Kinetic Study of Hydrodeoxygenation of Palmitic Acid as a Model Compound for Microalgae Oil over Pt/ γ -Al₂O₃

Lin Zhou* and Adeniyi Lawal

New Jersey Center for Microchemical Systems, Dept. of Chemical Engineering and Materials Science, Stevens Institute of Technology, 1 Castle Point on Hudson, Hoboken, NJ 07030, USA

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*Corresponding author,

Tel.; +1 201 216 8314; Fax: +1 201 216 8306; Email: lzhou4@stevens.edu

Abstract

The kinetics of hydrodeoxygenation (HDO) of palmitic acid over the 1% Pt/ γ -Al₂O₃ catalyst was investigated in a microreactor using integral method. Kinetic data were collected under process conditions of industrial interest but in the regime with negligible heat and mass transfer limitations. For the first time, rate equations derived from three kinetic models (Power law, Langmuir-Hinshelwood, and Eley-Rideal) were investigated in data fitting through nonlinear regression using Levenberg-Marquardt algorithm, and evaluated based on proposed statistical and thermodynamics criteria. H₂ was found to be adsorbed on the catalyst surface without dissociation, which is different from gaseous reaction with consistent dissociative adsorption of H₂. The apparent activation energy is 60.3 kJ/mol, which is lower than the intrinsic activation energy of 92.9 kJ/mol due to the exothermic adsorption of reactants. The proposed rate equations are expected to be applicable to liquid phase HDO of fatty acids, and not limited to palmitic acid. This complete kinetic study (including rate equations with specified kinetic parameters) fills an important knowledge gap in green diesel production from algae, and can be used for rational design of reactors and the determination of optimum operating conditions. Moreover, the presented work develops a systematic procedure for kinetic study by identifying the challenges that need to be overcome to obtain meaningful kinetic data.

1. Introduction

According to the International Outlook 2014 released by the U.S. Energy Information Administration (EIA), the world liquid fuels consumption will rise 38% by 2040.¹ As the biggest oil consumer of the world, the transportation sector is reported to account for about 20% of the global energy consumption.² About 80% of today's transportation fuels are derived from petroleum. It has been reported that processes involving petroleum account for 31% of CO₂ emissions, 24% of NO_x emissions and 41% of nmVOC (non-methane Volatile Organic Compounds),³ and constitute the predominant source of air pollution. In addition, because fossil fuel reserves are finite, petroleum is not sustainable in the long term. These factors have encouraged the research and development of biomass-derived fuels, the utilization of which is a low-net carbon process. Compared with lignocellulosic biomass, oleaginous feedstock, comprising mainly triglycerides and free fatty acids, has higher energy content.⁴ Microalgae, as a source of non-edible oleaginous feedstock, has attracted researchers' attention due to its fast growth rate and high oil content. As reported previously, microalgae oil contains mainly C14 to C20 fatty acids with C16 fatty acid being predominant in the *Nannochloropsis salina* strain, which is the workhorse of the algae industry.⁵

Based on the experience on upgrading of vegetable oil, hydrotreating, which produces green diesel, is comparatively more advantageous than transesterification, the product of which is biodiesel.⁶ Performance studies of hydrodeoxygenation (HDO), the most critical step in hydrotreating of microalgae oil⁵⁻⁷ and vegetable oil⁸⁻¹⁰ have been demonstrated over different catalysts. Through the study of a wide range of model compounds, the mechanism of HDO of triglycerides was established.^{7-8,11-12} The HDO process starts with the saturation of double bonds in the alkyl chain, and is followed by the cleavage of C-O bond to produce fatty acids. Then the carboxylic group will be hydrogenated to form fatty aldehyde, which is finally converted to an even-numbered carbon hydrocarbon through Hydrodehydrogenation (DHYD) with fatty alcohol as intermediate, or an odd-numbered carbon hydrocarbon via Hydrodecarboxylation (DCO2)/Hydrodecarbonylation (DCO). Previous studies^{7,13-15} have investigated the group 10 metals-based catalysts (Pt, Pd and Ni) in the HDO of lipids, including Triglycerides (TAG), fatty acid methyl esters (FAME), and free fatty acid (FFA). The results reveal that, over the group 10 metals-based catalysts, due to the similarities in their electronic structure, DCO route was preferred, and the hydrogenation of FFA to form aldehyde have been shown to be the rate-limiting step of the HDO reaction.^{7,13-15} The studies indicate that a cost-effective process of green diesel production from oleaginous feedstocks requires catalysts that demonstrate high activity in the conversion of carboxylic acids.¹³

