DEVELOPMENT OF NOEVL CATALYST FOR THE PRODUCTION OF BIO-DIESEL FROM CRUDE PALM OIL

DR.LEE KEAT TEONG

UNIVERSITI SAINS MALAYSIA
KAMPUS KEJURUTERAAN
2008

UNIVERSITI SAINS MALAYSIA

Laporan Akhir Projek Penyelidikan Jangka Pendek

Development of Novel Catalyst for the Production of Bio-Diesel from Crude Palm Oil

by

Dr. Lee Keat Teong
Prof. Abdul Rahman Mohamed
Prof. Subhash Bhatia

UNIVERSITI SAINS MALAYSIA

LAPORAN AKHIR PROJEK PENYELIDIKAN JANGKA *PENDEK*

FINAL REPORT OF SHORT TERM RESEARCH PROJECT

Sila kemukakan laporan akhir ini melalui Jawatankuasa Penyelidikan di Pusat Pengajian dan Dekan/Pengarah/Ketua Jabatan kepada Pejabat Pelantar Penyelidikan

24 MAR 200
UNIT EIT
Universiti Sains Ma

1. **Nama Ketua Penyelidik:** *Name of Research Leader* **Lee Keat Teong**

☐ Profesor Madya/ *Assoc. Prof.* ☑ Dr./ *Dr.* ☐ Encik/Puan/Cik *Mr/Mrs/Ms*

2. **Pusat Tanggungjawab (PTJ):** *School/Department* **School of Chemical Engineering**

3. **Nama Penyelidik Bersama:** *Name of Co-Researcher*
Prof. Abdul Rahman Mohamed
Prof. Subhash Bhatia

4. **Tajuk Projek:** *Title of Project* **Development of Novel Catalyst for the Production of Bio-Diesel from Crude Palm Oil**

5. **Ringkasan Penilaian/***Summary of Assessment:*	Tidak Mencukupi *Inadequate* 1		Boleh Diterima *Acceptable* 3	Sangat Baik *Very Good* 4	
i) **Pencapaian objektif projek:** *Achievement of project objectives*	☐	☐	☐	☐	☑
ii) **Kualiti output:** *Quality of outputs*	☐	☐	☐	☑	☐
iii) **Kualiti impak:** *Quality of impacts*	☐	☐	☐	☑	☐
iv) **Pemindahan teknologi/potensi pengkomersialan:** *Technology transfer/commercialization potential*	☐	☐	☑	☐	☐
v) **Kualiti dan usahasama :** *Quality and intensity of collaboration*	☐	☐	☑	☐	☐
vi) **Penilaian kepentingan secara keseluruhan:** *Overall assessment of benefits*	☐	☐	☐	☑	☐

6. Abstrak Penyelidikan
(Perlu disediakan di antara 100 - 200 perkataan di dalam **Bahasa Malaysia dan juga Bahasa Inggeris**. Abstrak ini akan dimuatkan dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & masyarakat luar).

Abstract of Research
(An abstract of between 100 and 200 words must be prepared in Bahasa Malaysia and in English).
This abstract will be included in the Annual Report of the Research and Innovation Section at a later date as a means of presenting the project findings of the researcher/s to the University and the community at large)

Sejak kebelakangan ini, penghasilan biodiesel telah mendapat perhatian ramai akibat peningkatan permintaan terhadap tenaga yang bersih, selamat dan boleh diperbaharui. Kaedah biasa bagi penghasilan biodiesel adalah dengan mencampurkan minyak tumbuh-tumbuhan dengan alkohol dan mangkin homogen (NaOH). Walau bagaimanapun, kaedah ini mempunyai banyak kekurangan seperti pembentukkan sabun, keperluan air yang banyak dan proses pemisahan yang kompleks. Sebaliknya pula, proses pemangkinan heterogen yang menggunakan mangkin pepejal mempunyai banyak kelebihan berbanding proses pemangkinan homogen. Selain daripada itu, pada masa kini, lebih daripada 90% biodiesel yang digunakan di dunia ini adalah dihasilkan daripada minyak '*rapeseed*'. Penghasilan biodiesel daripada '*rapeseed*' adalah dianggap tidak ekonomikal memandangkan minyak sawit adalah minyak masak yang paling murah di dunia. Justeru itu, tujuan penyelidikan ini adalah untuk membuktikan kemungkinan bagi menghasilkan biodiesel daripada minyak sawit dengan menggunakan Montmorillonite KSF sebagai mangkin heterogen. Proses transesterifikasi heterogen ini akan dikaji dengan menggunakan pendekatan rekabentuk ujikaji (DOE). Secara spesifik, kaedah permukaan tindakbalas berdasarkan empat pemboleh-ubah rekabentuk komposit terpusat (CCD) dengan $\alpha = 2$ akan digunakan. Pemboleh-ubah proses transesterifikasi yang dikaji adalah suhu, tempoh tindakbalas, nisbah metanol kepada minyak dan kuantiti mangkin. Didapati bahawa nilai penukaran minyak sawit kepada biodiesel boleh mencecah 78.7% pada keadaan tindakbalas berikut: suhu 155°C, tempoh tindakbalas 120 min, nisbah metanol kepada minyak 10:1 dan kuantiti mangkin 4%.

Production of biodiesel has become popular nowadays as a result of increasing demand for a clean, safe and renewable energy. The conventional method of producing biodiesel is by reacting vegetable oil with alcohol in the presence of homogenous catalyst (NaOH). However, this conventional method has some limitations such as the formation of soap, usage of lot wash water and complicated separation processes. On the other hand, heterogeneous process using solid catalysts has a lot of advantages over the homogenous methods. Apart from that, currently, more than 90% of world biodiesel is produced using rapeseed oil. Producing biodiesel from rapeseed oil is considered uneconomical, considering the fact that palm oil is currently the world cheapest vegetable oil. Therefore, the focus of this study is to show the feasibility of producing biodiesel from palm oil using montmorillonite KSF as the heterogeneous catalyst. The heterogeneous transesterification process was studied using design of experiment (DOE), specifically response surface methodology (RSM) based on four-variable central composite design (CCD) with $\alpha = 2$. The transesterification process variables were reaction temperature, reaction period, methanol/oil ratio, and amount of catalyst. It was found that the conversion of palm oil to biodiesel can reach up to 78.7% using the following reaction conditions; reaction temperature of 155 °C, reaction period at 120 min, ratio of methanol/oil at 10:1 mol mol^{-1} and amount of catalyst at 4%.

7. Sila sediakan laporan teknikal lengkap yang menerangkan keseluruhan projek ini.
[Sila gunakan kertas berasingan]
Applicant are required to prepare a Comprehensive Technical Report explaning the project.
(This report must be appended separately)

Please refer to the attachment for Comprehensive Technical Report.

Senaraikan kata kunci yang mencerminkan penyelidikan anda:
List the key words that reflects your research:

Bahasa Malaysia	*Bahasa Inggeris*
Biodiesel	Biodiesel
Transesterifikasi	Transesterification
Mangkin heterogen	Heterogeneous Catalyst
Montmorillonite KSF	Montmorillonite KSF

(c) **Latihan Sumber Manusia**
Training in Human Resources

i) Pelajar Sarjana:
Graduates Students
(Perincikan nama, ijazah dan status)
(Provide names, degrees and status)

Pelajar Siswazah

1. Jibrail Kansedo (P-JM0127) Master Program, Status: Completing soon

Pelajar Prasiswazah

1. Kho Moi Ling, Bachelor Degree, Status: Completed
2. Wong Wai Lin, Bachelor Degree, Status: Completed
3. Yee Kian Fei, Bachelor Degree, Status: In Progress
4. Hue Siew Ching, Bachelor Degree, Status: In Progress

ii) Lain-lain: Tiada
Others

9. Peralatan yang Telah Dibeli:
Equipment that has been purchased

1. Electrothermal Heating Mantle with OMNI Controller & Stirrer (ELE#OMCA)

29/02/08

Tandatangan Penyelidik
Signature of Researcher

Tarikh
Date

Komen Jawatankuasa Penyelidikan Pusat Pengajian/Pusat
Comments by the Research Committees of Schools/Centres

Penyelidikan telah tamat dengan jayanya seperti perancangan awal.

16/3

PROFESOR ABDUL LATIF AHMAD, CEng FIChemE
Dekan
Pusat Pengajian Kejuruteraan Kimia
Kampus Kejuruteraan
Universiti Sains Malaysia, Seri Ampangan
14300 Nibong Tebal, Seberang Perai Selatan
Pulau Pinang.

**TANDATANGAN PENGERUSI
JAWATANKUASA PENYELIDIKAN
PUSAT PENGAJIAN/PUSAT**
*Signature of Chairman
[Research Committee of School/Centre]*

Tarikh
Date

JABATAN BENDAHARI
UNIT KUMPULAN WANG AMANAH
UNIVERSITI SAINS MALAYSIA
KAMPUS KEJURUTERAAN
SERI AMPANGAN

PENYATA KUMPULAN WANG

TEMPOH BERAKHIR 31/01/2008

DR LEE KEAT TEONG

304.PJKIMIA.6035157

JUMLAH GERAN :- 18,800.00

NO PROJEK :-

PANEL :- J/PENDEK

PENAJA :- JANGKA PENDEK

Tempoh Projek:01/09/2005 - 31/08/2007

DEV. OF NOVEL CATALYSTS FOR THE PRODUCTION OF BIO-DIESEL FROM CRUDE PALM OIL

Vot	*Peruntukan* (a)	*Perbelanjaan sehingga 31/12/2007* (b)	*Tanggungan semasa 2008* (c)	*Perbelanjaan Semasa 2008* (d)	*Jumlah Perbelanjaan 2008* (c + d)	*Jumlah Perbelanjaan Terkumpul* (b+c+d)	*Baki Peruntukan Semasa 2008* (a-(b+c+d)
11000 GAJI KAKITANGAN AWAM	5,140.00	4,580.08	0.00	0.00	0.00	4,580.08	559.92
21000 PERBELANJAAN PERJALANAN DAN SARAHI	2,000.00	3,220.40	0.00	0.00	0.00	3,220.40	(1,220.40)
23000 PERHUBUNGAN DAN UTILITI	600.00	203.80	0.00	0.00	0.00	203.80	396.20
24000 SEWAAN	700.00	0.00	0.00	0.00	0.00	0.00	700.00
27000 BEKALAN DAN ALAT PAKAI HABIS	5,400.00	4,757.55	0.00	0.00	0.00	4,757.55	642.45
28000 PENYELENGGARAAN & PEMBAIKAN KECIL	660.00	0.00	0.00	0.00	0.00	0.00	660.00
29000 PERKHIDMATAN IKTISAS & HOSPITALITI	1,000.00	2,553.05	0.00	0.00	0.00	2,553.05	(1,553.05)
35000 HARTA-HARTA MODAL LAIN	3,300.00	3,472.00	0.00	0.00	0.00	3,472.00	(172.00)
	18,800.00	18,786.88	0.00	0.00	0.00	18,786.88	13.12
Jumlah Besar	18,800.00	18,786.88	0.00	0.00	0.00	18,786.88	13.12

COMPREHENSIVE TECHNICAL REPORT
UNIVERSITI SAINS MALAYSIA
SHORT TERM GRANT

Project Title: **Development of Novel Catalyst for the Production of Bio-Diesel from Crude Palm Oil**

Project Leader: **Dr. Lee Keat Teong**

1.0 Introduction

Due to escalating crude petroleum oil prices and the effect of global warming, a search for alternative fuels has gained significant attention over the years. Among the various sources of alternative energy, renewable energy from biomass presents a promising alternative to replace the conventional fossil fuels. In the recent years, a number of studies have shown that vegetable oil such as rapeseed [1], soybean [2-9] and sunflower seed [10-11] oil can be used as a source of biodiesel replacing conventional petroleum-derived diesel fuels. The biodiesel is produced through transesterification reaction where by the triglycerides present in vegetable oil is converted to fatty acid alkyl esters. Transesterification, also called alcoholysis, is the reaction of the triglycerides in the vegetable oil with alcohol to form a mixture of fatty acid alkyl esters and glycerol [12-16]. The fatty acid alkyl esters produced from this process is known as biodiesel which has become more attractive recently because it has almost the same properties and characteristic of petroleum-derived diesel. Several studies have shown that biodiesel produced from vegetable oil have viscosity close to petroleum-derived diesel fuel [17,18]. Their volumetric heating values are a little lower compared to the petroleum-derived diesel fuel, but they have high cetane and flash point values.

