dilute H<sub>2</sub> in Ar (6%) as the headspace gas at higher pressures (1.7 MPa). Using these conditions at higher temperatures (120 °C) resulted in the complete conversion of acetone into a mixture of C<sub>6</sub>, C<sub>9</sub>, and C<sub>12</sub> ketones (84% total carbon yield of C<sub>6</sub>-C<sub>12</sub> ketones, Scheme 3). Aromatic products



**Scheme 3.** Synthesis of C<sub>6+</sub> ketones and aromatics from acetone. Yields are based on carbon, as determined by <sup>1</sup>H NMR spectroscopy (see Supporting Information for more details). Conditions: acetone (2.72 mmol), cyclohexane (3.0 mL), Amberlyst 15 (0.20 g), Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (0.04 g), 24 h.

were also identified as minor products from the reaction using GC-MS analysis (Scheme 3), with mesitylene as the predominant aromatic compound present in approximately 1% carbon yield. An initial screening of condensation conditions revealed the necessity of both Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Amberlyst 15 to obtain good carbon yields of C<sub>9</sub> and higher ketones (Table S1 in the Supporting Information). Notably, replacement of Ni with either Pd/C or Ru/C under these conditions resulted in lower C<sub>9</sub> yields. In the case of Pd/C, a high selectivity for MIBK production was observed, as previously reported.<sup>[26]</sup>

The evolution of ketone species over time was examined by analyzing the acetone-condensation reaction products at various time points (Figure 1 A). In the first 6 h, acetone consumption was at a maximum, whereas subsequently MIBK and diisobutyl ketone (DIBK) production was at a maximum. Beyond 6 h, C<sub>9</sub> and C<sub>12</sub> products began to increase concomitantly with the decrease of MIBK. From these results, a general pathway for the production of the C<sub>6</sub>, C<sub>9</sub>, and C<sub>12</sub> ketones from acetone can be constructed (Figure 1 B). The initial condensation of acetone catalyzed by Amberlyst 15 and Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> produces MIBK, which in turn can be condensed with remaining acetone



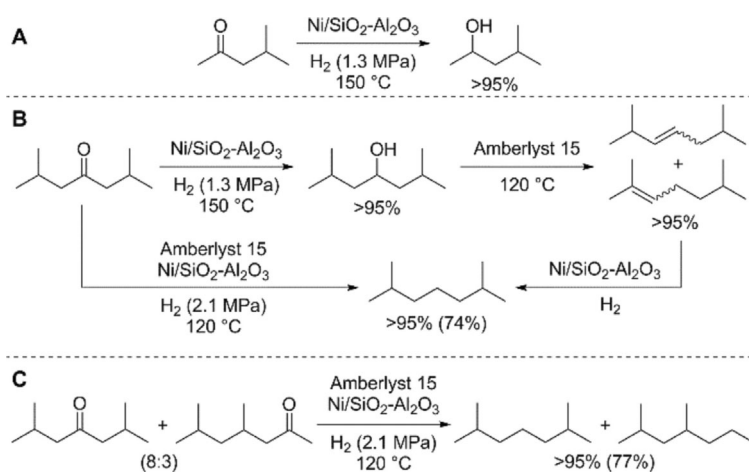
**Figure 1.** Consumption of acetone and formation of ketone products over time (A), and possible product formation pathways (B). Conditions: acetone (2.72 mmol), cyclohexane (3.0 mL), Amberlyst 15 (0.20 g), Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (0.04 g), Ar/H<sub>2</sub> (94:6; 1.7 MPa), 120 °C.

to form the two C<sub>9</sub> ketone species. The 2-methyl isomer of the C<sub>9</sub> ketone species can also condense with residual acetone (if present) to produce the C<sub>12</sub> ketone. However, the most likely contributing pathway for the production of the C<sub>12</sub> ketone is the self-condensation of MIBK. This is visualized in Figure 1A with the disappearance of MIBK over time and the gradual increase of the C<sub>12</sub> ketone. The time-dependent ketone product profiles demonstrate that this reaction can be optimized to provide the most desirable ketone product by altering the reaction conditions. The separation of the ketone products from acetone condensation should be easily accomplished by distillation given the difference in boiling points of these compounds (115, 165, and 220 °C for the C<sub>6</sub>, C<sub>9</sub>, and C<sub>12</sub> ketones, respectively; see Figure S11 and discussion in the Supporting Information for more details).