The effectiveness of a catalyst in a reaction can be evaluated through its activation energy for that reaction. Although numerous studies have been conducted on the hydrotreating of fatty acids, limited kinetic models with specified kinetic parameters have been reported. The Langmuir-Hinshelwood kinetic expression was rarely investigated for this hydrotreating process. Boda et al. explain the pressure effect on the HDO of caprylic acid over NiMo/ γ -Al₂O₃ and Pd/C using a rate equation derived from the competitive non-dissociative adsorption model. However, no kinetic parameters were determined for this system.¹³ Snare et al. studied the kinetics of HDO of stearic acid over 5%Pd/C without considering the role of H₂ in the derived rate equation. The

reported results show that the adsorption equilibrium constants for all reactants, intermediates and products are negligible, and the kinetic equation was reduced to a first order power-law form, which was found to be in good agreement with the experimental data.¹⁶ Due to the complexity of mechanistic model for the HDO reaction, most of the reported rate equations are in power-law form. The HDO kinetics of stearic acid based on a first order power law model was studied by Kumar et al, and the apparent activation energy was found to be 175.4 kJ/mol over 15wt.% Ni/ γ - Al_2O_3 ,¹⁷ which is greater than the value reported by Ayodele et al, 130.3 kJ/mol, over $\text{FeMoO}_x/\text{Zeol}$.¹⁸ Precious metal-based catalysts were found to be more effective in lowering activation energy than the base metal catalysts. The apparent activation energy of HDO of palm stearin fatty acid mixture over 5% Ru/ Al_2O_3 was reported to be 49.22 kJ/mol, with the order of 0.8 with respect to H_2 partial pressure and 1.2 to liquid reactant.¹⁹

Considering the fact that there are only a few of applications of precious metal-based catalyst in the hydrotreating industry, the presented work aimed at investigating the Pt catalyst, with the 1% loading level being most commonly used for precious metal-based catalysts. This catalyst has been previously shown to have excellent performance in the HDO of microalgae oil, including inhibition of CH_4 and coke formation.⁵ The objective of the current work is to establish a kinetic model with specified parameters that can be used in design of reactors for HDO of microalgae oil over Pt/ γ - Al_2O_3 , which makes both scientific and industrial contribution to the production of green diesel. In terms of complex reaction feedstocks, such as lingo-cellulosic bio-oils, the lumping kinetics approach can be used, in which the chemical species with similar chemical reactivity are grouped into pseudo-species, the so-called lumps.²⁰⁻²² However, since C16 fatty acids are the predominant fatty acids in microalgae oil, and the conversion of saturated FFA is the rate-limiting step, Palmitic Acid is used in this study as the model compound. The kinetic study results will be interpreted with the power law model, and the reaction mechanism will be presented via Langmuir-Hinshelwood and Eley-Rideal models.

2. Experimental Section

2.1 Materials

Reactants

Due to the complexity of biomass feedstocks (algae inclusive), a kinetic study similar to the presented work but applied to the real feedstock is theoretically not feasible, and the kinetic studies of major components (model compound) are widely used to obtain kinetic data for design purpose. As illustrated above, Palmitic Acid (P.A., $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$) is selected as the model compound of microalgae oil in hydrodeoxygenation. P.A. was purchased from Fisher Scientific with 98% purity. At room temperature, similarly to the flowability of microalgae oil, which is semisolid, P.A. is a solid (white flakes), therefore pre-heating will be needed for continuous processing in a flow reactor system. There is however an alternative and practically feasible approach to processing these semisolids or solids, and that is the co-processing with petroleum refinery middle distillates, such as gas oil. The petroleum refinery has existing infrastructure for supply of hydrogen, hence the co-processing of alga oil with refinery middle distillates makes

conversion of alga oil to green diesel practically realizable. Therefore, to make the proposed kinetic models applicable to hydrotreating of alga oil as it would be practiced industrially, (e.g.co-processing alga oil with petroleum refinery middle distillates, gas oil), the selected solvent should be a hydrocarbon that mimics the solvent properties of gas oil. In addition, it should also satisfy the following requirements: (1) not reactive under experimental conditions (2) high boiling point to maintain low vapor pressure under experimental condition (3) low melting point to keep it in melted state at room temperature. Based on all these considerations, n-dodecane (99+%, Alfa Aesar) is used as solvent in this study.

Limited by the HPLC pump operating temperature range (of 10 °C to 30 °C), feed solution cannot be preheated to increase the P.A. solubility in the feed reservoir. Therefore, 1g of P.A. is dissolved in 99g of dodecane to make 1wt% solution. In order to minimize the potential sources of errors from sample preparation and GC analysis, Eicosane ($C_{20}H_{42}$) was added into the feed solution as internal standard due to its thermal and chemical stability. The feed solution is sonicated for 2 hours to ensure complete mixing. Ultra-high purity (5.0 grade) Hydrogen was purchased from Praxair.

Catalyst

Based on our previous catalyst evaluation on hydrodeoxygenation of microalgae (*Nannochloropsis salina*) oil, to maximize the application of the proposed model and to provide reproducible and reliable kinetic models, 1% Pt/ γ - Al_2O_3 (Alfa Aesar) is used in the present kinetic study.⁵ Based on the previously published and extensive experimental studies from our group, including hydrogenation of o-nitroanisole,²³ and aromatic nitro ketone,²⁴ and the hydrodeoxygenation of different reactants at different concentrations (pyrolysis oil,²⁵ 2-methoxy-4-propylphenol,²⁶ and acetic acid²⁷), , using different catalysts in a microreactor, it was found that the reactions were not limited by internal mass transfer, when the particle size of the catalyst ranges from 75-150 μ m. Therefore, catalyst was ground and sieved to this particle size range, and the theoretical evaluation is considered to be adequate for estimating the internal mass transfer limitation effect.

