ORIGINAL PAPER

Catalytic Production of 1-Octadecanol from Octadecanoic Acid by Hydrotreating in a Plug Flow Reactor

Thomas M. Potts · Keiron Durant · Jamie Hestekin · Robert Beitle · Michael Ackerson

Received: 16 April 2013/Accepted: 13 June 2014/Published online: 28 June 2014 © AOCS 2014

Abstract 1-Octadecanol (stearic alcohol) has uses ranging from lubricants to perfumes. The production of 1-octadecanol from octadecanoic acid (stearic acid) was investigated in a liquid-phase trickle-bed reactor by hydrogenating octadecanoic acid using a Ni/Co/Mo sulfide catalyst. The primary reactions occurring in the reactor were the desired conversion of octadecanoic acid to 1-octadecanol and the subsequent undesired conversion of 1-octadecanol to octadecane. A model was developed to predict these two reactions. The model found to be most useful for this system was a series-parallel reaction first order in octadecanoic acid and 1-octadecanol and pseudozero order in hydrogen for both reactions. The activation energies of the first and second reactions were 63.7.8 and 45.6 kJ/mol, respectively. From these values, the conversion of octadecanoic acid and the selectivity to the desired product as functions of temperature, space velocity, and inlet octadecanoic acid concentration were estimated. The model predicts the maximum productivity of 1-octadecanol occurs at higher temperatures with short residence times. Parametric plots show productivity to be ≥ 0.48 g 1-octadecanol/g octadecanoic acid at 566 °F and a 0.1 h residence time.

Keywords Octadecanoic acid · 1-Octadecanol · Hydrogenation · Kinetics

T. M. Potts \cdot K. Durant \cdot J. Hestekin \cdot R. Beitle \cdot

M. Ackerson (🖂)

Ralph E. Martin Department of Chemical Engineering, University of Arkansas, Fayetteville, AR 72701, USA e-mail: mike.ackerson@processdyn.com

T. M. Potts e-mail: tpotts@uark.edu

Introduction

Low cost synthesis of vegetable oil source alcohols, especially for hexadecanol (cetyl alcohol) and octadecanol (stearyl alcohol), is becoming increasingly important commercially. Much has been reported in the literature on the hydrotreating of the fatty acids, but there are few reports on measuring the kinetic constants for these reactions [1, 2]. Octadecanoic acid has been studied to a lesser extent than other fatty acids, and the present study is intended to elucidate the kinetics of the hydrogenation of octadecanoic acid while considering the undesired conversion of 1-octadecanol to octadecane.

Adkins [3] first reported the catalytic hydrogenation of vegetable oils using a copper chromite catalyst. Others performed catalytic hydrogenation of acids to alcohols, usually at high temperature and pressure [4–6]. Copper chromite catalysts in various forms have been used to produce alcohols from vegetable and other crop oils [7, 8]. Because of the limitations of low surface area, low activity, and water stripping inherent in the use of copper chromite catalysts, studies turned to the use of noble metals [9] and multi-component metallic catalysts, especially Ru based catalysts [10–12]. We know of no other studies using Ni/ Co/Mo catalysts for the conversion of octadecanoic acid to 1-octadecanol.

Ackerson and Byars [13, 14] devised a variation of catalytic hydrogenation for the treatment of petrochemicals and other waste products and this process was applicable to 1-octadecanol synthesis. In their process, the solute (octa-decanoic acid) was pressurized with hydrogen in the saturated liquid state to minimize equipment size and operating costs. The process, known as IsoTherming, differs from conventional hydroprocessing in that all of the hydrogen required for the reaction is delivered solvated in

the liquid inert diluent to transport the reactants through the catalyst bed. Delivery of the hydrogen solvated in the liquid diluent avoids the need for a large hydrogen recycle system. Solvation is achieved by adding an inert diluent to the feed and dissolving the required amount of hydrogen into that feed. The reactant mixture then enters the reactor in the liquid state. The amount of inert diluent is determined by the solubility of hydrogen in the inert and the total amount of hydrogen required. The purpose of the liquid recycle is to carry the unreacted hydrogen back to the reactor and to act as a heat sink to remove the heat of reaction and limit the temperature rise through the bed allowing for a more isothermal operation. The reactor used in the present study did not employ recycling, but instead was operated in trickle-bed mode, which is one pass through the reactor. In this way, the reactor behaved as a plug flow reactor.

The hydrogenation of octadecanoic acid progresses in two reactions, shown as reactions 1 and 2.

