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ORIGINAL ARTICLE

Potential Vegetable-Based Diesel Fuels from Perkin Condensation of Furfuraldehyde and Fatty Acid Anhydrides

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Abstract Domestically produced biofuels may help to reduce dependence on imported oil for powering transportation and infrastructure in the future. In this report, we reacted medium-chain and long-chain fatty anhydrides (capric, caprylic, lauric, and palmitic) with furfuraldehyde by the Perkin condensation to produce 2-*n*-alkenylfurans. In the second step, the 2-*n*-alkenylfurans were hydrogenated to form 2-*n*-alkyltetrahydrofurans. Basic fuel property testing (melting point, density, kinematic viscosity, derived cetane number, and calorific value) of the 2-*n*-alkyltetrahydrofurans indicates they are potentially useful as fuels for diesel engines. The mixture composed of 2-octyl- and 2-decyltetrahydrofuran had the best combination of fuel properties including a low melting point (−39 °C), high cetane number (63.1), high flash point (98.2 °C), and low viscosity (2.26 mm^2 s^{-1}, 40 °C), which compares favorably with specifications for diesel #2 and biodiesel.

Keywords Diesel · Condensation · Carboxylic anhydride · Furfuraldehyde · Cetane number · Green chemistry

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Introduction

The US Navy requires tremendous volumes of liquid hydrocarbon fuels to power vehicles and equipment on land, at sea, and through the air to accomplish its missions all around the world (Office of the Assistant Secretary of Defense for Energy, Installations, and Environment, 2017). These fuels are mostly derived from foreign sources of crude oil, particularly from unstable regions, and this vulnerability to supply disruption is a strategic energy issue. In response to the National Defense Authorization Act of 2007, the Navy began initiatives such as the “Great Green Fleet” and “Green Hornet” to explore using biofuels (liquid fuels derived from biological sources) and other renewable energy sources to supplement traditional fossil fuels (Alexander, 2016; Department of the Navy and the Department of Energy and the Department of Agriculture, 2011; John Warner, 2006; Kiefer, 2013). The Navy’s land and marine vehicles are typically equipped with compression ignition engines (e.g., diesel engines), which require a special distillation fraction from crude oil refining commonly known as diesel fuel, named after the inventor of the technology Rudolf Diesel (Diesel, 1895). The compression ignition engine harnesses the phenomenon that hydrocarbons can undergo spontaneous combustion when compressed in the presence of air. Road grade diesel fuel (D#2) is a complex statistical mixture of paraffinic hydrocarbons in the range of C_9–C_{23} that also contains various amounts of isoparaffins (e.g., branched), cycloaliphatics, aromatics, and/or sulfur-containing hydrocarbons depending on the crude source and refining processes. Furthermore, testing has shown that for optimal diesel engine performance, straight-chain (e.g., normal) paraffins are most desirable because of their decreased ignition delay, lower

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Supporting information Additional supporting information may be found online in the Supporting Information section at the end of the article.

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autoignition temperature, and higher cetane number (Heck et al., 1998; Hellier et al., 2018; Wilson III, 2016). Owing to this particular range of petroleum distillate, diesel fuel (0.85 g mL^{-1}) has a higher density than both jet fuel (0.79 g mL^{-1}) and gasoline (0.73 g mL^{-1}) (Bacha et al., 2007). As a consequence, diesel fuel has more energy per unit volume (~10–15%); hence road and marine motorized transportation by diesel is historically more economical (greater miles per gallon) than those powered by gasoline.

During a research project to identify new and environmentally friendly degreasing solvents, several simple condensation reactions of the renewable, platform chemical furfuraldehyde (furan-2-carboxaldehyde) were studied to build more complex, fit-for-purpose liquids (Davis et al., 2016; Werpy and Peterson, 2004). Furfuraldehyde is made on the industrial scale by the acid-catalyzed pyrolysis of lignocellulose (Miner and Brownlee, 1929). While examining the Perkin reaction (Johnson, 1942; Perkin, 1886) between furfuraldehyde and carboxylic acid anhydrides, we noticed that along with the expected 2-*n*-alkyl-3-furanacrylic acids the reaction mixtures also contained a small but significant quantity of a 2-*n*-alkenylfurans formed presumably by in situ decarboxylation of the former (Fig. 1).

Although the Perkin reaction employing saturated fatty acid anhydrides has rarely been studied (Krafft and Rosiny, 1900; Papa and Schwenk, 1950; Rebrovic and Kilbarger, 1994), the resulting 2-*n*-alkenylfurans appeared interesting not only as solvents but might lead, after further chemical processing, to a sort of vegetable-based diesel fuel (Leitner et al., 2017). This report will describe some further results in Perkin condensation of furfuraldehyde with fatty acid anhydrides from medium-chain and long-chain fats (caprylic, capric, lauric, and palmitic). We show that 2-*n*-alkenylfurans can be isolated on a preparative scale and further transformed by mild hydrogenation to 2-*n*-alkyltetrahydrofurans (2RTHF), a lesser known class of compound now readily accessible by this synthetic route. Preliminary fuel property data were collected on the new 2RTHF including the derived cetane number (DCN), kinematic viscosity, flash point, heat of combustion, melting point, and density. Comparisons are made with data from Sudholt et al. (2015) who were the first to report cetane numbers for 2RTHF with short alkyl chains (methyl, ethyl, and butyl). The data show that 2RTHF are more similar to biodiesel than petroleum diesel and nevertheless might be useful as renewable blendstock for diesel fuels.

Materials and Methods

Chemicals

The caprylic/capric fatty acid mixture was obtained from ChemCeed LLC (Chippewa Falls, WI) and used as received. The lauric acid (99%), butyric anhydride, cetane (hexadecane), acetic anhydride (Ac_2O), furfuraldehyde (furan-2-carboxaldehyde), and anhydrous potassium acetate (KOAc) were obtained from Sigma-Aldrich (Milwaukee, WI). The furfuraldehyde was purified by fractional distillation (101 kPa), removing a small amount of water present by way of its lower boiling, binary azeotrope. Palmitic acid (95%) was obtained from Twin Rivers Technologies (Quincy, MA) and used as received.