Modifying the above condensation conditions enables access to molecules with varying functional groups through stepwise, or one-pot, defunctionalization reactions. For instance, MIBK can be readily hydrogenated to methyl isobutyl carbinol (MIBC) by Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> under moderate temperatures and H<sub>2</sub> pressures in excellent yield without solvent (Scheme 4A). Under identical conditions, DIBC can also be easily hydrogenated to diisobutyl carbinol (DIBC, Scheme 4B). Alkenes can be readily isolated from the resulting alcohols; as an example, a mixture of alkenes (di- and tri-substituted, *cis* and *trans* iso-

mers) was produced exclusively from DIBC by reaction with Amberlyst 15 in the absence of solvent. If desired, the alkenes are rapidly hydrogenated to alkanes using Ni/H<sub>2</sub>. Moreover, the combination of Amberlyst 15 and Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> can be used to affect the hydrodeoxygenation of ketones in a one-pot approach. For example, reaction of DIBK with H<sub>2</sub> in the presence of Amberlyst 15 and Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> afforded 2,6-dimethylheptane as the exclusive product, which was isolated in 74% yield (Scheme 4B) and fully characterized by MS as well as <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (see Supporting Information). This reaction is general and efficiently provides alkanes from methyl ketones as well. As a further example, we subjected neat technical-grade C<sub>9</sub>H<sub>18</sub>O (an 8:3 mixture of 2,6-dimethyl-4-heptanone and 4,6-dimethyl-2-heptanone) to the aforementioned conditions and obtained the corresponding mixture of alkanes exclusively in 77% isolated yield (Scheme 4C). Notably, we did not observe any isomerization of the methyl groups across the carbon chain, which was reported during hydrodeoxygenation of similar substrates using other catalyst systems.<sup>[27]</sup> This reaction was performed on >3 g-per-batch scale, and we have isolated >0.1 L of the C<sub>9</sub> alkanes to date. These step-wise and one-pot approaches enable access to a wide range of products using identical catalysts, a feature that is central to producing flexible product profiles on demand from biomass inputs.

As stated previously, biofuel production can be supported by the co-production of bioproducts. The products from the acetone condensation reaction are used commercially and are therefore inherently valuable. For example, current global production of MIBK is approximately 394 000 metric tons per year,<sup>[28]</sup> and it finds use as a solvent in resins, printing inks, and as an extraction solvent in the production of antibiotics.<sup>[25]</sup> The current U.S. spot market price of MIBK is approximately \$1587–1631 per metric ton.<sup>[29]</sup> Similarly, global production of DIBK is approximately 236 000 metric tons per year, and it is used as a solvent for extraction of iron and copper ores, among other applications.<sup>[25]</sup> The current U.S. spot price of DIBK is approxi-



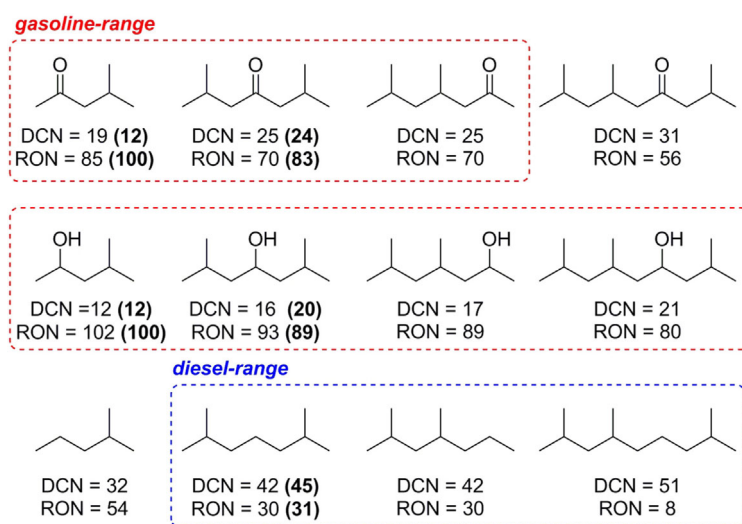
**Scheme 4.** (A) Hydrogenation of MIBK, (B) stepwise and one-step hydrogenation/hydrodeoxygenation reactions of DIBK, (C) one-step hydrodeoxygenation of C<sub>9</sub> ketones [solvent-free conditions, isolated yields in parentheses; in (B), the isolated yield stems from the one-pot hydrodeoxygenation of DIBK, see Supporting Information for full reaction conditions].

