

Green Heterogeneous Catalysis

Renewable Olefins from Biodiesel by Autothermal Reforming***Ramanathan Subramanian and Lanny D. Schmidt**

Olefins are the largest volume chemical intermediates produced in the chemical industry, with global annual production over 300 billion lbs per year (1 lb = 0.454 kg).^[1] Olefins are produced almost exclusively from ethane or other light alkanes (naphtha) in a process called steam cracking. This process involves homogeneous pyrolysis at approximately 800 °C in a tube furnace with a residence time of about 1 s. It has been estimated that 30 % of all pollution from chemical plants comes from steam cracking owing to NO_x emissions and unburned hydrocarbons in the flame required to heat the tube furnace.

Approximately 10 % of petroleum is consumed in the production of olefins and related chemicals. To reduce our reliance on fossil fuels, it would be desirable to produce olefins from renewable fuels that produce no net CO₂ emissions to contribute to global warming. To reduce pollution in olefins production, it would also be desirable to use partial oxidation rather than steam cracking. This possibility is discussed herein.

Biodiesel is the methyl ester formed by the reaction of triglyceride vegetable oils with methanol. From soy oil, there are five major ester compounds with the typical composition: methyl palmitate (12 %), methyl stearate (5 %), methyl oleate (25 %), methyl linoleate (52 %), and methyl linolenate (5 %).

[*] R. Subramanian, Prof. L. D. Schmidt
Department of Chemical Engineering and Materials Science
University of Minnesota
Minneapolis, MN 55455 (USA)
Fax: (+1) 612-626-7246
E-mail: schmidt@cems.umn.edu

[**] This research was partially sponsored by grant No. 518-6651 from the National Science Foundation. We gratefully acknowledge discussions with Christopher J. Cramer regarding reaction mechanisms. We thank Gregg A. Deluga for reviews and discussions.

Double bonds (all in the *cis* configuration) occur exclusively after carbon atoms 9, 12, and 15 for fatty acids containing one, two, and three double bonds, respectively.

We^[2] and others^[3] have shown that the partial oxidation of ethane or other light alkanes (naphtha) can be used to produce olefins in autothermal reactors with as high as 85 % selectivity for ethylene. We recently showed that higher alkanes, such as *n*-decane and *n*-hexadecane, can also be converted into olefins in high selectivity.^[4] However, olefinic esters, such as those contained in biodiesel, are not expected to be reformed under autothermal oxidation because of the carbon formation that is expected from the presence of double bonds. Moreover, the oxidation of aliphatic esters could result in substantial decarboxylation giving low-value products.

The apparatus and procedures reported herein have been described elsewhere for experiments with *n*-decane, *n*-hexadecane, and diesel fuel.^[4–6] Liquid fuels were injected into the reactor (Figure 1, inset) by using an automotive fuel injector that sprayed droplets onto the wall of a quartz tube heated to approximately 300 °C. The catalyst was a mixture of 2.5 % Rh and 2.5 % Ce deposited on α -Al₂O₃ ceramic foam from nitrate salt solutions, which was then dried and heated in an oven to 600 °C. Experiments were conducted at several flow rates, but only results at 4 standard litres min^{−1} are shown herein. Products were analyzed by dual column gas chromatography (GC) and by GC-mass spectrometry.

Figure 1 shows conversions of biodiesel and O₂ along with the back-face temperature of the catalyst plotted versus the carbon to oxygen (C/O) ratio, calculated assuming 18.8 carbon atoms per molecule. C/O = 1 represents one oxygen atom from O₂ per carbon atom in the biodiesel. It is seen that the conversions of biodiesel and of O₂ are > 90 % for most conditions.

Figure 2 shows the selectivities for the major products formed in the partial oxidation of biodiesel. The selectivities are based on H atoms for H₂ and C atoms for all other species. All H and C containing products add to 100 %. At C/O = 0.9, the selectivity for H₂ is 85 % and for CO is 80 %, as the C/O ratio increases, the selectivity towards these species decrease rapidly as the “total hydrocarbons” (that is, all products C₂ through C₁₅) increase. The total-combustion products CO₂ (not shown) remain < 13 % for all C/O ratios. Species C₂ through C₅ are almost exclusively olefins, and larger species comprise both olefins and olefinic esters.

Figure 3 shows the selectivity for the production of ethylene, propylene, 1-butene, and 1-pentene versus C/O ratio for biodiesel. Ethylene dominates the small olefins with a maximum of approximately 25 %, followed by propylene and smaller amounts of higher olefins.