2.2. Experimental Setup and Procedure

The schematic of the setup for kinetic study of P.A. hydrodeoxygenation is shown in Figure 1. Since meaningful kinetic data can only be collected in the region where heat and mass transfer limitations are all negligible, microreactor, which features enhanced mass and heat transfer characteristics, is used in this study. The inner diameter of the SS316L microreactor used was 0.762mm and the length was varied from 3cm to 13.3cm depending on the catalyst loading amount required by the experiment. Two pieces of 0.3175 cm outer diameter SS316L tubing packed with glass beads (90 μ m) were connected to the entrance and exit of the microreactor. In order to retain the packed particles in each tubing section, Hastelloy micro filter-cloth (200X1150 meshes, Unique Wire Weaving Co., Hillside, NJ) was placed at the end of each tubing. The reactor was then placed in an electric furnace with digital temperature control and readout, and a hand-held thermal meter was also used to further confirm the temperature in the furnace. It should be noted that the temperature in this study was reported as reactor wall

temperature. Two pressure transmitters were used to measure the pressure at the entrance and exit of the reactor, and the system pressure was adjusted by a back pressure regulator (BPR) installed downstream. The flow rate of compressed gas was regulated by the mass flow controller (sccm), which was calibrated routinely with an Agilent ADM 2000 universal gas flowmeter before and after each run. In order to prevent the precipitation of P.A. and the HDO product from dodecane, heat trace was added to keep the temperature of the region surrounding the reactor system at 22°C or slightly higher.

Before each run, reactor system was purged with hydrogen for 30 minutes at room temperature and atmospheric pressure to ensure the system was filled with pure hydrogen. Then, in situ reduction of fresh catalyst was conducted by increasing the system pressure to 500psig and temperature to 310°C with hydrogen flow rate of 50sccm. After adjusting to reaction temperature, pressure and hydrogen flow rate, and letting the system stabilize for 30 minutes, liquid feed was pumped by the HPLC pump to the T-mixer where it contacts the hydrogen feed to form a slug flow before entering the reactor. The reduction in the cross sectional area of the reactor system from the entrance to catalyst bed ensures the uniform wetting of the catalyst by the reagents. During the experiment, liquid sample was collected from the sample valve every hour and analyzed. The remaining product would flow into the gas-liquid separator, with liquid being condensed in the separator flask and gas being vented to the hood. After the experiment, the system was cleaned by first pumping hexane through it at 4ml/min for 30 minutes with the BPR fully opened, followed by purging with nitrogen for 1hour to get rid of any liquid residue from the system.

2.3. Product Analysis

Based on the analysis of the liquid product from a preliminary run, as depicted in Figure 2, the liquid products of HDO of P.A. were Pentadecane ($C_{15}H_{32}$), Hexadecane ($C_{16}H_{34}$), Hexadecanal ($C_{15}H_{31}CHO$), Hexadecanol ($C_{16}H_{33}OH$), and Palmityl Palmitate ($C_{15}H_{31}COOC_{16}H_{33}$), which confirmed the reaction mechanism previously reported for HDO of different fatty acids over different catalysts.⁷⁻⁸ The identification and quantification of all compounds in the liquid product was done using a Varian 450 Gas Chromatograph (GC) equipped with a CP-8400 Autosampler under the conditions listed below:

Column: ZB-FFAP capillary column (30m x 0.32mm x 1 μ m)
Oven Profile: 100°C (1min), 15°C/min to 160°C, 8°C/min to 260°C (35min)
Carrier Gas: Helium, 2.4ml/min
Injection: 280°C, 0.5 μ L, 1:10 split
Detector: FID, 280°C

External calibration was conducted before analyzing each batch of samples to obtain the response factor and retention time of each compound, which were used in the calculation of the concentration (mol/m³) of respective compounds. Since the feed solution was very dilute, which was essentially dodecane (99 wt %), the density of liquid flow was assumed unchanged before and after the reaction.

Therefore, the molar flow rate of P.A. at exit is defined as

$$F_{P.A.out} \left(\frac{\text{mol}}{\text{s}} \right) = \text{concentration of P.A. at exit} \times \text{liquid flow rate} \quad (1)$$

The yield of $C_{15}H_{32}$, the major product was calculated on the total product mass basis

$$C_{15}H_{32} \text{ Yield (\%)} = \frac{\text{total mass of } C_{15}H_{32} \text{ in product}}{\text{total mass of all HDO liquid products}} \times 100 \quad (2)$$

The yield of total product is defined as:

$$\text{Total Product Yield (\%)} = \frac{\text{Total moles of liquid products}}{\text{Total moles of the theoretical yield of liquid product}} \times 100 \quad (3)$$

Space-time consumption (STC) of P.A. is defined as

$$STC_{P.A.} = \frac{\text{moles of P.A. consumed/time}}{\text{mass of catalyst}} \quad (4)$$

Conversion of P.A. is defined as

$$\text{Conversion of P.A. (\%)} = \frac{\text{moles of P.A. consumed}}{\text{moles of P.A. fed}} \times 100 \quad (5)$$

After each run, a check was made to ensure that material balance was satisfied using the following equation:

$$-5\% < \frac{\text{moles of P.A. consumed} - \text{total moles of liquid product}}{\text{moles of P.A. consumed}} < 5\% \quad (6)$$

It should be noted that two moles of P.A. are required to form one mole of Palmityl Palmitate. Therefore, when performing the material balance, the number of moles of produced Palmityl Palmitate contributed to the total moles of liquid product was twice the moles of Palmityl Palmitate measured in product.

