Kinetics of Liquid Phase Catalytic Hydrogenation of Impure Soy Lecithin

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Abstract

Hydrogenation was carried out at different temperatures, hydrogen pressures and catalyst loadings and the observations were used to tune parameters of a kinetic model. The reaction products were analyzed by Wijj's method to find iodine value, which quantitatively yielded the degree of unsaturation; hence conversion. Impure soy lecithin was hydrogenated using 10% Pd/C catalyst in pressure reactor at comparably low pressure such as 1.5 Mpa until iodine number values drops in the range of 10-30 gI$_2$/100g from initial 105gI$_2$/100g. The best fits were obtained for a reaction that occurs in three stages: adsorption of lecithin onto the catalyst surface (rate controlling step), hydrogenation of adsorbed lecithin and desorption of the hydrogenated product. The order of the rate determining step with respect to lecithin and catalyst is 0.81 and 0.53 respectively while the activation energy is 3.0 kcal/mol. The order with respect to hydrogen pressure is 0.6. The enthalpy of hydrogenation and desorption was determined to be -18.61 kcal/mol and 20.35 kcal/mol respectively. The speed of agitation was sufficiently high enough to eliminate diffusional resistance. Hydrogenated lecithin provides products with increased stability with respect to oxidation, mostly applied in cosmetics and pharmaceutical preparations.

Keywords

Impure Soy Lecithin; Palladium Carbon; Catalytic Hydrogenation; Iodine Value; HPLC

Introduction

Lecithin, a natural emulsifying agent; naturally occurring mixture of the esters of stearic, palmitic and oleic acids, linked to the choline ester of phosphoric acid, plays an important role in cell metabolism and has great potential for use as a surfactant in cosmetics. Its use in cosmetics is limited due of its ready thermal and oxidative degradation: impure soy lecithin develops unpleasant odour upon its storage. The main cause of the instability is the presence of double bonds in the fatty acid esters present in the lecithin molecule which causes lecithin to develop rancidity on exposure to atmosphere. The double bond can be removed by

one of several techniques including hydrogenation [Li & Xu (2009)], hydroxylation, acylation [Resh et al. (1999)], sulfonation [March (1985)], etc. These techniques modify the physical as well as chemical properties of this compound. Of these, selective hydrogenation of the double bonds yields a product that retains most of the desirable properties of the lecithin but with improved stability to oxidation and thermal degradation.

The quality and physical properties of the final product during hydrogenation are greatly affected by the number of double bonds present in the oil, i.e. the iodine value and the *cis–trans*-isomers of fatty acid [Hunter (2005)].

Cole (1959) carried out hydrogenation of lecithin at low pressure (1.2-2.7 bar) in the presence of 10% palladium on charcoal catalyst in a mixture of chlorinated solvents such as methylene chloride and chlorobenzene and the temperature range from 0 to 80^{0}C. After filtration of the catalyst, chlorinated solvent and obtained product are with 60-80% yield. They also tried various other solvents such as benzene, ethyl acetate, methylene chloride, chlorobenzene and chloroform in order to increase the hydrogenation rate and thus reducing the operating pressure. However, the toxicity of chlorinated solvents and carcinogenic aromatics like benzene makes the process environmentally unfriendly and unsafe. Additionally, the stringent limits of the lowest possible content of the toxic solvents in the product put excessive economic burdens on the process.

Mounts et al. (1978) carried out hydrogenation of Soybean oil performed in an autoclave with copper-chromite catalyst which included a high-pressure scan 3.5, 7.0, and 21 MPa, at selected temperatures 110-170℃, agitator speed 1200-1400 rpm and at catalyst concentrations (0.05, 0.1, 0.2. and 0.4% copper). The samples were filtered to remove residual catalyst prior to analysis. Though the copper-chromite is most selective for hydrogenating the linolenic acid in

soyabean oil and other vegetable oils, drawback of commercially available copper-chromite catalysts is that they are much less active at low hydrogen pressures and spent catalyst presents a disposal problem. This is especially a problem since the hydrogenation of the lecithin requires higher temperature and pressure as compared to triglycerides.