Since biodiesel contains exclusively linear C₁₆ and C₁₈ fatty acids, its molecular weight and isomers should correspond closely to *n*-hexadecane which has been studied with rhodium catalysts.^[4] Since the catalyst used herein was Rh–Ce, we repeated all of the experiments reported above on this catalyst using *n*-hexadecane. These results are shown as open symbols and dashed curves in Figure 1, Figure 2, and Figure 3. It is seen that conversions and selectivities correspond closely between biodiesel and *n*-hexadecane. The maximum H₂

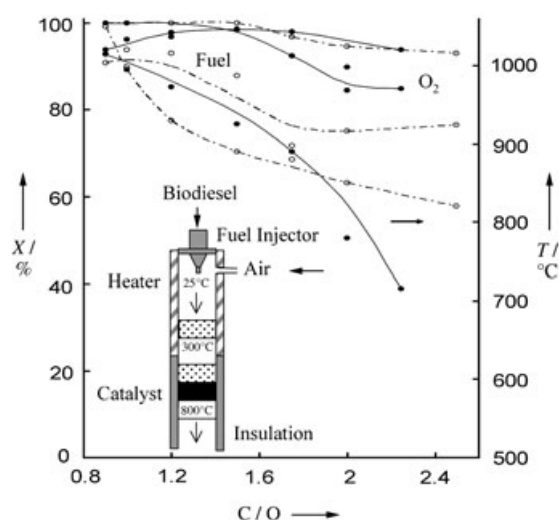


Figure 1. Fuel and oxygen conversions (*X*) and reactor temperature (*T*) versus C/O ratio for the partial oxidation of biodiesel (closed symbols and solid curves) and *n*-hexadecane (open symbols and broken lines). From the bottom, the first two curves indicate the temperatures (right-hand scale) for the partial oxidation of biodiesel (solid line) and *n*-hexadecane (broken line), the next two curves indicate fuel conversion (left-hand scale) for biodiesel (solid line) and *n*-hexadecane (broken line), and the top two curves indicate oxygen conversion (left-hand scale) for the partial oxidation of biodiesel (solid line) and *n*-hexadecane (broken line). The catalyst was a mixture of 2.5 % Rh and 2.5 % Ce deposited on an α -Al₂O₃ ceramic foam and the total flow rate was 4 standard litres min^{−1}, which corresponds to a catalyst contact time of approximately 5 ms. Liquid fuels were injected into the reactor using an automotive fuel injector. Cold air, admitted near the injector, rapidly mixed with the vaporized fuel with temperature and concentration gradients that minimized the potential for autothermal ignition before the reactor. Inset: schematic representation of the reactor.^[4–6]

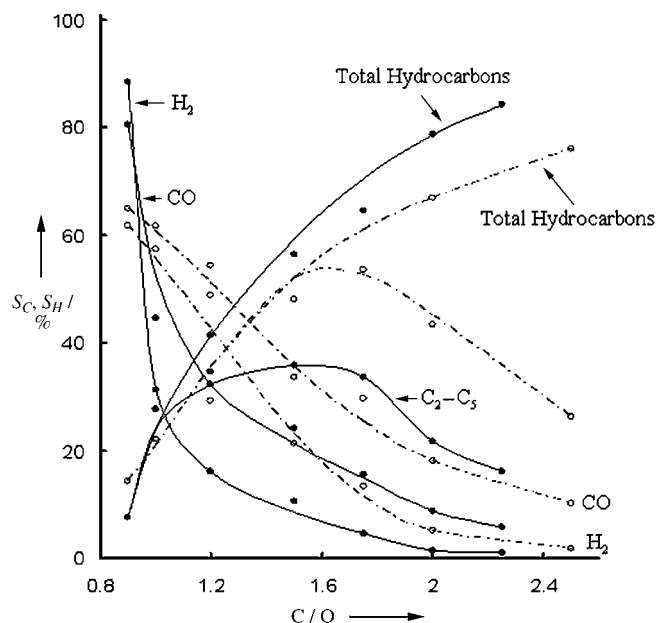


Figure 2. Selectivities *S* for the major products (H₂, CO, C₂–C₅ hydrocarbons, and total hydrocarbons) obtained from the autothermal oxidation of biodiesel with an Rh–Ce catalyst (closed symbols and solid curves) and from *n*-hexadecane over the same catalyst (open symbols and broken lines); see text for details.

