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Optimization of continuous hydrogenation of soybean lecithin using factorial design

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Abstract

Soybean lecithin containing a mixture of phospholipids (PLs) is an important co product obtained during soybean oil refining. Saturated rich PLs find several applications in food, cosmetic and pharmaceutical areas. The present study reports a simple, rapid, efficient and continuous hydrogenation process using 10% Pd/C catalyst at various temperatures and pressures. Degree of hydrogenation was monitored by fatty acid composition and iodine values (I.V). Maximum hydrogenation of 91.3% was obtained at 60°C and 20 bar pressure which showed an I.V of 3.89 as against the crude soybean lecithin having I.V 99.5. Design of experiments was carried to optimize the process.

Introduction

Soybean lecithin is an important by-product of oil processing obtained during the degumming step of oil refining. Soybean lecithin is a complex, naturally occurring mixture of phospholipids containing mainly phosphatidylcholine, phosphatidylethanolamine, phosphatidylinositol and phosphatidic acid. Soybean lecithin has potential as a multifunctional additive for food, pharmaceutical and other industrial applications (Dasheill, 1989; Endre and Szuhaj, 1996; Tomomi, 2010). Saturated fatty acid–rich phospholipids are being used in food, cosmetic and pharmaceutical applications. The presence of high stearic content improves the oxidative stability and decreases the hygroscopic nature of PLs which is responsible for several applications (Hubschier *et al*., 1959; Schaffner *et al*., 2002).

Lecithin can be hydrogenated to a stearin like solid that has higher oxidative stability. During catalytic hydrogenation, the unsaturated fatty acids of lecithin become saturated. The natural pigments present in the lecithin are also destroyed during hydrogenation and the products become white and off white in colour. Hydrogenation of lecithin is usually carried out using deoiled lecithin in solvent medium using classical hydrogenation in presence of the catalyst (Ziegelitz, 1995). Hydrogenation is carried out by treating lecithin with fine grained nickel (Szukalska, 2001; Joshia *et al*., 2006), palladium, rhodium or platinum catalyst at 75-100ºC, with pressures varying from 70 to 150 atm. Reaction times are generally greater than would be expected for triglycerides. Shinozaki and Sato (Shinozaki and Sato, 1934) carried out the hydrogenation of soybean lecithin using nickel catalyst under a hydrogen pressure above 80 atm. However, hydrogenation is complicated by simultaneous double bond isomerizations, which may be positional or geometrical when nickel is used as catalyst. Therefore many researchers emphasized that palladium on various supports is the viable industrial catalyst for lecithin hydrogenation. Song *et al.* (2010) has investigated the effect of several catalysts, such as NiCu-S, SRNA-2 and Pd/C on soy lecithin hydrogenation and found that hydrogenation of lecithin using 5%, Pd/C at 60ºC temperature, 1.5 MPa hydrogen pressure, for 3 h, gave a product with iodine value 25.4.

Naglic *et al.* (1997) predicted that partially hydrogenated lecithin obtained with catalytic transfer hydrogenation (CTH) could give an excellent product for cosmetic and commercial liposome formulations. PLs from partially hydrogenated soybean lecithin still contain some amount of linoleic acid, a fatty acid which is designated as essential fatty acid for healthy skin (Banik *et al*., 1999). On the other hand the amount of linolenic acid, a fatty acid which is oxidised most easily is minimized. Partially hydrogenated soybean lecithin is thus healthy for skin and at the same time has increased resistance to oxidation. Even though a number of articles (Smidovnik *et al.*, 1992; Leskovsek *et al*., 1994; Smidovnik *et al*., 1994; Banik *et al*., 1999; Mondal and Lalvani, 2000) were published on CTH of lipids, only one report appears on CTH of soybean

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lecithin (Naglic *et al*., 1997) where in the researchers used aqueous sodium formate solution and Pd/C as the hydrogen donor and catalyst respectively. The researchers used sodium formate as hydrogen donor and there is a possibility of retaining alkali residues in the reaction products.

In general, hydrogenation reactions involve a two step batch process i.e., reaction followed by filtration to remove the catalyst. However, in the present work we report a rapid, continuous and efficient process for hydrogenation of lecithin using a continuous flow hydrogenator. This technology promises high compatibility with multiphase catalytic hydrogenations and an efficient interaction between hydrogen, substrates and a catalyst to afford a smooth reaction (Jones *et al.*, 2006).

Experimental designs are used to obtain empirical relationships based on a mathematical model between one or more of the measured responses and a certain number of factors. Factorial design of experiements was applied to vegetable oil processing by various authors. Berrios *et al.* (2009) applied design of experiments in order to optimise the conditions for biodiesel production from lard. Boulifi *et al.* (2010) studied the storage stability of biodiesel made from corn oil over a storage time of 30 months and the optimum value for the variables affecting the process was determined using application of factorial design and response surface methodology. Hydrogenation of sunflower oil to oleomargarine was studied by Cepeda *et al.* (2008) using response surface methodology to predict the effect of reaction parameters on the overall rate constant of hydrogenation. This work reports for the first time application of design of experiments for the hydrogenation of soybean lecithin.

