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# Journal Name

## COMMUNICATION

# Conversion of Biomass-derived Fatty Acids and Derivatives into Hydrocarbons Using a Metal-Free Hydrodeoxygenation Process

Xing-Yu Li,[a] Rui Shang,[a] Ming-Chen Fu [a] and Yao Fu[*a]

**A metal-free hydrodeoxygenation process was developed for the production of hydrocarbons from biomass-derived fatty acids and derivatives. Biomass-derived fatty acids and derivatives were converted to alkane and alkene under mild reaction conditions. Furthermore, this catalytic system can also be applied to convert real biomass with satisfactory result.**

The decline of fossil fuel resource and the increasing demand of energy have stimulated people to search for alternative resources. Currently, the only known sustainable organic carbon source comes from biomass[1], and biomass is also considered as the only renewable feedstock to obtain liquid fuels[1]. Based on these reasons, utilization of biomass has attracted increasing attentions. The molecule structure of biomass-derived fatty acids and derivatives is similar with the structure of fuel from petrochemical industry. Thus, people have paid many efforts to convert these biomasses to fuel. Biodiesel, the first generation of biofuel, is produced by transesterification of triglyceride (a common biomass-derived fatty acid derivative) and primary alcohol (mainly methanol). Acid or base homogeneous or heterogeneous catalysts always play important roles in transesterification reactions[2-4], and lipase catalysis has also been applied to this field[5]. However, the fuels composed of fatty acid alkyl esters (FAAEs) have several drawbacks, such as low fluidity[6], high oxygen content[6], poor thermal oxidation stability[6] and polymerization of ester fuel molecule[2]. These disadvantages limit the application of ester biodiesel[6]. To solve these problems, people begin to seek for method that can directly convert biomass, especially biomass-derived fatty acids and derivatives to hydrocarbons.

Biodiesel usually represents long chain fatty acid methyl ester. To distinguish the two kinds of fuels, hydrocarbon obtained from biomass is called green diesel[2]. Some reviews[7] and patents[8] summarized methods to convert triglyceride to hydrocarbon by heterogeneous catalysis. Recently, Vardon et al.[9] reported a route using Pt-Re/C catalyst to convert long chain fatty acid to hydrocarbon. Wang et al.[10] accomplished production of long chain hydrocarbon from the aldol condensation product of furfural or 5-HMF by using a bimetal catalyst, $Pt/NbOPO_4$. The method using heterogeneous catalysis has turned out to be effective. However, some disadvantages still exist, such as using precious metals (for instance, Pt) and harsh reaction conditions (300 $^o$C).

The homogeneous Lewis acid, trispentafluorophenylborane $(B(C_6F_5)_3)$, can catalyze reduction reaction in combination with silane as reductant. This method was first reported by Piers group[11]. Subsequently, Piers[12], Yamamoto[13], and Chandrusekhar et al.[14] apply this catalysis system to reduction or hydrosilation of ketone, aldehyde, ether, ester and carboxylic acid[15]. Considering the mild reaction conditions and low cost of this reduction system, application of this method to the reduction of biomass evokes the interest of biomass-chemist recently. Cantat et al.[16] successfully accomplished C-O bond cleavage of lignin model compounds utilizing $B(C_6F_5)_3$ with $Et_3SiH$ as reducing agent. Gagne et al. reported inspiring work on hydrosilylative reduction of glucose into alkane by using Ir(III) pincer catalyst[17]. Then, Gagne et al.[18] discovered by replacing Ir(III) pincer catalyst with $B(C_6F_5)_3$, alkane can also be obtained from glucose under mild conditions. Alkane products from glucose or glucose-derivatives are mainly hexane or its isomers. For producing hydrocarbons with different carbon numbers (carbon number>10), hydrodeoxygenation of biomass-derived carboxylates is a better choice. Herein, we first-time applied $B(C_6F_5)_3$-catalyzed hydrosilylative reduction for the hydrodeoxygenation of biomass-derived fatty acids and derivatives to produce hydrocarbons. Both alkane and alkene can be produced in good yields.

