# Kinetic model for Hydrodeoxygenation of Stearic acid over Ni-MoS$_2$ Catalyst

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**Abstract:** Hydrodeoxygenation (HDO) of oils from bio-streams to liquid hydrocarbons is a novel catalytic process for the production of renewable fuels. In this study, the HDO of stearic acid over industrial catalyst NiMoS$_2$ was investigated varying several parameters like temperature, pressure and feed concentration. It's a first detailed kinetic study of a Ni-MoS$_2$/Al$_2$O$_3$ catalyst with selectivity for both decarbonation and direct-HDO reaction routes. A pseudo 1st order kinetic model was able to predict the evolution of intermediates (like octadecanol), final products and influence of H$_2$ pressure on selectivity.

**Keywords:** Hydrodeoxygenation, Kinetic model, NiMo catalyst.

## 1. Introduction (11-point boldface)

The world consumption of liquid fuels is predicted to reach to 112Mb/d by 2035. Out of which, 56% of demand will be from the transport sector alone due to the increased ownership of vehicles in emerging economies [1]. So, it is quite pertinent to find alternate sustainable routes to produce liquid transportation fuels. Catalytic hydrodeoxygenation (HDO) is a process which upgrades renewable feed like animal grease, forestry residue and waste oils to drop-in fuels. There are extensive studies on different aspects of HDO related to feeds, catalyst and reaction parameters in the open literature. While, kinetic studies and detailed modelling articles are limited to very few [2,3] concerning Ni and noble metal based catalysts. It is vital to develop a kinetic model with the industrial catalysts like (NiMo or CoMo on alumina) for scale-up, process design and elucidation of reaction mechanism. In this study, a kinetic model was developed based on a proposed reaction mechanism and its predictions were compared to experimental observations.

## 2. Experimental (or Theoretical)

Hydrodeoxygenation of Stearic acid was carried over Ni promoted molybdenum sulfide catalysts. A set of kinetic experiments were executed by varying temperature (275-325 °C), H$_2$ pressure (40-60 bar) and stearic acid concentration (2-8 wt%). Also, a few intermediates which are formed during HDO of stearic acid like octadecanal and octadecanol were used as feed as well for validation of the model.

The reactor mole balance consisted of a pseudo homogeneous ideal batch reactor model that comprised a series of differential equations for each component. Initially, a pseudo first order reaction kinetic model was used to estimate the rate constants and the activation energy for an assumed reaction scheme. The differential equations were solved numerically, and simultaneously the vapor-liquid equilibrium (VLE) was calculated based on the Predictive Soave-Redlich-Kwong (PSRK) equation of state. The VLE predictions of liquid phase component concentrations were used in the kinetic model.

## 3. Results and discussion

Fig. 1 compares the concentration profiles of reactants and products with time during HDO of stearic acid at 40 and 60 bar of H$_2$ pressure. The kinetic model is able to predict the trends of products (heptadecane and octadecane), reactants (stearic acid) and intermediates rather well. The experimental results indicate that the direct-HDO route producing C18 alkane is preferred at higher H$_2$ pressure as indicated by the relative quantities of C18/C17 alkane products. In addition a higher quantity of octadecanol (C18-OH) is formed at higher H$_2$ pressure because it is an intermediate of the direct-HDO route. The model was able to replicate these trends in selectivity since the direct-HDO route from octadecanal was first order with respect to $H_2$, whereas the decarbonylation route (DCO), leading to C17 alkane, was zero order. However the model over-predicts the effect of H2 pressure on selectivity probably because the pseudo first order model does not accurately reflect the actual reaction orders. In addition both the experiments and the model show that the C17 olefin is formed earlier compared to the C18 olefin. The model successfully predicts this trend because in the assumed reaction scheme for the HDO route an additional intermediate is formed, namely octadecanol, before the olefin whereas for DCO the olefin is produced directly from octadecanal.