In view of the above discussion and the existing literature on hydrogenation of Impure Soy lecithin, there is need to study the hydrogenation process using environmentally friendly solvents and lower pressures and temperatures of operations. In this work a hydrogenation of Impure Soy lecithin over Pd/C catalyst with ethanol-toluene mixture as solvent. The advantage of this process is that the solvent is relatively benign and the catalyst can be recovered and reused.

Materials and Methods

Materials

Impure Soy Lecithin was obtained from M/s Sonic Biochem, Indore, India. The rest of material such as 10% Pd/C (Particle size-6Micrometer), ethanol, toluene, acetone, Wijjs reagent, and all commercial grade chemicals were procured from standard reagent suppliers. All the reagents were laboratory grade.

Methods

In solvent mixture of ethanol/toluene (in the ratio of 7:3), 5gm of Impure Soy Lecithin was dispersed along with 10% Pd/C catalyst in an autoclave and schematic diagram shown in FIG. 1. The catalyst loading of 0.05-2.5% (based on lecithin content w/w) and the temperature range 40-80℃ were employed. The nitrogen gas pressure has been used for purging the reactor. During each run, the hydrogen partial pressure was held constant; the effect of hydrogen partial pressure was investigated for pressures between 0.3 MPa to 1.5 MPa. In all cases, the reaction was allowed to proceed for four hours. It was observed that the reaction became slower with an increase in toluene content in the solvent but we have not investigated this effect in detail.

During the four hours of each run, 5ml aliquots of the reaction mixture were withdrawn every 30 minutes. Each sample was cooled to room temperature and it was diluted with toluene and filtered through Buckner funnel in order to remove the catalyst. The catalyst could be reused with some processing but the regeneration and activation of the catalyst is not in the

scope of this work. The toluene layer obtained had acetone added to it and the liquid was concentrated by evaporation under vacuum to get a solid/gummy mass. It was later dried in a vacuum dryer to get the final product.
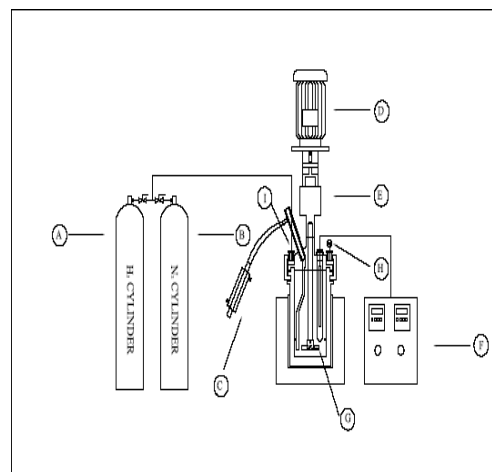

FIG. 1 SCHEMATIC DIAGRAM OF THE EXPERIMENTAL SETUP A-HYDROGEN CYLINDER, B- NITROGEN CYLINDER, C-SAMPLING PORT WITH, D-STIRRER DRIVE SYSTEM, E-MAGNETIC DRIVE, F-PRESSURE AND TEMPERATURE CONTROLLER, G-TURBINE TYPE IMPELLER, H- DISCHARGING PORT, I- CHARGING PORT.

Measure of Degree of Unsaturation (Iodine Value)