3. Results and Discussion

3.1. Mass Transfer Analysis

3.1.1. Analysis of External Mass Transfer Limitation

Based on the relevant fluid flow characterization study,²³ all the kinetic study data was collected in Taylor flow regime, comprising alternate liquid slugs and gas bubbles. The main external mass transfer resistances, for this three phase reaction of palmitic acid with hydrogen on the γ -alumina supported catalyst, occur at the gas-liquid and liquid-solid interfaces, with the former being predominant.⁶ Due to the dependence of mass transfer rates through interfaces on flow velocity, the overall external mass transfer limitation can be evaluated experimentally by studying the change of Space-time-consumption (STC) of P.A. at different superficial flow velocities. Superficial flow velocity was varied by changing gas and liquid flow rates and reactor length (the amount of catalyst), while keeping the other process conditions, including reactor ID, gas to liquid ratio, residence time, reaction temperature and pressure, constant.⁵ The

experimental results depicted in Figure 3 show that the STC of P.A. is independent of the superficial flow velocity in the studied range. That means the reaction is not limited by external mass transfer even at the lowest flow velocity of 0.49 m/s, which was subsequently chosen as the baseline velocity for the kinetic studies.

3.1.2. Analysis of Internal Mass Transfer Limitation

Internal mass transfer refers to the diffusion of reactants from the catalyst pellet pore entrance into the catalyst.²⁵ When the concentration profiles of reactants inside the pores show significant variation from the catalyst surface to its center, reactions are considered to be limited by internal mass transfer. This concentration variation through the catalyst pellet is estimated by calculating the Weisz-Prater parameter (C_{wp}) defined as:²⁸

$$C_{wp} = \frac{\text{actual reaction rate}}{\text{a diffusion rate}} = \frac{-r'_{A(obs)} \rho_P R^2}{D_e C_{AS}} \quad (7)$$

Where

$-r'_{A(obs)}$: Observed reaction rate, 1.066×10^{-3} g P.A./ g cat. /s.

ρ_P : Density of catalyst pellets, 0.29×10^6 g cat. /m³.

R: Characteristic diameter of the catalyst pellets, 112.5×10^{-6} m.

C_{AS} : Hydrogen concentration at the external surface of the catalyst pellets, which is the hydrogen solubility in dodecane approximately, 360 g/m³.

D_e : Effective diffusivity of hydrogen in the catalyst pellets, $D_e = (D_{AB} \Phi_p \sigma_c) / \tau$, where D_{AB} : Binary diffusivity of hydrogen in dodecane, 1.12×10^{-7} m²/s;²⁹ Φ_p : Porosity of the catalyst pellets, 0.5; σ_c : Catalyst constriction factor, 0.8 ; τ : catalyst tortuosity, 2.²⁵ Then, the D_e is calculated to be between 2.24×10^{-8} m²/s.

The calculated Weisz-Prater parameter is 0.485, which is less than 1. According to the definition of C_{wp} , the actual reaction rate in this study is less than the diffusion rate, and the reaction is not controlled by internal mass transfer.

3.2. Heat Transfer Analysis

Poor heat transfer characteristics will result in large temperature gradient within the reactor, which will mask the true kinetics of the reaction because reaction will occur in the

reactor at different rates due to the temperature gradient. Therefore, in order to ensure that experimental data collected reflect only the kinetics, heat transfer limitations will be analyzed for the following three regions: 1. Intra-particle ; 2. Interphase between the external surface of the particles and fluid adjacent to them; and 3. Inter-particle or intra-reactor (between the local fluid regions or catalyst particles), which reflects gradients within the reactor as a whole.²⁷ To determine whether heat transfer limitations exist in any domain depends on the values of literature defined criteria.³⁰⁻³¹ Mears³¹ suggested that when the Biot number (Bi) is much smaller than 10, the heat transfer resistances decrease in the order of inter-particle > inter-phase > intra-particle. The Biot number is the ratio of thermal resistance of the particle to that of the film around the particle.

$$Bi = \frac{\text{thermal resistance of the particle}}{\text{thermal resistance of the film around the particle}} = \frac{hd_p}{\lambda} \quad (8)$$

where: h (10-100 W/m²/k) is the heat transfer coefficient,³¹ d_p (112.5μm) is the diameter of the catalyst particle, and λ (in the order of 0.1 W/m/K³²) is the effective thermal conductivity of porous catalyst. In the present work, Bi << 10 indicating that inter-particle heat transfer limitations predominate compared to the other two. Inter-particle transport effects occur both radially and axially within the reactor.

Axial Heat Transfer Limitation When the ratio of axial length of the reactor to the catalyst particle size is much greater than 20, the axial heat transport effect can be neglected. In this study, the minimum ratio used for kinetic study is 267, thus the axial heat transfer limitation is negligible.