In the initial studies, the most common triglyceride, tristearin, was used as model substrate, $Et_3SiH$ was chosen as reductant. We tested the reaction using different amount of catalyst.

R=C₁₇H₃₅
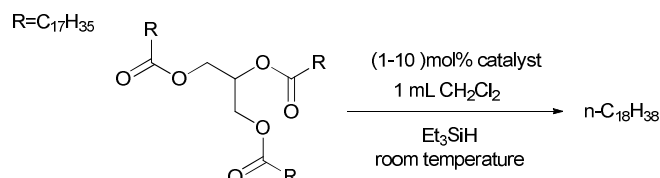


**Scheme 1.** Conversion of tristearin to octodecane at different amount of catalyst loading.

When 1 mol% of B(C₆F₅)₃ was used, the yield of target product octodecane was only 2% (Table 1, Entry 1). Increasing the catalyst loading to 3 mol% and 5 mol% resulted 40% and 81% yield respectively (Table 1, Entry 2 and 3). Further increase the catalyst loading to 10 mol% resulted 95% yield (Table 1, Entry 4). Prolonging reaction time (from 6 h to 24 h) at the same reaction conditions in Entry 1 can only increase the yield to 12% (Table 1, Entry 5). Control experiment without the B(C₆F₅)₃ catalyst showed no octodecane was generated (Table 1, Entry 6). Using 5 mol% of catalyst resulted slightly decreasing of the yield comparing with using 10 mol% of catalyst (Table 1, Entry 3, Entry 4). Considering the cost issue of the catalyst, we decide to use 5 mol% of catalyst to further study this process.

**Table 1.** Conversion of tristearin to octodecane at different catalyst loading

| Entry[a] | Loading | Time | Yield[b] |
|---|---|---|---|
| 1 | 1 mol% | 6 h | 2% |
| 2 | 3 mol% | 6 h | 40% |
| 3 | 5 mol% | 6 h | 92% |
| 4 | 10 mol% | 6 h | 95% |
| 5 | 1 mol% | 24 h | 12% |
| 6 | 0 | 6 h | 0 |

[a] B(C₆F₅)₃ as catalyst, 0.1 mmol tristearin, 18 equiv silane, room temperature. [b] Yields were determined by GC analysis

Next, we tested various factors affecting this proccess, including different type of silanes, dosage of silanes, solvents and reaction time.

To study the influence of reaction temperature, we tested reactions at different temperature. The results show increasing the temperature decreases the yield of octodecane (see Supporting Information). We chose ambient temperature as the optimized temperature for this reaction. Various silanes were tested (Table 2, Entries 1-6). Several silanes are competent reductant except triethoxysilane (Table 2, Entry 3). It is worth noting poly(methylhydrosiloxane) (PMHS), a cheap silane used in industry[16] also gave high yield (Table 2, Entry 6). Testing the dosage of silane (Table 2, Entry 1, Entries 7-11) showed satisfactory yield of octodecane can be got when 18 equiv silane was used. But when fatty acids and fatty acid methyl esters were substrates, 9 equiv silane was enough. Entries 12-17 showed the solvent effect of this reaction. Acetonitrile, dioxane, DMF, DMA and DMSO are all ineffective as solvent probably due to the poison of the boron catalyst by their lone pair electron (Entries 12-16). Except for dichloromethane, cyclohexane also gave good result (Table 2. Entry 17). It should be note for production of fuel, the alkane product and alkane solvent can be used without extra separation procedure. To avoid energy-intensive separation steps after the reaction, cyclohexane can be chosen as solvent for this reaction. According to the previous work[14, 15], B(C₆F₅)₃ acts as a Lewis acid catalyst to activate silane in the system. Based on this

mechanism, we speculated whether cheap metal Lewis acid could also catalyze this reaction. Some metal Lewis acids were tested, such as (OTf)₂Zn(II), (OTf)₂Fe(II) and AlCl₃. None of these Lewis-acid-metal-catalyst was effective even extending the reaction time to 24 h. At last, we studied the necessary reaction time of this reaction (Table 2. Entry 6, Entries 21-23). The result showed 6 h is necessary to achieve good conversion and yield.