Degree of unsaturation in the product was obtained from the iodine value according to the Wijj method [Jeeffery et al. (1991)].During each hydrogenation run samples were withdrawn at 30 minute intervals. 0.2 grams of the sample were mixed with 20 ml Wijj solution and 10 ml chloroform. It was then left in the dark for 30 minutes. Thereafter, 20 ml of 20% potassium iodide solution and 100 ml of distilled water was added. This was then titrated against 0.1M sodium thiosulfate (VI) solution. The experimental measurement error is +/- 0.05% for analysis of iodine value.
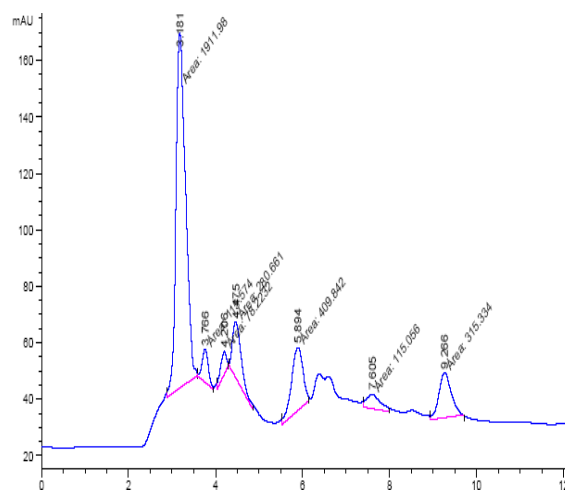

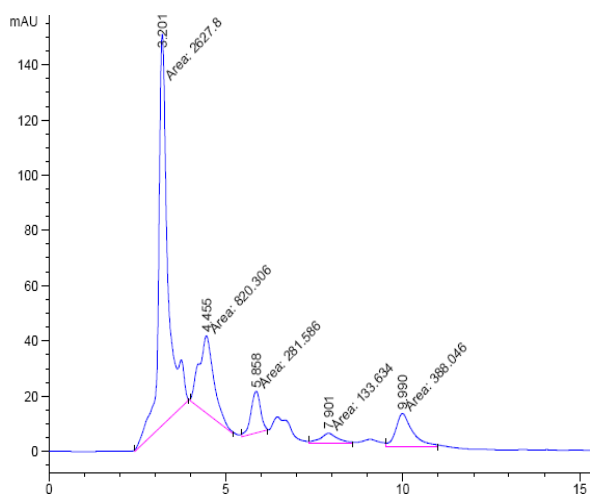FIG. 2 HPLC OF UNHYDROGENATED IMPURE SOY LECITHIN

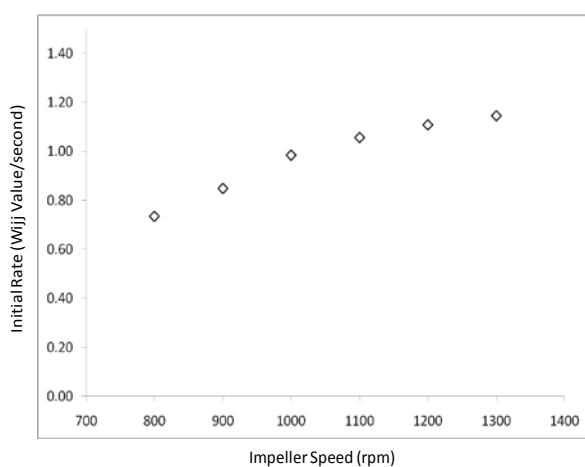FIG. **3** HPLC OF HYDROGENATED IMPURE SOY LECITHIN

FIG.4 INITIAL RATES OF REACTION (IN WIJJ VALUE PER SECOND) PLOTTED AGAINST IMPELLER SPEED (IN RPM). THE VARIATION WITH IMPELLER SPEED IS ONLY 3% BETWEEN 1200 AND 1300 RPM. CONSEQUENTLY, THE REACTION IS CONSIDERED IMPELLER INDEPENDENT AT 1200 RPM.
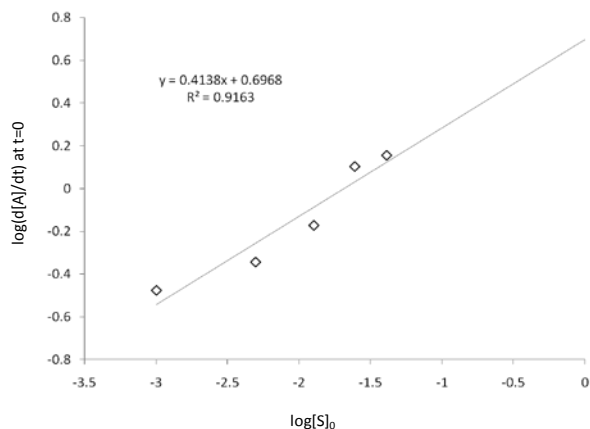