Materials and Methods

Crude soybean lecithin was procured from M/s Alpine Industries Ltd., Indore, India. Hexane used in the experiments was of analytical grade and was procured from M/s. Sd Fine chem. Pvt. Ltd., Mumbai. Hydrogenation of soybean lecithin was accomplished by employing a continuous flow hydrogenation device, H-Cube Midi™ (Thales Nano, Hungary) that incorporates *in-situ* hydrogen generation by electrolysis of deionized water and prepacked catalyst catridges containing 10% Pd/C, at 15 to 20 bar pressure and 30 to 60ºC temperature. The degree of conversion was established by monitoring the composition of reaction mixture after hydrogenation.

The fatty acid composition of soybean lecithin (soybean lecithin contained palmitic (18.52%), stearic (3.80%), oleic (25.29%), linoleic (48.25%), linolenic (4.14%) fatty acids) and hydrogenated soybean lecithin was determined by GC after converting them to fatty acid methyl esters (Christie, 1972). The analysis of methyl esters was carried out using GC Agilent 6890 series equipped with flame ionization detector. The stationary phase used was a capillary column, DB-225 MS (i.d. 0.25 mm, length 30 m). The oven temperature was programmed from 180 to 220ºC at 5ºC per minute and nitrogen with a flow rate of 35 mL/min was used as carrier. The injector and detector temperatures were maintained at 250 and 300ºC respectively. The area percentage was recorded using HP Chem Station Data System. Iodine value (IV) of the samples was determined using standard AOCS method (AOCS, 2003).

Experimental procedure

The system was allowed to run using hexane at a flow rate of 3 mL/min for 30 min. Then the system was pressurized to 20 bar at a temperature of 60ºC with hexane. Reaction mixture containing lecithin: hexane in ratio 1:19 (5 mL lecithin in 95 mL hexane, v/v) was homogenized and was allowed to pass through prepacked cartridge containing 10% Pd/C catalyst at 60ºC temperature. Pressure of 20 bar with a flow rate of 3 mL/min was used for hydrogenation. The sample was collected, desolventized and dried under reduced pressure. The fatty acid composition was determined using GC and the amount of unsaturation was determined by IV. Different experiments were carried out varying hydrogen pressure from 15 to 20 bar and temperature from 30 to 60ºC.

Results and Discussion

Hydrogenation using different process conditions showed that maximum hydrogenation occurred at 60ºC and 20 bar when 10% Pd/C was used as catalyst. Among the reactions carried out using 10% Pd/C, the rate of reaction increased with increase in pressure from 15 to 20 bar. The increase in degree of hydrogenation in case of 10% Pd/C at 60ºC and 20 bar was reflected in the reduction of iodine value (I V.) of the product (3.89 from 99.5). Among all the process conditions used the reaction rate was slow when lecithin was hydrogenated at 15 bar pressure and 30ºC temperature. However time taken for 90-92% hydrogenation using the described method was much less compared to conventional method which required 16 h for 85% hydrogenation. Further the product can be obtained directly without any filtration unlike the conventional method. Therefore the process reported is a simple, rapid and efficient which can be used as

Table 1. Experimental Design Matrix

Experiment Number	Order	Pressure bar	Temperature Deg C	Iodine value (IV)
1	1	15.00	30.00	56.25
2	8	15.00	30.00	57.89
3	12	15.00	30.00	54.36
4	2	20.00	30.00	25.33
5	5	20.00	30.00	26.92
6	11	20.00	30.00	25.04
7	3	15.00	60.00	40.63
8	7	15.00	60.00	41.28
9	9	15.00	60.00	40.14
10	4	20.00	60.00	3.89
11	6	20.00	60.00	3.25
12	10	20.00	60.00	4.18

Table 2. ANOVA for response surface linear model

Source	Sum of Squares	df	Mean Square	F Value	p-value
Model	4483.25	3	1494.42	1655.01	< 0.0001
A-pressure	3398.31	1	3398.31	3763.50	< 0.0001
B-temperature	1053.19	1	1053.19	1166.36	< 0.0001
AB	31.75	1	31.75	35.16	0.0010
Residual	5.42	6	0.90		
Cor Total	4492.65	11			

continuous method for the hydrogenation of lecithin.

A 2^2 factorial design of experiments have been used to determine the effect of process conditions on the continuous hydrogenation of lecithin such as temperature and pressure on degree of hydrogenation. The variables chosen were pressure and temperature while the response was iodine value. The effect of two independent variables (reaction temperature and pressure) on this system was studied. The dependent variable (referred to as a response) iodine value was experimentally measured. Temperature levels were 30°C and 60°C, pressure levels were 15 and 20 bar. All the experimental runs were performed at random and in triplicates for error estimation.

$$IV = 143.3400 - 4.77933 * A - 0.13456 * B - 0.043378 * A * B$$

The experimental design matrix and the iodine values are given in Table 1. The model was generated by fitting the response to the factors. The ANOVA for the response surface linear model is given in Table 2. Since the p-value for the model was lower than 0.05 there was a statistical relation between the response and the selected variables at 95% confidence level. Second-order models were obtained to predict the responses analyzed as a function of the variables. The following expression was obtained and it can be seen from the data analysis by ANOVA that the main effect of both pressure and temperature were negative on iodine value showing positive influence on the reduction in iodine value which in turn gives an indication of increase in conversion. The AVOVA results implies that the model is significant i.e., A, B, AB are significant.