Ignition Quality Test and DCN

The DCN of the 2RTHF (sample volume 100 mL) were collected by the Southwest Research Institute® (San Antonio, TX) using an ignition quality test (IQT) apparatus according to the published method (ASTM D6890, 2018). The ignition delay time (τ) for each fuel is measured

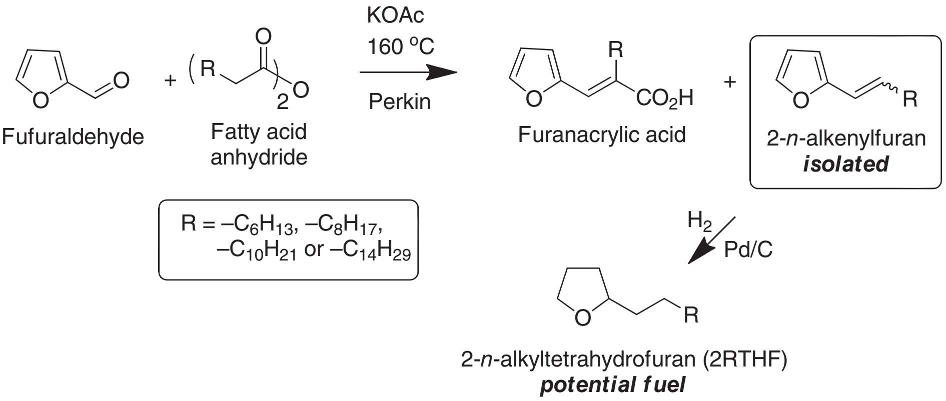


Fig. 1 Synthesis of 2-*n*-alkenylfuran by Perkin condensation of fatty acid anhydride and furfuraldehyde followed by catalytic hydrogenation to 2-*n*-alkyltetrahydrofuran (2RTHF)

(ms) and averaged over 32 combustion cycles. The DCN value is then calculated based on τ and the equations found in the standard method.

Melting Point

The melting points of the 2RTHF were determined by using a TA Instruments Q200 differential scanning calorimeter (DSC). Analyte (2–4 mg) in a hermetically sealed aluminum pan was cooled to −90 °C under a nitrogen atmosphere (50 mL min^{-1}) followed by slow heating to 30 °C at a rate of 5 °C min^{-1}. The intersection of the slopes of the base and the descending curve of the left side of the endothermic peak was taken as the melting point (Höhne et al., 1996). Complete DSC thermograms of the 2RTHF can be found in Figs S8–S11, Supporting Information.

Flash Point

The flash point data for the 2RTHF (sample volume 2 mL) were collected with a Grabner Instruments MiniFlash FLP using the closed cup method (ASTM D7094, 2017).

Density and Kinematic Viscosity

Density and kinematic viscosity of the 2RTHF were obtained simultaneously using an Anton-Paar SVM 3001 Stabinger viscometer by the published method (ASTM D4052-18, 2018). The instrument was injected with analyte (~3 mL) and set to run from 30 to 40 °C in 5 °C increments. The data were collected at 40 °C as this is the temperature specified in ASTM 975 for diesel fuels (ASTM D975, 2018). For safety reasons, the 2-*n*-butylTHF sample was run from −20 to 20 °C in 5 °C increments. The instrument was cleaned and dried between measurements of each analyte. Tables and charts of these data can be found in Tables S1 and S2 and Figs. S2 and S3, Supporting Information.

Bomb Calorimetry

The gross heats of combustion (H_c), or calorific values, of the 2RTHF were obtained using a Parr 6725 Semi-micro Calorimeter outfitted with a Parr Calorimeter Thermometer according to the standard method (ASTM D240, 2017). Benzoic acid was used as the internal standard (e.g., spike) for the tests and to calculate the energy equivalent of the instrument. Between each combustion measurement, the oxygen bomb was disassembled and cleaned with distilled water. The gross heat of combustion (H_c) was calculated from the average of three separate measurements of each analyte (70–90 mg). There was only 1.3% maximum SD in the measurements of each analyte, see Tables S3–S7 for the raw data tables. From H_c (kJ g^{-1}), the net heat of combustion (H_n) in kJ g^{-1} was calculated (Babrauskas, 1992; Jessup, 1960):

$$H_n = H_c - [21.96 \times (\text{weight fraction hydrogen of the analyte})]. \tag{1}$$

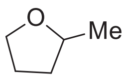
This equation deducts the enthalpy of vaporization of water, resulting from the complete oxidation of the hydrogen contained in the analyte.

Group Contribution Methodology to Predict Heat of Combustion

The gross heat of combustion (Q_c) for the 2RTHF was calculated using the data and method reported by Walters (2002). To illustrate the method, 2-methyltetrahydrofuran is calculated in the following manner. The 2-methyltetrahydrofuran molecule is broken into its basic structural moieties: ether (—O—), methylene (–CH_2–), and methyl (–CH_3). The number of each moiety (N_i), molecular weight (M_i), and heating value (H_i) are delineated according to the Walters model, Table 1. The heating values are then incorporated for the calculated gross heat of combustion (Q_c):

$$Q_c = \Sigma N_i H_i / \Sigma N_i M_i. \tag{2}$$

Table 1 Walters GCM heat of combustion values of 2-methyltetrahydrofuran

	Structural moiety (*i*)	N_i	M_i (g mol^{-1})	Group H_i (kJ mol^{-1})	N_iM_i (g)	N_iH_i (kJ)
	–CH_3	1	15	775	15	775
	–CH_2–	4	14	670	56	2,680
	–O–	1	16	−132	16	−132
		Total			87	3,323

Therefore, for 2-methyltetrahydrofuran, $Q_c = 3{,}323$ kJ/87 g = 38.19 kJ g^{-1}. Q_c for each of the family of 2RTHF was calculated similarly, simply differing in the number of $–CH_2–$ moieties.

Gas Chromatography–Mass Spectrometry

The analysis was conducted on an Agilent 5973N mass selective detection using a 6890N network gas chromatograph outfit with an Agilent J&W HP-5ms column (0.25 mm ID, 30 m length). The temperature program was 3 min at 40 °C and then the oven was ramped to 300 °C at a rate of 20 °C min^{-1} and held at the final temperature for 20 min. Injections (1 μL, CH_2Cl_2 solvent) were made splitless with a carrier gas (He) flow rate of 1 mL min^{-1} and at an inlet temperature of 275 °C. A portion of this data Figs. S4–S6 can be found in the Supporting Information.

Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy of the synthesized compounds was performed to ensure the correct chemical constitution and qualitative purity. Solutions for NMR analysis were made by dissolving the analyte (~20 mg) in deuterated chloroform ($CDCl_3$, 1 mL). All data were collected on a Bruker Avance II 300 MHz spectrometer (^1H at 300 MHz, ^{13}C at 75 MHz). NMR data (free-induction decay's) were processed using ACD/NMR Processor software (Advanced Chemistry Development Inc., Toronto, Ontario, Canada). All spectra were referenced to solvent or tetramethylsilane. Complete NMR spectra of all the compounds synthesized in this report can be found in Figs S12–S30, in the Supporting Information.

Elemental Microanalysis

In further support for the chemical identity and purity of the molecules made in this report, elemental microanalysis of the 2RTHF and their chemical intermediates were made by Atlantic Microlab, Inc. (Norcross, GA, USA).

Preparation of Fatty Acid Anhydrides

The preparation of the fatty acid anhydride from the fatty acids (caprylic/capric [2/1], lauric, and palmitic) was all done in the same manner exemplified by the synthesis of lauric anhydride detailed below.

Lauric Anhydride

A round-bottomed flask (3 L) equipped with a magnetic stirring bar and a reflux condenser was charged with lauric acid (1.09 kg, 5.4 mol) and Ac_2O (13.5 mol, 1.38 kg, 1.275 L, 2.5 equiv.). The mixture was heated with a heating mantle to boiling for 5 hours. Afterward, the reflux condenser was replaced with a distillation head and the reaction mixture was distilled at atmospheric pressure. Once the temperature of the distillate fell below 100 °C, the distillation was then conducted at reduced pressure (1.3 kPa) to remove the remaining portion of acetic acid. The distillation pot was allowed to cool to rt, during which time the reaction product solidified. No further purification was performed nor was necessary, m.p.: 37–40 °C; lit. 41.2–41.5 °C (Sonntag et al., 1954). ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 2.46 (triplet, $J = 7.6$ Hz, 4H), 1.67 (pentet, $J = 7.4$ Hz, 4H), 1.41–1.21 (multiplet, 32H), and 0.9 (triplet, $J = 6.9$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 169.84, 35.52, 32.12, 29.81, 29.79, 29.62, 29.54, 29.42, 29.09, 24.47, 22.89, and 14.32. Elemental analysis calculated for $C_{24}H_{46}O_3$ (382.6): C, 75.34; H, 12.12%. Found: C, 75.35; H, 12.26%.

Preparation of 2-n-Alkenylfuran

The preparation of 2-*n*-alkenylfurans by the Perkin reaction between fatty acid anhydrides and furfuraldehyde catalyzed by base was all done in the same manner, which is exemplified by the synthesis of the 2-*n*-octenylfuran/2-*n*-decenylfuran (2/1) mixture described below.

Cis/trans 2-n-Octenylfuran and cis/trans 2-n-Decenylfuran (2/1) Mixture

A two-necked, round-bottomed flask (2 L) equipped with a magnetic stirring bar was filled with a caprylic/capric anhydride mixture (401 g, 1.39 mol), furfuraldehyde (134 g, 115.5 mL, 1 equiv.), and anhydrous KOAc (137 g, 1 equiv.). The side neck was equipped with a thermometer to monitor the internal temperature. A reflux condenser was equipped to the other flask neck. The mixture was heated on a stir plate with a heating mantle with the Variac set to 40% power. During the heating up period, it was noticed that some liquid was distilling at ~100 °C while gas was evolving. The color of the reaction also changed to dark brown during once the mixture reached maximum temperature. After 5 hours, evolution of the gas had ceased. The heating was shut off to allow the mixture to cool down to ~100 °C. The thermometer was replaced with a glass stopper and the condenser was replaced with a short-path, reduced pressure distillation head. The heating mantle was turned on again and the mixture was distilled (1.3 kPa) to obtain a pale yellow liquid in the receiver (~100 g). The distillate was partitioned between hexanes (500 mL) and 1 M KOH (2 L). After allowing the phases to break, the organic layer was separated and washed with H_2O (1 L) followed by brine (1 L). The organic layer was dried over anhydrous $MgSO_4$

(10 g) for 20 min, filtered, and then the solvent was rotary evaporated. The residue was then distilled at reduced pressure (b.p. 84–94 °C, 13 Pa) to give the product as a pale yellow liquid (40 g, 16%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.43–7.31 (multiplet, 1H), 6.47–5.54 (multiplet, 4H), 2.56–2.12 (multiplet, 2H), 1.60–1.22 (multiplet, 15H), and 0.94 (triplet, $J = 7.2$ Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 153.41, 141.11, 131.44, 130.27, 118.49, 117.23, 111.02, 108.65, 105.80, 34.69, 32.84, 31.93, 31.78, 31.64, 29.53, 29.33, 29.26, 29.13, 28.92, 25.31, 22.71, 22.69, 22.66, and 14.11. Elemental analysis calculated for 1 $C_{12}H_{18}O$ + 0.5 $C_{14}H_{22}O$: C, 81.09; H, 10.39%. Found: C, 79.21; H, 10.14%.

Preparation of 2RTHF

The preparation of the 2RTHF by heterogeneous, catalytic hydrogenation of the 2-*n*-alkenylfurans was accomplished in the same manner exemplified by the synthesis of 2-*n*-dodecyltetrahydrofuran described below.

2-n-Dodecyltetrahydrofuran

A mixture of *cis*/*trans* 2-*n*-dodecenylfuran (129.17 g, 550 mmol), 5% Pd on carbon (10 g, 7.7 wt.%), and anhydrous THF (100 mL) was loaded into a pressure bottle and hydrogenated (275 kPa) on a Parr shaker apparatus. Uptake of hydrogen was completed after 1.5 hours. The mixture was filtered through diatomaceous earth to remove the catalyst and the solvent was rotary evaporated. The crude product was distilled at reduced pressure (b.p. 90–107 °C, 13 Pa) to obtain the pure product as a colorless liquid (123 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 3.93–3.61 (multiplet, 3H), 2.02–1.78 (multiplet, 3H), 1.58–1.16 (multiplet, 25H), and 0.88 (triplet, $J = 7$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 79.43, 67.55, 35.75, 31.92, 31.38, 29.76, 29.67, 29.64, 29.62, 29.60, 29.35, 26.41, 25.70, 22.67, and 14.08. Elemental analysis calculated for $C_{16}H_{32}O$ (240): C, 79.93; H, 13.42%. Found: C, 79.97; H, 13.37%.

