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Article

# Catalytic Hydrothermal Deoxygenation of Stearic Acid with Ru/C: Effects of Alcohol- and Carboxylic Acid-Based Hydrogen Donors

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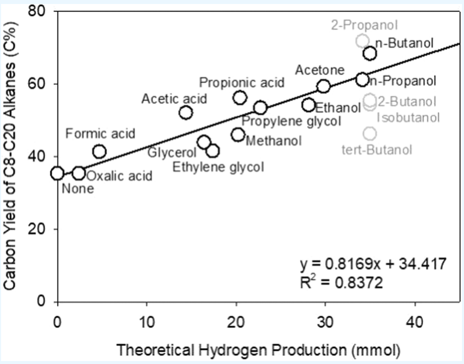
**ABSTRACT:** Catalytic hydrothermal processing is a promising technology for the production of biofuels used in transportation to alleviate the energy crisis. An important challenge for these processes is the need for an external supply of hydrogen gas to accelerate the deoxygenation of fatty acids or lipids. It follows that in situ-produced hydrogen can improve process economics. This study reports on the use of various alcohol and carboxylic acid amendments as sources for in situ hydrogen production to accelerate Ru/C-catalyzed hydrothermal deoxygenation of stearic acid. Addition of these amendments significantly increases yields of liquid hydrocarbon products, including the major product heptadecane, from stearic acid conversion at subcritical conditions (330 °C, 14−16 MPa during the reaction). This research provided guidance for simplifying the catalytic hydrothermal process of biofuel production, making the production of the desired biofuel in one pot possible without the need for an external $H_2$ supply.



## 1. INTRODUCTION

In recent years, due to the depletion of nonrenewable fossil fuels and increasing global concern for environmental pollution, biofuels have received increasing attention.[1] Biofuels derived from lipid materials, such as vegetable oils, animal fats, waste oils, and microalgae oils, have become attractive alternatives.[2] In addition, population growth and economic development produced growing quantities of waste. The production of waste lipids, including waste vegetable oil, waste animal fat residuals from meat animal processing facilities, and sewer trap grease, in the U.S. exceeds 10 billion pounds per year.[2] In China, more than 11 billion pounds of waste cooking oil is produced per year, some of which is recollected, recolored, and blended with fresh vegetable oil for resale, posing a significant threat to public health. Thus, identifying economically and environmentally sustainable pathways for converting waste lipids into viable biofuels can help to alleviate the energy crisis and provide an attractive alternative to unsafe reuse practices.

The main components of lipids are triglycerides and free fatty acids. Under hydrothermal conditions, triglycerides are rapidly hydrolyzed to free fatty acids and a glycerol coproduct. At present, there are two main deoxygenation strategies for converting fatty acids into alkane fuels, hydrodeoxygenation (HDO) and decarboxylation/decarbonylation (DCX/DCN).[3,4] The presence of excess hydrogen ($H_2$) in the reaction matrix serves both as an activator for some catalytic metals and metal oxide supports[5,6] and as a direct participant in HDO reactions.[7] In the absence of $H_2$, many unsaturated compounds are stable and will adsorb to and poison the active catalytic sites.[8−10] Some unsaturated compounds can also undergo polymerization reactions, producing coking deposits that can also contribute to catalyst deactivation[11] and reduce carbon recovery.[12]

Compared with externally supplied $H_2$, which requires an on-site delivery, $H_2$ produced in situ from organic coproducts or co-constituent amendments like glycerol,[5,13] methanol,[13,14] and formic acid[15] is an attractive alternative.[16] This can lower the net costs for production of hydrocarbon fuels. For example, the biodiesel industry produces a surplus of glycerol as a coproduct that is increasingly becoming a problem, so the use of such byproducts to accelerate the lipid and fatty acid deoxygenation process is a promising strategy for waste valorization. Hollak et al.[13] have verified the positive effect of glycerol on the hydrothermal deoxygenation of triglycerides and fatty acids over a Pd/C catalyst without an external hydrogen supply. Vardon et al.[17] employed glycerol as a hydrogen-generating amendment in the hydrogenation and deoxygenation of fatty acids over a Pt−Re/C catalyst in an inert atmosphere. They found that in situ-generated $H_2$ from glycerol accelerated both hydrogenation and decarboxylation reactions, even though the latter reaction does not include $H_2$. Similarly, the $Pt-Ni/Al_2O_3$ catalyst was reported to promote the aqueous phase reforming of glycerol, supporting the

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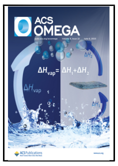

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Table 1. Products after Hydrothermal Reactions with Hydrogen Donors as Feedstock Alone

| | | | | products (mmol) | | | |
|---|---|---|---|---|---|---|---|
| entry | feedstock | reaction time (h) | conversion (C%)[aa] | $CH_4$ | $C_2H_6$ | $CO_2$ | $H_2$ |
| 1 | methanol | 2.5 | 97.9 | 4.57 | 0.00 | 2.03 | 1.47 |
| 2 | ethanol | 2.5 | 95.7 | 6.58 | 0.00 | 2.39 | 0.90 |
| 3 | *n*-propanol | 2.5 | 86.0 | 6.87 | 0.09 | 2.32 | 0.79 |
| 4 | *n*-butanol | 2.5 | 74.5 | 6.38 | 0.00 | 2.31 | 0.87 |
| 5 | ethylene glycol | 2.5 | 59.3 | 2.52 | 0.00 | 1.61 | 0.54 |
| 6 | propylene glycol | 2.5 | 71.3 | 3.95 | 0.02 | 2.10 | 0.81 |
| 7 | glycerol | 2.5 | 100.0 | 5.40 | 0.08 | 1.90 | 0.83 |
| 8 | 2-propanol | 2.5 | 48.1 | 4.02 | 0.37 | 1.48 | 1.91 |
| 9 | *n*-propanol | 0 | 58.8 | 3.74 | 0.87 | 1.78 | 1.02 |
| 10 | propylene glycol | 0 | 69.6 | 3.79 | 0.10 | 2.03 | 0.77 |
| 11 | glycerol | 0 | 79.0 | 3.10 | 0.03 | 2.43 | 0.94 |