Transesterification process is catalyzed by catalysts with both, acidic and basic sites. Currently, all the transesterification process goes through the homogenous transesterification process by mainly using potassium hydroxide as the catalyst [12-16]. In the homogeneous transesterification process, the catalysts used are in the same phase as the reactants/products. However, homogeneous transesterification process using potassium hydroxide presents certain disadvantages. Among some of the disadvantages are the formations of soap in the product mixture leading to additional cost required for the separation of soap from the biodiesel. Apart from that, the formation of soap has also led to the loss of triglycerides molecules that can be used to form biodiesel. Since the catalyst and the reactants/products are in similar phase, the separation of products (biodiesel) from the catalyst becomes complex. These disadvantages make the current (homogeneous transesterification process) expensive, complex and uneconomical. In order to overcome these limitations, researchers are now looking for alternative routes to produce biodiesel from vegetable oil. One of the possible solutions is by using heterogeneous transesterification process whereby solid catalyst is used. Recent researches have shown that there are various types of catalyst that can be used in the heterogeneous transesterification process. Jitputti *et al.* [19] studied the transesterification of coconut oil and palm kernel oil using zirconium oxide-based and zinc oxide-based catalyst, while Suppes *et al.* [2] used zeolite and metal catalyst for the conversion of soybean oil to biodiesel. In other research, heterogeneous base [20], $Na/NaOH/Al_2O_3$ [21] and metal complexes [22] are used as the catalyst.

Currently more than 90% of the world biodiesel is produced from rapeseed oil. However, due to the high price of rapeseed seed oil, the use of biodiesel replacing conventional petroleum-derived diesel oil can only be used in developed countries in Europe and USA. In order to overcome this problem, researchers have been trying to source for other types of vegetable oil that is cheaper such as palm oil [23], jatropha oil [24,25], soybean oil [3-9], canola oil [26] and even waste cooking oil [27,28]. Since palm oil is the worlds' cheapest vegetable oil, it presents a promising alternative as a feedstock for biodiesel production replacing rapeseed oil. Nevertheless the study on converting palm oil to biodiesel using heterogeneous reaction is still very limited.

Thus, in this study, the feasibility of producing biodiesel from palm oil using montmorillonite KSF as the heterogeneous catalyst will be presented. Statistical design of experiments will be used to accumulate and analyze information on the effect of process variable on the conversion of palm oil to biodiesel rapidly and efficiently using minimum number of experiments. As illustrated in the later section, this method was found superior than the conventional method of studying one variable at one time while keeping the rest constant.

2.0 Materials and Methods

2.1 Materials

Purified palm oil was purchased from Yee Lee Edible Oils Sdn Bhd, Malaysia and methanol from R & M Chemicals, UK. Montmorillonite KSF, methyl heptadecanoate (internal standard) and standard references for methyl esters analysis; methyl myristate, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate were obtained from Fluka Chemie, Germany. The catalyst, montmorillonite KSF, has humidity of ≤ 12 %, free acid of 8 – 12 %, and has its surface partially laid with H_2SO_4. The properties of palm oil are given in the Table 1 [29].

Table 1: Properties of palm oil

Fatty acids	Percentage (%)
Lauric	0.1
Myristic, C14	1.0
Palmitic, C16	42.8
Stearic, C18	4.5
Oleic, C18	40.5
Linoleic, C18	10.1
Linolenic	0.2
Other/Unknown	0.8

2.2 Design of experiments

The experimental design selected for this study is a Central Composite Design (CCD) that helps in investigating linear, quadratic, cubic and cross-product effects of the four transesterification process variables (independent) on the conversion of palm oil to biodiesel (response). The four transesterification process variables studied are reaction temperature, reaction period, ratio of oil to methanol and amount of catalyst. Table 2 lists the range and levels of the four independent variables studied. The CCD comprises a two-level fractional factorial design (½ × 2^4 = 8), eight axial or star points and five center points. The value of α for this CCD is fixed at 2. The complete design matrix of the experiments employed and results are given in Table 3. All variables at zero level constitute to the center points and the combination of each of the variables at either its lowest (-2.0) level or highest (+2.0) level with the other variables at zero level constitute the axial points. The experiment sequence was randomized in order to minimize the effects of the uncontrolled factors.

Table 2: Levels of the transesterification process variables chosen for this study

Variable	Coding	Unit	Levels				
			- 2	- 1	0	+ 1	+ 2
Reaction temperature	x_1	°C	50	80	120	155	190
Reaction period	x_2	min	60	120	180	240	300
Ratio of oil/methanol	x_3	mol mol^{-1}	1:4	1:6	1:8	1:10	1:12
Amount of catalyst	x_4	%	1	2	3	4	5

Table 3: Experimental design matrix and results

Catalyst Code	Experimental variables				Conversion, %
	Reaction temperature (°C)	Reaction period (min)	Ratio of oil/ methanol (mol mol^{-1})	Amount of catalyst (% g)	
K01	+1	+1	+1	-1	71.63
K02	+1	+1	-1	-1	59.10
K03	+1	-1	+1	+1	78.69
K04	-1	+1	-1	+1	5.07
K05	+1	-1	-1	+1	55.10
K06	-1	-1	+1	-1	3.92
K07	-1	+1	+1	+1	5.43
K08	-1	-1	-1	-1	2.90
K09	-2	0	0	0	0.79
K10	+2	0	0	0	74.34
K11	0	-2	0	0	14.49
K12	0	+2	0	0	60.05
K13	0	0	-2	0	36.52
K14	0	0	+2	0	51.39
K15	0	0	0	-2	32.54
K16	0	0	0	+2	61.98
K17	0	0	0	0	55.07
K18	0	0	0	0	50.88
K19	0	0	0	0	55.75
K20	0	0	0	0	55.07
K21	0	0	0	0	55.75

Each response of the transesterification process was used to develop a mathematical model that correlates the conversion of palm oil to the transesterification process variables studied through first order, second order and interaction terms, according to the following second order polynomial equation,

$$Y = b_o + \sum_{j=1}^{4} b_j x_j + \sum_{ij=1}^{4} b_{ij} x_i x_j + \sum_{j=1}^{4} b_{jj} x_j^2 \tag{1}$$

where Y is the predicted conversion of palm oil to biodiesel, mol mol^{-1}, x_i and x_j represent the variables or parameters, b_o is the offset term, b_j is the linear effect, b_{ij} is the first order interaction effect and b_{jj} is the squared effect.

2.3 Model fitting and statistical analysis

Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) was used for regression analysis of the experimental data to fit the second order polynomial equation and also for evaluation of the statistical significance of the equation developed.

2.4 Activity study

Transesterification reactions were carried out in a low pressure batch reactor with a magnetic stirrer, as shown in the Figure 1. Mixture of palm oil, catalyst and methanol was charged into the reactor. The mixing intensity of the magnetic stirrer was set at 190-200 rpm. The reaction temperature, duration, ratio of oil/methanol and amount of catalyst (montmorillonite KSF) were set according to the values as proposed in the DOE shown in Table 3. The excess methanol from the samples was removed using rotary evaporator. The upper layer of the sample was separated from the bottom layer and was analyzed to detect biodiesel content.

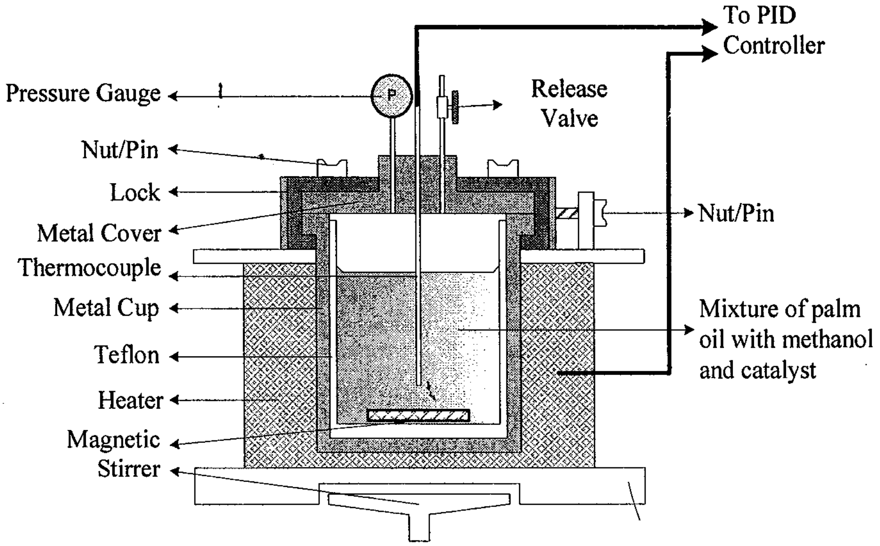


Figure 1: Schematic diagram of the experimental set-up for the transesterification process

2.5 Analysis

The resulting products from the transesterification processes were analyzed using Gas Chromatography (GC) by means of Inert Cap WAX capillary column (30 mm x 0.25 mm, I.D. 0.25 μm) to identify the presence of methyl esters (biodiesel) in the sample. Helium was used as the carrier gas. Oven temperature at 120 °C was initially hold for 1 minute and then increased to 220 °C (hold 15 minute) at a rate of 4 °C min^{-1}. The temperatures of the injector and detector were set at 220 °C and 250 °C respectively. A quantity of 1 μl from each sample was injected into the column. Methyl heptadecanoate was used as internal standard for the calculation of the conversion. The conversions of the transesterification processes were calculated as mol ratio of methyl esters produced to palm oil used divided by 3. The formula is given as:

$$\text{Conversion, \%} = \frac{\text{Total mol of methyl esters}}{3 \times \text{Total mol of oil}} \times 100\,\% \tag{2}$$

3.0 Results and Discussion

3.1 Development of regression model equation

A central composite design (CCD) was used to develop a correlation between the transesterification reaction variables to the conversion of palm oil to biodiesel. The complete design matrix and conversion of palm oil to biodiesel (responses) are listed in Table 3. As can be seen from Table 3, the conversion of palm oil to biodiesel range from 0.79% to 78.69%. Runs K17 to K21 at the center point of the design are to determine the experimental error. As the result of conversion of these five runs were quite consistent, single replicate experimental run is essential in this study. Apart from that, from results of these five runs, the experimental error for the conversion of palm oil to biodiesel could be calculated as 1.2%.

By using multiple regression analysis, the response (conversion of palm oil to biodiesel) obtained in Table 3 was correlated with the four transesterification reaction variables/parameters studied using the polynomial equation as shown in Equation (1). The coefficients of the full regression model equation and their statistical significance were determined and evaluated using Design-Expert 6.0.6 software. The final equation in terms of actual value after excluding the insignificant terms (identified using Fisher's Test) is

$$\begin{aligned} Y = {} & 54.50 + 18.39x_1 + 11.39x_2 + 4.20x_3 + 7.36x_4 - 5.02x_1^2 - 5.09x_2^2 - 3.42x_3^2 - \\ & 2.60x_4^2 + 6.52x_1x_2 + 4.34x_1x_3 + 11.31x_1x_4 - 12.51x_2x_4 \end{aligned} \tag{3}$$

Positive sign in front of the terms indicates synergistic effect, while negative sign indicates antagonistic effect. Equation (3) shows that the conversion of palm oil to biodiesel has a linear and quadratic effect on the four transesterification process variables studied. Apart from that, interactions between the variables also effect the conversion of palm oil to biodiesel.

3.2 Model adequacy check

The quality of the model developed could be evaluated from their coefficients of correlation. The value of R for Equation (3) is 0.9846. The high value of R (very close to 1) shows that there is a very good agreement between the experimental and predicted value from the model. On the other hand the value of R^2 for Equation (3) is 0.9515. It implies that 95.15% of the total variation in the conversion of palm oil to biodiesel responses is attributed to the experimental variables studied. The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in Table 4. Based on a 95% confidence level, the model was tested to be significant as the computed F value (42.67) is much higher than the theoretical $F_{0.05\,(12,8)}$ value (3.28), indicating that the regression model is reliable in predicting the conversion of palm oil to biodiesel. Apart from that, each term in the model was also tested to be significant at a 95% confidence level as the computed F values for the respective terms are higher than the theoretical $F_{0.05\,(1,8)}$ value (5.32). From these statistical tests, it was found that the model is adequate for predicting the conversion of palm oil to biodiesel within the range of variables studied.