2-n-Octyltetrahydrofuran and 2-n-Decyltetrahydrofuran (2/1) Mixture

The product was distilled at reduced pressure (13 Pa) to obtain the pure compound as a colorless liquid that had a mild floral odor. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 3.92–3.57 (multiplet, 3H), 2.0–1.73 (multiplet, 3H), 1.58–1.14 (multiplet, 17H), and 0.84 (triplet, $J = 7$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 79.38, 67.48, 35.71, 31.85, 31.34, 29.73, 29.58, 29.57, 29.55, 26.37, 25.66, 22.61, and 14.01. Elemental analysis calculated for $2C_{12}H_{24}O$ + $1C_{14}H_{28}O$: C, 78.55; H, 13.18%. Found: C, 77.71; H, 12.86%.

2-n-Hexadecyltetrahydrofuran

The product was distilled at reduced pressure (140–150 °C, 13 Pa) to obtain the pure compound as a colorless liquid that slowly became a crystalline slush when stored at room temperature overnight. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 3.91–3.66 (m, 3H), 2.04–1.77 (m, 3H), 1.51–1.22 (m, 31H), and 0.89 (triplet, $J = 7$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 79.46, 67.57, 35.76, 31.94, 29.78, 29.71 (overlapping signals), 29.68, 29.64, 29.62, 29.38, 26.43, 25.72, 22.70, and 14.11. Elemental analysis calculated for $C_{20}H_{40}O$ (296.5): C, 81.01; H, 13.60%. Found: C, 81.27; H, 13.77%.

2-n-Butyltetrahydrofuran

Reduced pressure distillation (58–62 °C, 1.3 kPa) gave this compound as a colorless, mobile liquid with a strong floral odor. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 3.95–3.51 (multiplet, 3H), 2.02–1.69 (multiplet, 3H), 1.61–1.13 (multiplet, 7H), and 0.85 (triplet, $J = 7.2$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 79.34, 67.47, 35.37, 31.31, 28.52, 25.64, 22.74, and 13.95. Elemental analysis calculated for $C_8H_{16}O$ (128): C, 74.94; H, 12.58%. Found: C, 73.27; H, 12.25%.

Results and Discussion

Preparation of 2RTHF

The Perkin reaction is a well-known carbon–carbon bond-forming condensation between an aldehyde and a carboxylic acid anhydride catalyzed by base. Although furfuraldehyde is widely available, medium-chain and long-chain fatty acid anhydrides are not commercial products. The latter can be made by reaction of their acid chlorides with acetic anhydride or by dehydration with dicyclohexylcarbodiimide (Selinger and Lapidot, 1966; Sonntag et al., 1954). These methods require solvents and expensive and/or hazardous reagents such as thionyl chloride. Instead, dehydration of the fatty acids (caprylic, capric, lauric, and palmitic) to their anhydrides was effected by heating in excess acetic anhydride followed by distillative decomposition of the intermediate acetic–fatty acid mixed anhydride (Albitzky, 1900; Wallace Jr. and Copenhaver, 1941). NMR spectra (^{1}H and ^{13}C) of the fatty acid anhydrides can be found in the Figs S12–S15. Although this method can also form fatty ketones by decarboxylation, we did not run into this problem or such by-products were generated in small quantity that they did not otherwise interfere with the intended chemistry (Stipp and Kluesener, 1995). The caprylic and capric acids were a commercial mixture obtained from distillation of coconut oil, a 2:1 ratio, respectively, and no attempt to separate the two symmetrical anhydrides was made (Cermak et al., 2012; Combs, 1985). Using this fatty acid anhydride mixture created a mixed 2-*n*-alkenylfuran and RTHF, which were also not separated.

With the fatty acid anhydrides and furfuraldehyde in hand, the Perkin reaction conditions chosen were a molar equivalent mixture of fatty acid anhydride:furfuraldehyde:potassium acetate. The most expedient scale to run was ~1.5 mol of fatty acid anhydride, which produced a reaction mixture that could be magnetically stirred. The reactions were heated to 160 °C for 5 hours. Working up the reaction by water/organic solvent extraction was severely complicated by the fact that the aqueous base generated a soap solution and concomitant emulsion. Instead, the reaction mixture was distilled at reduced pressure, which gave a distillate containing varying proportions of 2-*n*-alkenylfuran, acetic, and fatty acids. The distillate was then extracted with aqueous potassium hydroxide to remove the by-products acetic and fatty acids. Afterward, the pure 2-*n*-alkenylfurans were obtained by distillation as *cis*/*trans* regioisomeric mixtures of the alkene, Fig. S1a.

The proton NMR spectra clearly distinguished these isomers, which together created a complicated aromatic region. The isomeric –CH_2– bonded to alkene are clearly differentiated in the 2–2.5 ppm region. The *cis* isomer has an alkene signal with characteristic ~11 Hz coupling in the 5.5 ppm region (Fig. 2).

In addition, gas chromatography–mass spectrometry (GCMS) showed that the *cis*/*trans* ratio was typically 1/2, which corroborates the NMR signal integrations (Figs S4 and S6). No optimization of the reactions conditions and product yield were made. From these fatty acid anhydrides,2-*n*-alkenylfurans were obtained in approximately 15–20% yield. The complete NMR spectra (^{1}H and ^{13}C) of 2-*n*-alkenylfurans can be found in the Figs S18–S22. A survey of the literature found only two reports of further decarboxylation under the Perkin conditions of furfuraldehyde with the short, branched carboxylic anhydrides, isobutyl and isovaleric (Baeyer, 1877; Schaarschmidt et al., 1918). In these two instances, the 2-alkenylfurans were the sole products isolated. It has already been shown that neat furanacrylic acid will undergo decarboxylation to 2-vinylfuran, albeit at much higher temperature, by heating at 300–320 °C in a tube furnace (Moureu et al., 1927; Wagner, 1947). Although these decarboxylated 2-*n*-alkenylfurans were obtained in low yield, the conditions for their formation were rather mild in contradistinction with those effecting decarboxylation of fatty acids (transition metals, >300 °C) (Fu et al., 2011; Knothe et al., 2017; Mohite et al., 2014; Wu et al., 2016).