[a] conversion (C %) = $\left(1 - \frac{\text{moles of carbon in feedstock after reaction}}{\text{moles of carbon in feedstock before reaction}}\right) \times 100\%$

complete hydrogenation and partial deoxygenation of fatty acids.[18,19] Kim et al.[2] applied the Pt−Re/C material to convert real waste oils (e.g., waste vegetable oil, sewer trap grease) into diesel-like hydrocarbons without external chemical inputs, employing the glycerol produced from lipid hydrolysis for in situ $H_2$ generation via aqueous phase reforming. Hwang et al.[15] examined the hydrothermal deoxygenation of crude jatropha oil over the Pd/C catalyst using formic acid as an amendment. They found that addition of formic acid increased the deoxygenation and initial resistance to catalyst deactivation significantly. In addition to glycerol and formic acid, a variety of alcohols and carboxylic acids can also generate $H_2$ in situ through aqueous phase reforming, steam reforming, and water−gas shift reactions.[20,21] However, the net effects of these amendments on hydrothermal deoxygenation reactions of long-chain fatty acids (e.g., stearic acid, oleic acid) remain unclear.

As far as we know, there are very few studies examining the efficacy of different low-molecular-weight organics for in situ production of hydrogen and their net effects on hydrothermal deoxygenation reactions of long-chain fatty acids. In the present study, we explored the promotion effects of a series of alcohol and carboxylic acids of low molecular weight on hydrothermal reactions of stearic acid catalyzed by Ru/C. Previous work from our team demonstrated stearic acid decarboxylation and alkane cracking reactions with Ru/C yield mixtures of liquid alkane and gaseous products that are dependent upon the headspace composition, with reaction rates being significantly accelerated under $H_2$ headspace.[5] Under a $N_2$ headspace, the reaction of an intact lipid was also found to be faster than the reaction of stearic acid due to in situ generation of $H_2$ by aqueous phase reforming of the glycerol.[5] Building on this finding, the current study aims to (1) screen potential hydrogen-forming amendments for their effects on the deoxygenation of stearic acid; (2) explore the relationships between characteristics of hydrogen donors and the net yield of stearic acid-derived hydrocarbon products; and (3) obtain insights that can be used to identify convenient, economical, and environmentally friendly strategies for producing liquid biofuels.

## 2. EXPERIMENTAL SECTION

**2.1. Chemicals.** Stearic acid (98%), *n*-butanol (99%), and ethanol (99.5%) were obtained from Macklin. The powdered Ru/C (5 wt %) catalyst and alkane standard solution C8−C20 were purchased from Sigma-Aldrich. Acetic acid (99.5%), sodium acetate (99.5%), 1-propanol (99%), 1,2-propanediol (99%), ethylene glycol (99.5%), propanol (99.5%), *n*-butanol (99%), and formic acid (99.5%), were obtained from Keshi. Methanol (99.5%), glycerol (99%), isopropyl alcohol (99.7%), iron (99.9%), and aluminum (99.9%) were obtained from Chuandong Chemical. Dichloromethane (high-performance liquid chromatography (HPLC) grade) was obtained from Knowles. Mixed standard samples of gas products were purchased from Dalian Special Gases.

**2.2. Catalytic Hydrothermal Conversion Experiments.** Hydrothermal reactions were conducted in 50 mL high-pressure batch reactors. Reactor parts were washed with ethanol and dried in an oven to remove any residual materials. In a typical experiment, 2 g of stearic acid, 8 mL of water, and 0.2 g of the Ru/C catalyst were loaded into the reactor. The reactor vessel was then pressurized with the desired headspace gas ($N_2$ or $H_2$) and purged for three cycles before starting the reaction. The headspace pressure was then increased to the desired initial value corrected to 25 °C. The reactor temperature was raised to 330 °C at a rate of ~10 °C $min^{-1}$ (heat-up time ~1 h) with constant stirring at high speed (500 rpm) applied for the desired reaction time. Time zero was set to be the time at which the reaction temperature reached the target value. Once the reaction time elapsed, the reactor was quenched to room temperature by placing it in a cooling water bath. After the reaction, a gas headspace sample was collected with a gas sampling bag for further analysis. All liquid products were recovered by extraction with dichloromethane. Mass transfer limitation could be neglected because of the small catalyst particle size and high stirring speed. Where indicated, triplicate reactions were performed independently to determine experimental variability, with error bars representing standard deviations.

**2.3. Reaction Product Analysis.** The liquid hydrocarbon products were directly analyzed by gas chromatography (GC, Agilent, 7890B) with a flame ionization detector (FID) using an HP-5 capillary column (liquid samples). The injection and detection temperatures were both 250 °C. The column temperature was increased from 100 to 250 °C at a ramp rate of 20 °C $min^{-1}$. High-purity $N_2$ (99.999%) served as the carrier gas. $CH_4$, $C_2H_6$, $H_2$, CO, and $CO_2$ gas products were analyzed by a GC (Shimadzu, GC2014CAT) with a thermal