Table 4: Analysis of variance (ANOVA) for the regression model equation and coefficients

Source	Sum of squares	Degrees of freedom	Mean of squares	F-test
Model	13390.31	12	1115.86	42.67
x_1	2704.80	1	2704.80	103.43
x_2	1037.86	1	1037.86	39.69
x_3	282.58	1	282.58	10.81
x_4	433.36	1	433.36	16.57
x_1^2	632.50	1	632.50	24.19
x_2^2	651.22	1	651.22	24.90
x_3^2	294.00	1	294.00	11.24
x_4^2	169.18	1	169.18	6.47
$x_1 x_2$	169.91	1	169.91	6.50
$x_1 x_3$	150.86	1	150.86	5.77
$x_1 x_4$	511.90	1	511.89	19.57
$x_2 x_4$	626.25	1	626.25	23.95
Residual	209.21	8	26.15	

Figure 2 shows the experimental values versus predicted values using the model equation developed. A line of unit slope, i.e. the line of perfect fit with points corresponding to zero error between experimental and predicted values is also shown in Figure 2. This plot therefore visualizes the performance of the model in an obvious way. The results in Figure 2 demonstrated that the regression model equation provided a very accurate description of the experimental data, indicating that it was successful in capturing the correlation between the four transesterification process variables to the conversion of palm oil to biodiesel.

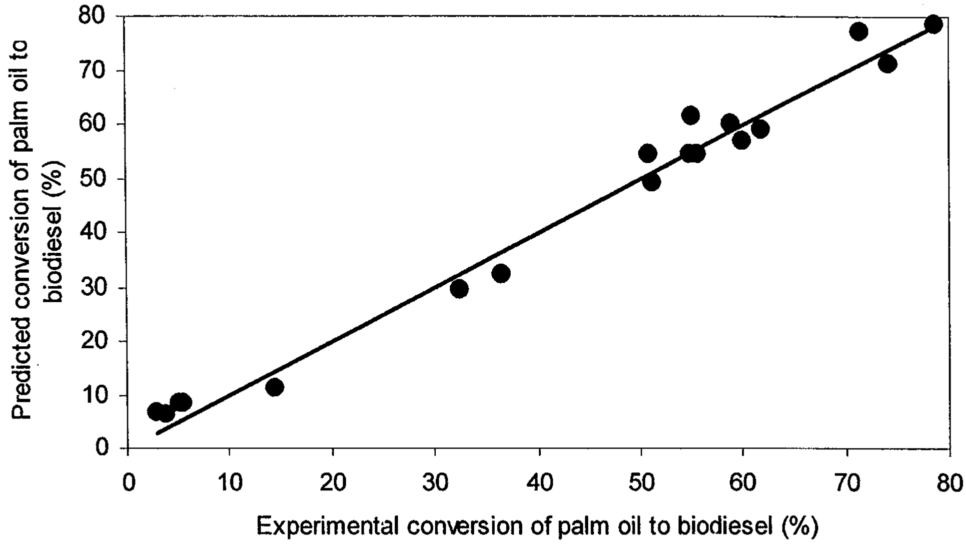


Figure 2: Experimental versus predicted conversion of palm oil to biodiesel

3.3 Effects of transesterification process variables

From Table 4, it was observed that among the four individual variables studied, reaction temperature (x_1) has the largest effect on the conversion of palm oil to biodiesel (due to the highest F value) followed by reaction period (x_2). Ratio of oil/methanol (x_3) and amount of catalyst (x_4) have similar least significant effect on the conversion of palm oil to biodiesel. The quadratic term of (x_1) and (x_2) were fairly significant on the conversion of palm oil to biodiesel compared to that of (x_3) and (x_4). The other significant terms include the effect of interaction between variables, particularly between variables (x_2) and (x_4) and between variables (x_1) and (x_4). Longer reaction period allows sufficient time for the transesterification process to occur completely, or at least, until the maximum level. Higher reaction temperature allows transesterification reactions occur at accelerated rate since there's supply of more energy to the reactions. On the other hand, larger amount of catalyst used will results in higher conversion of triglycerides to biodiesel because of higher availability of active sites. Apart from that, higher ratio of oil/methanol, 1:10, gives higher conversion as excess methanol is required to push the transesterification reaction forward. All these results are in agreement with those reported in the literature [13].

The results in Table 3 show that the transesterification process variables have great effect on the conversion of palm oil to biodiesel. The highest conversion was achieved at a reaction temperature of 155 °C, reaction period of 240 min or 4 hr, oil/methanol ratio of 1:10 and amount of catalyst of 4%. Whereas the lowest conversion was obtained at a reaction temperature of 50 °C, reaction period of 3 hr, oil/methanol ratio of 1:8 and amount of catalyst of 3%. These results illustrate that there is a great possibility in improving the conversion of palm oil to biodiesel with proper selection of transesterification process variables using montmorillonite KSF as the catalyst. The ability of montmorillonite KSF to catalyze the transesterification reactions, at any rate, is due to the acidic properties of the catalyst itself. Montmorillonite KSF has free acid of 8-12%, and its surface partially laid with H_2SO_4. H_2SO_4 is known as a typical strong acid, and since the transesterification reactions can be catalyzed with acid or base, therefore the strong acidity of this montmorillonite KSF will definitely contribute to the high conversion of palm oil to biodiesel.

However, since the maximum conversion occurs at the border of the experimental variables selected for this study, optimum experimental conditions to obtain the highest conversion cannot be derived (except for the experimental conditions at the border of the design variables). This finding was also supported by the model developed using the DOE software whereby no maximum conversion was located within the experimental domain examined. Therefore, the model developed by the DOE software was used to facilitate a straight forward examination of the effects of the variables and their interaction towards the conversion of the transesterification process. Among the four interaction terms that were found to have significant effect on the conversion of palm oil to biodiesel, emphasis were given to the interaction between (x_2) and (x_4) and between variables (x_1) and (x_4).

Figure 3 shows the changes in conversion with varying reaction temperature at 2% and 4% catalyst. The other two process variables; reaction period and ratio of oil to methanol were kept constant at 180 min and 1:8 respectively. It is generally perceived that higher percentage of catalyst used will results in higher conversion of triglycerides to biodiesel because of higher availability of active sites. However, this perception may not always be true. Referring to Figure 3, the conversion of oil to biodiesel was found to be lower at 4% catalyst as compared to 2% catalyst when the reaction temperature was lower than 95 °C. This may suggest the real interactions between the supplied energy (heat) and the active site on the catalyst itself. The active sites on the catalysts may require a certain amount of energy to be activated. At lower temperature, smaller percentage of catalyst, 2%, will reach the activation energy more quickly than the 4% catalyst because the ratio of active site to energy (heat) is smaller. In other words, the total energy required to activate the whole active sites on the 2% catalyst is much smaller than those for 4% catalyst. Thus, lower temperature (small energy) may just be enough to activate the whole active site on the 2% catalyst but not for the 4% catalyst because of the assumption of fair distribution of energy to all active sites. Thus, the transesterification reactions by 2% catalysts will commence sooner, while the 4% catalyst will show delay in transesterification reactions. However, as activation energy for all catalyst in the 4% is fully achieved at higher temperature, the reactions will proceed rapidly and subsequently exceeds to that of 2% catalyst. Thus, only when the reaction temperature is sufficient to activate all the active sites of the catalyst, then only the perception that higher amount of catalyst will results in higher conversion applies. These results demonstrate the capability of using systematical statistical design where by the effect of interaction between variables can be identified easily as compared to the conventional method of studying one variable at one time.

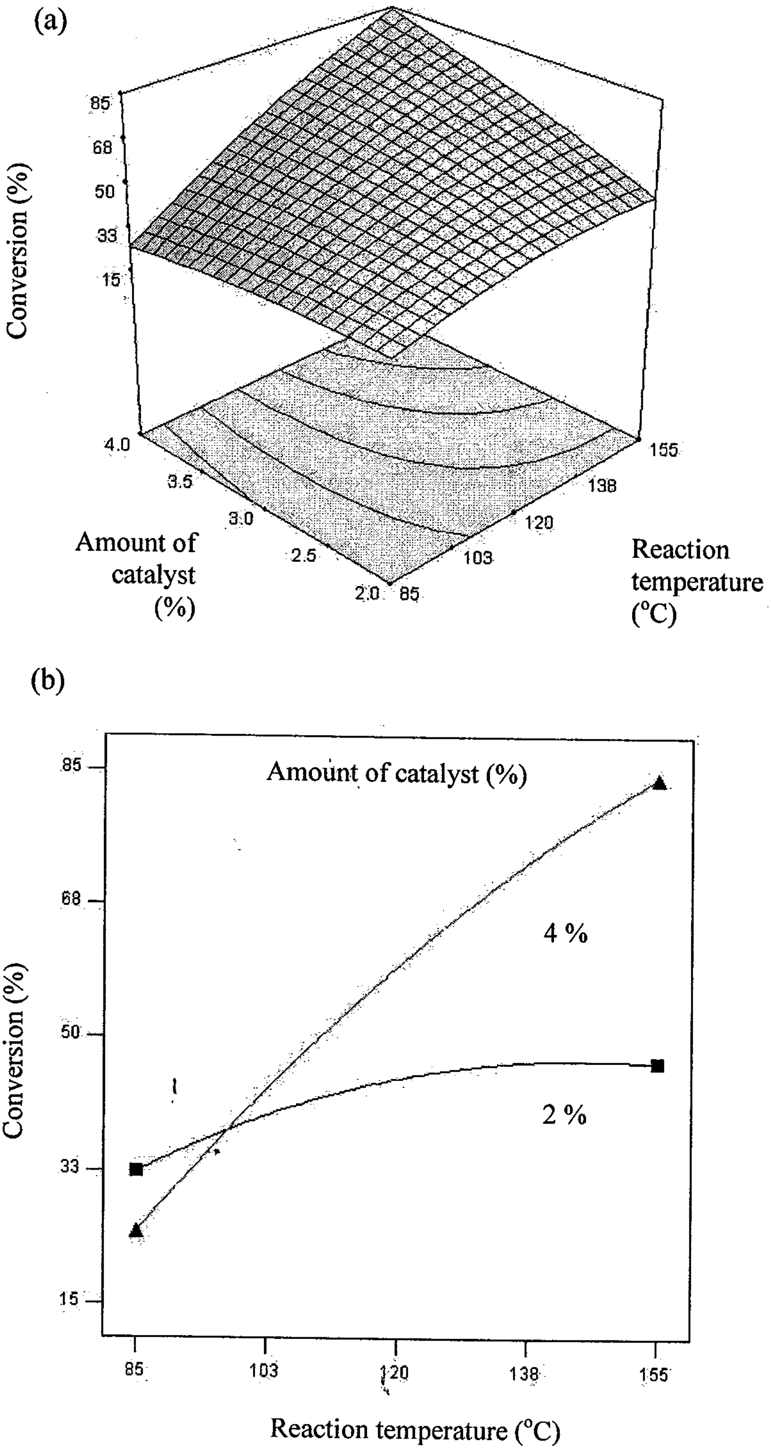
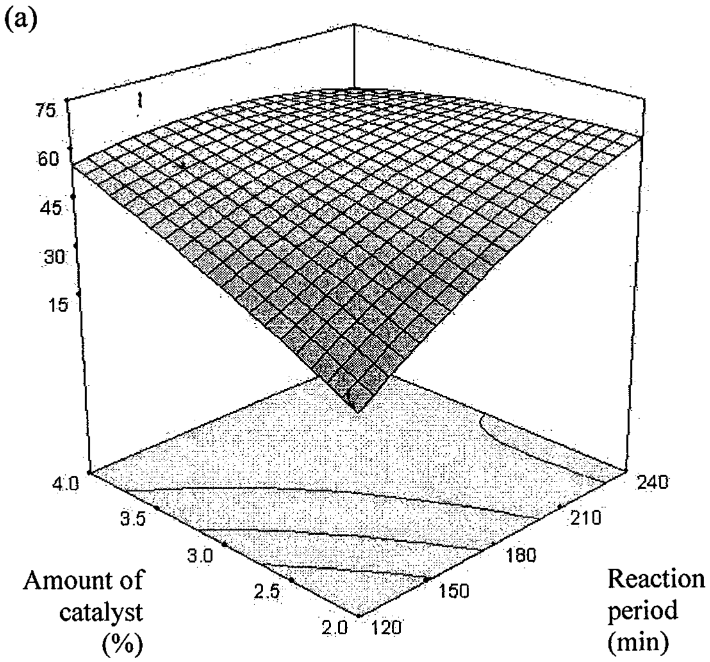


Figure 3: Effect of reaction temperature and amount of catalyst on the conversion of palm oil to biodiesel; (a) response surface plot and (b) two-dimensional drawing.