Radial Heat Transfer Limitation Radial heat transport limitations could be evaluated by calculating Damkohler number (Da) for heat transfer,³⁰ and comparing it to the value of 0.4(RT_w/E_a), as shown by the equation below:

$$Da = \left| \frac{-\Delta H(-R_{obs})(1-\varepsilon)R_0^2}{\lambda T_w(1+b)} \right| < 0.4 \frac{RT_w}{E_a} \quad (9)$$

When the above inequality holds, the radial temperature difference in the reactor would be less than 5% of average cross-sectional temperature.

In this work, where

- ΔH=49.7X10³ J/mol is the heat of reaction.
- -R_{obs}=4.34 mol/m³/s is observed reaction rate at temperature (T_w) of 633.15K.
- ε=0.3 is the bed porosity.
- R₀=0.000381m is the inner radius of the microreactor.
- b=0 is the ratio of diluent to catalyst volume.
- E_a=60.30 X10³ J/mol is activation energy.

the left side (0.000346) is much smaller than the right side (0.0349), indicating that the radial temperature gradient in the reactor is negligible. Based on the heat transfer analysis, the kinetic study experiment was not conducted in the heat transfer controlling regime.

3.3. Catalyst Activity and Selectivity

Microalgae oil, as reported previously,⁵⁻⁶ is a complex material. In addition to the oxygen atom O, the non-lipids portion also contains heteroatoms like N, S, P, which may cause catalyst deactivation. According to our experience with microalgae upgrading techniques, the deactivation study using model compounds is of limited significance, and therefore, not included in this presented kinetic study.

As is well known to researchers in industrial catalysis, fresh catalysts are always super active before subsequently stabilizing in performance in the reactor system. The initial decrease in catalyst activity is not considered as deactivation but the transition to stability. Industrial catalysis texts make reference to this behavior in performance of fresh catalysts. It has also been confirmed in previous performance study on HDO of microalgae oil over 1% Pt catalyst, which showed that the catalyst activity and selectivity reached stable state around 4 to 5-hour time-on-stream.⁵ As shown in Figure 4 (a)& (b), with the lowest catalyst loading used in this study, the stability of catalyst activity and selectivity was studied in terms of P.A. conversion and the yield of main product, C₁₅H₃₂ respectively. The activity of the catalyst dropped rapidly during the first 5 hours, and then remained stable for 5 hours; while its selectivity didn't change much with time-on-stream. The stability of catalyst performance can always be preserved by increasing catalyst loading.⁵⁻⁶ Moreover, catalyst regeneration, which was conducted every 2 hours on-stream following the same catalyst reduction procedure, was found to be effective in restoring the catalyst performance, as reflected by the total product yield (Figure 4 (c)). Therefore, all kinetic data was collected between 8 to 10 hours on-stream time, during which the catalyst deactivation effect was negligible.

3.4. Kinetic Study

3.4.1 Experimental results

Preliminary results showed that the lowest conversion of P.A. obtained in the shortest microreactor, 3cm (14.2 mg 1% Pt catalyst), at process conditions of interests, was higher than 10%. Therefore, integral method is used in this kinetic study. By performing mole balance on P.A. in the microreactor, the consumption rate of P.A. in HDO is expressed through measurable process parameters, and is given by

$$\frac{dF_{P.A.}}{dw} = r_{P.A.} \quad (10)$$

where, w is the weight of catalyst in g, and $F_{P.A.}$ is the molar flow rate of P.A., mol/s. Since 99% of the processed liquid feed was dodecane, the liquid volume flow rate at the entrance and exit was considered to be unchanged, and $F_{P.A. \text{ out}}$ can be calculated by multiplying P.A. concentration (mol/m³) by liquid flow rate (m³/s). The consumption rate of P.A., $r_{P.A.}$, will be substituted by rate equations derived from proposed reaction mechanisms, which is a function of reactants concentration and reaction temperature. With negligible heat and mass transfer limitations, $r_{P.A.}$ is constant radially, but changes axially along the reactor due to the change in reactants concentration, i.e., $r_{P.A.} = f(z)$ where z is the reactor axial coordinate. It is challenging practically to measure the $r_{P.A.}$ locally along the reactor. Therefore, experiments were conducted in reactors

with different length but same catalyst packing density. As shown in Figure 5 and Figure 6, by plotting $F_{P.A. \text{ out}}$ vs. weight of catalyst, $F_{P.A. \text{ out}}$ were found to change with catalyst weight in an exponential manner, therefore, the reaction rate can be calculated by numerically differentiating the corresponding exponential functions.

3.4.2 Kinetic modelling

The obtained kinetic data from 3.4.1. was fitted to different rate equations. It should be noted that, since the pressure of H_2 is the commonly used process parameter in the control of hydrotreating process, H_2 pressure was used in all proposed rate equations, but not the concentration of dissolved H_2 .

The kinetic parameters in each rate equation were estimated through nonlinear regression using Levenberg-Marquardt algorithm in Polymath. The goodness of fit of the kinetic models was evaluated by comparing the reaction rates obtained from the model with the experimental data. The statistical information in the Polymath results was used to assess the quality of the proposed model. Also, the obtained kinetic parameters had to satisfy certain constraints for model discrimination:

- 1) Reaction rate constants and adsorption equilibrium constants should be positive.
- 2) Activation energy should be positive.
- 3) $R^2 > 95\%$.
- 4) The 95% confidence interval should be much less than the corresponding value itself.