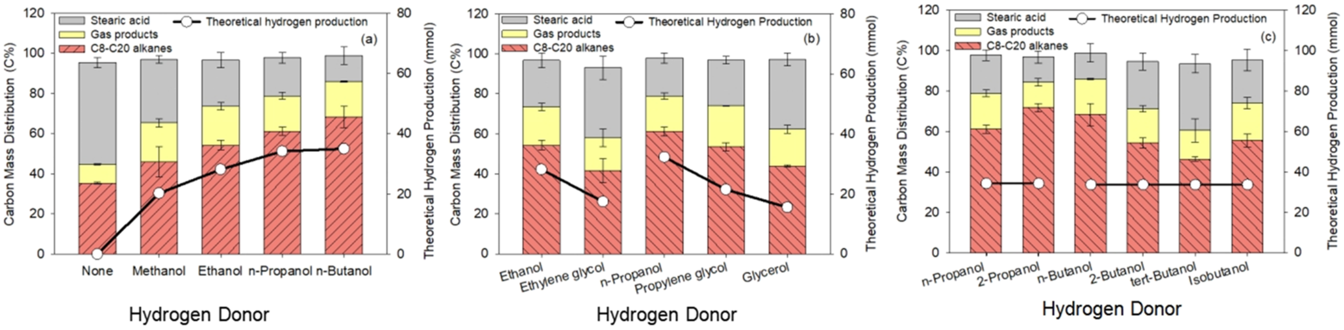

**Figure 1.** Effects on Ru/C-catalyzed deoxygenation of stearic acid with or without hydrogen donor amendments. Reaction conditions: 2 g of stearic acid, 0.216 g of the hydrogen donor, 0.2 g of the Ru/C catalyst, 8 g of $H_2O$, initial headspace gas = 1 MPa $N_2$, 330 °C, 2.5 h.

conductivity detector (TCD), a P−N packed column, and a 13× column. The carrier gas was high-purity Ar (99.999%). The injection and detection temperatures were both 150 °C.

Stearic acid was used as a model compound for investigating the synergistic reaction of fatty acids and hydrogen donors over Ru/C. The conversion was calculated as the number of moles of C in the reacted stearic acid divided by the number of moles of C loaded with the stearic acid. Yields were calculated as the number of moles of C in each product divided by the total number of moles of C loaded with the stearic acid. Selectivity was calculated as the number of moles of C in each product divided by the total number of moles of C in the reacted stearic acid.

## 3. RESULTS AND DISCUSSION

**3.1. Different Alcohols as Hydrogen Donors.** Under subcritical hydrothermal conditions, stearic acid is converted by Ru/C into a mixture of alkane products similar to petroleum-derived diesel and a variety of gas products, including short-chain alkanes, $CO_2$, and $H_2$.[5] For simplicity, C-containing gases, such as $CH_4$, $C_2H_6$, and $CO_2$, are collectively referred to as gas products below. We confirmed in situ $H_2$ production from several alcohols by Ru/C in separate experiments where alcohol was added to the reactor without stearic acid. (Table 1). The results show that the conversion rates of all alcohols are between 48 and 100% in 2.5 h, and a large fraction of $H_2$ has been produced during the initial heat-up stage. It is also found that most of the carbon in alcohols was converted into $CH_4$, $C_2H_6$, and $CO_2$ via aqueous phase reforming, direct dehydrogenation, and water−gas-shift reactions.[22,23] Surprisingly, after 2.5 h of reaction, all of the alcohols produce similar amounts of $H_2$ in addition to the main gas product, $CH_4$. The conversion rate of glycerol reached 79% during the heat-up stage and further climbed to 100% in 2.5 h (Figure S1). Further, the reaction of glycerol showed that the selectivity to $CH_4$ increased continuously with increased reaction time. This is consistent with the fact that $H_2$ and $CO_2$ formed initially, subsequently being converted to $CH_4$ (i.e., methanation reaction) in the absence of other sinks for $H_2$. However, we speculate that the methanation reaction will be less important in matrices containing stearic acid or other fatty acids for two reasons. First, fatty acid adsorption to catalyst-active sites may limit the reaction between dissolved $H_2$ and $CO_2$ species. Second, fatty acids will compete with $CO_2$ for hydrogen. Furthermore, in matrices containing stearic acid, most carbon in the hydrogen donors was transformed into gas products. We also verified the effect of glycerol dosage on stearic acid conversion (Figure S2). With increasing the glycerol dosage from 0.216 to 0.864 g, the conversion of stearic acid and the amount of gas products increased steadily, but the yields of liquid products increased first and then decreased. This indicates that excessive hydrogen donors would lead to a large production of $H_2$, which enlarges the cracking reaction and then increases the formation of gas products but suppresses the yield of liquid products. Similar conclusions were also reported by Ouyang et al.[24] and Yfanti and Lemonidou.[22]

The actual transformation of the hydrogen donor is complex and continuous. However, the $H_2$ formation of the hydrogen donor can be estimated with the help of theoretical hydrogen production, which refers to the hydrogen production with this presumption of the conversion of the hydrogen donor into $H_2$ and $CO_2$ through aqueous phase reforming, steam reforming, and water−gas shift reactions under hydrothermal conditions eqs 1−9[20,25,26]

$$\begin{aligned}\text{methanol: } & CH_3OH + H_2O \\ & \rightarrow CO + H_2O + 2H_2 \\ & \rightarrow CO_2 + 3H_2\end{aligned} \tag{1}$$

$$\text{ethanol: } CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \tag{2}$$

$$\begin{aligned}n-\text{propanol: } & CH_3CH_2CH_2OH + 5H_2O \\ & \rightarrow 3CO_2 + 9.5H_2\end{aligned} \tag{3}$$

$$\begin{aligned}n-\text{butanol: } & CH_3CH_2CH_2CH_2OH + 7H_2O \\ & \rightarrow 4CO_2 + 12H_2\end{aligned} \tag{4}$$