Figure 4 shows the changes in conversion with varying reaction period at 2% and 4% catalyst. The other two process variables; reaction temperature and ratio of oil to methanol were kept constant at 120 °C and 1:8 respectively. As in Figure 4, at shorter reaction period, 2% catalyst showed a significant lower conversion of palm oil to biodiesel compared to that of 4% catalyst. However, the conversion by 2% catalyst continues to steadily increase until it subsequently exceeds to that of 4% catalyst after 210 minutes of reaction. On the other hand, the 4% catalyst showed a fairly constant conversion for most of the time and slightly dropped when the reaction period is beyond 210 minutes. From this behavior, it can be said that the equilibrium of the reactions is reached rapidly with 4% catalyst, and after reaching the equilibrium, the transesterification reactions may become stagnant or start to reverse. The equilibrium of transesterification reactions by 2% catalyst may only reached after longer reaction time because of smaller active site availability, thus defines the staging increment of conversion by 2% catalyst from 120 min to 240 min. After all, the total rate of reactions, be it transesterification or reversed reaction, may directly be influenced by the total active sites of the catalyst, whereby higher active sites will accelerate both reactions.

4.0 Conclusion

Based on the experimental result obtained, it can be concluded that montmorillonite KSF could be used as an effective catalyst for the conversion of palm oil to biodiesel. However, future research on this catalyst is still required to investigate wider range of the parameters, and also new possible parameters which can be included in the reaction process such as the mixing intensity, reaction pressure and so forth.



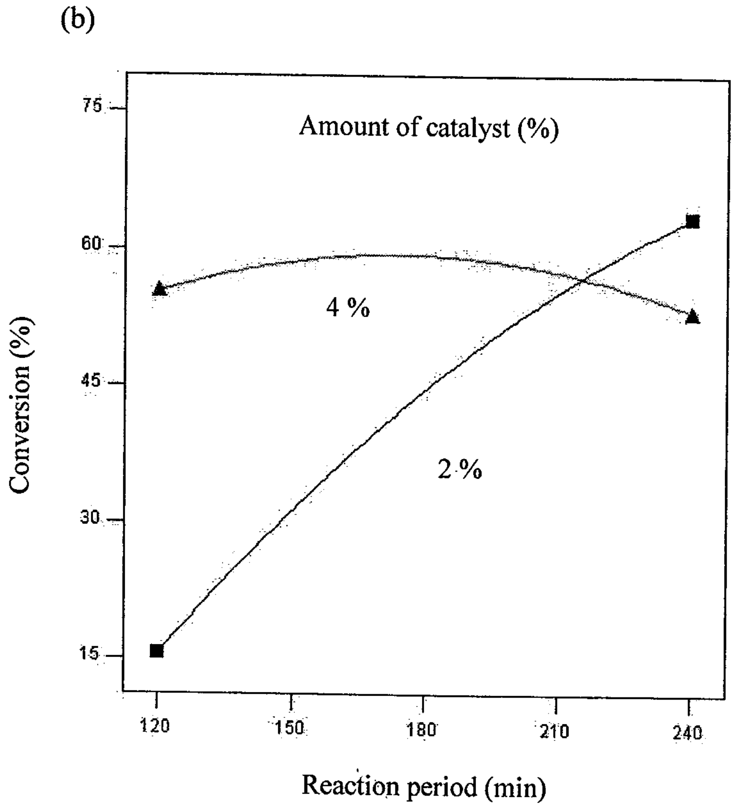


Figure 4: Effect of reaction period and amount of catalyst on the conversion of palm oil to biodiesel; (a) response surface plot and (b) two-dimensional drawing.

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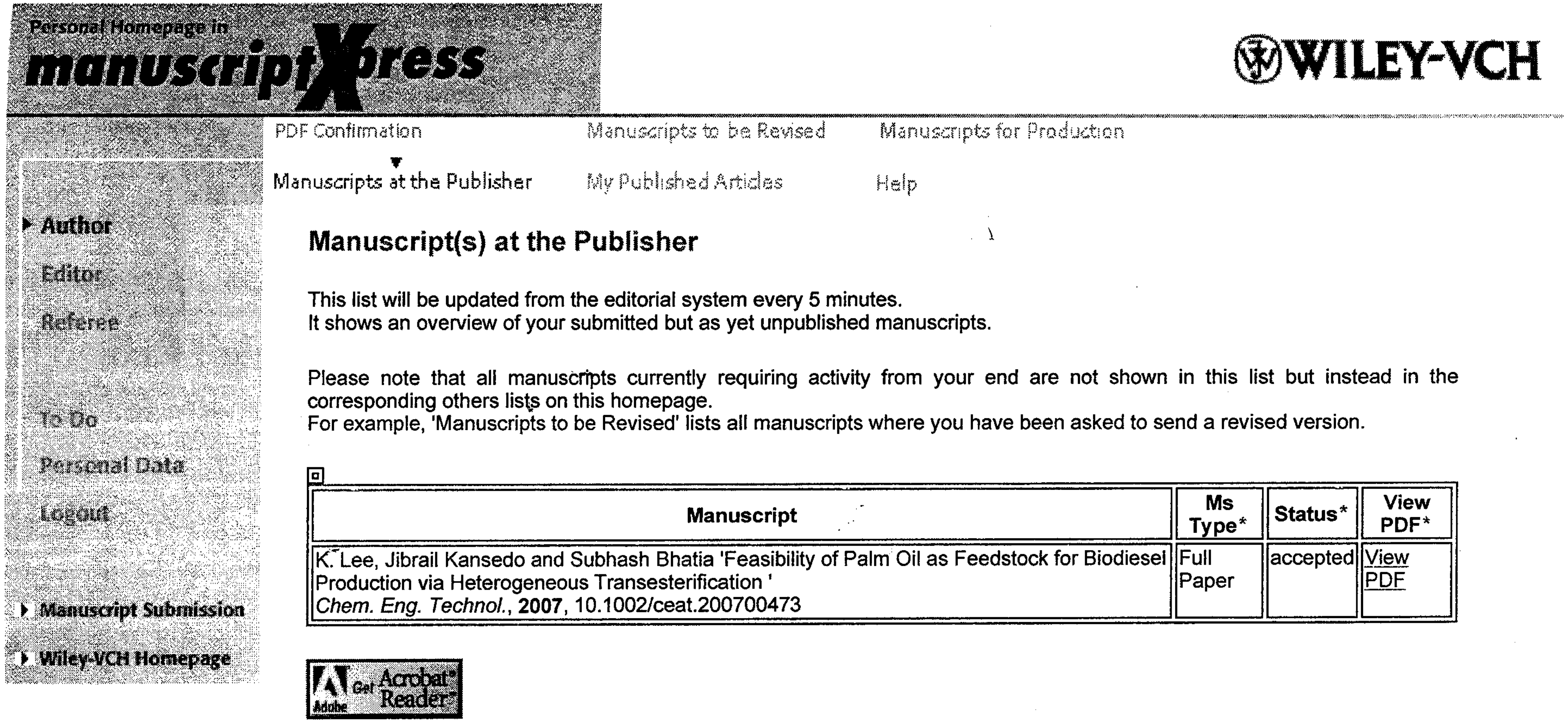

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Feasibility of Palm Oil as Feedstock for Biodiesel Production via Heterogeneous Transesterification

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Abstract

Production of biodiesel has become popular nowadays as a result of increasing demand for a clean, safe and renewable energy. Biodiesel is made from natural renewable sources such as vegetable oils and animal fats. The conventional method of producing biodiesel is by reacting vegetable oil with alcohol in the presence of homogenous catalyst (NaOH). However, this conventional method has some limitations such as the formation of soap, usage of lot wash water and complicated separation processes. On the other hand, heterogeneous process using solid catalysts has a lot of advantages over the homogenous methods. Apart from that, currently, more than 90% of world biodiesel is produced using rapeseed oil. Producing biodiesel from rapeseed oil is considered uneconomical, considering the fact that palm oil is currently the world cheapest vegetable oil. Therefore, the focus of this study is to show the feasibility of producing biodiesel from palm oil using montmorillonite KSF as the heterogeneous catalyst. The heterogeneous transesterification process was studied using design of experiment (DOE), specifically response surface methodology (RSM) based on four-variable central composite design (CCD) with $\alpha = 2$. The transesterification process variables were reaction temperature, x_1 (50-190 ^{o}C), reaction period, x_2 (60-300 min), methanol/oil ratio, x_3 (4-12 mol mol^{-1}) and amount of catalyst, x_4 (1-5% wt). It was found that the conversion of palm oil to biodiesel can reach up to 78.7% using the following reaction conditions; reaction temperature of 155 ^{o}C, reaction period at 120 min, ratio of methanol/oil at 10:1 mol mol^{-1} and amount of catalyst at 4%. From this study, it was shown that montmorillonite KSF catalyst can be used as a solid catalyst for biodiesel production from palm oil.

Keywords : biodiesel; transesterification; heterogeneous catalysts; montmorillonite KSF

1. Introduction

Due to escalating crude petroleum oil prices and the effect of global warming, a search for alternative fuels has gained significant attention over the years. Among the various sources of alternative energy, renewable energy from biomass presents a promising alternative to replace the conventional fossil fuels. In the recent years, a number of studies have shown that vegetable oil such as rapeseed [1], soybean [2-9] and sunflower seed [10-11] oil can be used as a source of biodiesel replacing conventional petroleum-derived diesel fuels. The biodiesel is produced through transesterification reaction where by the triglycerides present in vegetable oil is converted to fatty acid alkyl esters.

Transesterification, also called alcoholysis, is the reaction of the triglycerides in the vegetable oil with alcohol to form a mixture of fatty acid alkyl esters and glycerol [12-16]. The fatty acid alkyl esters produced from this process is known as biodiesel which has become more attractive recently because it has almost the same properties and characteristic of petroleum-derived diesel. Several studies have shown that biodiesel produced from vegetable oil have viscosity close to petroleum-derived diesel fuel [17,18]. Their volumetric heating values are a little lower compared to the petroleum-derived diesel fuel, but they have high cetane and flash point values.

Transesterification process is catalyzed by catalysts with both, acidic and basic sites. Currently, all the transesterification process goes through the homogenous transesterification process by mainly using potassium hydroxide as the catalyst [12-16].

In the homogeneous transesterification process, the catalysts used are in the same phase as the reactants/products. However, homogeneous transesterification process using potassium hydroxide presents certain disadvantages. Among some of the disadvantages are the formations of soap in the product mixture leading to additional cost required for the separation of soap from the biodiesel. Apart from that, the formation of soap has also led to the loss of triglycerides molecules that can be used to form biodiesel. Since the catalyst and the reactants/products are in similar phase, the separation of products (biodiesel) from the catalyst becomes complex.

These disadvantages make the current (homogeneous transesterification process) expensive, complex and uneconomical. In order to overcome these limitations, researchers are now looking for alternative routes to produce biodiesel from vegetable oil. One of the possible solutions is by using heterogeneous transesterification process whereby solid catalyst is used. Recent researches have shown that there are various types of catalyst that can be used in the heterogeneous transesterification process. Jitputti *et al.* [19] studied the transesterification of coconut oil and palm kernel oil using zirconium oxide-based and zinc oxide-based catalyst, while Suppes *et al.* [2] used zeolite and metal catalyst for the conversion of soybean oil to biodiesel. In other research, heterogeneous base [20], $Na/NaOH/Al_2O_3$ [21] and metal complexes [3] are used as the catalyst.

Currently more than 90% of the world biodiesel is produced from rapeseed oil. However, due to the high price of rapeseed seed oil, the use of biodiesel replacing conventional petroleum-derived diesel oil can only be used in developed countries in

Europe and USA. In order to overcome this problem, researchers have been trying to source for other types of vegetable oil that is cheaper such as palm oil [22], jatropha oil [23,24], soybean oil [3-9], canola oil [25] and even waste cooking oil [26,27]. Since palm oil is the worlds' cheapest vegetable oil, it presents a promising alternative as a feedstock for biodiesel production replacing rapeseed oil. Nevertheless the study on converting palm oil to biodiesel using heterogeneous reaction is still very limited.