mately \$2930–3050 per metric ton.<sup>[30]</sup> To contextualize these figures, U.S. spot prices of acetone have varied considerably, but have been as low as \$400–500 per metric ton in 2015,<sup>[31]</sup> which demonstrates the value in upgrading acetone to either of these two possible products.

To assess the potential for these products to be employed as drop-in fuel replacements, we predicted their corresponding derived cetane numbers (DCNs) and research octane numbers (RONs). This was accomplished using a group-contribution method based on functional-group additivity previously reported for DCN prediction<sup>[32]</sup> in combination with a previously reported relationship between RON and DCN.<sup>[33]</sup> Although this method provides only predictions, this approach yields a first approximation of the suitability of a given molecule for either gasoline or diesel applications.<sup>[34]</sup> The results of this analysis are presented in Figure 2 and demonstrate that the C<sub>6</sub>, C<sub>9</sub>, and

more valuable than the obtained alkane and the reaction requires H<sub>2</sub>. Furthermore, this fact exemplifies the need to perform preliminary fuel-property analyses because alkanes are not necessarily the most ideal fuel targets for a given input.<sup>[36]</sup> In addition to the molecules highlighted in Figure 2, mesitylene is a known octane booster for gasoline fuel with a RON > 120,<sup>[37]</sup> making this aromatic byproduct a potentially desirable fuel blendstock as well.

In conclusion, we have presented a simple and inexpensive dual catalyst system (Amberlyst 15 and Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) for the upgrading of acetone to fuels and chemicals. Both steps of our upgrading process (i.e., condensation and hydrodeoxygenation) can be accomplished with the same catalyst system by simply modifying the reaction conditions, which enables product profiles that can be tuned to market demand. The catalyst system offers high selectivity for producing ketones during acetone condensation as well as high carbon efficiency (see Table S2 for a more detailed comparison to previous reports). The simplicity and ready commercial availability of the catalysts, combined with the mild conditions, offer an attractive route for the upgrading of bio-derived acetone. By evaluating the chemical market and the initial fuel properties, we are confident that this process supplies relevant molecules to both sectors rather than presuming a certain class of molecule is inherently important. By doing this initial analysis, we have also determined that the drive towards hydrocarbons is not always necessary and in certain cases will lead to more expensive processes, using more resources to produce a product with less value than the starting material. Current efforts are focused on developing this chemistry in flow, full fuel-property testing, and techno-economic and life-cycle analyses, and will be described in due course.



**Figure 2.** Predicted DCN and RON for select molecules that can be produced using this process. DCN measured using ASTM D6890 and corresponding calculated RON are bolded and presented in parentheses.

C<sub>12</sub> ketones and alcohols are predicted to be suitable for gasoline drop-in fuel replacement based on their respective predicted RONs (with the exception of the C<sub>12</sub> ketone). Alternatively, the branched C<sub>9</sub> and C<sub>12</sub> alkanes are predicted to be suitable diesel drop-in fuel replacements based on their predicted DCNs. To support these predictions, a subset of these compounds was subjected to testing using the Ignition Quality Tester (IQT)<sup>[35]</sup> to obtain experimental DCNs (Figure 2; bold values in parentheses). The DCN values obtained using this method (and the corresponding RON values) strongly agree with the predictions above.

Notably, 2-methylpentane (derived from the hydrodeoxygenation of MIBK) is not predicted to be a suitable gasoline or diesel substitute, which is in contrast to previous claims regarding its applicability as a gasoline drop-in replacement fuel.<sup>[13,27]</sup> This is an important consideration given that hydrodeoxygenation of MIBK would cause a negative impact on the economics of an industrial process because MIBK is inherently

## Experimental Section

The details of the experiments are provided in the Supporting Information.