$$\text{ethylene glycol: } (CH_2OH)_2 + 2H_2O \rightarrow 2CO_2 + 5H_2 \tag{5}$$

$$\begin{aligned}\text{propylene glycol: } & CH_2OH - CH_2 - CH_2OH + 4H_2O \\ & \rightarrow 3CO_2 + 8H_2\end{aligned} \tag{6}$$

$$\begin{aligned}\text{glycerol: } & CH_2OH - CHOH - CH_2OH + 3H_2O \\ & \rightarrow 3CO_2 + 7H_2\end{aligned} \tag{7}$$

$$\begin{aligned}2-\text{propanol: } & CH_3 - CH_2OH - CH_3 + 5H_2O \\ & \rightarrow 3CO_2 + 9.5H_2\end{aligned} \tag{8}$$

$$tert-\text{butanol: } C(CH_3)_3OH + 7H_2O \rightarrow 4CO_2 + 12H_2 \tag{9}$$

First, we compared the effects of adding different alcohol-based amendments on Ru/C-catalyzed reactions of stearic acid (Figure 1). For comparison, we evaluated four monohydric alcohols (methanol, ethanol, *n*-propanol, and *n*-butanol) (Figure 1a), three polyhydric alcohols (ethylene glycol, propylene glycol, and glycerol) (Figure 1b), and their isomers (2-propanol, 2-butanol, *tert*-butanol, *iso*-butanol) (Figure 1c) as amendments to stearic acid reactions with a headspace containing 1 MPa $N_2$ prior to heating up to the target reaction temperature (330 °C). Compared to the amendment-free reaction, significant promotion of stearic acid deoxygenation was observed when the four monohydric alcohols were added, with the promotion climbing with an increased carbon number in hydrogen donors (Figure 1a). This is consistent with the trends in theoretical hydrogen production for these amendments eqs 1−4. It is also worth mentioning that when using *n*-butanol as the hydrogen donor, the carbon yield of C8−C20 products is comparable to that observed for the stearic acid reaction under a $H_2$ headspace (Figure S3), indicating the possibility of replacing an external supply of hydrogen with alcohol-based solution amendments.

Next, the promotion effect of alcohols possessing different numbers of hydroxyl groups was examined. As shown in Figure 1b, increasing the number of alcoholic groups in the amendments led to lower C8−C20 alkane yields. For example, substituting ethanol with ethylene glycol reduced the C8−C20 alkane yield from 54 to 42%. A similar phenomenon was also observed for *n*-propanol (1-OH group; 61%), propylene glycol (2-OH group; 53%), and glycerol (3-OH group; 44%). This trend may result from the fact that demand for H atoms to form $H_2O$ instead of $H_2$ increases as the number of O atoms increases in the amendments. Therefore, we speculate that the smaller proportion of O atoms in the hydrogen donor, the more $H_2$ it yields and the greater the net effect on the deoxygenation of stearic acid.

The isomer effect of propanol and butanol was also studied. The promotion of stearic acid conversion with 2-propanol as an amendment (72% C8−C20 products) was higher than that observed with *n*-propanol (61%), whereas switching from *n*-butanol to 2-butanol, *tert*-butanol, and *iso*-butanol markedly reduced the yields of C8−C20 alkanes from 68 to 54, 46, and 55%, respectively. Hence, even though these isomers have the same theoretical $H_2$ production, their net effects on the deoxygenation of stearic acid varied greatly. The position of the hydroxyl group on the alcohol molecule has a great influence on the aqueous phase reforming reaction. Under hydrothermal conditions, *n*-propanol was dehydrogenated to active aldehyde intermediates, while 2-propanol was dehydrogenated to acetone.[22] The aldehyde intermediates can quickly convert into ethane and CO, but acetone can further promote the deoxygenation of stearic acid (Figure S4) as a hydrogen donor. Of the four isomers, n-butanol has the highest C8−C20 alkane yield (Figure 1c). In general, secondary alcohols are more prone to dehydrogenation than primary alcohols, and the hydrogen formation rate of 2-butanol has been reported to be faster than *n*-butanol.[27] But the reason for the greater net effect of *n*-butanol on stearic acid deoxygenation remains unclear. The *tert*-butanol cannot be converted to a ketone and $H_2$ due to the absence of a H atom on the tertiary carbon connecting to the alcoholic hydroxyl group. The net effect of *iso*-butanol is analogous with 2-butanol, possibly due to their similar α-hydrogen activities.[22]

Reaction conditions: 0.216 g of feedstock, 0.2 g of the Ru/C catalyst, 8 g of $H_2O$, initial headspace gas = 1 MPa $N_2$, reaction temperature 330 °C. The reaction time of 0 h means there was only the heating up for this feedstock to the predetermined reaction temperature, and the heating up time was about 45 min.

### 3.2. Different Carboxylic Acids as Hydrogen Donors.

We also examined the effects of several carboxylic acids as hydrogen donor amendments for accelerating the deoxygenation of stearic acid (Figure 2). Like alcohol-based amendments, the addition of carboxylic acids increased the yield of the total hydrocarbon products. In addition, most carbon in the carboxylic acids was transformed into $CO_2$ and $CH_4$ in the conversion processes.[28,29] Formic acid, acetic acid, and propionic acid increased C8−C20 alkane yields from 35% (no amendment) to 41, 52, and 56%, respectively. The reason may be that as the ratio of C/O or H/O in the carboxylic acid increases, the amount of $H_2$ produced increases eqs 10−13

