

Ethanolysis of Soybean Oil into Biodiesel : Process Optimization via Central Composite Design

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A process for production of ethyl ester for use as biodiesel has been studied. The sodium hydroxide catalyzed transesterification of soybean oil with ethanol was carried out at different molar ratio of alcohol to oil, reaction temperature and catalyst amount for a constant agitation in two hours of reaction time. Central composite design and response surface methodology were used to determine optimum condition for producing biodiesel. It was found that ethanol to oil ratio and catalyst concentration have a positive influence on ester conversion as well as interaction effects between the three factors considered. An empirical model obtained was able to predict conversion as a function of ethanol to oil molar ratio, reaction temperature and catalyst concentration adequately. Optimum condition for soybean ethyl ester production was found to be moderate ethanol to oil ratio (10.5 : 1), mild temperature range (70°C) and high catalyst concentrations (1.0%wt), with corresponding ester conversion of 93.0%.

Key Words : Biodiesel, Ethyl Ester, Soybean Oil, Optimization, Central Composite Design

Nomenclature

C : Catalyst concentration
I_C : Coefficient of catalyst concentration effect
I_R : Coefficient of ethanol to oil molar ratio effect
I_T : Coefficient of temperature effect
I_{CR} : Coefficient of interaction effect between catalyst concentration and molar ratio
I_{CT} : Coefficient of interaction effect between catalyst concentration and temperature
I_{RT} : Coefficient of interaction effect between molar ratio and temperature
I_{RCT} : Coefficient of interaction effect between molar ratio, catalyst concentration and temperature
R : Molar ratio of ethanol to vegetable oil

T : Reaction temperature
X_C : Coded variable for catalyst concentration
X_R : Coded variable for ethanol to oil molar ratio
X_T : Coded variable for reaction temperature
Y : Yield or conversion efficiency to ethyl ester

1. Introduction

Demand for diesel fuel in Thailand is rising with the growth of the country's industrial economy. With ascending rate of diesel consumption, shrinking crude oil reserves and limited refining capacity, Thailand is heavily dependent upon imports of crude petroleum and petroleum products. Imported diesel oil accounts for a large proportion in the country's energy imports (Wibulswas, 2002). Recent economic and political factors make supplies of petroleum uncertain and give rise to tremendous price escalation. It is naturally logical that research and development for alternatives to partial or total substitution of diesel fuels have been carried out. Among the

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many different types of alternative fuels, vegetable oils and their derivatives appear to be most promising choices. The idea of using vegetable oils as diesel fuel substitute is not new but very attractive especially in countries rich in oleaginous plants and poor in petroleum resources, like Thailand. Vegetable oils are widely available, biodegradable and nontoxic, have low emissions profiles, and are made from renewable resources (Ma and Hanna, 1999). Utilization of vegetable oils will also help increase the incomes of farmers and reduce expenditure of foreign exchange required for imported petroleum products.

However, due to differences in characteristics of vegetable oils and diesel fuels, such as heating value, viscosity, chemical composition, boiling point, there exist a few difficulties in obtaining acceptable engine operations. Generally, in short term engine tests, the vegetable oils performed well. Problems arise only after the engine has been tested with the vegetable oil for long periods of operation time (Bhattacharyya and Reddy, 1994). These problems include lubricating oil contamination, carbon deposits on engine surfaces and injection problems. Fundamentally, high viscosity appears to be a property at the root of many problems associated with direct use of these oils as engine fuels (Pryde, 1983). Several approaches to reduce viscosity and its associated problems have been explored, including blends with lighter fuel oils, preheating, transesterification, microemulsions with solvents, and pyrolysis or thermal cracking (Graboski and McCormick, 1998; Ma and Hanna, 1999).

Esterified vegetable oils in form of methyl ester or ethyl ester (known as biodiesel) have received the most attention worldwide and have become the predominant vegetable oil fuels used in Europe, USA and Asia (Shay, 1993; Graboski and McCormick, 1998; Ma and Hanna, 1999; Srivastava and Prasad, 2000; Fukuda et al., 2001; Ryu and Oh, 2003). Transesterification is a common and well established chemical reaction in which vegetable oil reacts with alcohol in the presence of an alkaline or acidic catalyst. Common alcohols used are methanol and ethanol. The most commonly preferred catalysts are sodium

hydroxide, sodium methoxide (NaOCH_3), and potassium hydroxide as alkaline catalysts and sulfuric, sulphonic and hydrochloric acids as acid catalysts (Canakci and Van Gerpen, 1999). In this study, our research efforts have been directed to improvement in the use of soybean oil as fuel via transesterification with ethanol. Soybean is grown locally and has shown potential for mass production in Northern provinces of Thailand and ethanol can be produced from agricultural renewable sources. The effect of excess alcohol, reaction temperature and catalyst concentration on conversion efficiency will be examined. Optimization using the central composite design of experiments and response surface methodology (Sanchez et al., 1997; Vicente et al., 1998; Kim and Heo, 2003) will be adopted. The aim of the present work is to optimize the yield in terms of these fundamental process variables.