 $R-COOH + 2H_2 \rightarrow R-CH_2OH + H_2O \tag{1}$

 $R-CH_2OH + H_2 \rightarrow R-CH_3 + H_2O$ (2)

The first of these reactions is the hydrogenation of the octadecanoic acid to 1-octadecanol, and the second reaction is the hydrogenation of 1-octadecanol to octadecane. For producing 1-octadecanol, the first reaction is desired whereas the second reaction is not. A determination of kinetic parameters that describe Eqs. 1 and 2 was sought to develop a simple model for the IsoTherming process as a function of the parameters typically adjusted for optimal conditions (temperature, pressure, feed). Such a modeling effort forms the basis of a sensitivity analysis to predict productivity (mol alcohol formed/mol acid fed).

Experimental Procedures

Experimental determinations of the rate constants and hydrogen reaction order were performed in a series of hydrogenation reactions of octadecanoic acid. A schematic of the reactor, a pilot-scale IsoTherming catalytic hydrogenation reactor used for the study is shown in Fig. 1. The catalyst selected was a nickel-cobalt-molvbdenum mixture on trilobal aluminum oxide. The reactor was a 5/8 in. 316 stainless-steel tube with stainless-steel screen end caps. The lower end was filled with a short layer of small glass balls to hold the catalyst in place. 90 mL of packing was slowly added with vibration and tamping. The catalyst was then topped with a second layer of glass balls. The reactor was installed in the system, and once leak tight, the catalyst was activated by sulfiding with 10 % butanethiol in light paraffin solvent over a period of approximately 8 h.

It was necessary to solvate the octadecanoic acid in warm diluent so that it could be pumped into the system. The diluent chosen was a mixed light-paraffin solvent. The feed stream consisted of the octadecanoic acid and light-paraffin solvent mixture at 5 wt% octadecanoic acid. The reactor temperature was varied from 248 to 450 °F, while the space velocity, the reciprocal of the residence time of the feed in the reactor, was varied between 0.5 and 2.0 h⁻¹. The hydrogen flow rate was varied so that it was approximately eight times (by mole ratio) that of the octadecanoic acid. This was done so that hydrogen would not be the limiting reactant. Sampling was done after temperatures and pressures had reached a steady state and approximately two system volumes (about 200 mL) of feed solution had passed through the system. Samples were approximately



Fig. 1 Schematic of the hydrogenation system

100 mL in size. Once started, the system was operated continuously until all samples were completed.

Analysis of the feed material and each of the various collected product samples was done on an HP5890 gas chromatograph (GC). The GC was equipped with a 30-m HP-1 capillary column (Agilent Technologies, Santa Clara, CA, USA). Detection of the sample was achieved with a flame ionization detector. Data acquisition and reduction was done with the Agilent ChemStation software installed on a personal computer.

Reactions 1 and 2 were used in a plug flow reactor model to determine the concentrations of octadecanoic acid, C_A , hydrogen, C_B , 1-octadecanol, C_C , and octadecane, C_D . Various kinetic models were tested to represent each reaction. The coupled differential equations for the rate of concentration changes for this system are shown as Eqs. 3-6:

$$\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}t} = -\frac{k_1 C_{\mathrm{A}} C_{\mathrm{B}}^n}{\mathrm{denominator}} \tag{3}$$

$$\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}t} = -\frac{k_1 C_{\mathrm{A}} C_{\mathrm{B}}^n}{\mathrm{denominator}} - \frac{k_2 C_{\mathrm{C}} C_{\mathrm{B}}^n}{\mathrm{denominator}} \tag{4}$$

$$\frac{\mathrm{d}C_{\mathrm{C}}}{\mathrm{d}t} = \frac{k_1 C_{\mathrm{A}} C_{\mathrm{B}}^n}{\mathrm{denominator}} - \frac{k_2 C_{\mathrm{C}} C_{\mathrm{B}}^n}{\mathrm{denominator}}$$
(5)

$$\frac{\mathrm{d}C_{\mathrm{D}}}{\mathrm{d}t} = -\frac{k_1 C_{\mathrm{C}} C_{\mathrm{B}}^n}{\mathrm{denominator}} \tag{6}$$

where *t* was the time that the reactant spent in the reactor, k_i were the two rate constants, *n* was the reaction order with respect to hydrogen. Eqs. 3–6 include the provision for chemisorption, with the denominators capable of representing adsorption of all species:

denominator =
$$1 + \sum K_i C_i$$
 (7)

Note that this representation of the system assumes reactions on the surface of the catalyst govern the conversion of acid to alcohol and alkane, respectively. Alternate forms would include external or internal mass transfer limitations, or a combination thereof, owing to the possibility of boundary layer formation or diffusional limitations about or within a catalyst particle, respectively.