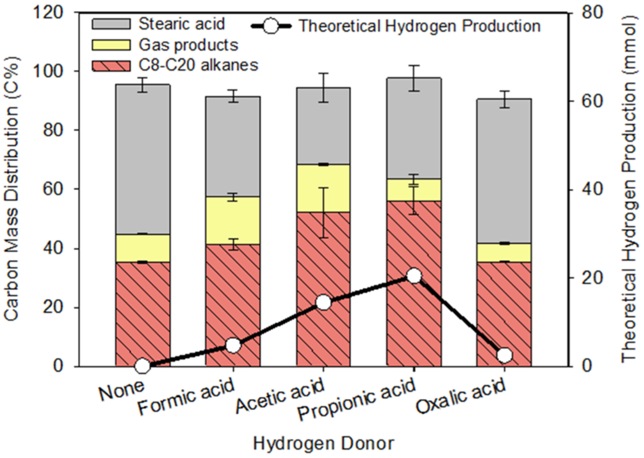

**Figure 2.** Effects of different carboxylic acid hydrogen donor amendments on Ru/C-catalyzed deoxygenation of stearic acid. Reaction conditions: 2 g of stearic acid, 0.216 g of the hydrogen donor, 0.2 g of the Ru/C catalyst, 8 g of $H_2O$, initial headspace gas = 1 MPa $N_2$, 330 °C, 2.5 h.

$$\text{formic acid: } HCOOH \rightarrow CO_2 + H_2 \quad (10)$$

$$\text{acetic acid: } CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2 \quad (11)$$

$$\text{propionic acid: } CH_3CH_2COOH + 4H_2O \rightarrow 3CO_2 + 7H_2 \quad (12)$$

$$\text{oxalic acid: } HOOC - COOH \rightarrow 2CO_2 + H_2 \quad (13)$$

In addition to producing $H_2$ in situ via aqueous phase reforming, steam reforming, and water−gas shift reactions, amending reaction solutions with carboxylic acids may affect the solution pH. We measured the initial and final pH of the reaction when using carboxylic acids as hydrogen donors and found that the initial pH before the reaction was negatively correlated with the carbon yield of C8−C20 alkanes (Table 2). After the reaction, the pH increased significantly, suggesting that the carboxylic hydrogen donors were converted into neutral substances during the deoxygenation of stearic acid. To assess the importance of the initial solution pH on stearic acid reactions, we compared the effects of amending solutions with acetic acid versus its conjugate base, sodium acetate (which has comparable theoretical $H_2$ production). Application of sodium

**Table 2. pH Changes in the Reactions of Ru/C-Catalyzed Deoxygenation of Stearic Acid with Different Hydrogen Donor Amendments**[aa]

| compound | none | formic acid | acetic acid | propionic acid | oxalic acid |
|---|---|---|---|---|---|
| before reaction | 5.6 | 1.9 | 2.5 | 2.7 | 1.1 |
| after reaction | 6.6 | 5.1 | 4.9 | 4.9 | 3.2 |

[a] Reaction conditions: 2 g of stearic acid, 0.216 g of a hydrogen donor, 0.2 g of the Ru/C catalyst, 8 g of $H_2O$, initial headspace gas = 1 MPa $N_2$, 330 °C, 2.5 h.

acetate in place of acetic acid raised the initial pH from 2.5 to 8.9, but the yield of C8−C20 alkanes from stearic acid was found to be similar (Figure S5), indicating that solution pH had little effect on the net deoxygenation of stearic acid. We also measured the carbon distribution of the alkane products in the presence or absence of hydrogen donors (Figure 3) and found that the compositions of alkane products are almost identical in all systems, with C17 being the dominant one.

### 3.3. Correlation between the Carbon Yield of Liquid Hydrocarbons and Theoretical $H_2$ Production.

As demonstrated in Figure 4, the carbon yield of C8−C20 alkanes displayed a positive correlation with the theoretical $H_2$ production of different linear alcohol and carboxylic acid amendments ($R^2$ = 0.84), supporting a conclusion that the promotion of stearic acid reactions is attributed to in situ generation and availability of $H_2$ in the reaction matrix. Breaking out carboxylic acid- and alcohol-based amendments separately, we see a stronger correlation for the former ($R^2$ = 0.97; Figure S6a) than for the latter ($R^2$ = 0.88; Figure S6b). This suggests a more consistent mechanism for in situ $H_2$ generation from carboxylic acid- than from alcohol-based amendments. Based on the results of the correlation, it is feasible to predict the net effect of a low-molecular homologous series of alcohols and carboxylic acids according to the theoretical maximum production of hydrogen.

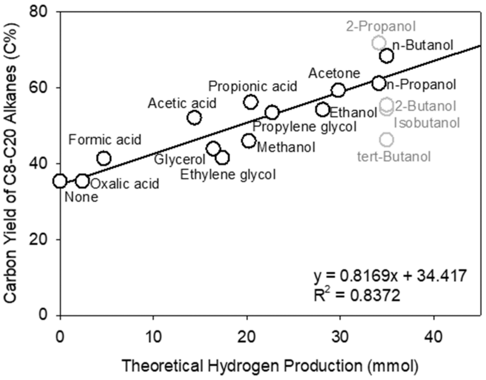

**Figure 4.** Correlation between the yield of liquid hydrocarbon products and theoretical hydrogen production for different hydrogen donor amendments. Reaction conditions: 2 g of stearic acid, 0.216 g of the hydrogen donor, 0.2 g of Ru/C catalyst, 8 g of $H_2O$, initial headspace gas = 1 MPa $N_2$, 330 °C, 2.5 h. Isomers, such as 2-propanol, 2-butanol, *tert*-butanol, and *iso*-butanol are displayed in gray color in this figure but are not involved in the fitting.