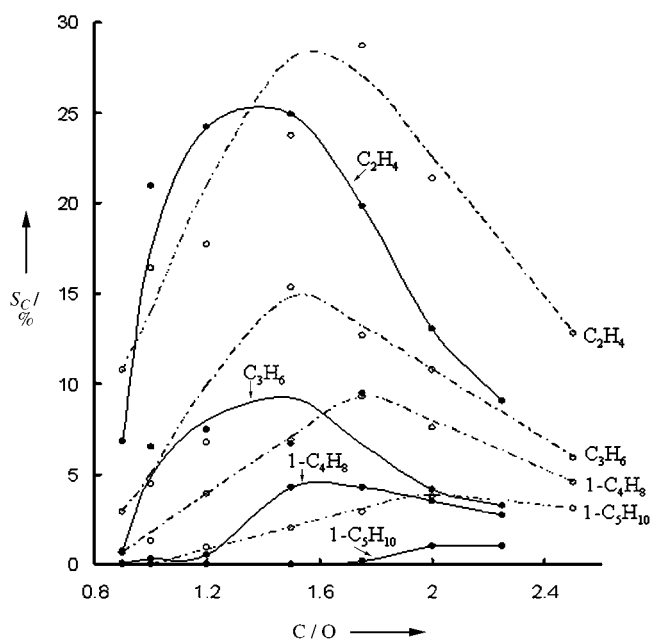


Figure 3. Selectivity S for the formation of ethylene, propylene, 1-butene, and 1-pentene versus C/O ratio from the partial oxidation of biodiesel (closed symbols and solid curves) and n -hexadecane (open symbols and broken lines). Methane is the only significant saturated alkane for which the selectivity is less than 8% (not shown).

selectivity appears to be higher for biodiesel, but this is sensitive to the exact C/O ratio and reactor temperatures. The GC chromatograms of the products from biodiesel and n -hexadecane indicate that α -olefins and olefinic esters are formed from biodiesel, but only α -olefins are formed from n -hexadecane. Figure 4 shows plots of selectivities for different species versus the chain length of the products.

All of these processes are initiated by surface oxidation reactions on the rhodium surface that produces primarily H_2 , H_2O , CO , and CO_2 . These reactions occur near the entrance of the catalyst (probably within the first millimeter) where the surface is nearly free of carbon.^[4] Most or all of the other products including olefins and olefinic esters arise from homogeneous reactions that occur after most O_2 has been consumed,^[4] and rapid quenching within 20 ms prevents secondary reactions that would make many products. Further, most of the ester linkages survive the 800 °C of the reactor.

We never observed deactivation or extinction of the reaction under any conditions up to $C/O = 3$ for at least 50 h and this strongly indicates that carbon in the catalyst is not forming in sufficient quantities to block the rhodium surface sites that are required for oxidation reactions. Once all the O_2 has been consumed, we believe that the rhodium sites are carbon covered (up to 5% carbon by weight of the monolith), but this does not cause time-dependent results, so a steady state is rapidly obtained.

For n -hexadecane the process is fitted quite well assuming a very simple mechanism, dissociation of the parent molecule into two radicals [Eq. (1)] followed by the elimination of the H atom on the carbon atom in the position β to the radical [Eq. (2)] to produce the corresponding α -olefins.

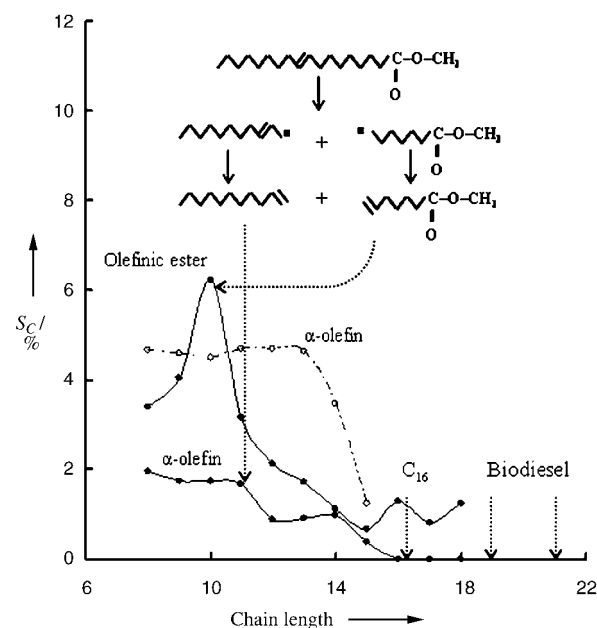
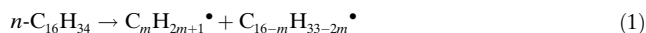


Figure 4. Plots of selectivities S for different species versus the chain length of the products observed at $C/O = 2.25$. 90% of the molecules present in biodiesel have a double bond between the ninth and tenth carbon atoms. Dissociation occurs mostly near this double bond because the allylic radical thus formed is resonance stabilized, this leads to a large amount of olefinic ester with a chain length of C_{10} . In contrast, n -hexadecane undergoes random C–C scission, which leads to nearly equal amounts of all α -olefins up to C_{14} (open symbols and broken line).



The alternative to β -H elimination is β -scission of C–C bond [Eq. (3)] which produces ethylene and a smaller alkyl radical.