The reactions were assumed to be first order with respect to octadecanoic acid and to 1-octadecanol as suggested by Patterson [15]. The Arrhenius equation was used to examine temperature effects:

$$k_i = a_i e^{-\frac{\omega_i}{RT}} \tag{8}$$

Г.

where a_i is the frequency factor for each reaction, E_i is the activation energy for each reaction, R is the ideal gas constant and T is the absolute temperature.

A MatLab (The MathWorks, Inc., Natick, MA, USA) program was written to determine the rate constants from the system of differential equations that minimized a least squares criteria (lsq):

$$lsq = \sum (C_{i,reactorexit} - C_{i,predicted})^2$$
(9)

where the reactor exit concentrations are compared to those values predicted from the model. To perform this least squares minimization, 17 sets of conditions (all at 2,000 psig) were integrated from t = 0 to t = tau, defined as the residence time in the reactor.

Finally, the values of k_i , a_i , and E_i generated from the first MatLab routing were used as input for a sensitivity analysis to investigate the space defined by tau, temperature, and pressure, in all 44 sets of conditions. In the above treatment, the value of the hydrogen concentration in diluent was required. In the absence of direct measurement capability, the hydrogen concentrations were estimated with an Aspen (AspenTech, Burlington, MA, USA) simulation. This simulation was tested for validity by comparing results from the simulation to experimental values reported by those determined by Park [16]. Good agreement with these values was obtained using a multicomponent flash calculation with the Peng-Robinson equation of state. The Aspen simulation molar fractions of hydrogen in alkane agreed with the experimental values within 10 %. Based on this finding, we assumed that the Aspen simulation could be used to generate the hydrogen molar fractions at the experimental conditions.

Results and Discussion

All the octadecanoic acid was converted to 1-octadecane when the temperature was above 351 °F at the space velocities used, and those data points were deemed not useful for the modeling. Temperatures in the range of 300-450 °F and were examined at three pressures (700, 1400 and 2,000 psi). The values tested for the reaction order for hydrogen, n, were $-\frac{1}{2}$, 0, $\frac{1}{2}$, 1, 2, and with provision for chemisorption by inclusion of a denominator typical of a Hougan-Watson expression. Testing of the permutations of Eqs. 3-6, i.e., with different *n* values, inclusion or absence of a denominator led to a "best fit" of first order in all species (acid, alcohol, and hydrogen). Figures 2 and 3 are Arrhenius plots that indicate the fit used to calculate E_i for each reaction, with the activation energies for the two reactions given in Table 1. The activation energy of the first reaction was very comparable to those obtained by Chen et al. [18] for lactic acid (56.6 kJ/mol) and propionic acid (67.1 kJ/mol). Chen and coworkers did not consider the second reaction, however, we found that the second reaction happens to a significant degree and must be considered.

Figures 4, 5, 6 and 7 were used as figures of merit to indicate the effectiveness of the model to describe





 Table 1
 Arrhenius constants for the hydrogenation of octadecanoic acid

	Frequency factor (s^{-1})	Energy of activation (kJ/mol)
Reaction 1 (dehydration of octadecanoic acid)	3.20×10^{7}	63.7
Reaction 2 (dehydration of 1-octadecanol)	3.81×10^5	45.6

various effluent concentrations of acid, alcohol, alkane, respectively. In the figures, perfect agreement between model and experiment would be indicated by a direct variation (y = cx) with *c* equal to unity. Good agreement for all three species were observed by comparing the line y = x between experimental and modeled values. The figures have slopes equal to 1.01 (acid), 1.01 (alcohol),

and, 0.93 (alkane), which are close to the desired value of 1.0. In its present form, the model over predicts the three major species of interest; this is likely to have occurred because other byproducts could have been formed but were not accounted for in the model. Nevertheless, good agreement between experimental and calculated values allowed for a sensitivity analysis to be performed.