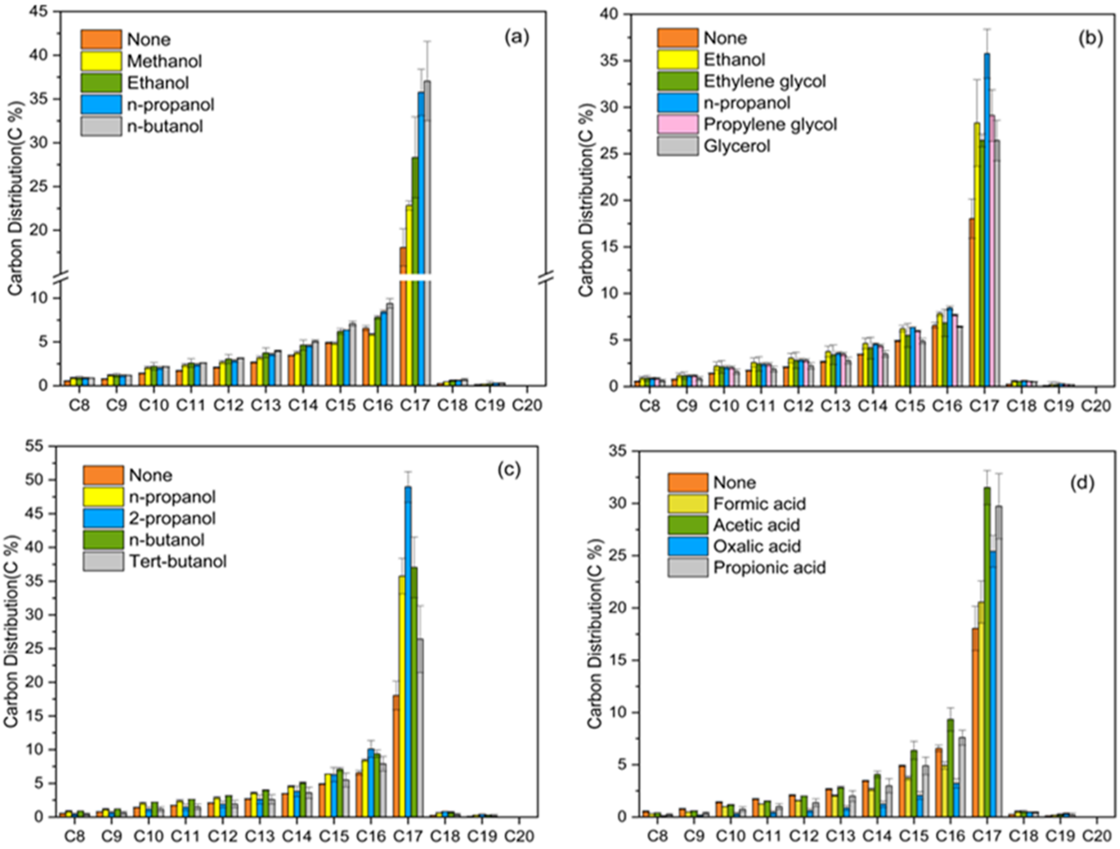

**Figure 3.** Carbon distribution in alkane products with monohydric alcohols (a), polyhydric alcohols (b), isomeric alcohols (c), and carboxylic acids (d). Reaction conditions: 2 g of stearic acid, 0.216 g of a hydrogen donor, 0.2 g of the Ru/C catalyst, 8 g of $H_2O$, initial headspace gas = 1 MPa $N_2$, 330 °C, 2.5 h.

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## 4. CONCLUSIONS

Both alcohol and carboxylic acid amendments were found to promote the hydrothermal conversion of stearic acid to liquid hydrocarbon products over Ru/C. Further, there is a positive correlation between the yields of C8−C20 alkanes and the theoretical $H_2$ production predicted for the low-molecular homologous series of alcohols and carboxylic acids. For monohydric n-alcohol, the longer its carbon chain, the better the effect of promoting the deoxygenation on stearic acid. For polyhydric alcohols, the ratio of O atoms in the molecule is negatively correlated with the deoxygenation effect of stearic acid. Regarding the isomers of alcohols, the net effects on stearic acid should be estimated based on the position of the hydroxyl group in the carbon chain, and the order obtained in this study is 2-propanol > *n*-propanol; *n*-butanol > 2-butanol ≈ *iso*-butanol > *tert*-butanol. We believe that this result is an important complement to current hydrogen donor research studies and provides researchers with a reference for hydrogen donor selection that has not been covered in previous reports.

Thus, the introduction of hydrogen donor amendments from low-cost supplies (e.g., waste products) can not only promote the deoxygenation of fatty acids and elevate the production of liquid biofuels but also reduce the need for external $H_2$ supplies, which is promising for lowering the cost of biofuels from the hydrothermal deoxygenation process.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c01975.

> Time dependence of products during the reaction of glycerol alone; reaction with different dosages of glycerol; comparison of products with either an external $H_2$ supply or using *n*-butanol or 2-propanol hydrogen donors; comparison of products from acetone; *n*-butanol or 2-propanol hydrogen donors; comparison of products from acetic acid and sodium acetate; and correlation between carbon yield of liquid hydrocarbons and theoretical hydrogen production (PDF)

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### Notes

The authors declare no competing financial interest.