Finally, 2-*n*-alkenylfurans were reduced by catalytic hydrogenation (275 kPa H_2, 5% Pd/C) in tetrahydrofuran solvent to remove all unsaturation and furnish 2RTHF. These reductions were very facile with a 5–10 wt.% loading of 5% palladium on the carbon catalyst, typically completing in 1 hour. 2-RTHFs were isolated by distillation and the yields were approximately 90%, Fig. S1b. Proton NMR showed all of the aromatic and alkene resonances between 5–8 ppm chemical shift were eliminated and the characteristic

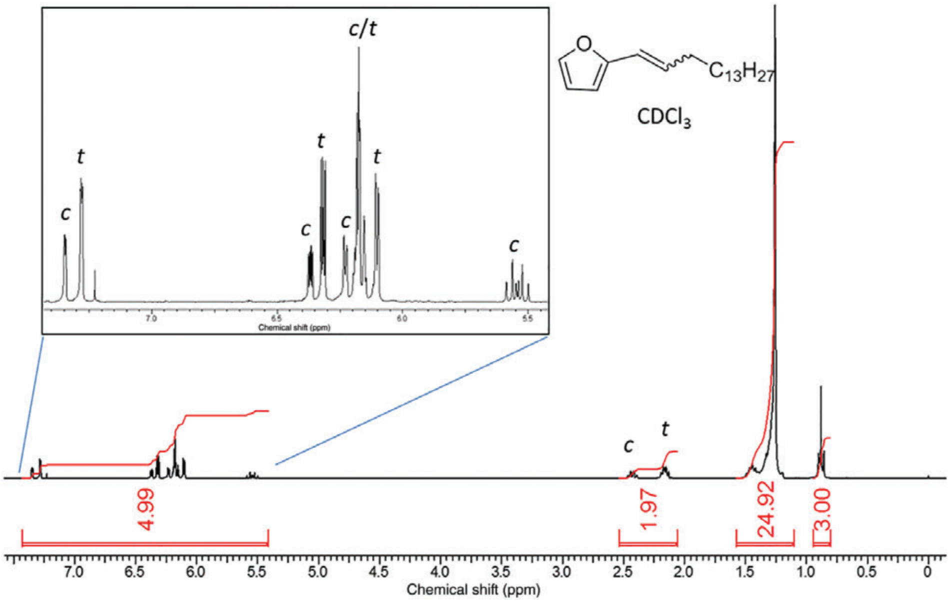


Fig. 2 Proton NMR spectrum of pure *cis*/*trans* 2-*n*-hexadecenylfuran from Perkin condensation

complicated splitting pattern and chemical shift for substituted THF were observed at 1.75 and 3.75 ppm (Fig. 3).

Gas chromatography–mass spectrometry showed that 2RTHF had excellent purity (>97%). The complete NMR spectra (^{1}H and ^{13}C) and GCMS traces of the 2RTHF can be found in the Figs 25–30; Figs S5 and S7. Although the pot residues from the distillations were not analyzed further, the mass balance was likely high-boiling, alcohol by-products from THF ring opening known to occur in nickel-catalyzed hydrogenation of 2-hydroxymethylfuran (Lukes and Nelson, 1956).

For comparison purposes, 2-butylTHF was also synthesized by the Perkin route because it was shown to have an adequate cetane number for diesel (Sudholt et al., 2015). Although details of their synthesis of 2-butylTHF were not included, others have synthesized this compound using more complicated synthetic methods than the one described here (Julis and Leitner, 2012; Xu et al., 2011). The synthesis details and NMR spectra (^{1}H and ^{13}C) of 2-*n*-butenylfuran and 2-butylTHF can be found in the Figs S16, S17, S23 and S24.

Fuel Property Analyses of the 2RTHF with Comparison to D#2, Naval Distillate Fuel, Biodiesel, and Related Structures

The successful synthesis of relatively large quantities (~100 g) of 2RTHF allowed for a preliminary study of their properties related to liquid fuels in particular the diesel range. Only some of the basic fuel properties were examined using analytical instruments and services available including: melting point, flash point, kinematic viscosity, calorific value, and DCN. These data were compared with the corresponding data, related data, and/or specifications given for two diesel-type fuels: diesel 2 (D#2) and biodiesel (B100). Diesel #2 is the typical road-grade fuel found at automotive service stations in North America (ASTM D975, 2018). Biodiesel (B100), a specific chemical category of biofuel, is by definition monoalkyl esters of animal or vegetable fatty acids (ASTM D6751, 2015). Because 2RTHF are biogenic, they can also be classified as a form of biofuel. In addition, they are oxygenated hydrocarbons so comparison with B100 seemed to be appropriate.

Melting Point and Flash Point

The flash point of an organic compound is the temperature at which a spark can ignite the compound into combustion in a standard air atmosphere. In the series of 2RTHF, there is an obvious trend of increasing flash point temperature as the alkyl group length increases, Table 2. 2-ButylTHF had a very low flash point (<20 °C) that is well below the minimum flash point cutoffs for D#2 (52 °C) and B100 (93 °C). This derivative is, therefore, highly flammable and will likely have a high evaporation rate owing to its low molecular weight. The mixed 2RTHF had a flash point of 98.2 °C, which is just above the minimum for B100. The mixed 2RTHF is composed of two components, 2-octylTHF and 2-decylTHF. These would require separation before their individual flash points could be measured. However, the flashpoint of 2-octylTHF must be less than 2-decylTHF based on molecular weight. The higher