Selected rate equations derived from different kinetic models are listed in Table 1.

a. Empirical modeling (Power-law)

With the assumption that the adsorption of reaction intermediates and products was negligible, HDO rate of P.A. was fitted to the power law model (Table 1), in which, $r_{P.A.}$ is the consumption rate of P.A., k_{rxn} is the rate constant, $C_{P.A.}$ is the P.A. concentration, P_{H_2} is the hydrogen partial pressure, and α and β are reaction orders. Values of α or $\beta \approx 1$ indicate a weak adsorption of reactants on catalyst surface, whereas much lower values of the order ($\ll 1$) will imply a strong adsorption.³³

b. Mechanistic conjecture

In a typical heterogeneous catalytic reaction, three sequential steps are involved: a) Adsorption of reactants onto catalyst surface; b) Surface reaction; c) Desorption of the products from the catalyst surface. The reaction mechanisms giving rise to the reaction rates of HDO of P.A. can be described via two different approaches:

- (1) Langmuir-Hinshelwood mechanism, which assumes both reactants are adsorbed on the catalyst surface. In this study, rate equations derived from both single-site and dual-site dissociative and non-dissociative adsorption of H_2 and P.A. mechanisms were investigated and evaluated through data fitting, where k_{rxn} is the rate constant, K_{H_2} and

$K_{P.A.}$ are the equilibrium adsorption constants of H_2 and P.A. respectively. Based on the statistical constraints stated above, the experimental data was best fitted to the rate model that assumes the rate-limiting step to be surface reaction with dual-site non-dissociative adsorption of H_2 and P.A..

- (2) Eley-Rideal mechanism. Due to the steric constraint and the geometric requirement for site adsorption,³⁴ one reactant is adsorbed, while the other non-adsorbed reactants remains in the fluid phase. According to the model fitting results, H_2 was adsorbed on the catalyst surface without dissociation, and reacted with P.A. molecule from the bulk phase.

The two types of mechanistic models are based on different assumptions on the adsorption step. For LHHW model, both reactants are adsorbed on the catalyst surface, while only one reactant is adsorbed on the catalyst surface for the Eley-Rideal mechanism. Therefore, both mechanisms were considered. The proposed Langmuir-Hinshelwood rate equation reduces to Eley-Rideal rate equation at low P.A. concentration ($K_{P.A.}C_{P.A.} \ll 1$), and also they can both be shown to convert to a form with a reaction order of 1 with respect to each reactant, which confirms the validity of the power law model. For example, when $1 \ll K_{P.A.}C_{P.A.}$ and $K_{H_2}P_{H_2} \ll 1$, Langmuir-Hinshelwood model simplifies to $r_{P.A.} = k_{rxn}K_{H_2}P_{H_2}$, which indicates the reaction order of H_2 is 1.

Based on the criteria listed above, as shown in Table 2, three rate equations derived from (1) power law, (2) Langmuir-Hinshelwood mechanism with the assumption of due site non-dissociative H_2 and P.A., and (3) Eley-Rideal mechanism with the assumption of non-dissociative adsorption of H_2 and non-adsorbed P.A., were found to fit the experimental data well, and were considered for further calculation of kinetic constants. All kinetic parameters listed in Table 1 were assumed to follow the Arrhenius relation, $K_i = A_i e^{-E_i/RT}$. By plotting $\ln K_i$ against $1/T$, all pre-exponential factors (A, B, C), as well as the Activation Energy (E_a) and Heat of adsorption (ΔH_{H_2} , $\Delta H_{P.A.}$) are determined from intercept and slope of Arrhenius plot (Table 2). It needs to be stated that, since no independently measurable thermodynamic data for adsorption equilibrium constants was involved, the regression analysis of the experimental data was performed purely on mathematical basis. Therefore, the thermodynamic significance of the adsorption constants cannot be established.

The activation energy (60.3 kJ/mol) obtained from Power Law and Eley-Rideal models is in fact an apparent activation energy, affected by the adsorption terms, which is typically lower than the intrinsic activation energy (92.9 kJ/mol) obtained from Langmuir-Hinshelwood model.^{19,35} Compared to the activation energy reported previously in the literature (175.4 kJ/mol,¹⁷ 130.3 kJ/mol,¹⁸ mentioned in Introduction section) for other base metal-based catalysts, 1%Pt/ γ - Al_2O_3 appears to be more effective in lowering the energy barrier of HDO, thereby enhancing the conversion rate of P.A.. As expected, the adsorption step is exothermic, and negative ΔH value was obtained. The small adsorption heat of H_2 obtained from mechanistic model indicates the weak adsorption of H_2 onto the catalyst surface, which is in agreement with the power law model results with $\beta \approx 1$. Furthermore, H_2 was found to be non-dissociative when

adsorbed on catalyst surface in this study, and similar results were also reported elsewhere.^{19,24,26,36} It should be stated that, in gaseous reactions, H₂ was generally found to adsorb on precious metal catalyst, especially Pt, with dissociation. In contrast, in the current work, our observations indicate that the adsorption of H₂ on catalyst surface is affected by the presence of the liquid reagent, therefore, the derived rate equations only apply to liquid phase HDO. However, based on the previously reported experimental studies, which conclude that the HDO rates of different fatty acids are independent of the fatty acid chain length,³⁷⁻³⁹ the derived rate equations are also applicable to other fatty acids with different chain lengths.