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Supporting Information for

# Catalytic Hydrothermal Deoxygenation of Stearic Acid with Ru/C: Effects of Alcohol- and Carboxylic Acid-Based Hydrogen Donors

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**This Supporting Information includes six figures.**

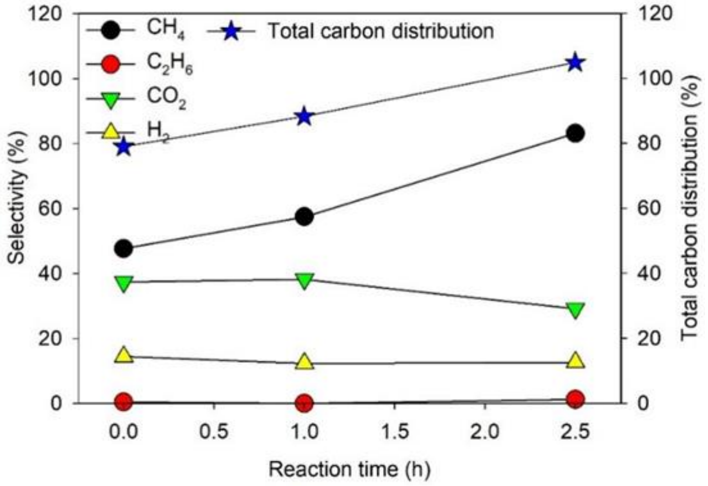

**Figure S1.** Time dependence of products measured during catalytic hydrothermal reaction of glycerol alone. Reaction conditions: 0.216 g glycerol, 0.2 g Ru/C catalyst, 8 g $H_2O$, initial headspace gas = 1 MPa $N_2$, temperature 330 ºC.

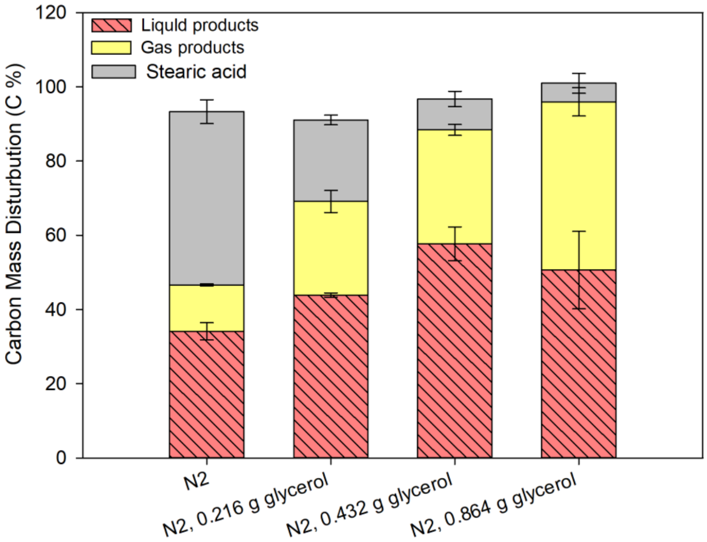

**Figure S2.** Hydrothermal deoxygenation reaction of stearic acid under different dosages of glycerol. Reaction conditions: 2 g stearic acid, 0.2 g Ru/C catalyst, 8 g $H_2O$, 330 ºC, 2.5 h; initial headspace gas = 1 MPa $H_2$ or 1 MPa $N_2$ with different amounts of glycerol added to reaction mixture.

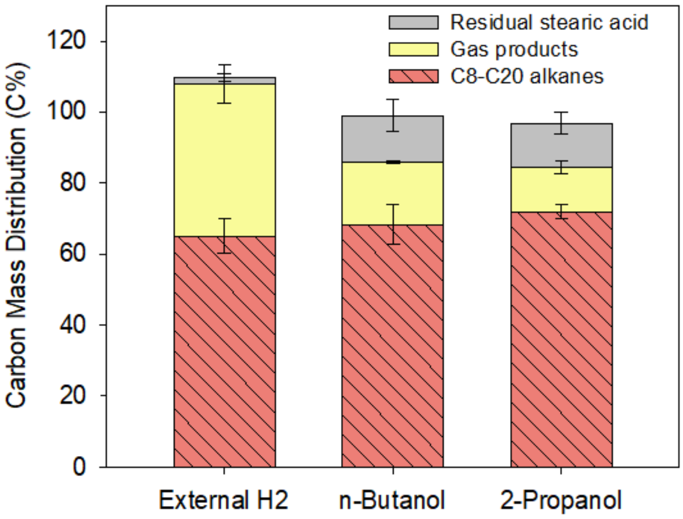

**Figure S3.** Comparison of the carbon distribution of products following catalytic reaction of stearic acid with either an external $H_2$ supply or in-situ produced $H_2$ using n-butanol or 2-propanol hydrogen donors. Reaction conditions: 2 g stearic acid, 0.2 g Ru/C catalyst, 8 g $H_2O$, 330 °C, 2.5 h; initial headspace gas = 1 MPa $H_2$ or 1 MPa $N_2$ with 0.216 g of n-butanol or 2-propanol added to reaction mixture.

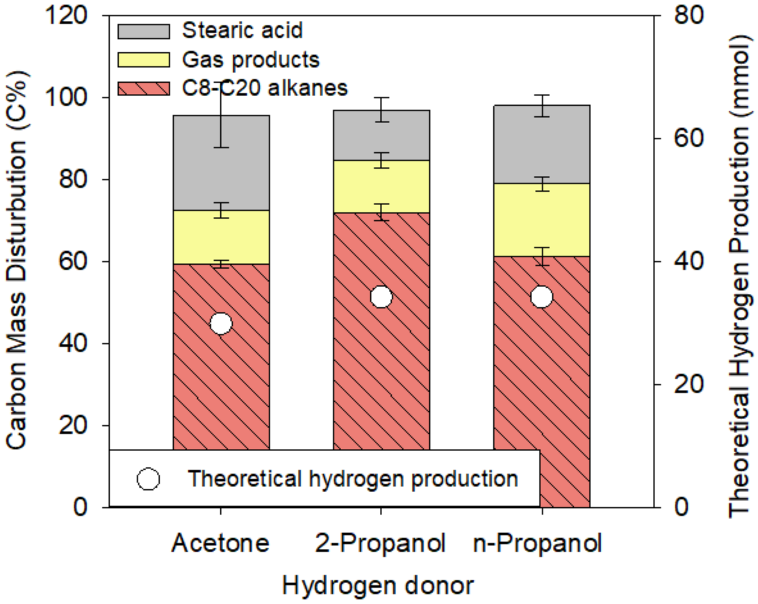

**Figure S4.** Comparison of the carbon distribution of products following catalytic reaction of stearic acid with acetone as hydrogen donor amendments. Reaction conditions: 2 g stearic acid, 0.216 g hydrogen donor, 0.2 g Ru/C catalyst, 8 g $H_2O$, initial headspace gas = 1 MPa $N_2$, 330 °C, 2.5 h. Theoretical hydrogen generation from acetone is described by the following reaction stoichiometry (eq. S1), and that for 2-propanol and n-propanol are described in eqs. 3 and 8.