2. Materials and Methods

2.1 Materials

In this experiment, soybean oil (with free fatty acid $\sim 1.0\%$) obtained from a local food store and ethanol (research grade, 99.8%) purchased from Merck, Germany, were used as reactants for transesterification. The base catalyst used was sodium hydroxide (commercial grade) which was provided by O.V. Chemicals, Thailand.

2.2 Biodiesel preparation procedure

A laboratory-scale reactor in the form of a 1000 cm^3 glass flask was used. Each 200- cm^3 sample of soybean oil was dehumidified to remove moisture to below 0.6% by heating to 120°C for 30 min prior to placing in the flask. The flask was heated and stirred by a combination of hot plate and a magnetic stirrer. At the same time, the pre-determined amount of catalyst was dissolved in an appropriate volume of ethanol to obtain required molar ratio of ethanol to oil for each sample. It was necessary to heat the ethanol slightly with stirring to completely dissolve the catalyst. When the required reaction temperature was reached for the oil, the mixture of ethanol and dissolved catalyst was then added. Stirring

and heating were set in such a way that temperature was kept constant throughout the reaction at atmospheric pressure. After 120 min of reaction time, the reaction was stopped, distilled water was added and the mixture was allowed to cool and left to settle to separate into two layers; the ester product formed the upper layer and the byproduct glycerin formed the lower layer. The ester layer was later separated in a separating funnel and washed with 40 cm³ of distilled water each time until the washings were neutral. Afterwards, the wet ester was dried at 120°C for 30 min and filtered. The end product was analyzed for viscosity (ASTM D88), flash point (ASTM D93), pour point (ASTM D97), heat capacity (ASTM D240) and specific gravity (ASTM D1298). Each experiment was conducted at least four times and the results were averaged. In all cases, the results were within 7.5%.

2.3 Central composite experimental design

A central composite design (CCD) of experiments, originally developed by Box and Wilson (1951), is one of the most efficient classes of designs capable of generating a response surface. Several factors at several levels can generate a response surface. The minimum number of levels and factors is three for a second order model. The CCD with three independent variables requires 15 treatments. Eight treatment combinations are located at the vertices of a cube. Six additional points (star points) are considered at a distance α along the three axes. One more point is at the center of the cube and corresponds to a (0, 0, 0) level of the

three factors. CCD was used to determine the optimum values of three quantitative factors chosen, namely, molar ratio of ethanol to oil (X_R), reaction temperature (X_T) and catalyst concentration (X_C). The response measured was degree of conversion (Y) of oil to ethyl ester after 120 min. The levels chosen for each factor in this study were based on the properties of the reactants, the operating limits of the experimental apparatus, practical consideration and previous literature (Muniyappa et al., 1996). Molar ratio of ethanol to oil was taken at 6 : 1, 10.5 : 1, 15 : 1, 19.5 : 1 and 24 : 1. The reaction temperatures chosen and catalyst concentrations tested were 40, 65, 70 and 90°C and 0.75, 0.85, 0.875 and 1.0%wt, respectively. The experimental matrix for 2ⁿ factorial design was shown in Table 1 where n is factor number. Real values and coded values (+1, -1) for the three factors were given. A minus one (-1) represents the low level and a plus one (+1) represents the high level for each factor. Additional runs were performed at the centre point, coded 0, and extra number of star points, coded -0.5, -0.2, +0.2, +0.5, to estimate the overall curvature effect on the response surface (Montgomery, 2001). Composite designs are useful for sequential experimentation in which the cube portion is used to allow estimation of the first order effects and the later addition of the star points permits second order terms to be added to the model and estimated (Kim and Heo, 2003). Systematic errors were avoided by randomized order of experimental runs.