FIG. 5 ORDER WITH RESPECT TO S. PLOT OF LOGARITHM OF INITIAL RATE $\mathbf{LOG}\left(-\frac{d[A]}{dt}\right)_0$ VS LOGARITHM OF INITIAL CATALYST CONCENTRATION $\mathbf{LOG}[S]_0$.THE SLOPE OF THIS PLOT IS M, THE ORDER WITH RESPECT TO [S], $m = \mathbf{0.41} \pm \mathbf{0.13}$ (**95% CONFIDENCE INTERVAL**).

High Performance Liquid Chromatography (HPLC)

The analysis of Impure Soy Lecithin and hydrogenated

Soy Lecithin was carried out using HPLC [Zhao et al. (2010)]. HPLC system (Agilent Technologies, India 1200 Series) consisted of Chem Station software, model G1322A degasser, model G1311A quaternary pump, auto sampler, model G1316A column oven and variable wavelength UV-visible detector. The separation was performed on Agilent Eclipse plus C18 column (4.6 X 100mm, 3.5μm). The mobile phase consisted of acetonitrile, methanol, and water in the ratio of 60:30:10 v/v. All the mobile phase solvents used were of HPLC grade filtered through 0.22 μm filter paper and sonicated for 20 min to remove any dissolved gases to avoid air entrapment in the HPLC system. Isocratic system of mobile phase was used for the elution of Impure Soy Lecithin at a flow rate of 0.3ml min^{-1} at constant column temperature of 30℃ and a wavelength of 210 nm was used for detection. All the samples were prepared by dissolving unhydrogenated and hydrogenated samples in methanol to get 1mg/ml concentration and filtered through 0.22 μm Pall filter. 10 μl of sample was injected into the column. FIG. 2 shows number of impurities in impure soy lecithin with the PC, PE, and PI (see nomenclature) peaks. Unhydrogented PC shows the area of 1911.98 mAU in FIG. 4. From FIG.5, it can be said that the PC, PE, and PI shows retention time of 3.201, 4.455 and 5.858 respectively and others are impurities and to be removed by separation and purification process. Hydrogenated PC shows the area of 2627.8mAU in FIG. 3.
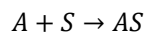
Results and Discussion

Agitation Speed

The hydrogenation of Impure Soy Lecithin is a heterogeneous system involving two miscible solvents namely ethanol and toluene and the solid catalyst palladium on carbon. The diffusional process (mass transfer) of Impure Soy Lecithin and molecular hydrogen getting transported to active catalyst center depends upon the intensity of turbulence in the liquid phase [List et al. (1981)]. In order to study the effect of agitation, experiments at different impeller speeds were conducted at 80℃ and the initial rates of reaction, measured in terms of rate of reduction of Iodine (Wijj) value were plotted against the impeller speed as shown in FIG. 4. It was observed that the reduction in Iodine Value (Wijj Value) decreases rapidly with an increase in the speed of agitation until 1200 rpm, thereafter, the effect of agitation was minimal. Hence, all subsequent reactions were carried out at an agitator speed of 1200 rpm.

Reaction Mechanism

The data was fitted using a kinetic model as described below.

1) Adsorption of Lecithin (A) onto Catalyst (S) to Yield Adsorbed Lecithin (AS):

$$A + S \rightarrow AS$$

This reaction is assumed to be the rate controlling step. The order of reaction with respect to A is n and with respect to S is m. Since the mechanism within the catalyst particle is not studied in detail, the model is made with the "fudge" parameters m and n. In subsequent analysis, the step 1 will be further resolved to yield a sequence of elementary steps each with integral order of reactant. The rate of reaction with respect to A can be written as follows:

$$\frac{d[A]}{dt} = -k_A [A]^n [S]^m \tag{1}$$

Here, the kinetic constant is modeled using the Arrhenius equation as:

$$k_A = k_{Ao} \exp\left(-\frac{E_A}{RT}\right) \tag{2}$$

Where k_{Ao} and E_A are constants to be fitted.