Thus, in this study, the feasibility of producing biodiesel from palm oil using montmorillonite KSF as the heterogeneous catalyst will be presented. Statistical design of experiments will be used to accumulate and analyze information on the effect of process variable on the conversion of palm oil to biodiesel rapidly and efficiently using minimum number of experiments. As illustrated in the later section, this method was found superior than the conventional method of studying one variable at one time while keeping the rest constant.

2. Materials and Methods

2.1 Materials

Purified palm oil was purchased from Yee Lee Edible Oils Sdn Bhd, Malaysia and methanol from R & M Chemicals, UK. Montmorillonite KSF, methyl heptadecanoate (internal standard) and standard references for methyl esters analysis; methyl myristate, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate were obtained from Fluka Chemie, Germany. The catalyst, montmorillonite KSF, has humidity of ≤ 12 %, free acid of 8 – 12 %, and has its surface partially laid with H_2SO_4. The properties of palm oil are given in the Tab. 1 [28].

2.2 Design of experiments

The experimental design selected for this study is a Central Composite Design (CCD) that helps in investigating linear, quadratic, cubic and cross-product effects of the four transesterification process variables (independent) on the conversion of palm oil to biodiesel (response). The four transesterification process variables studied are reaction temperature, reaction period, ratio of oil to methanol and amount of catalyst. Tab. 2 lists the range and levels of the four independent variables studied. The CCD comprises a two-level small factorial design ($\frac{1}{2} \times 2^4 = 8$), eight axial or star points and five center points. The value of α for this CCD is fixed at 2. The complete design matrix of the experiments employed and results are given in Tab. 3. All variables at zero level constitute to the center points and the combination of each of the variables at either its lowest (-2.0) level or highest (+2.0) level with the other variables at zero level constitute the axial points. The experiment sequence was randomized in order to minimize the effects of the uncontrolled factors.

Each response of the transesterification process was used to develop a mathematical model that correlates the conversion of palm oil to the transesterification process variables studied through first order, second order and interaction terms, according to the following second order polynomial equation,

$$Y = b_o + \sum_{j=1}^{4} b_j x_j + \sum_{ij=1}^{4} b_{ij} x_i x_j + \sum_{j=1}^{4} b_{jj} x_j^2 \qquad (1)$$

where Y is the predicted conversion of palm oil to biodiesel, mol mol^{-1}, x_i and x_j represent the variables or parameters, b_o is the offset term, b_j is the linear effect, b_{ij} is the first order interaction effect and b_{jj} is the squared effect.

2.3 Model fitting and statistical analysis

Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) was used for regression analysis of the experimental data to fit the second order polynomial equation and also for evaluation of the statistical significance of the equation developed.

2.4 Activity study

Transesterification reactions were carried out in a low pressure batch reactor with a magnetic stirrer, as shown in the Figure 1. Mixture of palm oil, catalyst and methanol was charged into the reactor. The mixing intensity of the magnetic stirrer was set at 190-200 rpm. The reaction temperature, duration, ratio of oil/methanol and amount of catalyst (montmorillonite KSF) were set according to the values as proposed in the DOE shown in Tab. 3. The excess methanol from the samples was removed using rotary evaporator. The upper layer of the sample was separated from the bottom layer and was analyzed to detect biodiesel content.

2.5 Analysis

The resulting products from the transesterification processes were analyzed using Gas Chromatography (GC) by means of Inert Cap WAX capillary column (30 mm x 0.25 mm, I.D. 0.25 μm) to identify the presence of methyl esters (biodiesel) in the sample. Helium was used as the carrier gas. Oven temperature at 120 °C was initially hold for 1 minute and then increased to 220 °C (hold 15 minute) at a rate of 4 °C min^{-1}. The temperatures of the injector and detector were set at 220 °C and 250 °C respectively. A quantity of 1 μl from each sample was injected into the column. Methyl heptadecanoate was used as internal standard for the calculation of the conversion. The conversions of the transesterification processes were calculated as mol ratio of methyl esters produced to palm oil used divided by 3. The formula is given as:

$$\text{Conversion, \%} = \frac{\text{Total mol of methyl esters}}{3 \times \text{Total mol of oil}} \times 100\,\% \qquad (2)$$

3. Results and Discussion

3.1 Development of regression model equation

A central composite design (CCD) was used to develop a correlation between the transesterification reaction variables to the conversion of palm oil to biodiesel. The complete design matrix and conversion of palm oil to biodiesel (responses) are listed in Tab. 3. As can be seen from Tab. 3, the conversion of palm oil to biodiesel range from 0.79% to 78.69%. Runs K17 to K21 at the center point of the design are to determine the experimental error. As the result of conversion of these five runs were quite consistent, single replicate experimental run is essential in this study. Apart from that, from results of these five runs, the experimental error for the conversion of palm oil to biodiesel could be calculated as 1.2%.

By using multiple regression analysis, the response (conversion of palm oil to biodiesel) obtained in Tab. 3 was correlated with the four transesterification reaction variables/parameters studied using the polynomial equation as shown in Equation (1). The coefficients of the full regression model equation and their statistical significance were determined and evaluated using Design-Expert 6.0.6 software. The final equation in terms of actual value after excluding the insignificant terms (identified using Fisher's Test) is

$$\begin{aligned} Y = {} & 54.50 + 18.39x_1 + 11.39x_2 + 4.20x_3 + 7.36x_4 - 5.02x_1^2 - 5.09x_2^2 - 3.42x_3^2 - \\ & 2.60x_4^2 + 6.52x_1x_2 + 4.34x_1x_3 + 11.31x_1x_4 - 12.51x_2x_4 \end{aligned} \tag{3}$$

Positive sign in front of the terms indicates synergistic effect, while negative sign indicates antagonistic effect. Equation (3) shows that the conversion of palm oil to biodiesel has a linear and quadratic effect on the four transesterification process variables studied. Apart from that, interactions between the variables also effect the conversion of palm oil to biodiesel.

3.2 Model adequacy check

The quality of the model developed could be evaluated from their coefficients of correlation. The value of R for Equation (3) is 0.9846. The high value of R (very close to 1) shows that there is a very good agreement between the experimental and predicted value from the model. On the other hand the value of R^2 for Equation (3) is 0.9515. It implies that 95.15% of the total variation in the conversion of palm oil to biodiesel responses is attributed to the experimental variables studied. The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in Tab. 4. Based on a 95% confidence level, the model was tested to be significant as the computed F value (42.67) is much higher than the theoretical $F_{0.05\,(12,8)}$ value (3.28), indicating that the regression model is reliable in predicting the conversion of palm oil to biodiesel. Apart from that, each term in the model was also tested to be significant at a 95% confidence level as the computed F values for the respective terms are higher than the theoretical $F_{0.05\,(1,8)}$ value (5.32). From these statistical tests, it was found that the model is adequate for predicting the conversion of palm oil to biodiesel within the range of variables studied.

Figure 2 shows the experimental values versus predicted values using the model equation developed. A line of unit slope, i.e. the line of perfect fit with points corresponding to zero error between experimental and predicted values is also shown in Figure 2. This plot therefore visualizes the performance of the model in an obvious way. The results in Figure 2 demonstrated that the regression model equation provided a very accurate description of the experimental data, indicating that it was successful in capturing the correlation between the four transesterification process variables to the conversion of palm oil to biodiesel.

3.3 Effects of transesterification process variables

From Tab. 4, it was observed that among the four individual variables studied, reaction temperature (x_1) has the largest effect on the conversion of palm oil to biodiesel (due to the highest F value) followed by reaction period (x_2). Ratio of oil/methanol (x_3) and amount of catalyst (x_4) have similar least significant effect on the conversion of palm oil to biodiesel. The quadratic term of (x_1) and (x_2) were fairly significant on the conversion of palm oil to biodiesel compared to that of (x_3) and (x_4). The other significant terms include the effect of interaction between variables, particularly between variables (x_2) and (x_4) and between variables (x_1) and (x_4). Longer reaction period allows sufficient time for the transesterification process to occur completely, or at least, until the maximum level. Higher reaction temperature allows transesterification reactions occur at accelerated rate since there's supply of more energy to the reactions. On the other hand, larger amount of catalyst used will results in higher conversion of triglycerides to biodiesel because of higher availability of active sites. Apart from that, higher ratio of oil/methanol, 1:10, gives higher conversion as excess methanol is required to push the transesterification reaction forward. All these results are in agreement with those reported in the literature [13].

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However, since the maximum conversion occurs at the border of the experimental variables selected for this study, optimum experimental conditions to obtain the highest conversion cannot be derived (except for the experimental conditions at the border of the design variables). This finding was also supported by the model developed using the DOE software whereby no maximum conversion was located within the experimental domain examined. Therefore, the model developed by the DOE software was used to facilitate a straight forward examination of the effects of the variables and their interaction towards the conversion of the transesterification process. Among the four interaction terms that were found to have significant effect on the conversion of palm oil to biodiesel, emphasis were given to the interaction between (x_2) and (x_4) and between variables (x_1) and (x_4).

Figure 3 shows the changes in conversion with varying reaction temperature at 2% and 4% catalyst. The other two process variables; reaction period and ratio of oil to methanol were kept constant at 180 min and 1:8 respectively. It is generally perceived that higher percentage of catalyst used will results in higher conversion of triglycerides to biodiesel because of higher availability of active sites. However, this perception may not always be true. Referring to Figure 3, the conversion of oil to biodiesel was found to be lower at 4% catalyst as compared to 2% catalyst when the reaction temperature was lower than 95 °C. This may suggest the real interactions between the supplied energy (heat) and the active site on the catalyst itself. The active sites on the catalysts may require a certain amount of energy to be activated. At lower temperature, smaller percentage of catalyst, 2%, will reach the activation energy more quickly than the 4% catalyst because the ratio of active site to energy (heat) is smaller. In other words, the total energy required to activate the whole active sites on the 2% catalyst is much smaller than those for 4% catalyst. Thus, lower temperature (small energy) may just be enough to activate the whole active site on the 2% catalyst but not for the 4% catalyst because of the assumption of fair distribution of energy to all active sites. Thus, the transesterification reactions by 2% catalysts will commence sooner, while the 4% catalyst will show delay in transesterification reactions. However, as activation energy for all catalyst in the 4% is fully achieved at higher temperature, the reactions will proceed rapidly and subsequently exceeds to that of 2% catalyst. Thus, only when the reaction temperature is sufficient to activate all the active sites of the catalyst, then only the perception that higher amount of catalyst will results in higher conversion applies. These results demonstrate the capability of using systematical statistical design where by the effect of interaction between variables can be identified easily as compared to the conventional method of studying one variable at one time.

Figure 4 shows the changes in conversion with varying reaction period at 2% and 4% catalyst. The other two process variables; reaction temperature and ratio of oil to methanol were kept constant at 120 °C and 1:8 respectively. As in Figure 4, at shorter reaction period, 2% catalyst showed a significant lower conversion of palm oil to biodiesel compared to that of 4% catalyst. However, the conversion by 2% catalyst continues to steadily increase until it subsequently exceeds to that of 4% catalyst after

210 minutes of reaction. On the other hand, the 4% catalyst showed a fairly constant conversion for most of the time and slightly dropped when the reaction period is beyond 210 minutes. From this behavior, it can be said that the equilibrium of the reactions is reached rapidly with 4% catalyst, and after reaching the equilibrium, the transesterification reactions may become stagnant or start to reverse. The equilibrium of transesterification reactions by 2% catalyst may only reached after longer reaction time because of smaller active site availability, thus defines the staging increment of conversion by 2% catalyst from 120 min to 240 min. After all, the total rate of reactions, be it transesterification or reversed reaction, may directly be influenced by the total active sites of the catalyst, whereby higher active sites will accelerate both reactions.

4. Conclusion

Based on the experimental result obtained, it can be concluded that montmorillonite KSF could be used as an effective catalyst for the conversion of palm oil to biodiesel. However, future research on this catalyst is still required to investigate wider range of the parameters, and also new possible parameters which can be included in the reaction process such as the mixing intensity, reaction pressure and so forth.

Acknowledgement

The authors would like to thank Universiti Sains Malaysia for providing fund for this project.