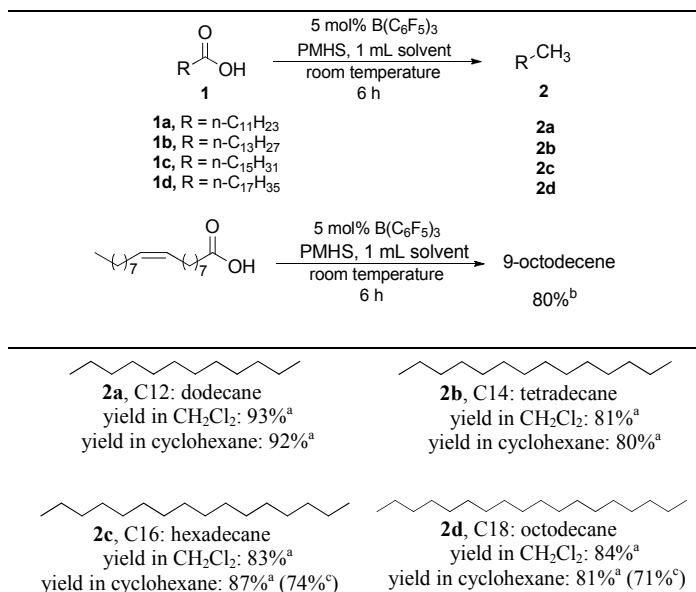**Table 2.** Yields of alkane under different conditions

| Entry[a] | Silane | Time | Solvent | Yield[b] |
|---|---|---|---|---|
| 1 | 18 equiv Et₃SiH | 6 h | CH₂Cl₂ | 92 |
| 2 | 18 equiv Et₂MeSiH | 6 h | CH₂Cl₂ | 97 |
| 3 | 18 equiv (EtO)₃SiH | 6 h | CH₂Cl₂ | -- |
| 4 | 18 equiv Ph₂SiH₂ | 6 h | CH₂Cl₂ | 96 |
| 5 | 18 equiv Et₂SiH₂ | 6 h | CH₂Cl₂ | 88 |
| 6 | 18 equiv PMHS[c] | 6 h | CH₂Cl₂ | 91 |
| 7 | 3 equiv Et₃SiH | 6 h | CH₂Cl₂ | 0 |
| 8 | 6 equiv Et₃SiH | 6 h | CH₂Cl₂ | 52 |
| 9 | 9 equiv Et₃SiH | 6 h | CH₂Cl₂ | 62 |
| 10 | 12 equiv Et₃SiH | 6 h | CH₂Cl₂ | 71 |
| 11 | 15 equiv Et₃SiH | 6 h | CH₂Cl₂ | 88 |
| 12 | 18 equiv PMHS | 6 h | CH₃CN | 0 |
| 13 | 18 equiv PMHS | 6 h | dioxane | 5 |
| 14 | 18 equiv PMHS | 6 h | DMF | 0 |
| 15 | 18 equiv PMHS | 6 h | DMA | 0 |
| 16 | 18 equiv PMHS | 6 h | DMSO | 0 |
| 17 | 18 equiv PMHS | 6 h | cyclohexane | 93 |
| 18[d] | 18 equiv PMHS | 24 h | CH₂Cl₂ | 0 |
| 19[e] | 18 equiv PMHS | 24 h | CH₂Cl₂ | 0 |
| 20[f] | 18 equiv PMHS | 24 h | CH₂Cl₂ | 0 |
| 21 | 18 equiv PMHS | 0.2 h | CH₂Cl₂ | 13 |
| 22 | 18 equiv PMHS | 0.5 h | CH₂Cl₂ | 28 |
| 23 | 18 equiv PMHS | 4 h | CH₂Cl₂ | 60 |