It is interesting to note that Patterson [15] reported a pseudo-zero order dependency for the hydrogenation of fats and oils, which, upon quick examination, would conflict with this study. Since the value of n (hydrogen order) determined to be the best fit of the data was n = 1, and the IsoTherming process is designed to run with excess hydrogen as evident by the presence of gas phase throughout the reactor, one could present k_i as the product of the rate constant and liquid phase hydrogen



Fig. 5 Comparison of

experimental and predicted final

concentrations of 1-octadecanol



concentration. For the case of IsoTherming, rate constants that are pseudo-zero order for hydrogen are easily obtained from our data and the Aspen simulation (data not shown). Hydrogen concentration independence was further tested by estimating the Biot number for a catalyst particle. The Biot number is defined by:

$$B_i = \frac{X_{\rm L}k_{\rm c}}{D_{\rm TA}^e} \tag{10}$$

where

 B_i is the dimensionless Biot number,

 $X_{\rm L}$ is the characteristic length (m),

 $D_{\rm TA}^e$ is the mass diffusivity (Pa m²/s), and

 \bar{k}_c is the mass transfer coefficient (m/s), as given in Eq. 11:

$$\bar{k}_{\rm c} = \frac{\dot{n}_{\rm A}}{A\Delta C_{\rm A}} \tag{11}$$

In Eq. 11,

 $\dot{n}_{\rm A}$ is the mass transfer rate (mol/s), A is the effective mass transfer area (m²), $\Delta C_{\rm A}$ is the concentration difference driving the diffusion (mol/m3)

Measurement of the catalyst particles determined that they were, on average, $0.52 \text{ mm} \times 2.02 \text{ mm}$ long and with a mass of 0.0043 g so that

 $X_{\rm L} = 2.5 \times 10^{-4}$ m (the radius of one catalyst particle) A = 3.17 × 10⁻⁶ m² (the surface area of one catalyst particle)

 $D_{TA}^{e} = 3.11$ Pa m²/s (tabulated value from Wicks *et al.* [17]





Productivity of 1-Octadecanol as a Function of Temperature, Residence Time and Pressure



Fig. 7 Predicted productivity of 1-octadecanol per gram of octadecanoic acid at varying temperatures, space velocities and pressures

As a limiting (maximum) case, one flow rate of hydrogen going into the reactor was 3.54×10^{-5} mol/s and there was 66.7 g of catalyst in the reactor, so the molar feed rate associated with one particle was $\dot{n}_{\rm A} = 2.36 \times 10^{-9}$ mol/s. For our reactor, $\Delta C_{\rm A} = 600$ mol/m³, the maximum change in concentration of the hydrogen in the reactor assuming that all acid was converted to alkane. Thus, the mass diffusivity was 1.24×10^{-6} m/s and the Biot number was 0.001375. Since this number is very small, we expect the hydrogen concentration to be essentially constant in the liquid phase. This low value indicated that the maximum possible consumption of hydrogen within a catalyst particle was greatly exceeded by the hydrogen available in the liquid phase for the reaction. One possible concern with the above calculation was the use of the particle radius as the characteristic length. Since it was beyond the scope of this work to define the boundary layer associated with mass transport to the catalyst, geometric considerations for the maximum thickness of such a layer to be on the order of the catalyst particle size. We expect the actual boundary layer to be much smaller because of the superficial velocity of the liquid through the reaction, with the mass transfer coefficient calculable with a variety of correlations.

The above argument supporting the fact that hydrogen, treated either as a first order or pseudo-zero order component, manifests itself as an excess reactant and permits one to strongly examine the kinetic expression describing IsoTherming with respect to the acid feed concentration. Based on the Biot number calculations and Arrhenius dependency of the data, it is likely that the Axens catalyst was operated under conditions that were not diffusion limited since no break in the slopes of Figs. 2 and 3 were observed. The values of k_i determined by the model are the observed reaction rate constant, the product of the intrinsic value times and the interparticle effectiveness factor $(k_{\text{intrinsic}} \eta)$. In the absence of catalyst physical property data, the effectiveness factor cannot be calculated. Nevertheless, the k_i values can be used to examine the sensitivity of the system to various combinations of temperature, pressure and feed since the value of η for a first-order reaction is independent of external concentration.

The 1-octadecanol is the desired product and maximization of this product can be studied with parametric plots based on the developed model. One such parametric plot is shown in Fig. 7. The trends shown in Fig. 7 indicate that better productivity was achieved at higher temperatures with higher space velocities, i.e., shorter residence times in the reactor. Although our experimental work found complete conversion to the undesired product octadecane at temperatures above 351 °F, this was at relatively long residence times. The trend analysis presented in Fig. 7 predicts that optimum productivity in this reactor for 1-octadecanol would occur at 566 °F with a residence time of 0.1 h. Further investigations will explore the data space around this set of conditions to confirm that the model developed can predict conditions of high productivity. Minor modifications to the hardware will enable these investigations. Thus, we have shown that by understanding the reaction kinetics of both reactions one can achieve high productivity without having to change catalysts.