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**Keywords:** biofuels · bioproducts · catalysis · condensation · hydrodeoxygenation

- [1] P. Gerland, A. E. Raftery, H. Sevcikova, N. Li, D. Gu, T. Spoorenberg, L. Alkema, B. K. Fosdick, J. Chunn, N. Lalic, G. Bay, T. Buettner, G. K. Heilig, J. Wilmoth, *Science* **2014**, *346*, 234–237.
- [2] J. J. Bozell, G. R. Petersen, *Green Chem.* **2010**, *12*, 539–554.
- [3] A. Corma, S. Iborra, A. Vely, *Chem. Rev.* **2007**, *107*, 2411–2502.
- [4] J. Murray, D. King, *Nature* **2012**, *481*, 433–435.
- [5] G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044–4098.
- [6] J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem. Int. Ed.* **2007**, *46*, 7164–7183; *Angew. Chem.* **2007**, *119*, 7298–7318.
- [7] A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, Jr., J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, *Science* **2006**, *311*, 484–489.
- [8] J. C. Serrano-Ruiz, J. A. Dumesic, *Energy Environ. Sci.* **2011**, *4*, 83–99.
- [9] U.S. Department of Energy. **2011**. *U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry*. R. D. Perlack, B. J. Stokes (Leads), ORNL/TM-2011/224. Oak Ridge National Laboratory, Oak Ridge, TN. [http://energy.gov/sites/prod/files/2015/01/f19/billion\\_ton\\_update\\_0.pdf](http://energy.gov/sites/prod/files/2015/01/f19/billion_ton_update_0.pdf).
- [10] M. J. Bidy, R. Davis, D. Humbird, L. Tao, N. Dowe, M. T. Guarnieri, J. G. Linger, E. M. Karp, D. Salvachúa, D. R. Vardon, G. T. Beckham, *ACS Sustainable Chem. Eng.* **2016**, *4*, 3196–3211.
- [11] *Bioproducts to Enable Biofuels Workshop Summary Report*, U.S. Department of Energy, Office of Energy Efficiency & Renewable Energy, Bioenergy Technologies Office **2015**. [http://energy.gov/sites/prod/files/2015/12/f27/bioproducts\\_to\\_enable\\_biofuels\\_workshop\\_report.pdf](http://energy.gov/sites/prod/files/2015/12/f27/bioproducts_to_enable_biofuels_workshop_report.pdf).
- [12] C. M. Moore, R. W. Jenkins, A. D. Sutton, U.S. Patent Application No. 62/327,254. Filed April 25th 2016.
- [13] A related preliminary report was recently published on using Pd-impregnated hydrotalcite: X. Sheng, N. Li, G. Li, W. Wang, A. Wang, Y. Cong, X. Wang, T. Zhang, *Green Chem.* **2016**, *18*, 3707–3711.
- [14] A. Multer, N. McGraw, K. Hohn, P. Vadlani, *Ind. Eng. Chem. Res.* **2013**, *52*, 56–60.
- [15] K. Min, S. Kim, T. Yum, Y. Kim, B.-I. Sang, Y. Um, *Appl. Microbiol. Biotechnol.* **2013**, *97*, 5627–5634.
- [16] A. Corma, O. de La Torre, M. Renz, *Energy Environ. Sci.* **2012**, *5*, 6328–6344.
- [17] P. Anbarasan, Z. C. Baer, S. Sreekumar, E. Gross, J. B. Binder, H. W. Blanch, D. S. Clark, F. D. Toste, *Nature* **2012**, *491*, 235–239.
- [18] E. R. Sacia, M. Balakrishnan, M. H. Deaner, K. A. Goulas, F. D. Toste, A. T. Bell, *ChemSusChem* **2015**, *8*, 1726–1736.
- [19] S. Sankaranarayananpillai, S. Sreekumar, J. Gomes, A. Grippo, G. E. Arab, M. Head-Gordon, F. D. Toste, A. T. Bell, *Angew. Chem. Int. Ed.* **2015**, *54*, 4673–4677; *Angew. Chem.* **2015**, *127*, 4756–4760.
- [20] E. Grousseau, J. Lu, N. Gorret, S. E. Guillouet, A. J. Sinskey, *Appl. Microbiol. Biotechnol.* **2014**, *98*, 4277–4290.