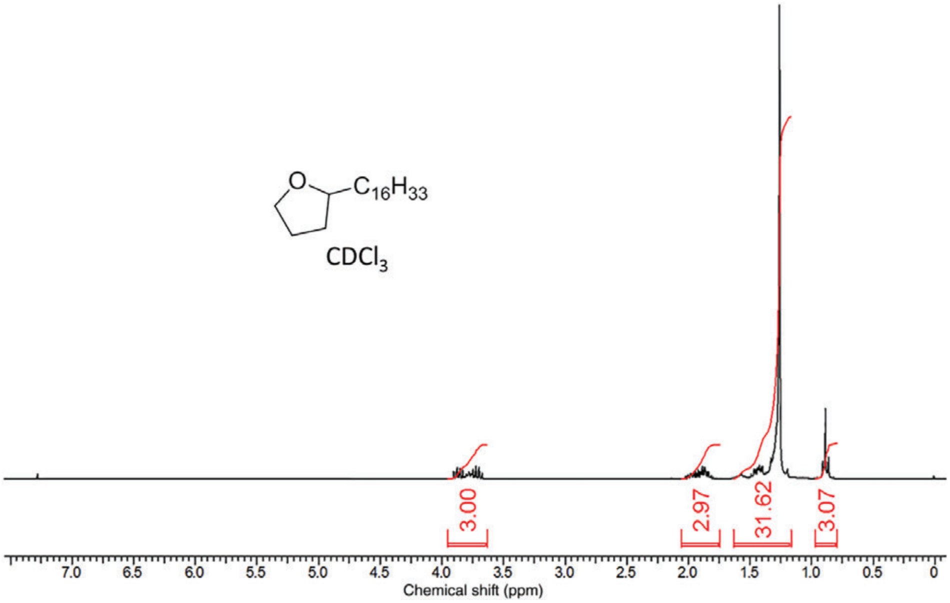


Fig. 3 Proton NMR spectrum of pure 2-*n*-hexadecyltetrahydrofuran made from palmitic acid

Table 2 Flash points and melting points and cloud points of 2RTHF and D#2 and B100

	Molecular formula	Flash point (°C)	Melting point (°C)	Cloud point (°C)	References
2-butylTHF	$C_8H_{16}O$	<20	< −90		
2-octylTHF/2-decylTHF[a]	$C_{12.6}H_{25.3}O$[a]	98.2	−39		
2-dodecylTHF	$C_{16}H_{32}O$	145.5	0.4		
2-hexadecylTHF	$C_{20}H_{40}O$	183.1	20.5		
D#2		≥52		−12	ASTM D975 (2018); Diemand (1991)
B100		≥93		−2 to 3	ASTM D6751 (2015); Knothe (2008)

[a] 2/1 mixture.

homolog 2RTHF each had flash points (145.5 and 183.1 °C) well above the minimum limits for these diesel fuels.

The effect of cold temperatures on diesel fuels is very important because waxes or other components can fall out of solution and cause clogging of fuel injectors and prevent the engine from running properly. The cloud point test is typically used to study the low temperature operability of diesel fuels and the cloud point is the minimum temperature at which the fuel becomes cloudy or hazy in appearance. Diesel #2 is a mixture composed of hundreds of different compounds, which results in a lower cloud point. Although B100 is also a mixture, it may be composed of an order of magnitude fewer compounds and generally has a higher cloud point. The 2RTHF made in this study are unimolecular or bimolecular in the case of 2-octylTHF/2-decylTHF mixture. Thus, they are more likely to freeze below ambient temperatures. Therefore, the melting point was a more appropriate measurement for the 2RTHF, although not typically specified for diesel fuels. Future work will measure cloud and pour points of the 2RTHFs to quantify these parameters.

At room temperature, all of the 2RTHF were liquids except for 2-hexadecylTHF, which slowly crystallized on the bench. The melting points of the 2RTHF were collected by DSC, see Figs S8–S11. 2-ButylTHF did not show a melting point over the temperature range studied (−90 to 30 °C) so this value must be lower than −90 °C, Table 2. The 2-butylTHF differs only by C_2H_2 with 2-methylTHF, which has a melting point of −136 °C (Sigma-Aldrich, 2018). As the length of the alkyl chain increased, the melting point of 2RTHF also increased. The mixed 2RTHF had a melting point of −39 °C well below either cloud point of D#2 (−12 °C) and soybean B100 (−2 to 3 °C). The binary mixed RTHF only showed a single melting endotherm, in contrast binary mixtures of fatty acid methyl esters showed two endotherms, one for each component (Dunn, 2008). 2-DodecylTHF had a melting point of 0.4 °C that is just within measurements for soybean B100 (−2 to 3 °C). The highest homolog 2-hexadecylTHF had a melting point of 20 °C almost exactly 20 °C higher than 2-dodecylTHF and was well above cloud point specifications for D#2 and B100.

Density and Kinematic Viscosity

The density of liquids fuels is important because their energy content is commonly related to volume rather than mass. The viscosity of liquid fuels is also important, especially for diesels, because it can change according to temperature. The kinematic viscosity is the significant viscosity measurement for fuels because it is the ratio of dynamic viscosity to density. Density and kinematic viscosity are typically measured at 40 °C for diesel fuels. Owing to the

Table 3 Comparison of densities (ρ), kinematic viscosities (kv) of 2RTHF and D#2 and B100

	Molecular formula	T (°C)	ρ (g mL^{-1})	kv (mm^2 s^{-1})	References
2-butylTHF	$C_8H_{16}O$	20	0.857	1.17	
2-octylTHF/2-decylTHF[a]	$C_{12.6}H_{25.3}O$[a]	40	0.851	2.26	
2-dodecylTHF	$C_{16}H_{32}O$	40	0.838	4.17	
2-hexadecylTHF	$C_{20}H_{40}O$	40	0.839	7.27	
D#2		40		1.9–4.1	Bacha et al. (2007); ASTM D975 (2018)
		15	0.85		
B100		40	0.867	1.9–6.0	ASTM D6751 (2015); Doll et al. (2008)

[a] 2/1 mixture.

low flash point of 2-butylTHF (<20 °C), its measurements were made up to 20 °C to minimize evaporation and provide better safety margin. The viscosities of the 2RTHF increased with increasing length of the alkyl chain, Table 3. Among the 2RTHF, the viscosity roughly doubled with each addition of four carbons to the alkyl chain. 2-ButylTHF had water-like viscosity (1.17 $mm^2\ s^{-1}$), which was slightly low compared to specifications for D#2 and B100 ($\geq 1.9\ mm^2\ s^{-1}$). 2-ButylTHF behaved more like gasoline ($< 1\ mm^2\ s^{-1}$ at 38 °C) than a diesel fuel. The mixed 2RTHF (2.26 $mm^2\ s^{-1}$) and 2-dodecylTHF (4.17 $mm^2\ s^{-1}$) each had viscosities within the D#2 and B100 fuel specifications. However, 2-hexadecylTHF had the highest viscosity (7.27 $mm^2\ s^{-1}$) of the 2RTHF group, even outside the range of B100 ($\leq 6.0\ mm^2\ s^{-1}$).