2) Hydrogenation of Adsorbed Lecithin to Hydrogenated Product (CS) Using Hydrogen Gas (H2) under Pressure:

$$H_2 + AS \leftrightarrow CS$$

This reaction is assumed to proceed rapidly and reaches its equilibrium condition. The equilibrium constant (K_{AS}) can be written as:

$$K_{AS} = \frac{[CS]}{P_{H_2}[AS]} \tag{3}$$

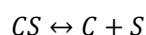K_{AS} can be represented as a function of temperature by:

$$\Delta G_{AS}^0 = -RT \ln K_{AS} \tag{4}$$

Where ΔG_{AS}^0 is the free energy change associated with the hydrogenation reaction averaged over the temperature range of $40\,^\circ C$ to $80\,^\circ C$, which can be further expressed as

$$\Delta G_{AS}^0 = \Delta H_{AS}^0 - T\Delta S_{AS}^0 \tag{5}$$

Here ΔH_{AS}^0 and ΔS_{AS}^0 are the enthalpy and entropy change, respectively, accompanying the hydrogenation reaction averaged over the temperature range of $40\,^\circ C$ to $80\,^\circ C$.

3) The Last Step in the Reaction Scheme Is Desorption of the Adsorbed Hydrogenated Lecithin (CS) to Give the Hydrogenated Lecithin Product (C) and Regenerate the Catalyst (S):

$$CS \leftrightarrow C + S$$

This step proceeds rapidly so that the equilibrium may be assumed. The equilibrium constant (K_{CS})

can be written as :

$$K_{CS} = \frac{[C][S]}{[CS]} \tag{6}$$

K_{CS} can be represented as a function of temperature by:

$$\Delta G_{CS}^0 = -RT \ln K_{CS} \tag{7}$$

Where ΔG_{CS}^0 is the free energy change associated with the desorption reaction averaged over the temperature range of $40\,^\circ C$ to $80\,^\circ C$, which can be further expressed as follows:

$$\Delta G_{CS}^0 = \Delta H_{CS}^0 - T\Delta S_{CS}^0 \tag{8}$$

Here ΔH_{CS}^0 and ΔS_{CS}^0 are the enthalpy and entropy change, respectively, accompanying the desorption reaction averaged over the temperature range. Additionally, assuming no hydrogenated lecithin is initially present; we have the following mass balance equations:

$$[A]_0 = [A] + [AS] + [CS] + [C] \tag{9}$$

Here, $[A]_0$ is the concentration of lecithin taken initially.

For the catalyst mass balance:

$$[S]_0 = [S] + [AS] + [CS] \tag{10}$$

Hence, from (3), (6), (9) and (10) we can write the following expressions for [C] and [S]:

$$[C] = \frac{[A]_0 - [A]}{\kappa[S] + 1} \tag{11}$$

And,

$$[S] = \frac{[S]_0}{\kappa[C] + 1} \tag{12}$$

Where,

$$\kappa = \frac{1}{K_{CS}}\left(1 + \frac{1}{P_{H_2} K_{AS}}\right) \tag{13}$$

Eliminating [S] from equations (11) and (12) gives,

$$[C]^2 + \alpha[C] - \beta = 0 \tag{14}$$

Where,

$$\alpha = \frac{1}{\kappa} + [S]_0 - ([A]_0 - [A]) \tag{15}$$

And, $\beta = \frac{[A]_0 - [A]}{\kappa} \tag{16}$

Hence, using the quadratic formula and noting that $[C] \geq 0$,

$$[C] = \frac{-\alpha + \sqrt{\alpha^2 + 4\beta}}{2} \tag{17}$$

The rate of reaction can be obtained by substituting equations (17) and (12) in equation (1).