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List of Tables

Table 1. Properties of palm oil

Fatty acids	Percentage (%)
Lauric, C-12:0	0.1
Myristic, C-14:0	1.0
Palmitic, C-16:0	42.8
Stearic, C-18:0	4.5
Oleic, C-18:1	40.5
Linoleic, C-18:2	10.1
Linolenic, C-18:3	0.2
Other/Unknown	0.8

Table 2. Levels of the transesterification process variables chosen for this study

Variable	Coding	Unit	Levels				
			- 2	- 1	0	+ 1	+ 2
Reaction temperature	x_1	°C	50	80	120	155	190
Reaction period	x_2	min	60	120	180	240	300
Ratio of oil/methanol	x_3	mol mol^{-1}	1:4	1:6	1:8	1:10	1:12
Amount of catalyst	x_4	%	1	2	3	4	5

Table 3. Experimental design matrix and results

Catalyst Code	Experimental variables				Conversion, %
	Reaction temperature (°C)	Reaction period (min)	Ratio of oil/ methanol (mol mol^{-1})	Amount of catalyst (% g)	
K01	+1	+1	+1	-1	71.63
K02	+1	+1	-1	-1	59.10
K03	+1	-1	+1	+1	78.69
K04	-1	+1	-1	+1	5.07
K05	+1	-1	-1	+1	55.10
K06	-1	-1	+1	-1	3.92
K07	-1	+1	+1	+1	5.43
K08	-1	-1	-1	-1	2.90
K09	-2	0	0	0	0.79
K10	+2	0	0	0	74.34
K11	0	-2	0	0	14.49
K12	0	+2	0	0	60.05
K13	0	0	-2	0	36.52
K14	0	0	+2	0	51.39
K15	0	0	0	-2	32.54
K16	0	0	0	+2	61.98
K17	0	0	0	0	55.07
K18	0	0	0	0	50.88
K19	0	0	0	0	55.75
K20	0	0	0	0	55.07
K21	0	0	0	0	55.75

Table 4. Analysis of variance (ANOVA) for the regression model equation and coefficients

Source	Sum of squares	Degrees of freedom	Mean of squares	F-test
Model	13390.31	12	1115.86	42.67
x_1	2704.80	1	2704.80	103.43
x_2	1037.86	1	1037.86	39.69
x_3	282.58	1	282.58	10.81
x_4	433.36	1	433.36	16.57
x_1^2	632.50	1	632.50	24.19
x_2^2	651.22	1	651.22	24.90
x_3^2	294.00	1	294.00	11.24
x_4^2	169.18	1	169.18	6.47
$x_1 x_2$	169.91	1	169.91	6.50
$x_1 x_3$	150.86	1	150.86	5.77
$x_1 x_4$	511.90	1	511.89	19.57
$x_2 x_4$	626.25	1	626.25	23.95
Residual	209.21	8	26.15	

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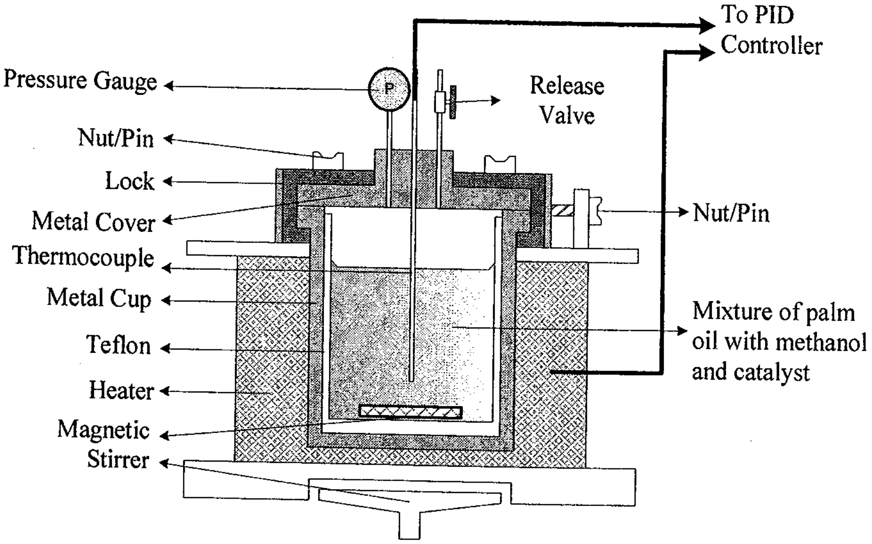

Figure 1. Schematic diagram of the experimental set-up for the transesterification process

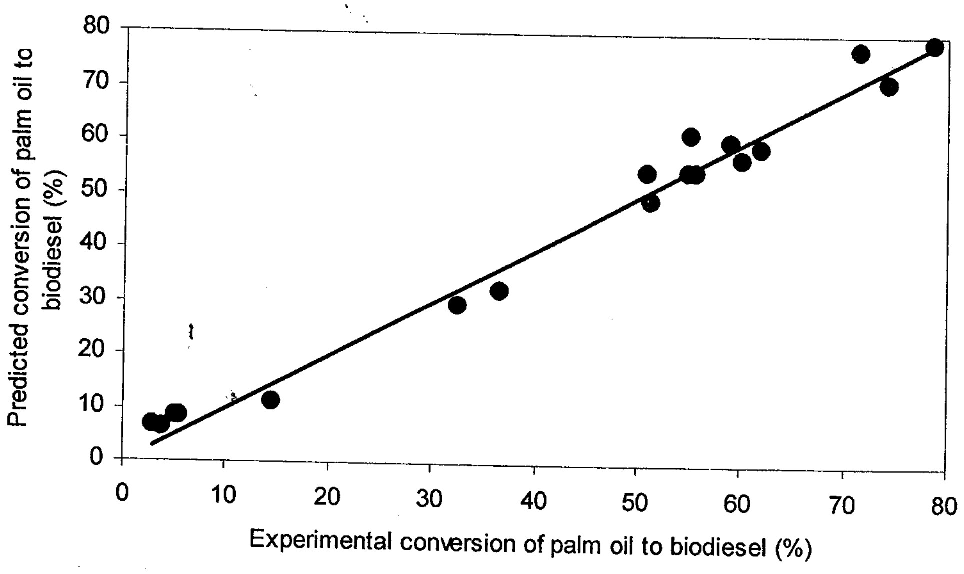

Figure 2. Experimental versus predicted conversion of palm oil to biodiesel

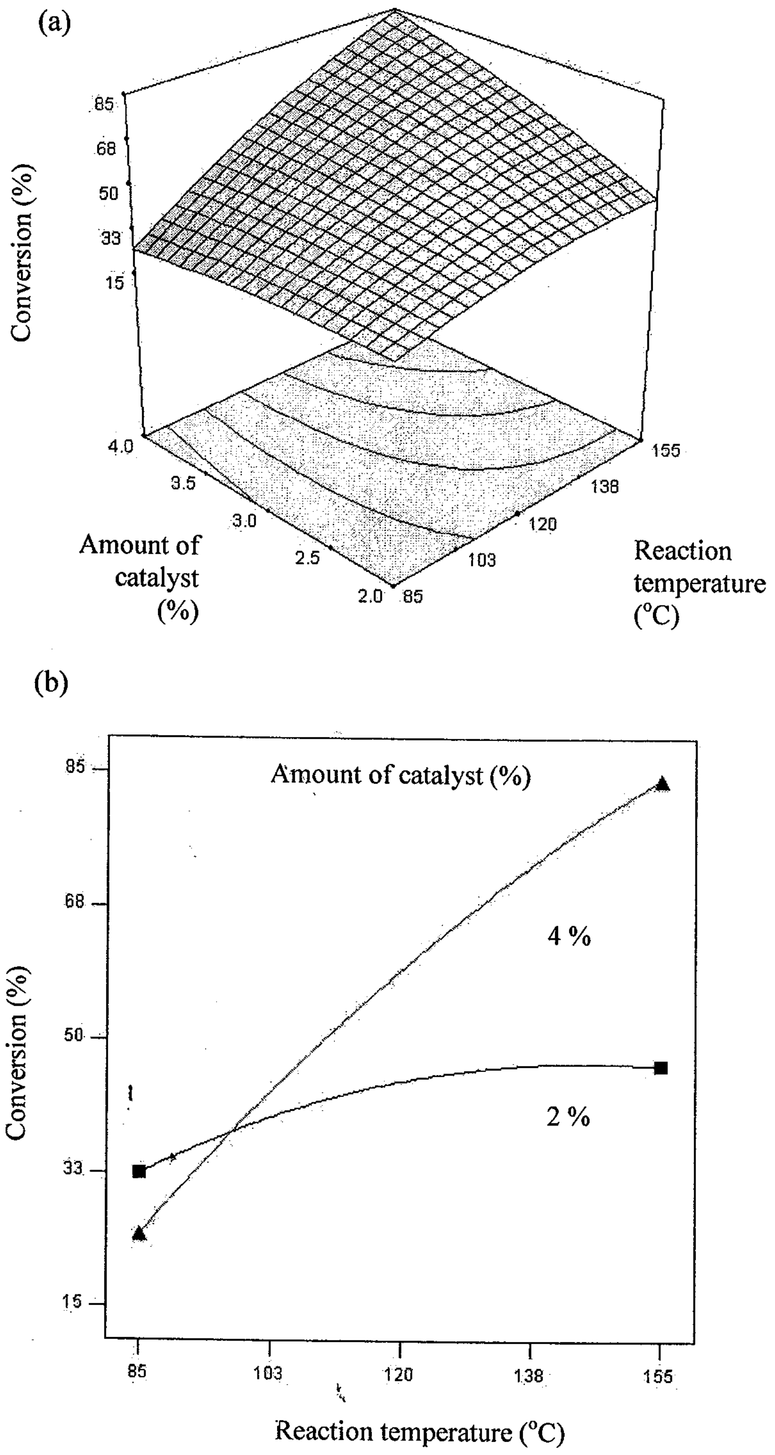

Figure 3. Effect of reaction temperature and amount of catalyst on the conversion of palm oil to biodiesel; (a) response surface plot and (b) two-dimensional drawing.

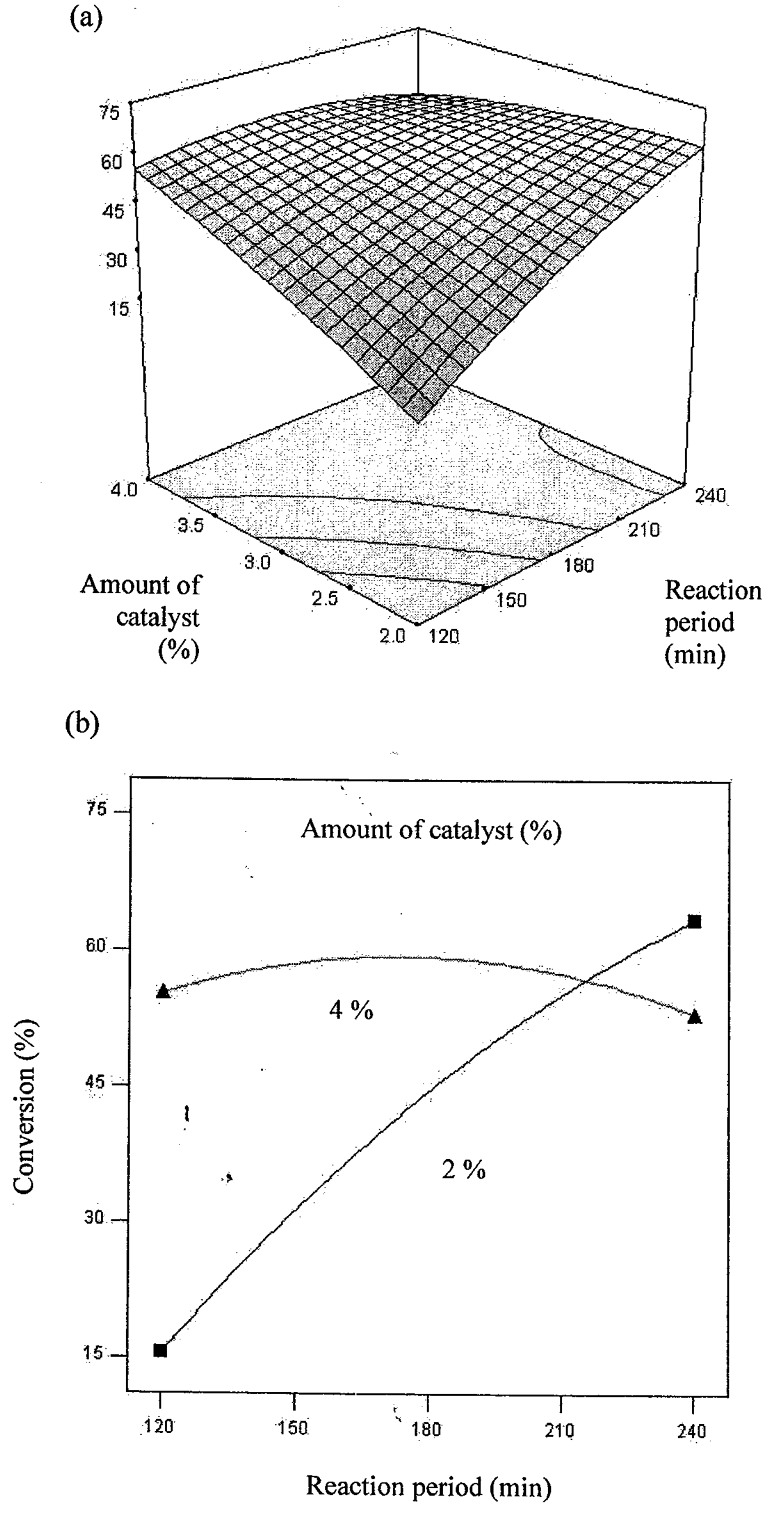

Figure 4. Effect of reaction period and amount of catalyst on the conversion of palm oil to biodiesel; (a) response surface plot and (b) two-dimensional drawing.