Table 1 Experimental matrix for the central composite design and resulting yields

Run	R	T (°C)	C (%wt)	X_R	X_T	X_C	Y (%)
1	6 : 1	40	0.75	-1	-1	-1	62.5
2	6 : 1	40	1.0	-1	-1	+1	72.3
3	6 : 1	90	0.75	-1	+1	-1	46.3
4	6 : 1	90	1.0	-1	+1	+1	55.5
5	24 : 1	40	0.75	+1	-1	-1	70.3
6	24 : 1	40	1.0	+1	-1	+1	81.3
7	24 : 1	90	0.75	+1	+1	-1	66.3
8	24 : 1	90	1.0	+1	+1	+1	69.3

Run	R	T (°C)	C (%wt)	X _R	X _T	X _C	Y (%)
9	15:1	65	0.875	0	0	0	81.0
10	15:1	65	0.875	0	0	0	85.0
11	15:1	65	0.875	0	0	0	87.0
12	15:1	65	0.875	0	0	0	82.0
13	6:1	40	0.85	-1	-1	-0.2	71.5
14	6:1	70	0.75	-1	+0.2	-1	66.3
15	6:1	70	0.85	-1	+0.2	-0.2	75.4
16	6:1	70	1.0	-1	+0.2	+1	75.3
17	6:1	90	0.85	-1	+1	-0.2	52.1
18	24:1	40	0.85	+1	-1	-0.2	80.3
19	24:1	70	0.75	+1	+0.2	-1	78.6
20	24:1	70	0.85	+1	+0.2	-0.2	82.7
21	24:1	70	1.0	+1	+0.2	+1	83.7
22	24:1	90	0.85	+1	+1	-0.2	67.6
23	10.5:1	40	0.75	-0.5	-1	-0.2	87.0
24	10.5:1	40	0.85	-0.5	-1	-0.2	89.3
25	10.5:1	40	1.0	-0.5	-1	-0.2	91.3
26	10.5:1	70	0.75	-0.5	0.2	-1	88.3
27	10.5:1	70	0.85	-0.5	0.2	-0.2	90.7
28	10.5:1	70	1.0	-0.5	0.2	+1	93.0
29	10.5:1	90	0.75	-0.5	0.2	-1	74.2
30	10.5:1	90	0.85	-0.5	0.2	-0.2	74.2
31	10.5:1	90	1.0	-0.5	0.2	+1	84.3
32	15:1	40	0.75	0	-1	-0.2	81.7
33	15:1	40	0.85	0	-1	-0.2	82.0
34	15:1	40	1.0	0	-1	+1	74.3
35	15:1	70	0.75	0	+0.2	-1	84.7
36	15:1	70	0.85	0	+0.2	-0.2	84.6
37	15:1	70	1.0	0	+0.2	+1	88.7
38	15:1	90	0.75	0	+1	-1	71.7
39	15:1	90	0.85	0	+1	-0.2	73.3
40	15:1	90	1.0	0	+1	+1	77.7
41	19.5:1	40	0.75	+0.5	-1	-0.2	77.5
42	19.5:1	40	0.85	+0.5	-1	-0.2	77.0
43	19.5:1	40	1.0	+0.5	-1	-0.2	83.0
44	19.5:1	70	0.75	+0.5	0.2	-1	80.4
45	19.5:1	70	0.85	+0.5	0.2	-0.2	84.6
46	19.5:1	70	1.0	+0.5	0.2	+1	85.3
47	19.5:1	90	0.75	+0.5	+1	-0.2	68.7
48	19.5:1	90	0.85	+0.5	+1	-0.2	70.3
49	19.5:1	90	1.0	+0.5	+1	-0.2	71.3

3. Results and Discussion

The conversions to ethyl ester obtained experimentally for each run are shown in the last column of Table 1 and statistically analyzed using an SPSS package. The three main effects and interaction effect were estimated and found to be significant, given from the test of statistical significance in Table 2. Inspection of the statistical analysis results suggests that the ethanol to oil molar ratio is the most important among the main factors, affecting the conversion efficiency ($I_R=0.203$), followed by the catalyst concentration ($I_C=0.163$). Change in the reaction temperature ($I_T=-0.433$) did not prove to significantly influence the ester yield. Interaction effect between molar ratio and temperature was found to be more significant ($I_{RT}=0.074$) than catalyst concentration—temperature, and molar ratio—catalyst concentration interactions. It should be noted that the main effects of molar ratio as well as catalyst concentration were more significant than the interaction effects which were evident from higher positive value of coefficient I .