Fitting Data

For each run, the concentration of lecithin in terms of Iodine Value was obtained at the interval of 30 minutes. The results were used to tune the adjustable parameters in the reaction mechanism. To determine the order of reaction with respect to S, the logarithm of initial rates of reaction equation 1 was plotted against logarithm of concentration i.e. $\ln\left(-\frac{d[A]}{dt}\right)$ vs $\ln[S]_0$ for

temperature of 80℃ and hydrogen pressure (P_{H_2}) of 1.5 MPa. The obtained plot gives a straight line, whose slope is m, the order of reaction with respect to [S], as shown in FIG.5. The value of m obtained from FIG.5 was 0.41 ± 0.13.

Now, the order with respect to [A] is not straight-forward to determine since the initial concentrations of [A] are all the same for all our runs. The order with respect to hydrogen was similarly obtained as 0.6 (see figure 6).
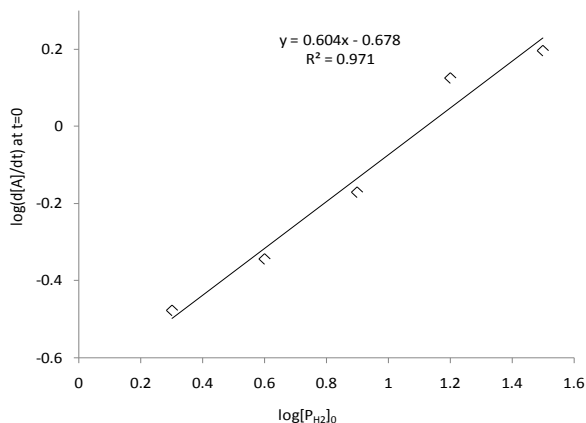

FIG. 6 ORDER WITH RESPECT TO HYDROGEN PRESSURE. PLOT OF LOGARITHM OF INITIAL RATE $\log\left(-\frac{d[A]}{dt}\right)_0$ VS LOGARITHM OF HYDROGEN PRESSURE $\log[P_{H_2}]$ THE SLOPE OF THIS PLOT IS THE ORDER WITH RESPECT TO HYDROGEN.

There is another parameter that we can readily obtain from our preliminary data; and that is the activation energy E_A, from the Arrhenius plot (shown in FIG. 7) for initial rates of reaction for $P_{H_2} = 1.5$ MPa and $[S]_0 = 0.2$ g-catalyst/100g-reaction mixture at temperatures between 40℃ and 80℃. The slope of this plot is, $-E_A/R$, where, R is the universal gas constant. Hence, the value obtained E_A is $2.76 \pm 0.41 \frac{kcal}{mol}$ (95% confidence interval using student-t test).
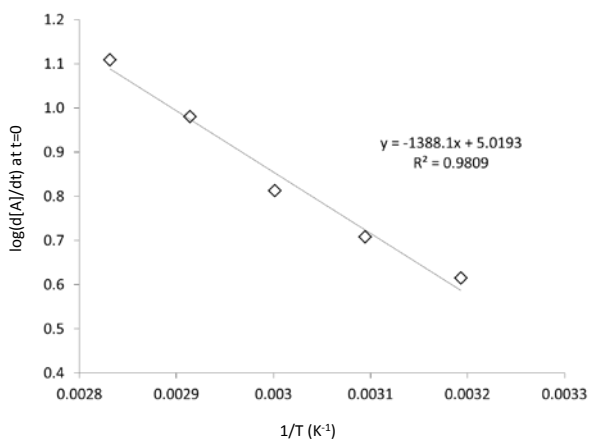

FIG. 7 ACTIVATION ENERGY E_A. PLOT OF LOGARITHM OF INITIAL RATE $\log\left(-\frac{d[A]}{dt}\right)_0$ VS 1/T (THE INVERSE REACTION

TEMPERATURE). THE SLOPE OF THIS PLOT IS $-E_A/R$, WHERE E_A IS THE ACTIVATION ENERGY FOR THE CONTROLLING STEP AND R IS THE UNIVERSAL GAS CONSTANT. HENCE $\frac{E_A}{R} = 1388 \pm 205\ K$ (95% confidence interval) I.E. $E_A = 2.76 \pm 0.41 \frac{kcal}{mol}$.