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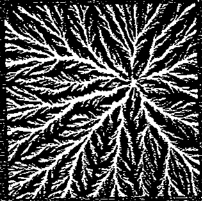
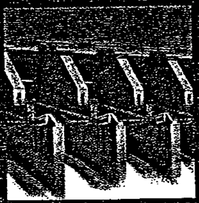
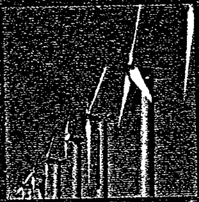


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Transesterification of Palm Oil to Biodiesel Using Solid Catalyst

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Being the cheapest vegetable oil in the world, palm oil from Malaysia has a very bright potential to be converted to renewable liquid fuels such as biodiesel. In this study, the conversion of palm oil to biodiesel via heterogeneous transesterification route using three different types of solid catalyst were investigated. The transesterification reaction was carried out in a batch reactor over a wide range of operating conditions; reaction temperature ranging from 65 to 150°C and reaction period ranging from 0 to 180 min. The effect of oil to methanol ratio and catalyst loading was also investigated. The results obtained using the solid catalyst was then compared to those obtained using homogeneous catalyst (potassium hydroxide). The three types of solid catalyst studied, sodium carbonate (Na_2CO_3), trisodium phosphate (Na_3PO_4) and trisodium phosphate dodecahydrate ($Na_3PO_4.12H_2O$) was found to exhibit very promising results, suggesting that they could be suitable alternatives to homogenous catalysts for the production of biodiesel from palm oil. Generally, the conversion of palm oil to biodiesel was found to increase at higher reaction temperature and reaction time. Among the three types of catalyst studied, trisodium phosphate was found to exhibit the highest activity for the conversion of palm oil to biodiesel.

Potential of crop residues as energy source in Pakistan

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Pakistan is an agrarian country. Biomass is the main source of energy in the country like other many developing countries and accounts for about 37% of total primary energy supply mix. About 68% of country's population lives in rural areas and are linked with agriculture. Traditionally, the rural masses have been dependent on fuel wood and agro-residues due to poverty and non-availability of local fossil resources in the country. The people in rural areas meet about 95% of their domestic fuel needs by burning biomass such as wood, crop residues, animal dung etc in traditional inefficient cook stoves. The crop residues has 17% share in total biomass consumption in rural household sector of Pakistan. In the present study, the energy potential of crop residue has been estimated and presented. The paper concludes that agricultural crop residue has theoretical energy potential of about 35 MTOE. About half of the crop residues produced in the country could be utilized as energy source for cooking, heating and co-generation purposes. Residues of crops like sugar cane, cotton and rice are of paramount significance for energy point of view.

Transesterification of Palm Oil to Biodiesel Using Solid Catalyst

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Being the cheapest vegetable oil in the world, palm oil from Malaysia has a very bright potential to be converted to renewable liquid fuels such as biodiesel (methyl esters). In this study, the conversion of palm oil to biodiesel via heterogeneous transesterification route using three different types of solid catalyst were investigated. The transesterification reaction was carried out in a batch reactor over a wide range of operating conditions; oil to methanol ratio ranging from 1:6 to 1:18 and reaction period ranging from 1 to 4 h. The effect of catalyst loading was also investigated. The results obtained using the solid catalyst was then compared to those obtained using homogeneous catalyst (potassium hydroxide). The three types of solid catalyst studied, sodium carbonate (Na_2CO_3), trisodium phosphate (Na_3PO_4) and trisodium phosphate dodecahydrate ($Na_3PO_4.12H_2O$) was found to exhibit very promising results, suggesting that they could be suitable alternatives to homogenous catalysts for the production of biodiesel from palm oil. Generally, the yield of methyl esters was found to increase at higher reaction period. Among the three types of catalyst studied, trisodium phosphate was found to exhibit the highest yield for the conversion of palm oil to methyl esters.

Keywords: biodiesel, catalyst, palm oil.

1. Introduction

The increasing crude oil prices and the effect of global warming have instigated the need for an alternative fuel. In the recent years, many research has shown that vegetable oils such as rapeseed, sunflower oil, palm oil and soybean oil are potential renewable resources that can be converted to biodiesel, replacing the petroleum-based diesel oil [1-5]. Currently, more than 95% of the world biodiesel are produced from rapeseed oil and sunflower oil. However, since palm oil is one of the world's cheapest vegetable oil, it has a bright future to be made the main feed stock for biodiesel production in the near future. What make the potential even greater is that palm oil is at least US$ 200 (US$ 1 = RM 3.77) a tonne cheaper than rapeseed oil.

Vegetable oil is converted to biodiesel mainly through the transesterification process in which triglycerides present in vegetable oil such as palm oil reacts with alcohol and is converted to fatty acid alkyl esters (or simply, methyl esters). The fatty acid alkyl esters produced from this process is known as biodiesel which has become more attractive recently because it has almost the same properties and characteristic of petroleum-based diesel.

Transesterification process is catalyzed by catalysts with both, acidic and basic sites. Currently, most of the transesterification process goes through the homogenous transesterification process by mainly using potassium hydroxide as the catalyst. However, homogeneous transesterification process presents certain disadvantages such as the separation of catalyst after the reaction and the difficulty in recovering pure glycerol. On the other hand, heterogeneous transesterification process has the potential to overcome the homogeneous transesterification process. Recently, it was reported that sodium phosphates compounds can act as a reactive heterogeneous catalyst for the transesterification process of rapeseed oil to biodiesel (methyl esters) [6]. Therefore, the aim of this study to investigate the possibility of using 3 different sodium phosphates compounds for heterogeneous transesterification of palm oil to biodiesel (methyl esters). The yield of methyl esters in the heterogeneous reaction was then compared with those obtained from the conventional homogeneous reaction. One of the three sodium phosphates compounds will also be selected for optimization study.

2. Methods

2.1 Materials

The palm oil used in this study is commercial grade refined palm oil. Typical fatty acid composition of palm oil is given in Table 1 indicating that the two most significant fatty acids in palm oil are palmitic acid and oleic acid. The homogeneous catalyst used is potassium hydroxide (KOH) while the heterogeneous catalyst used are sodium carbonate (Na_2CO_3), trisodium phosphate (Na_3PO_4) and trisodium phosphate dodecahydrate ($Na_3PO_4.12H_2O$). All the chemicals used were supplied from Merck including methanol.

Table 1: Fatty Acid Composition in Palm Oil

Fatty Acids	Composition
C12:0 Lauric	0.2%
C14:0 Myristic	1.1%
C16:0 Palmitic	44.0%
C18:0 Stearic	4.5%
C18:1 Oleic	39.2%
C18:2 Linoleic	10.1%
Others	0.9%

2.2 Experimental apparatus and procedure

The transesterification reaction was carried out in a 250 ml round bottom flask reactor equipped with heater, temperature controller, mechanical stirrer and reflux condenser. For the homogeneous reaction, 100 ml of palm oil was loaded in the reactor. Then, KOH (1% (w/w) with respect to oil) was dissolved in methanol (6:1 (methanol:oil) molar ratio) and the resulting solution was added in the reactor. The reaction was timed as soon as the KOH/methanol solution was added in the reactor and was continued for 1 h under heating at the boiling point of methanol. Upon completion, the mixture was transferred to a separatory funnel, allowing glycerol to separate by gravity overnight. Upon separation of glycerol, the mixture was distilled to remove the excess methanol and then washed with excess water several times to remove KOH and the remaining glycerol and methanol. The methyl ester phase was then analyzed to calculate the biodiesel yield. In the heterogeneous reactions, the amount of solid catalyst used was based on the mol ratio of oil to catalyst of 1:0.04. The procedure to run the heterogeneous reaction is similar to the homogeneous reaction except that after the removal of excess methanol through distillation, the methyl ester phase is filtered to remove the solid catalyst. Apart from that, the reaction time, amount of catalyst used and oil to methanol ratio was also changed accordingly in some reactions.

2.3 Analytical methods

The methyl ester content in the transesterification product was analyzed using a Hewlett Packard 5890/II gas chromatography equipped with a flame ionization detector. NUKOL column is used with the following specifications: 15 m in length, 0.53 mm internal diameter and a film thickness of 0.5 μm. Other main operating parameters are: helium as carrier gas; injector temperature of 220 °C; detector temperature of 250 °C; temperature program of 80 – 220 °C at 10 °C/min; injection sample volume of 0.2 μL.

3.0 Results and Discussion

Table 2 shows the yield of methyl ester using KOH as the homogeneous catalyst and various other sodium phosphates compounds as the heterogeneous catalysts. All the transesterification reactions were carried out according to the homogeneous transesterification reaction as described earlier so that comparison can be made. When KOH is used as the catalyst, the yield of methyl ester was found to be 91.5%. This value was found to agree well with those reported in the literature [7].

Table 2 : Yield of methyl ester using various catalysts

Catalyst	Yield (%)
KOH	91.5
Na_2CO_3	16.7
Na_3PO_4	26.4
$Na_3PO_4.12H_2O$	25.4

On the other hand, the yield of methyl ester using various other solid catalyst were found to be significantly lower. This is most probably due to the short reaction period and low reaction temperature used in the reaction. It was reported that heterogeneous catalyst generally requires higher reaction temperature or longer reaction time [8]. Never the less, the results in Table 2 shows that the three sodium compounds indeed has a potential to be utilized as a heterogeneous catalyst for the conversion of palm oil to biodiesel (methyl esters). Among the three types of sodium phosphate compound catalysts studied, Na_3PO_4 was selected to be further studied in order to increase the yield of methyl ester.

Figure 1 shows the effect of reaction time on the yield of methyl esters when Na_3PO_4 is used as the solid catalyst. The yield of methyl esters was found to increase when the reaction time was increased from 1 h to 2 h. However, beyond 2 h, no further increase in the yield of methyl esters was observed. This result indicated that the transesterification reaction was completed after 2 h of reaction period.

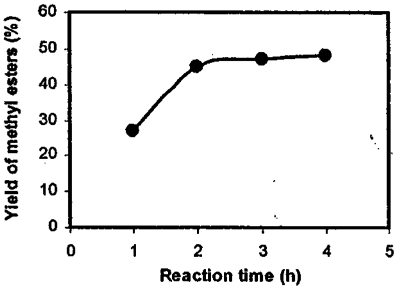

Figure 1 : Effect of reaction time on the yield of methyl esters. Oil:methanol:catalyst molar ratio of 1:6:0.04

Figure 2 shows the effect of oil to methanol ratio on the yield of methyl esters. From Figure 2, it was observed that the optimum oil to methanol ratio is about 1:9, giving a methyl esters yield of about 80%. It was reported in the literature that for typical homogeneous transesterification reaction, the optimum oil to methanol ratio should be about 1:6 [8]. However, as indicated from the results in Figure 2, higher amount of methanol is required to push the reaction towards the formation of methyl esters when Na_3PO_4 is used as the catalyst. Higher oil to methanol ratio reduces the yield of methyl esters generally due to the increased solubility of glycerol.