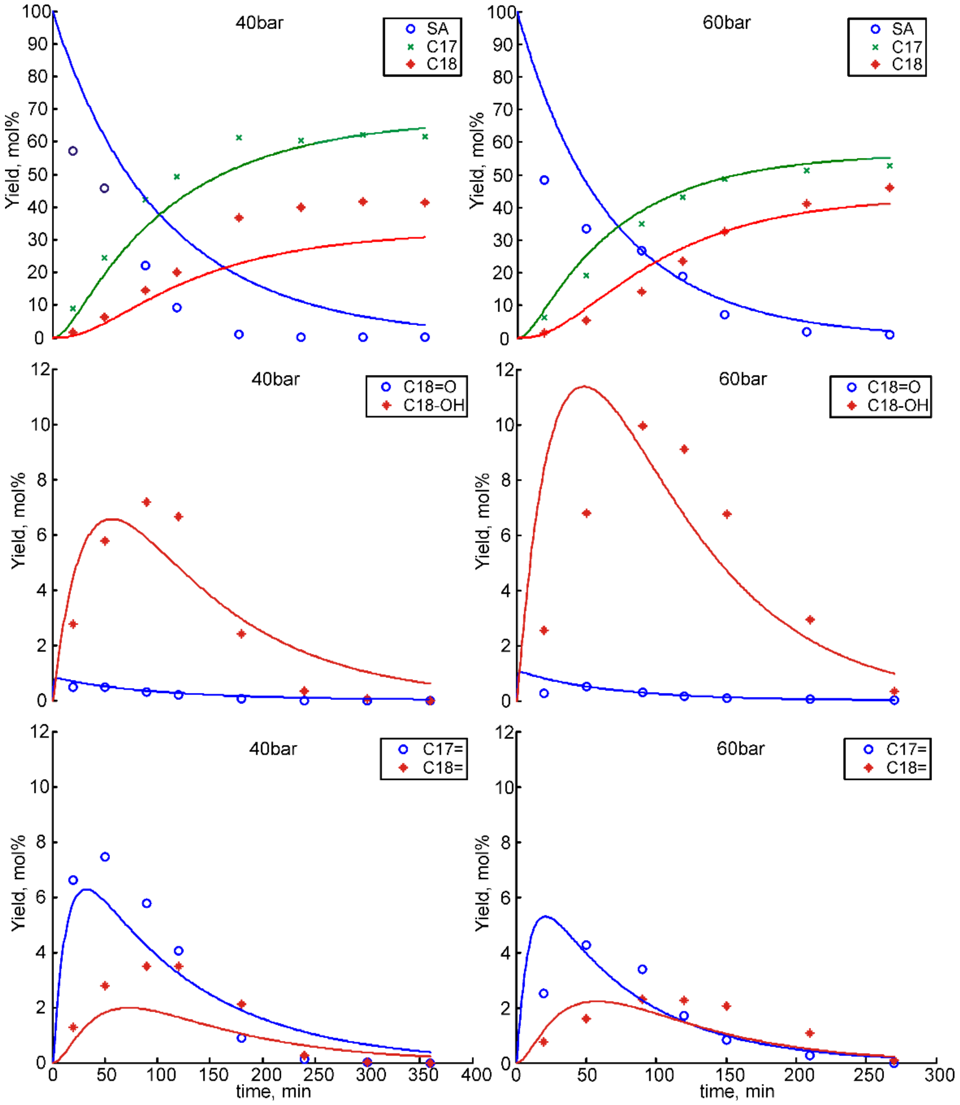

**Figure 1.** Results for HDO of 5 wt% stearic acid (SA) in dodecane at 300°C and under $H_2$ pressure of 40 bar (left panels) and 60 bar (right panels). Final products are heptadecane (C17) and octadecane (C18) and intermediates are 1-octadecanol (C18-OH), octadecanal (C18=O), heptadecene (C17=) and octadecene (C18=). Experimental results are symbols and model simulations are curves of corresponding colors.

## 4. Conclusions

A pseudo first order kinetic model was able to reasonably well predict the evolution of intermediates and final products for HDO over a Ni-$MoS_2$ catalyst. In addition the model was able to reproduce the influence of $H_2$ pressure on the selectivity for direct-HDO and DCO reaction routes.

## References

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