# Deoxygenation of triglycerides to olefins and paraffins on PtSnK catalysts

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#### Introduction

Triglycerides from vegetable oils or animal fats are a potential source of fuels and chemicals. Transesterification of triglycerides with methanol is commonly used to convert triglycerides to so-called biodiesel, which consists of fatty acid methyl esters (FAMEs). This conversion method, which uses homogeneous catalyst, is efficient and well understood. However, the FAMEs have some undesirable fuel properties<sup>1-3</sup>. A more desirable diesel fuel alternative would be conversion to straight chain hydrocarbons comparable to conventional diesel. A selective conversion path to olefins would also be valuable for the production of feedstocks for a variety of specialty chemicals as well<sup>4</sup>. Here we report on our studies of deoxygenation of triglycerides over PtSnK catalysts.

#### **Materials and Methods**

The catalyst (1%Pt,1.3%Sn,1.5%K/SiO<sub>2</sub>) was prepared by incipient wetness impregnation. The triglycerides used were trilaurin (glyceryl tridodecanoate), trimyristin (glyceryl trimyristate), and palm kernel oil (PKO). The major component of PKO is trilaurin (about 50%) while the remainder is a mixture of other triglycerides including trimyristin. The trilaurin and trimyristin were obtained from Sigma Aldrich; the PKO was obtained from Mountain Rose Herbs. All reactions were carried out in the liquid phase in semi-batch mode, in which the reactant (triglyceride) was charged to the 300 ml. stirred reactor (Parr Corp.). Flowing He continuously removed vapor phase products. For all experiments, the reaction temperature was 320 °C and the reaction pressure was 45 psig. Initial charges to the reactor were 5-10 g triglyceride in 140 ml hexadecane solvent and 2 g catalyst. The gas phase effluent flowed through two condensers to remove all condensable products. Reactor contents were periodically sampled and analyzed by gas chromatography.

## **Results and Discussion**

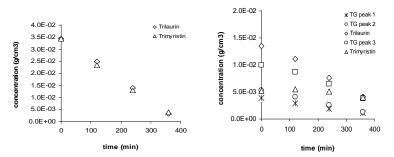
Results of deoxygenation of trilaurin and trimyristin in separate experiments are shown in Figure 1a. Deoxygenation of trilaurin occurs readily under the experimental conditions of these reactions. Primary products are C11 olefins and paraffins, with small amounts of cracking products from the hydrocarbon chains, and small amounts of C2 and C3 oxygenates from the glycerol head group of the triglyceride. Deoxygenation of trimyristin also takes place readily, with primary products being C13 olefins and paraffins instead of C11. Deoxygenation of PKO is more complex since PKO consists of a combination of triglycerides. Results are shown in Figure 1b. Based on typical PKO analyses (which also correspond well with observed GC peak elution times), component TG1 is a triglyceride with one C12 chain

and two C10 chains; TG2 has two C12 chains and one C10 chain; and TG3 has two C12 chains and one C14 chain.

Interestingly, while rates of conversion of trilaurin and trimyristin conversion are comparable in separate experiments (Figure 1a), trimyristin conversion is significantly inhibited in the mixtures. In one additional experiment, a mixture of PKO and trimyristin was reacted under conditions identical to experiments of Figure 1; trimyristin conversion was negligible, while rate of conversion of all other components was decreased but still significant. In a similar experiment, a mixture of PKO and trilaurin showed rapid conversion of all components except the trimyristin, for which conversion was again negligible. Calculations suggest that mass transfer limitations do not affect the measured kinetics under these experimental conditions.

## Significance

Catalytic deoxygenation of triglycerides is a potential route for production of "green" diesel fuel or hydrocarbons which substitute for petrochemical feedstocks for specialty chemicals.



**Figure 1.** Conversion of triglycerides. (a) conversion of trilaurin and trimyristin in separate experiments. (b) conversion of five triglycerides in PKO).

### References

- . Geyer, S.M., Jacobus, M.J., and Lestz, S.S. Trans. ASAE 27, 375 (1984).
- 2. Peterson, C.L., Korus, R.A., Mora, P.G., and Madsen, J.P. *Trans. ASAE* 30, 28 (1987).
- 3. Demirbas, A., Energy Convers. Manage. 44 (13), 2093 (2003).
- Bressler, D.C., Maher K.D., Bioresource Technology 98, 2351 (2007).