4. Conclusions

Kinetic study on hydrodeoxygenation of microalgae oil using palmitic acid as a model compound has been conducted over reduced 1% Pt/ γ -Al₂O₃ in a microreactor. In order to develop a kinetic model that can be applied at temperatures and pressures relevant to industrial process conditions, all kinetic data was collected over the range of temperature of 340 to 360°C, pressure of 300 to 500 psig at constant hydrogen to oil ratio of 1000 SmL/mL. Based on the heat and mass transfer analysis and catalyst stability study, all kinetic data was collected in the regime with negligible mass and heat transfer limitations and stable catalyst activity and selectivity. Rate equations derived from three different models (Power Law, Langmuir-Hinshelwood, and Eley-Rideal models) were investigated in data fitting through nonlinear regression using Levenberg-Marquardt algorithm in Polymath, and the best fitted rate equations were reported based on the proposed model discrimination constraints. In this presented gas-liquid reaction, H₂ was found to be adsorbed on the catalyst surface without dissociation, which is different from gaseous reaction with consistent dissociative adsorption of H₂. The apparent activation energy is 60.3 kJ/mol, which is lower than the intrinsic activation energy of 92.9 kJ/mol due to the exothermic adsorption of reactants. The proposed rate equations are applicable to liquid phase HDO of fatty acids, and not limited to palmitic acid.

The kinetic model we present in this work can be used for the preliminary sizing of the reactor and the techno-economic analysis (TEA) of this hydrotreating process. The challenges that need to be overcome to obtain meaningful kinetic data have been identified. Finally, a systematic procedure for kinetic study has been developed, which when adopted, will minimize the number of kinetic study experiments that need to be performed. Therefore, we consider our work to be an important asset to this green diesel production process.

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Figure 1. Schematic of Kinetic Study Setup

Figure 2. Chromatograms of preliminary experimental product (29.4 mg catalyst, 1.0 wt% P.A. in dodecane, 0.25 ml/min, Temperature=375°C, Reaction pressure=500 psig, H₂ flow rate=250 sccm)

Figure 3. Effect of superficial flow velocity on space-time consumption of Palmitic acid. (1.0 wt% P.A. in dodecane, Temperature = 360 °C, H₂ pressure = 500 psig, Residence time = 0.06s, H₂/Liquid feed = 1000 SmL/mL).

Figure 4. Stability of catalyst activity and selectivity (14.2 mg catalyst, 1.0 wt% P.A. in dodecane, Temperature=350°C, Reaction pressure=500 psig, (a) & (b) 0.2ml/min, H_2 flow rate=200 sccm, (c) 0.15ml/min, H_2 flow rate=150 sccm, on-stream regeneration every 2 hours).

Figure 5. Dependence of Palmitic acid molar flow rate at exit on catalyst load at different reaction temperature (1.0 wt% P.A. in dodecane, 0.2ml/min, H_2 pressure = 500 psig, H_2 flow rate=200 sccm).

Figure 6. Dependence of Palmitic acid molar flow rate at exit on catalyst load at different reaction Pressure (1.0 wt% P.A. in dodecane, 0.2ml/min, Reaction Temperature =360°C, H₂ flow rate=200 sccm).

Table 1 Estimation of kinetic parameters from different kinetic models at 350°C.