Conclusions

1-Octadecanol was made in a liquid-phase trickle-bed catalytic reactor by the catalytic hydrogenation of octadecanoic acid. A model of the parallel-series reactions was generated and correlated to experimental values of hydrogenation conducted in a plug flow reactor at pressures of 700, 1,400 and 2,000 psig (13.8 MPa) hydrogen and at varying temperatures and space velocities. The model most useful for this system was found to be a series-parallel reaction first order in octadecanoic acid and pseudo-zero order in hydrogen. The Arrhenius frequency factors and the activation energies for both reactions have been estimated. The activation energy of the first reaction was 63.7 kJ/mol and the activation energy of the second reaction was 45.6 kJ/mol. From these values, the conversion of octadecanoic acid and the selectivity to the desired product as functions of temperature, space velocity, reactor pressure, and inlet octadecanoic acid concentration were presented. The model predicts maximum productivity of 1-octadecanol per mass of octadecanoic acid occurs at higher temperatures with short residence times.

Acknowledgments The authors acknowledge Mr. John Coleman of Process Dynamics who provided training, manpower, and technical support during the processing and Dr. Glen Ackridge of Process Dynamics who assisted with analysis of the reaction products. Funding was provided by the Ralph E. Martin Department of Chemical Engineering and the Ford Foundation.

References

- 1. Costa J, Cunill F, Izquierdo JF (1984) Kinetic study of gas phase catalytic hydrogenation of furfural. An Quim Ser A 80:586–592
- Soner E, Dogu T, Yorulmaz Y (1996) Kinetics of hydrogenation of furfural to furfuryl alcohol over copper chromite catalyst and optimum regeneration procedures. Arabian J Sci Eng 21:321–332
- Adkins H, Connor R (1931) Catalytic hydrogenation of organic compounds over copper chromite. J Am Chem Soc 53:1091–1095
- Willemart A, Loury M, Everaerts P (1948) The preparation of dodecyl alcohol by catalytic hydrogenation of the total esters of coconut butter. Oleagineux 3:68–71
- Richardson AS (1945) Catalytic hydrogenation of fatty acids to form alcohols, US Patent 2375495
- Aly M, Baumgarten E (2001) Hydrogenation of hexanoic acid with different catalysts. Appl Catal A 210:1–12
- 7. Hoffmann AN, Montgomery JB (1955) Tall-oil alcohols, US Patent 2727885
- Nakaoka H, Mototani M (2003) Liquid vegetable unsaturated alcohol and process for producing the same, JP Patent 2003089393
- Manyar HG, Paun C, Pilus R, Rooney DW, Thompson JM, Hardacre C (2010) Highly selective and efficient hydrogenation of carboxylic acids to alcohols using titania supported Pt catalysts. Chem Commun (Cambridge, UK) 46:6279–6281
- Deshpande VM, Ramnarayan K, Narasimhan CS (1990) Studies on ruthenium-tin boride catalysts. II. Hydrogenation of fatty acid esters to fatty alcohols. J Catal 121:174–182
- Sanchez MA, Mazzieri VA, Sad MR, Grau R, Pieck CL (2011) Influence of preparation method and boron addition on the metal function properties of Ru-Sn catalysts for selective carbonyl hydrogenation. J Chem Technol Biotechnol 86:447–453
- Miyake T, Makino T, Taniguchi S, Watanuki H, Niki T, Shimizu S, Kojima Y, Sano M (2009) Alcohol synthesis by hydrogenation of fatty acid methyl esters on supported Ru-Sn and Rh-Sn catalysts. Appl Catal A 364:108–112
- Ackerson MD, Byars MS (1998) Two phase hydroprocessing. US Patent 9859019
- Ackerson MD, Byars MS (2005) Two-phase hydroprocessing with an eliminated hydrogen recirculation, US Patent 20050082202
- Patterson HBW (2011) Hydrogen process techniques. In: List GR, King JW (eds) Hydrogenation of fats and oils: theory and practice. AOCS Press, Urbana, IL, pp 33–48

- Park J, Robinson RL, Gasem AM (1995) Solubilities of hydrogen in heavy normal paraffins at temperature from 232.2 to 423.2 C and pressures to 17.4 MPa. J Chem Eng Data 40:241–244
- 17. Wicks J, Wicks CE, Rorrer RE, Wilson RE (2008) Fundamentals of momentum, heat and mass transfer, 5th edn. NJ, Wiley, Hoboken, p 692
- Chen Y, Jin R, Qin L (1995) Preparation of 1-octadecanol from methyl stearate by catalytic hydrogenation. Huaxue Shijie 36:423–425