Now, the rest of the parameters are not amenable to such exercise because the differential equation [1] is not tractable to solve analytically. Hence, we have solved it numerically using a Levenberg-Marquadt least-squares algorithm via the SciPy library of numerical tools [Jones et al. (2011)] in Python 2.6. However, we will compare the value of m and E_A obtained from the numerical fit of all data with the value obtained from the analysis of FIG. 7 and as a test of the validity of the fitting. All graphs were plotted using the Matplotlib library of Python 2.6 [Hunter (2007)]. The result of the full numerical fit appears in Table 1.

TABLE1 VARIOUS PARAMETER FITTED VALUES OF KINETIC CONSTANTS.

Fitted Parameter	Optimized Value	Unit	Variation
k_{A0}	0.1227	$\dfrac{(Wijj\ Units)^{1-n}\left(\frac{g-cat}{100g-mix}\right)^{-m}}{s}$	
E_{A0}	3.0	kcal/mol	2.76 ± 0.41(from FIG. 7)
n	0.81		
m	0.53		0.41 ± 0.13(from FIG. 5)
ΔH^0_{AS}	-18.61	kcal/mol	
ΔS^0_{AS}	-0.0886	kcal/(mol.K)	
ΔH^0_{CS}	20.35	kcal/mol	
ΔS^0_{CS}	0.0985	kcal/(mol.K)	

Discussion

It was clear that the value of m and E_A obtained from the full numerical fit is within the error of those obtained from linear regression, which validated our assumption for the adsorption of lecithin as the rate controlling step. The enthalpy of hydrogenation of lecithin appears to be -18.6 kcal/mol. Normally, enthalpies of hydrogenation of double bonds are around -30.0 kcal/mol [Hao et al. (2010), Timothy et al. (1988)]. The difference of about 10 kcal/mol can be straight forwardly attributed to the fact that the hydrogenation is not of the free lecithin but the adsorbed moiety and part of the bond-breaking may have occurred on the catalyst surface. The order of reaction with respect to lecithin was 0.81 with respect to the catalyst 0.53 and with respect to hydrogen 0.6. The reaction mechanism proposed was therefore not the whole story and we will subsequently work on elucidating a fuller mechanism by conducting

experiments with different catalyst morphologies. The activation energy of 2.76 kcal/mol was low compared to typical values greater than 8 kcal/mol. However, previous work [Hao et al. (2010)] has shown that activation energy for double bond hydrogenations may be lower than 1 kcal/mol.

Conclusions

Hydrogenation of Impure soy lecithin was carried out using solution of ethanol, toluene and palladium carbon as catalyst. The Pd/C catalyst was found to be a suitable catalyst for the hydrogenation of impure soy lecithin. The adsorption of lecithin onto the catalyst surface was determined to be the rate controlling step. The order of reaction with respect to lecithin concentration was 0.81 while that with respect to catalyst concentration was 0.53 and with respect to hydrogen was 0.6. The next step in the process elucidated the reaction steps that led to the fractional orders. Also, overall heat of reaction has been yet to be obtained. Once this parameter is obtained, the model may be used directly in reactor design. The kinetics gleaned from this work can be further used to design commercial scale reactors for mass production of this product using our catalyst. A more general model will be put forward in subsequent communications.

Nomenclature

Phosphatidylcholine (PC), Phosphatidyletanolamine (PE), Phosphatidylinositol (PI), Palladium carbon (Pd/C), High Performance Liquid Chromatography (HPLC), Activation Energy (E_A), Milli absorbance (mAU), Rotation per minute (rpm), Hydrogen pressure (P_{H_2}), Mega Pascal (MPa).

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