Acetone: $C_3H_6O + 5H_2O \rightarrow 3\ CO_2 + 8\ H_2$ (eq. S1)

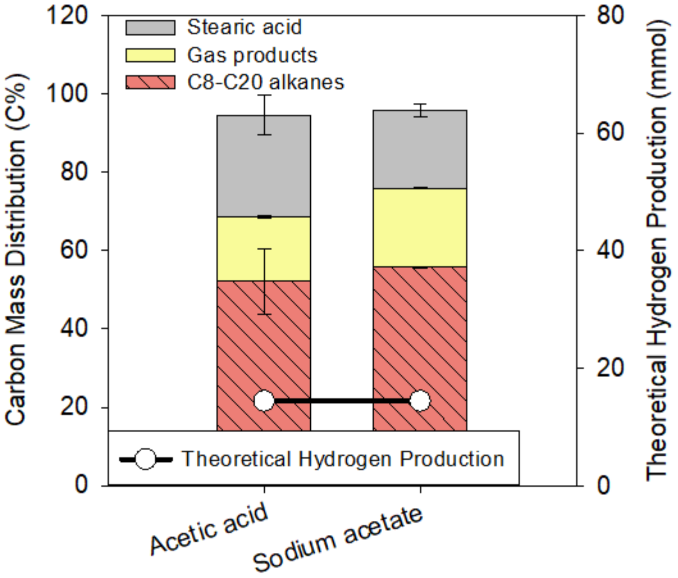

**Figure S5.** Comparison of the carbon distribution of products from catalytic reaction of stearic acid with acetic acid and sodium acetate as hydrogen donor amendments. Reaction conditions: 2 g stearic acid, 0.216 g hydrogen donor, 0.2 g Ru/C catalyst, 8 g $H_2O$, initial headspace gas = 1 MPa $N_2$, 330 °C, 2.5 h.

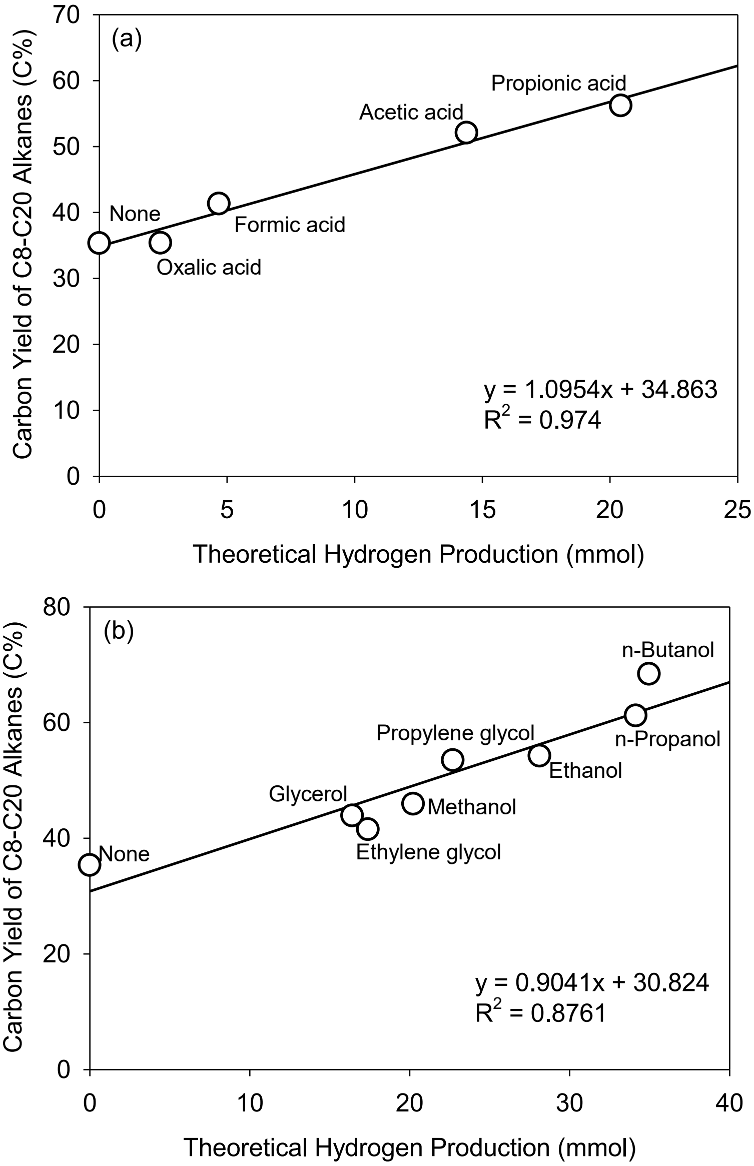

**Figure S6.** Correlation between the carbon yield of liquid hydrocarbons and theoretical hydrogen production from addition of (a) alcohol and (b) carboxylic acid hydrogen donors to the reaction solution. Reaction conditions: 2 g stearic acid, 0.216 g hydrogen donor, 0.2 g Ru/C catalyst, 8 g $H_2O$, initial headspace gas = 1 MPa $N_2$, 330 °C, 2.5 h.