Another clear trend among the 2RTHF (0.85–0.83 g mL^{-1}) was that density decreased as the alkyl chain length increased, Table 3, which paralleled the density (0.859–0.849 g mL^{-1}) in the family of fatty acid methyl esters (caprylate, laurate, palmitate, and stearate) (Pratas et al., 2010). The density of mixed 2RTHF (0.851 g mL^{-1}) was in specification for D#2 (0.85 g mL^{-1}) although the latter is measured at 15 °C. Although density at 40 °C is not a specification for B100, densities of all of the 2RTHF were slightly less than the density of commercial soybean B100 (0.867 g mL^{-1}).

Heat of Combustion

Energy content is an important property of liquid fuels, because it correlates with the fuel's capacity to do work. The energy content or calorific value of a fuel can be determined by measuring the heat released during its combustion, always an exothermic process. The energy content of the 2RTHF was measured by oxygen bomb calorimetry. As an internal check of our experimental methods, the gross heat of combustion (H_c) of the reference fuel cetane was measured and our value (47.03 kJ g^{-1}) differed by less than 1% to data found by Fraser and Prosen (1955). Combustion of hydrocarbons by oxygen yields carbon dioxide and water. H_c obtained using a bomb calorimeter is the sum of the heat output of both the combustion of the analyte *and* heat released during condensation of the by-product water vapor contained in the closed system. H_c is also referred to as the higher heating value. In contrast, an internal combustion engine is an open system because the resulting water vapor escapes along with the exhaust fumes from the combustion cylinder. Thus, the additional heating value from water condensation is not captured by the engine. For this reason, with liquid fuels it is more useful to compare net heats of combustion (H_n), also known as lower heating values. When the molecular formula of the analyte is known, it is straightforward to calculate H_n from H_c (Jessup, 1960).

H_n increased as the alkyl chain lengthened among the 2RTHF, from 34.75 kJ g^{-1} for 2-butylTHF up to 40.18 kJ g^{-1} for 2-hexadecylTHF, Table 4. Although H_n is not a specification for B100, apart from 2-butylTHF, all of the higher 2RTHF had H_n exceeding the measured value for soybean B100 (37.7 kJ g^{-1}). However, the energy content of the 2RTHF all fell short of the measurement for D#2 (42.64 kJ g^{-1}). Even 2-hexadecylTHF with the longest alkyl chain of the group was 6% less than H_n of D#2. 2-DodecylTHF (39.72 kJ g^{-1}), which differs from parent cetane (43.73 kJ g^{-1}) by replacement of two hydrogen atoms by one oxygen atom, lost ~10% energy content by that change in oxidation.

When large quantities of calorific data have been collected on a wide range of organic chemical structures, it is possible to build models to predict the heating value of new organic molecules. The group contribution method (GCM) reported by Walters (2002) was used to predict the heating value (Q_c) of 2RTHF. As can be seen from Table 4, the GCM predictions were remarkably close, only 3–7% higher than H_c. Nevertheless, these data demonstrate that GCM is a useful tool for predicting heats of combustion of organic compounds. To approach the D#2 energy specification (H_c = 45.30 kJ g^{-1}) with a 2RTHF analog, GCM predicts that the 2RTHF would need to be made from behenic anhydride (2-docosanylTHF; Q_c = 45.17 kJ g^{-1}). And, because the GCM estimates were found to be a little high, a 2RTHF with $H_c > 45$ kJ g^{-1} would likely need to be made from very long-chain fatty acid > C_{22}.

Derived Cetane Number

The cetane number (CN) of a fuel is a dimensionless value showing the relative ranking of a fuel's autoignition characteristics versus the primary reference fuel cetane (hexadecane, $C_{16}H_{34}$), which is assigned CN = 100. Fuels with a higher CN have better combustion performance characteristics for compression ignition engines. The traditional method to obtain the CN of a test fuel is using the Cooperative Fuel Research (CFR) engine; however, this method requires a large sample volume (1 L) (ASTM D613, 2018). Instead, a more recent method employing an IQT apparatus was used to determine the DCN for the 2RTHF (ASTM D6890, 2018). Combustion analysis by IQT requires just 100 mL of the sample and we could prepare 2RTHF on this scale. It has already been shown that these two CN evaluations correlate well (Allard et al., 1997; Wilson III, 2016; Yanowitz et al., 2017), and so for the purposes of the comparative discussion below, CN and DCN are assumed equivalent.

During the project, the related research by Sudholt et al. (2015) on the combustion characteristics of 2RTHF with short *n*-alkyl chains (methyl, ethyl, and butyl) was

Table 4 Experimental gross (H_c), net (H_n) and calculated gross (Q_c) heats of combustion data of 2RTHF and cetane, D#2 and B100

	Molecular formula	H_c (kJ g^{-1})	H_n (kJ g^{-1})	Q_c (kJ g^{-1})	References
2-butylTHF	$C_8H_{16}O$	37.49	34.75	40.48	
2-octylTHF/2-decylTHF[a]	$C_{12.6}H_{25.3}O$[a]	41.06	38.18	43.06	
2-dodecylTHF	$C_{16}H_{32}O$	42.64	39.72	43.92	
2-hexadecylTHF	$C_{20}H_{40}O$	43.14	40.18	44.66	
Cetane	$C_{16}H_{34}$	47.03	43.73	48.36	
D#2		45.30	42.64		Boruff et al. (1982); Bacha et al. (2007)
B100 (soy)		40.4	37.7		Barabás and Todoruţ (2011)

[a] 2/1 mixture.