The experimental results of this analysis were used to develop a linear equation which shows the relationships between degree of conversion, molar ratio of ethanol to oil, reaction temperature and catalyst concentration. By considering the coded values, the following expression was

obtained :

$$Y = 77.942 + 2.958X_R - 5.422X_T + 2.065X_C + 1.315X_{RT} + 0.297X_{RC} + 0.159X_{TC} - 3.655X_{RTC} \quad (1)$$

The linear model appeared to sufficiently describe the system with acceptable correlation ($r=0.91$). However, a higher order was considered to be able to lessen the curvature effect of these variables on yield and provide better predictions throughout the region of interest. The data was therefore fitted to the full second order model and the parameters of the model were determined by multiple regression analysis.

$$Y = 87.46 + 2.969X_R - 6.035X_T + 2.091X_C + 1.370X_{RT} - 0.239X_{RC} - 0.696X_{TC} - 2.757X_{RTC} - 11.772X_R^2 - 8.000X_T^2 + 1.288X_C^2 \quad (2)$$

The second order model can be plotted as a three dimensional surface representing the response as a function of the three factors. Figs. 1 to 4 show percentage ester conversion versus catalyst concentration and reaction temperature for each ethanol to oil molar ratio considered. The yield appears to increase with catalyst concentration. Maximum conversion was observed for sodium hydroxide concentration of 1.0% by weight. Nonetheless, increase in catalyst amount will eventually result in saponification leading to formation of soap. The molar ratio of ethanol to oil is one of the most important variables affecting ester conversion. Stoichiometric ratio for ethanol to

Table 2 Statistical analysis for the experimental design and results

Number of factor :	3
Degree of freedom :	7
Main effects :	$I_R=0.203, I_T=-0.433, I_C=0.163$
Interaction effects :	$I_{RT}=0.074, I_{RC}=0.016, I_{TC}=0.001, I_{RTC}=-1.610$
Significant test :	Student's t
Confidence level :	95%
Average of experimental runs :	77.17
Standard deviation :	0.107
Student's t -value :	1.979
Confidence interval :	± 0.082
Response model :	
(First order)	$Y = a_0 + a_1X_R + a_2X_T + a_3X_C + a_4X_{RT} + a_5X_{RC} + a_6X_{TC} + a_7X_{RTC}$
(Second order)	$Y = a_0 + a_1X_R + a_2X_T + a_3X_C + a_4X_{RT} + a_5X_{RC} + a_6X_{TC} + a_7X_{RTC} + a_8X_R^2 + a_9X_T^2 + a_{10}X_C^2$

oil is 3 : 1. In practice, molar ratio higher than theoretical value would be needed to drive the reaction to completion. From the results, the highest conversion was obtained at the 10.5 : 1 molar ratio. The molar ratio of 6 : 1 gave unsatisfactory yield. Higher molar ratio did not prove to have significant contribution to an increase in ester yield. Gain in ester conversion efficiency was marginal when temperature was increased from 40 to 70°C. Further increase in temperature to 90°C resulted in a dramatic reduction in yield

because major ethanol loss occurred due to the fact that the temperature at this level was above the boiling point of ethanol. Optimum condition for soybean ethyl ester production was found to be moderate ethanol to oil ratio (10.5 : 1), mild temperature range (70°C) and high catalyst concentrations (1.0%wt), with corresponding ester conversion of 93.0%.

The biodiesel produced from soybean oil in this study was sent to Department of Industrial Chemistry, Chiang Mai University for testing to

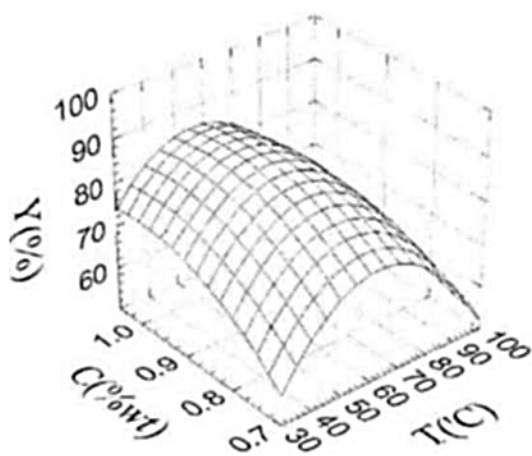


Fig. 1 Response surface of ethyl ester conversion versus catalyst concentration and temperature for molar ratio of 6 : 1

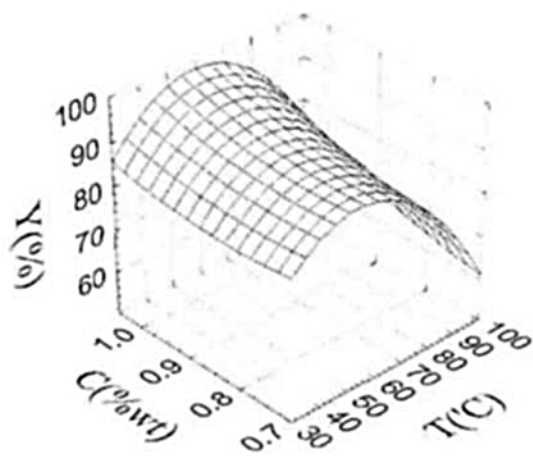


Fig. 3 Response surface of ethyl ester conversion versus catalyst concentration and temperature for molar ratio of 15 : 1