[a] 0.1 mmol tristearin, 5 mol% B(C₆F₆)₃ as catalyst, 1 mL solvent, room temperature. [b] Yields were determined by GC analysis. [c] PMHS is poly(methylhydrosiloxane). [d] 5 mol% (OTf)₂Zn as catalyst. [e] 5 mol% Fe(OTf)₂ as catalyst. [f] 5 mol% AlCl₃ as catalyst.

A series of biomass-derived fatty acids (Table 3), including lauric acid (C12), myristic acid (C14), palmitic acid (C16), as well as stearic acid (C18) were tested under the optimized condition. Various alkane products can be generated in good yield. Hydrocarbons with high boiling point, such as hexadecane and octodecane, were isolated. Unsaturated fatty acid, oleic acid is also

an amenable substrate. 9-octadecene was generated in good yield with the double bond unreacted.
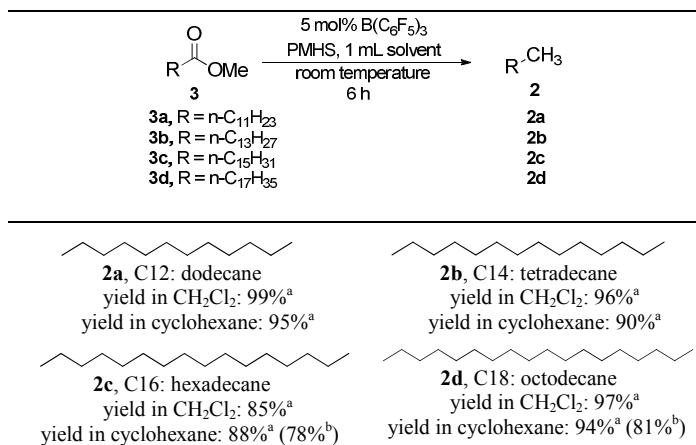
**Table 3.** Conversion of various biomass-derived fatty acids to hydrocarbons



1a, R = n-C$_{11}$H$_{23}$  2a
1b, R = n-C$_{13}$H$_{27}$  2b
1c, R = n-C$_{15}$H$_{31}$  2c
1d, R = n-C$_{17}$H$_{35}$  2d



9-octodecene

80%[b]

**2a**, C12: dodecane
yield in CH$_2$Cl$_2$: 93%[a]
yield in cyclohexane: 92%[a]

**2b**, C14: tetradecane
yield in CH$_2$Cl$_2$: 81%[a]
yield in cyclohexane: 80%[a]

**2c**, C16: hexadecane
yield in CH$_2$Cl$_2$: 83%[a]
yield in cyclohexane: 87%[a] (74%[c])

**2d**, C18: octodecane
yield in CH$_2$Cl$_2$: 84%[a]
yield in cyclohexane: 81%[a] (71%[c])

[a] 0.1 mmol substrate, 9 equiv PMHS, 1 mL solvent, room temperature, yields determined by GC analysis. [b] Yield were determined by GC-MS analysis. [c] Isolated yield