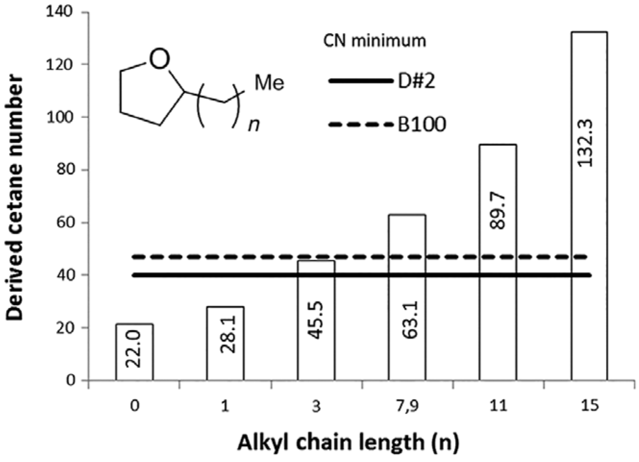


Fig. 4 Chart of derived cetane numbers (DCN) vs. chain length of 2RTHF from this study together with those of Sudholt et al. (2015) determined by IQT (ASTM D6890, 2018)

discovered. The DCN data for the latter 2RTHF and the higher homologs from this study are collected in Fig. 4. One can clearly see the trend of increasing DCN as the alkyl chain is lengthened, from methyl = 22.0 up to hexadecyl = 132.3. 2-MethylTHF and 2-ethylTHF are poor diesel fuels with low DCN. 2-ButylTHF appears to be the cutoff among this chemical class for adequate diesel combustion properties among the 2RTHF because the US minimum CN for D#2 is 40. However, 2-butylTHF falls slightly below the CN specification for B100 of 47. All of the 2RTHF made in this study well exceed the CN minimums for D#2 and B100. The long-chained 2RTHF seem to behave in compression ignition engines much like long linear alkanes that also have short ignition delays.

The DCN values of the 2RTHF and cetane values of diesel fuels are collected in Table 5. Included in the table are data for cetane (DCN = 100.5), which shows the close correlation between the CFR and IQT cetane number methods. As the chain length in 2RTHF increased, the ignition delay time (τ) decreased. Short ignition delay is favorable and indicates the fuel is less likely to cause knock in a diesel engine. τ for 2RTHF (3.18–2.03 ms) were well below that measured for D#2 (4.95 ms) and corn B100 (3.79 ms), although τ is not a specification of either fuel. It should be pointed out that fuels with fast ignition ($\tau < 3.1$ ms) such as 2-dodecyl- and 2-hexadecyl-THFs fall outside of the fuel data set used to create the DCN calculations (ASTM D6890, 2018; Dahmen and Marquardt, 2015). Tripling the

Table 5 Derived cetane number (DCN) and ignition delay time (τ) for 2RTHF and cetane number (CN) for diesel fuels

	Molecular formula	τ (ms)	DCN[a]	CN[b]	References
2-methylTHF	$C_5H_{10}O$		22.0		Sudholt et al. (2015)
2-ethylTHF	$C_6H_{12}O$		28.1		Sudholt et al. (2015)
2-butylTHF	$C_8H_{16}O$		45.5		Sudholt et al. (2015)
2-octylTHF/2-decylTHF[c]	$C_{12.6}H_{25.3}O$[c]	3.18	63.1		
2-dodecylTHF	$C_{16}H_{32}O$	2.47	89.7		
2-hexadecylTHF	$C_{20}H_{40}O$	2.03	132.3		
Cetane	$C_{16}H_{34}$		100.5	100	ASTM D613 (2018); Yanowitz et al. (2017)
D#2		4.95		≥40	Zheng et al. (2012); ASTM D975 (2018)
B100		3.79[d]		≥47	ASTM D6751 (2015); Wasfi (2017)

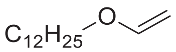
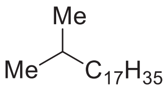
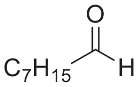
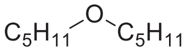
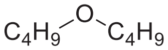
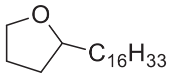
[a] ASTM D6890 (2018).

[b] ASTM D613 (2018).

[c] 2/1 mixture.

[d] Corn B100.

Table 6 Fuels reported with DCN > 100 by IQT

Fuel	Structure	DCN	Reference
Dodecyl vinyl ether		101.7	Dahmen and Marquardt (2015)
2-methyloctadecane		104.4; 104	Dahmen and Marquardt (2015); Yanowitz et al. (2017)
Octanal		109; 102.5	Dahmen and Marquardt (2015); Yanowitz et al. (2017)
Dipentyl ether		111	Yanowitz et al. (2017)
Dibutyl ether		115.4	Dahmen and Marquardt (2015)
2-hexadecyltetrahydrofuran		132.3	This work

chain length of 2-butylTHF to 2-dodecylTHF leads to roughly doubling of the DCN value. Adding oxygen to parent hydrocarbon cetane (100), as in 2-dodecylTHF (89.7), resulted in lower DCN.

Interestingly, the DCN of 2-hexadecylTHF (132) was higher than any recorded CN measured by CFR or IQT based on a recent compilation of 497 organic compounds by Yanowitz et al. (2017). Those six fuels with DCN > 100, along with 2-hexadecylTHF, are collected in Table 6. It is interesting to note that five of these six compounds are oxygenated hydrocarbons and of the latter, four are ethers including 2-hexadecylTHF. With little or no branching to their structure, ethers tend to promote autoignition and, therefore, have a higher CN (Dahmen and Marquardt, 2015), thus ethers have been studied as diesel fuels and cetane improving additives (Bailey et al., 1997; Chen et al., 2017; Lipkin, 1940; Park and Lee, 2013).

Conclusions

Although the yield was low (~20%), we were able to isolate and characterize 2-*n*-alkenylfurans on a preparative scale from the Perkin condensation of fatty acid anhydrides and furfuraldehyde. The conditions of the Perkin reaction are very "green" as there is no solvent, no heavy metal catalyst, relatively low temperature, and shows potential of recyclability of the by-product fatty acid. The unsaturated 2-*n*-alkenylfurans were easily transformed into hexahydro-derivatives, 2RTHF, by heterogeneous, palladium-catalyzed, low-pressure hydrogenation in high yield. 2RTHF made from caprylic, capric, lauric, and palmitic acids were tested as diesel fuels and had cetane numbers ranging from 63 to 132, which are much greater than the minimum specifications for US diesel #2 (40) and biodiesel (47). Increasing the length of the alkyl chain in 2RTHF also increased their melting points up to room temperature limiting the possibility of their use as a diesel fuel directly. Apart from short-chain members, the energy content of 2RTHF was equal or greater than biodiesel. Low-temperature operability was improved with a mixed 2RTHF, which had a low melting point (−39 °C) well below the cloud point specifications of D#2 and biodiesel. Further low temperature operability of 2RTHF may result with unsaturated fatty acids (e.g., oleic) and/or whole cut fatty acid mixtures as raw material inputs. Studies to better understand this manifold of the Perkin reaction and improve the poor yield of the process just described are currently underway.

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Conflict of Interest The authors declare that they have no conflict of interest.

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