- [21] G. W. Huber, J. N. Chheda, C. J. Barrett, J. A. Dumesic, *Science* **2005**, *308*, 1446–1450.
- [22] A. D. Sutton, F. D. Waldi, R. Wu, M. Schlaf, L. A. Silks, J. C. Gordon, *Nat. Chem.* **2013**, *5*, 428–432.
- [23] S. Sreekumar, Z. C. Baer, E. Gross, S. Padmanaban, K. Goulas, G. Gunbas, S. Alayoglu, H. W. Blanch, D. S. Clark, F. D. Toste, *ChemSusChem* **2014**, *7*, 2445–2448.
- [24] F. G. Klein, J. T. Banchemo, *Ind. Eng. Chem.* **1956**, *48*, 1278–1286.
- [25] H. Siegel, M. Eggersdorfer in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2000**.
- [26] C. U. Pittman, Jr., Y. F. Liang, *J. Org. Chem.* **1980**, *45*, 5048–5052.
- [27] M. A. Alotaibi, E. F. Kozhevnikova, I. V. Kozhevnikov, *Chem. Commun.* **2012**, *48*, 7194–7196.
- [28] V. Guevarra "Chemical Profile: Europe MIBK", ICIS Chemical Business **2013**. <http://www.icis.com/resources/news/2013/12/06/9733220/chemical-profile-europe-mibk/>.
- [29] A. Yanelli "US MIBK Ends Month Flat", ICIS Chemical Business **2016**. <http://www.icis.com/resources/news/2016/05/27/10002716/us-mibk-ends-month-flat-at-lowest-level-of-the-year/>.
- [30] Figure based on price per metric ton from retail vendors.
- [31] D. Hall "Outlook '16: Sellers to benefit from US phenol/acetone shifts", ICIS Chemical Business **2016**. <http://www.icis.com/resources/news/2016/01/05/9951468/outlook-16-sellers-to-benefit-from-us-phenol-acetone-shifts/>.
- [32] M. Dahmen, W. Marquardt, *Energy Fuels* **2015**, *29*, 5781–5801.
- [33] G. T. Kalghatgi, *Soc. Automot. Eng. SP* **2005**, *SP-1972*, 203–220. <http://papers.sae.org/2005-01-0239/>.
- [34] In general, this method is suitable for an initial screening for low RON molecules that should be disregarded before further in-depth fuel property testing, and we recognize that this does not replace certified RON and cetane testing.
- [35] *ASTM D 6890, Standard Test Method for Determination of Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils by Combustion in a Constant Vol. Chamber*, American Society for Testing and Materials (ASTM), West Conshohocken, **2011**. <http://www.astm.org/Standards/D6890>.
- [36] R. W. Jenkins, C. M. Moore, T. A. Semelsberger, C. J. Chuck, J. C. Gordon, A. D. Sutton, *ChemSusChem* **2016**, *9*, 922–931.
- [37] A. Demirbas, M. A. Balubaid, A. M. Basahel, W. Ahmad, M. H. Sheikh, *Pet. Sci. Technol.* **2015**, *33*, 1190–1197.

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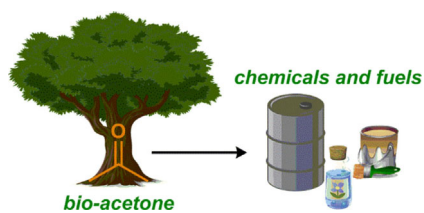
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## COMMUNICATIONS

C. M. Moore, R. W. Jenkins, M. T. Janicke,  
W. L. Kubic, Jr., E. Polikarpov,  
T. A. Semelsberger, A. D. Sutton\*



**Synthesis of Acetone-Derived C<sub>6</sub>, C<sub>9</sub>,  
and C<sub>12</sub> Carbon Scaffolds for Chemical  
and Fuel Applications**



**Combine and conquer:** A simple, inexpensive catalyst system (Amberlyst 15 and Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) is described for the upgrading of acetone to a range of chemicals and potential fuels. Stepwise hydrodeoxygenation of the produced ketones can yield branched alcohols, alkenes, and alkanes, thus providing a tunable product profile of bioproducts, bio-fuels, and potential chemical precursors.