Model	Expression	Parameters	Model Discrimination 95% Confidence	R ²
Power Law	$r_{P.A.} = -k_{rxn} C_{P.A.}^{\alpha} P_{H_2}^{\beta}$	$k_{rxn} = 3.94\text{e-}11 \text{ m}^3\text{s}^{-1}\text{g}^{-1}\text{kPa}^{-0.99}$ $\alpha = 1.02$ $\beta = 0.990$	1.12e-12 1.18e-2 4.49e-3	0.998
Eley-Rideal	$r_{P.A.} = -\frac{k_{rxn} C_{P.A.} P_{H_2}}{1 + K_{H_2} P_{H_2}}$ <ul style="list-style-type: none">• Non-dissociative adsorption of H₂• Non-adsorbed P.A.	$k_{rxn} = 3.68\text{e-}11 \text{ m}^3\text{s}^{-1}\text{g}^{-1}\text{kPa}^{-1}$ $K_{H_2} = 3.70\text{e-}6 \text{ kPa}^{-1}$	2.28e-15 2.17e-8	0.999
	$r_{P.A.} = -\frac{k_{rxn} C_{P.A.} (P_{H_2})^{0.5}}{1 + (K_{H_2} P_{H_2})^{0.5}}$ <ul style="list-style-type: none">• Dissociative adsorption of H₂• Non-adsorbed P.A.	$k_{rxn} = 1.51\text{e-}9 \text{ m}^3\text{s}^{-1}\text{g}^{-1}\text{kPa}^{-0.5}$ $K_{H_2} = 1.12\text{e-}33 \text{ kPa}^{-1}$	1.06e-10 3.01e-18	0.955
Langmuir-Hinshelwood	$r_{P.A.} = -\frac{k_{rxn} K_{P.A.} C_{P.A.} K_{H_2} P_{H_2}}{(1 + K_{P.A.} C_{P.A.})(1 + K_{H_2} P_{H_2})}$ <ul style="list-style-type: none">• Dual site adsorption• Non-dissociative adsorption of H₂• Non-dissociative adsorption of P.A.	$k_{rxn} = 2.15 \text{ mol s}^{-1}\text{g}^{-1}$ $K_{P.A.} = 4.60\text{e-}6 \text{ m}^3 \text{ mol}^{-1}$ $K_{H_2} = 3.72\text{e-}6 \text{ kPa}^{-1}$	1.21e-3 2.60e-9 2.12e-9	0.999
	$r_{P.A.} = -\frac{k_{rxn} C_{P.A.} P_{H_2}}{(1 + K_{P.A.} C_{P.A.})(1 + (K_{H_2} P_{H_2})^{0.5})^2}$ <ul style="list-style-type: none">• Dual site adsorption• Dissociative adsorption of H₂• Non-dissociative adsorption of P.A.	$k_{rxn} = 3.72\text{e-}11 \text{ m}^3\text{s}^{-1}\text{g}^{-1}\text{kPa}^{-1}$ $K_{P.A.} = 1.06\text{e-}6 \text{ m}^3 \text{ mol}^{-1}$ $K_{H_2} = 3.77\text{e-}8 \text{ kPa}^{-1}$	4.27e-15 1.74e-6 3.90e-10	0.999
	$r_{P.A.} = -\frac{k_{rxn} C_{P.A.} P_{H_2}}{(1 + K_{P.A.} C_{P.A.} + K_{H_2} P_{H_2})^2}$ <ul style="list-style-type: none">• Single site adsorption• Non-dissociative adsorption of H₂• Non-dissociative adsorption of P.A.	$k_{rxn} = 3.68\text{e-}11 \text{ m}^3\text{s}^{-1}\text{g}^{-1}\text{kPa}^{-1}$ $K_{P.A.} = 9.90\text{e-}7 \text{ m}^3 \text{ mol}^{-1}$ $K_{H_2} = 1.84\text{e-}6 \text{ kPa}^{-1}$	2.86e-15 9.15e-7 1.09e-8	0.999
	$r_{P.A.} = -\frac{k_{rxn} C_{P.A.} (P_{H_2})^{0.5}}{(1 + K_{P.A.} C_{P.A.} + (K_{H_2} P_{H_2})^{0.5})^2}$ <ul style="list-style-type: none">• Single site adsorption• Dissociative adsorption of H₂• Non-dissociative adsorption of P.A.	$k_{rxn} = 1.98\text{e-}9 \text{ m}^3\text{s}^{-1}\text{g}^{-1}\text{kPa}^{-0.5}$ $K_{P.A.} = 9.50\text{e-}4 \text{ m}^3 \text{ mol}^{-1}$ $K_{H_2} = 0 \text{ kPa}^{-1}$	1.56e-10 5.90e-4 8.54e-8	0.963

Table 2 Summary of kinetic constants for different kinetic models.

Model	Expression	Parameters
Power Law	$r_{P.A.} = -k_{rxn} C_{P.A.}^{\alpha} P_{H_2}^{\beta}$ $k_{rxn} = A e^{-\frac{E_a}{RT}}$	$A = 4.31 \text{e-}6 \text{ m}^3 \text{s}^{-1} \text{g}^{-1} \text{kPa}^{-0.99}$ $E_a = 60.3 \text{ kJ/mol}$ $\alpha = 1.02$ $\beta = 0.990$
Eley-Rideal	$r_{P.A.} = -\frac{k_{rxn} C_{P.A.} P_{H_2}}{1 + K_{H_2} P_{H_2}}$ $k_{rxn} = A e^{-\frac{E_a}{RT}}$ $K_{H_2} = B e^{-\frac{\Delta H_{H_2}}{RT}}$	$A = 3.99 \text{e-}6 \text{ m}^3 \text{s}^{-1} \text{g}^{-1} \text{kPa}^{-1}$ $E_a = 60.3 \text{ kJ/mol}$ $B = 2.00 \text{e-}6 \text{ kPa}^{-1}$ $\Delta H_{H_2} = -3.18 \text{ kJ/mol}$
Langmuir-Hinshelwood	$r_{P.A.} = -\frac{k_{rxn} K_{P.A.} C_{P.A.} K_{H_2} P_{H_2}}{(1 + K_{P.A.} C_{P.A.})(1 + K_{H_2} P_{H_2})}$ $k_{rxn} = A e^{-\frac{E_a}{RT}}$ $K_{H_2} = B e^{-\frac{\Delta H_{H_2}}{RT}}$ $K_{P.A.} = C e^{-\frac{\Delta H_{P.A.}}{RT}}$	$A = 1.27 \text{e+}8 \text{ mol s}^{-1} \text{g}^{-1}$ $E_a = 92.9 \text{ kJ/mol}$ $B = 1.31 \text{e-}6 \text{ kPa}^{-1}$ $\Delta H_{H_2} = -5.42 \text{ kJ/mol}$ $C = 2.38 \text{e-}8 \text{ mol m}^{-3}$ $\Delta H_{P.A.} = -27.3 \text{ kJ/mol}$