Meanwhile, we also used corresponding biomass-derived fatty acids esters as substrate (Table 4), including methyl laurate, methyl myristate, .methyl palmitate and methyl stearate. Isolated yields of hexadecane and octodecane were also obtained. The yield of alkane from ester is relatively higher compared with using carboxylic acid. A possible explanation for this observation is carboxylic anion coordinates with boron atom of the catalyst reduces the activity of the boron catalyst.
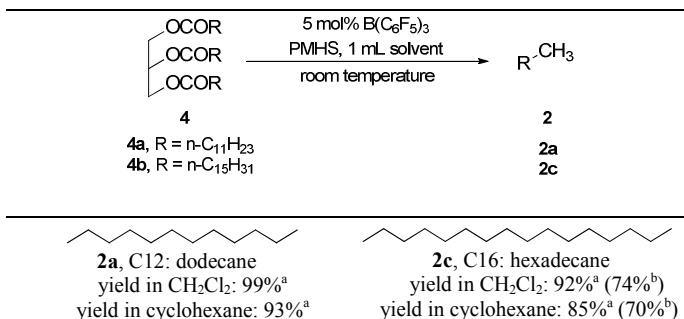
**Table 4.** Conversion of various biomass-derived fatty acids esters to hydrocarbons



3a, R = n-C$_{11}$H$_{23}$  2a
3b, R = n-C$_{13}$H$_{27}$  2b
3c, R = n-C$_{15}$H$_{31}$  2c
3d, R = n-C$_{17}$H$_{35}$  2d

**2a**, C12: dodecane
yield in CH$_2$Cl$_2$: 99%[a]
yield in cyclohexane: 95%[a]

**2b**, C14: tetradecane
yield in CH$_2$Cl$_2$: 96%[a]
yield in cyclohexane: 90%[a]

**2c**, C16: hexadecane
yield in CH$_2$Cl$_2$: 85%[a]
yield in cyclohexane: 88%[a] (78%[b])

**2d**, C18: octodecane
yield in CH$_2$Cl$_2$: 97%[a]
yield in cyclohexane: 94%[a] (81%[b])

[a] 0.1 mmol substrate, 9 equiv PMHS, 2 mL solvent, room temperature, yields were determined by GC analysis. [b] Isolated yield

Glyceride such as laurin and palmitin could be converted to dodecane and hexadodecane in excellent yield (Table 5). Considering the advantage of using alkane solvent, we tried all reactions using cyclohexane as solvent, alkane products of high yields were also obtained in cyclohexane

**Table 5.** Conversion of glyceride to hydrocarbons



4a, R = n-C$_{11}$H$_{23}$  2a
4b, R = n-C$_{15}$H$_{31}$  2c

**2a**, C12: dodecane
yield in CH$_2$Cl$_2$: 99%[a]
yield in cyclohexane: 93%[a]

**2c**, C16: hexadecane
yield in CH$_2$Cl$_2$: 92%[a] (74%[b])
yield in cyclohexane: 85%[a] (70%[b])

[a] 0.1 mmol substrate, 18 equiv PMHS, room temperature, 1 mL solvent, yields were determined by GC analysis. [b] Isolated yield

Applying this conversion to real biomass was also conducted. Commercially available colza oil (olein, 55 wt%-65 wt%[19]) and olive oil (olein, 67 wt%[19]) gave satisfactory results (mole ratio of PMHS and olein is 9:1). We could get 12.7 mg olefin from 40 mg colza oil and 14.3 mg olefin from 40 mg olive oil (detected by GC-MS, See Supporting Information). It should be pointed out although commercially available colza oil and olive oil contained small amount of water. Alkane product could be still generated in satisfactory yield without pre-dehydration of the biomass oil. This observation showed the catalytic system can tolerate small amount of water, which was also confirmed by Gagne's report[18]. It should also be noted, by using PMHS as reducing agent, the products could be easily separated due to the conversion of PMHS to insoluble residue of siloxane[14].

## Conclusions

In summary, we report a metal-free method to convert biomass-derived fatty acids and derivatives to hydrocarbons under mild condition. By using B(C$_6$F$_5$)$_3$ as catalyst and PHMS as reducing agent, alkane and alkene were produced in good to excellent yields under room temperature in alkane solvents. This method is also proved to be competent for the direct conversion of plant oil to hydrocarbon, and providing a useful method for upgrading biodiesel to liquid hydrocarbon fuel.

## Notes and references

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