This reaction can continue producing ethylene until the final radical is ethyl or propyl which dehydrogenates to form ethylene or propylene. Since β -H elimination has a lower activation energy than the elimination of the alkyl to form ethylene, it is predicted that high temperature (lower C/O ratio) favors small olefins and low temperature (high C/O ratio) favors longer-chain olefins (Figure 2 and Figure 3).

Biodiesel is of course more complex than n -hexadecane because of the ester group and because there is at least one double bond in 90% of the molecules (shown in Figure 4 for methyl oleate). Dissociation should occur mostly at C–C bonds because the C=C and C–O bonds are stronger. The most likely C–C bond dissociation occurs where the activation is lowest and, this is where the allylic radical stabilizes one of the radicals as a resonance structure, $R = C-C \cdot$ and $R-C=C \cdot$.

Since in soy oil the first double bond always occurs between the ninth and tenth carbon atom in the fatty acid, the most likely dissociation location in 90% of biodiesel mole-

cules occurs between the eighth and ninth carbon atoms (Figure 4).

From these radicals, the ester radical will undergo β -H elimination to produce an olefinic ester with a chain length of ten carbon atoms. The allylic radical will eliminate H to form an α -olefin with 11 carbon atoms.

This simple argument predicts that the dominant olefinic ester will have a chain length of C_{10} . Note from Figure 4 that this is exactly the maximum selectivity observed in the olefinic ester. Since the olefin side of the dissociated radicals can continue to dissociate, it is predicted that α -olefins with 11 carbon atoms or less but seldom more are produced, as shown in Figure 4.

Vegetable oils are widely produced throughout the world, and their production is increasing rapidly.^[7] These supplies are probably adequate to replace production of most small olefins with renewable sources instead of petroleum. The short-chain-olefin selectivities we obtain from biodiesel are only around 40%, but all the other products (H_2 , CO, α -olefins, and olefinic esters) all have considerable value. Only the CO_2 produced is irretrievably lost as a valuable chemical, so 90% of the carbon in vegetable oils can in principle be converted into chemicals and fuels by autothermal reforming. Olefins typically are priced at about \$0.25 per lb, so vegetable oil below \$3 per gallon should be a competitive source of olefins (\$0.20 per lb). An industrial olefins plant is capable of producing up to 1 billion lb per year by steam cracking. Our process produces about 1 lb per day from a 3 cm² reactor, 1 cm in depth, so a reactor would have to be approximately 4.5 meters diameter to match the output of the industrial olefin plant. We have not optimized flow rates, catalyst, preheat, or other variables, so it is likely that improvements in efficiency and yield will be possible. The H_2 selectivity was approximately 85% at the lowest C/O ratio (0.9). Higher H_2 selectivities can be obtained by using H_2O dilution to lower the temperature and increase the CO_2/CO ratio by promoting the water gas shift reaction in staged reactors.^[8,9]

Ultimately, it will be necessary to replace fossil fuels by renewable fuels because of issues of supply, global warming, and pollution. The constraints on using renewable fuels as an energy source are considerable because of their limited supply and the need to produce energy at low cost. However, chemicals have a much higher value and require smaller amounts of material than fuels, so the production of chemicals from renewable fuels appears to be less difficult.

The simplicity of the products and product distribution obtained from biodiesel indicates that the mechanism could be as simple as that outlined in Figure 4. The process produces both short-chain and longer-chain olefins and olefinic esters. Since both short-chain olefins and short-chain olefinic esters have considerable value in polymer and copolymer production, this process could be quite attractive as an alternative to making polymers from fossil fuels.

Received: May 26, 2004

Revised: September 14, 2004

Keywords: alkenes · fatty acids · green chemistry · heterogeneous catalysis · oxidation

- [1] R. Deng, F. Wei, Y. Jin, Q. Zhang, Y. Jin, *Chem. Eng. Technol.* **2002**, 25, 711–716.
- [2] A. S. Bodke, D. A. Olschki, L. D. Schmidt, E. Ranzi, *Science* **1999**, 285, 712–715.
- [3] A. Beretta, P. Forzatti, E. Ranzi, *J. Catal.* **1999**, 184, 469–478.
- [4] J. J. Krummenacher, K. N. West, L. D. Schmidt, *J. Catal.* **2003**, 215, 332–343.
- [5] D. A. Hickman, L. D. Schmidt, *Science* **1993**, 259, 343–346.
- [6] D. A. Goetsch, L. D. Schmidt, *Science* **1996**, 271, 1560–1562.
- [7] A. Demirbas, *Energy Sources* **2003**, 25, 721–728.
- [8] G. A. Deluga, J. R. Salge, L. D. Schmidt, X. E. Verykios, *Science* **2004**, 303, 993–997.
- [9] C. Wheeler, A. Jhalani, E. Klein, S. Tummala, L. D. Schmidt, *J. Catal.* **2004**, 123, 191–199.