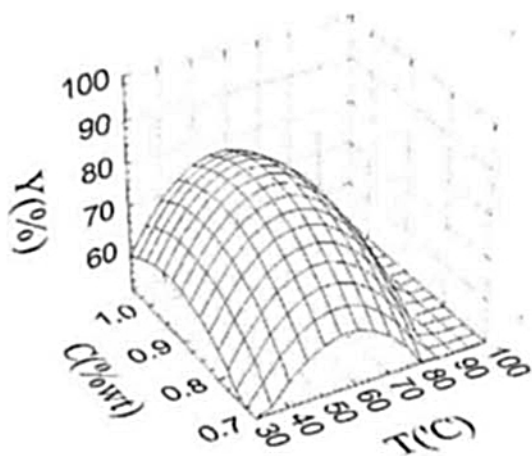


Fig. 2 Response surface of ethyl ester conversion versus catalyst concentration and temperature for molar ratio of 10.5 : 1

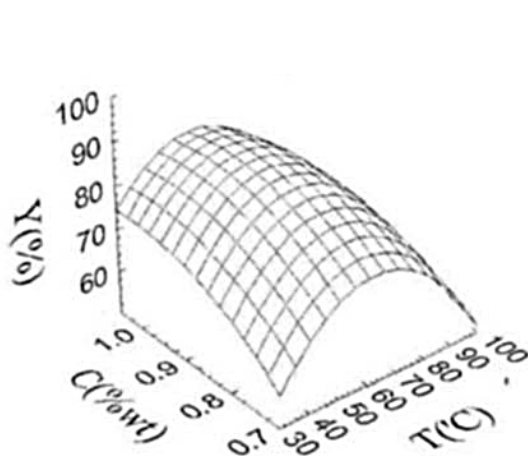


Fig. 4 Response surface of ethyl ester conversion versus catalyst concentration and temperature for molar ratio of 24 : 1

Table 3 Properties of soybean ethyl ester produced in this study and local diesel fuel

Property	Diesel	Biodiesel	Procedure
Viscosity @ 40°C (cSt)	5.9	5.5—6.7	ASTM D88
Specific gravity @ 15°C (kg/cm ³)	0.835	0.862—0.863	ASTM D1298
Heating value (MJ/kg)	46.2	39.8—40.7	ASTM D240
Flash point (°C)	77.0	155—170	ASTM D93
Pour point (°C)	-14.0	-6.0—-3.0	ASTM D97
Cloud point (°C)	-2.2	-3.0—-1.0	ASTM D2500

assess its potential as a petroleum based diesel fuel substitute. Tests results with local diesel fuel were presented in Table 3. A very good approximation of biodiesel to the characteristics of diesel fuel was obtained. The viscosity and specific gravity were found to be in similar magnitude. The energy content of the biodiesel based on heating value was slightly lower for the biodiesel, compared to the diesel fuel, being about 90% by mass and about 95% by volume of diesel fuel. The difference was not considered to be very significant. While the cloud point was in similar range, the pour point was higher. Nonetheless, there should not be any difficulty in cold starts. The greatest difference was in the flash point which was markedly higher for the biodiesel which implied better security in handling and storage.

4. Conclusions

In this research study, evaluation of soybean oil conversion to ethyl ester at atmospheric pressure for 120 min of reaction time has been investigated as a function of molar ratio of ethanol to oil, reaction temperature and sodium hydroxide concentration. Process optimization was performed by application of the central composite design and surface response method. The following conclusions may be drawn from the present study.

(1) Molar ratio of ethanol to oil and catalyst concentration were found to have a positive influence on conversion efficiency whereas reaction temperature did not prove to be dominant factor. Interaction effects between these factors were also significant. Highest conversions were obtained at moderate molar ratios of ethanol to

oil, relatively high temperatures and high catalyst concentrations.

(2) An empirical second order model relating molar ratio of ethanol to oil, reaction temperature and catalyst concentration was obtained to predict degree of conversion to ester. The model was found to represent the experimental data adequately.

(3) Biodiesel fuel was found to have similar physico-chemical properties to commercial diesel fuel.

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