The regression equation and the determination

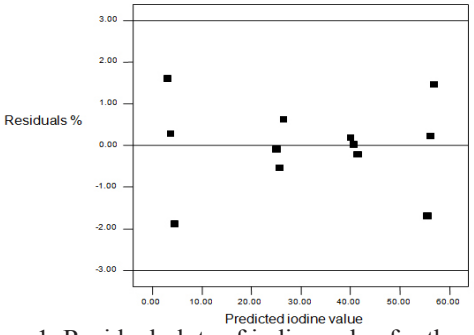

Figure 1. Residual plots of iodine value for the model

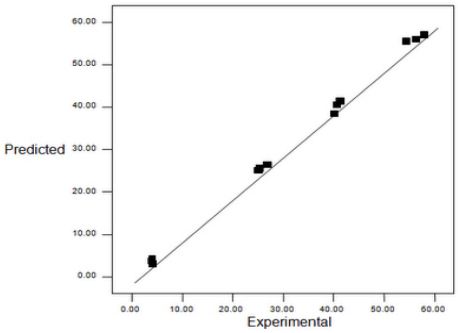

Figure 2. Predicted values vs. experimental values for the model

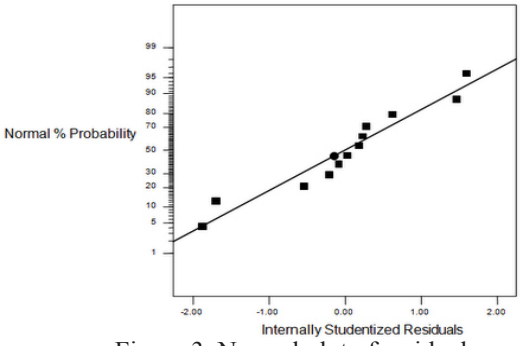

Figure 3. Normal plot of residuals

coefficient (R^2) were evaluated to test the fit of the model. In this case, the value of the determination coefficient was 0.9988. The predicted R^2 square value (0.9952) is in good agreement with adjusted R^2 square value (0.9982).

Figure 1 shows the residual distribution over the observed values for the response studied. A good fit was observed because the residual distribution does not follow a trend with regard to the predicted variables. The model accurately represents the influence of iodine value over the experimental range studies as all the residuals are less than 1.6 and the same is proved by the plot of experimental values vs predicted values as shown in Figure 2. The comparison of the experimental and calculated responses for the model show the agreement between the observed and predicted values. The figure shows that the mathematical model used for the prediction of the response provides good agreement for the experimental data. Figure 3 shows the normal probability plot of the residuals indicating a good

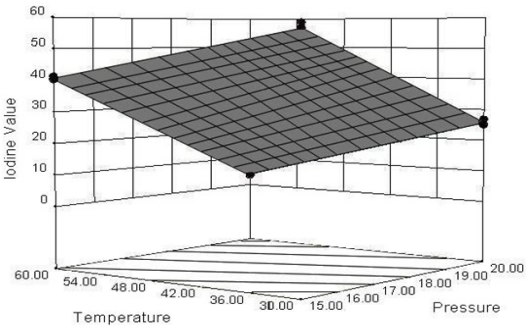

Figure 4. Response surface plot of iodine value as a function of temperature and pressure

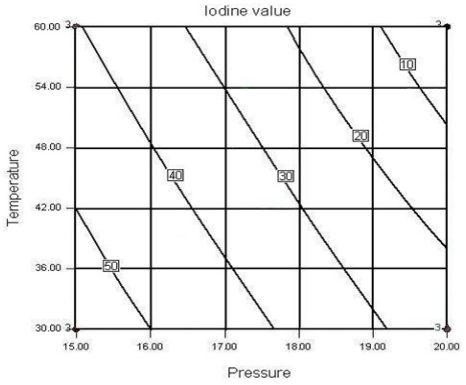

Figure 5. Contour plots of iodine value as a function of temperature and pressure

validity for the linear regression model. Figure 4 shows the 3D response surface graph of the regression equation and the contour plot is given in Figure 5.

The statistical analysis of the experimental studies shows the effect of both temperature and pressure on the iodine value. The interaction between the variables is negative. It is interesting to notice that the random distribution of the residuals (Figure 2) shows the absence of a trend which also indicates that the mathematical model is adequate since it does not detect any inconsistency between experimental and calculated values. It must be emphasized, that the model equation is an empirical equation that describes the relation between the iodine value and the reaction conditions in our experimental reactor.

Conclusions

A continuous hydrogenator was employed for the hydrogenation of lecithin which is a rapid, simple and efficient process. The effect of process parameters such as temperature and pressure has been studied. A 2^2 factorial design of experiments have been employed for the process optimization.

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