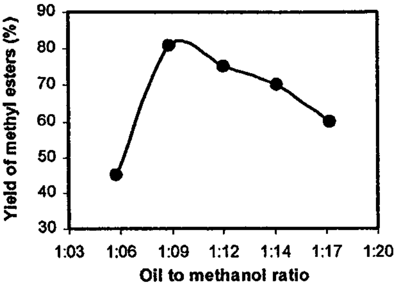

Figure 2 : Effect of oil to methanol ratio on the yield of methyl esters. Oil:catalyst molar ratio of 1:0.04 and reaction time of 2 h.

Figure 3 shows the effect of the amount of catalyst on the yield of methyl esters. The yield of methyl esters was found to increase from about 27% to 65% when the amount of catalyst used was increased from 0.5 g to 1.5 g. However, when the amount of catalyst was further increased, a slight dropped in the yield of the methyl esters was observed. This is probably due to the excess amount of the catalyst that interferes with the transesterification reaction.

4.0 Conclusion

This study has demonstrated that sodium phosphate compounds especially trisodium phosphate (Na_3PO_4) has the potential to be utilized as a solid catalyst for heterogeneous transesterification of palm oil to biodiesel (methyl esters). With specific reaction conditions (optimum conditions), the yield of methyl esters was found to be able to achieve as high as 80% (almost similar to the yield of homogeneous transesterification reaction).

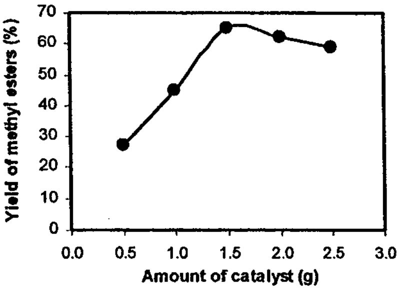

Figure 3 : Effect of amount of catalyst on the yield of methyl esters. Oil:methanol molar ratio of 1:6 and reaction time of 1 h.

Acknowledgement

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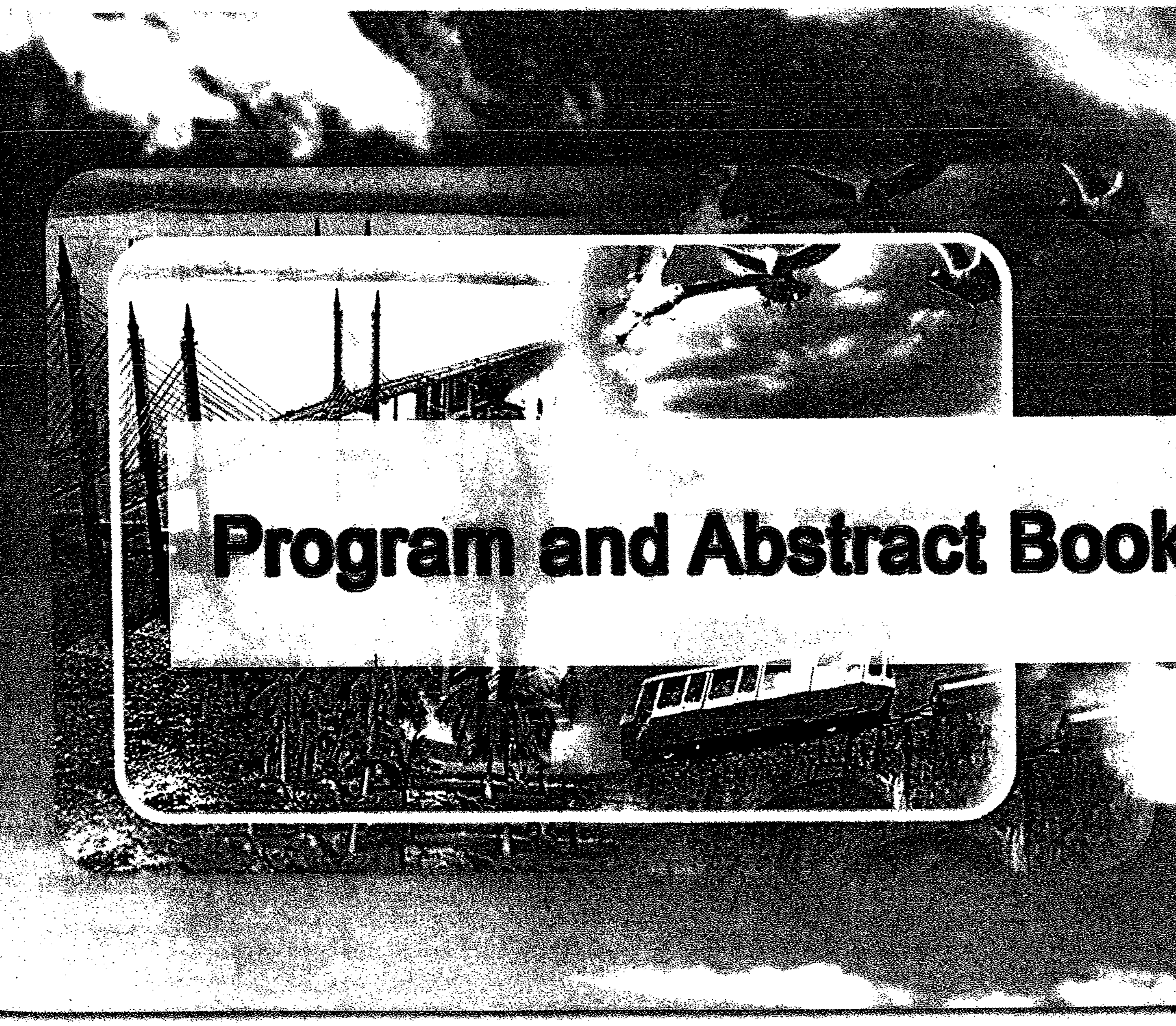

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DEVELOPMENT OF NOVEL CATALYSTS FOR THE PRODUCTION OF BIODIESEL FROM CRUDE PALM OIL: A REVIEW

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ABSTRACT

The production of bio-diesel has become more important and popular recently due to the increasing global demand for clean fuel and the increasing price of petrodiesel. As generally known, biodiesel can be produced by transesterification, thermal cracking (pyrolysis), microemulsions or by direct use and/or blending of vegetable oils. However, among these four methods, transesterification proves the most suitable and promising method, considering the cost, simplicity and yield of the process. In addition, almost all of the commercial productions of biodiesel are currently by transesterification methods. Transesterification reaction can be categorized to either catalytic or non-catalytic. Under these two categories, they can be further subdivided into various methods. Thus, the aim of this paper is to describe the various methods available for biodiesel synthesis from crude palm oil.

Keywords: Biodiesel; Transesterification; Biodiesel Catalysts; Supercritical Methanol

PRODUCTION OF BIODIESEL FROM VEGETABLE OILS: A REVIEW

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The production of bio-diesel has become more important and popular recently due to the increasing global demand for clean fuel and the increasing price of petrodiesel. As generally known, biodiesel can be produced by transesterification, thermal cracking (pyrolysis), microemulsions or by direct use and/or blending of vegetable oils. However, among these four methods, transesterification proves the most suitable and promising method, considering the cost, simplicity and yield of the process. In addition, almost all of the commercial productions of biodiesel are currently by transesterification methods. Transesterification reaction can be categorized to either catalytic or non-catalytic. Under these two categories, they can be further subdivided into various methods. Thus, the aim of this paper is to describe the various methods available for biodiesel synthesis from crude palm oil.

Keywords: Biodiesel; Transesterification; Biodiesel catalysts; Supercritical methanol

INTRODUCTION

Currently, the production of bio-diesel has gained its importance and popularity due to the increasing demand for clean fuel and the rising price of petro-diesel. Biodiesel is made from renewable sources which is environmental friendly [1-8]. These advantages had boosted the exploration using biodiesel as an alternative source of energy. The benefits of using biodiesel includes lower emissions of harmful gases, better lubricity and a renewable source as compared to the conventional petrodiesel [1-8].

During the last two decades, several new technologies have been developed and utilized to meet the increasing demand for biodiesel. Biodiesel is generally produced by the transesterification of vegetable oils and/or animal fats. The transesterification reaction can proceed either with or without the presence of catalysis. The catalytic technology for the production of biodiesel can be further divided into homogenous and heterogeneous process. In the homogenous process, the catalyst is in the same phase as the reactants and products. Whereas for heterogeneous, solid catalysts are commonly used. The catalyst for homogenous and heterogeneous can also be divided to acidic and basic/alkaline. Production of biodiesel via enzymatic route has also been attracting a lot of interest lately. Lipases are currently the most commonly used enzymes in the studies related to enzymatic production of biodiesel. Recently, several other emerging technologies have also been reported, such as the utilization of membrane reactor and the development of micro-reactor to produce biodiesel [6]. Figure 1 summarizes the various technologies and emerging technologies for the production of biodiesel. The subsequent sections will discuss further on each of the technologies presented in Figure 1.

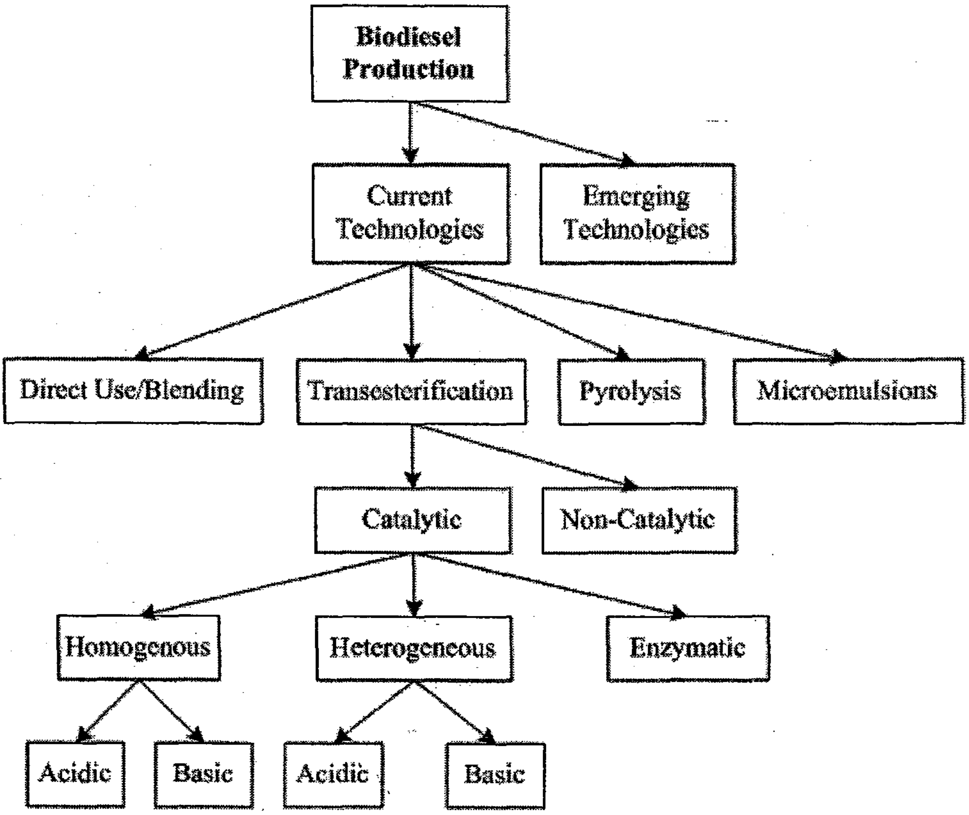

Figure 1: Classification of biodiesel productions

NON-CATALYTIC PRODUCTION OF BIODIESEL

The use of supercritical fluids is the most common practice in the non-catalytic transesterification studies. Supercritical alcohol, a type of supercritical fluids, is the most frequently used. Many papers related to the production of biodiesel using supercritical alcohol has been reported in the literature [9-12].

A recent study by Madras *et al.* [13], they have reported the transesterification of sunflower oil in supercritical methanol and supercritical ethanol at various temperatures (200 – 400 °C) at 200 bar. Alongside with the supercritical alcohols, they reported the use of another supercritical fluid (supercritical carbon dioxide) for comparison purpose. They investigated various factors such as the effect of enzyme loading, ratio of oil to alcohol, reaction time and temperature. In this study, they found that nearly complete conversion was obtained for the thermal reactions in supercritical methanol and ethanol, but only 30 % conversion was obtained in the enzyme-catalyzed reactions in supercritical carbon dioxide.

Apart from avoiding the use of catalysts, the utilization of supercritical fluids in the transesterification process is to eliminate the problem caused by the presence of water and free fatty acids in the oils. It was widely reported that in any conventional transesterification process, the presence of free fatty acids and water can cause some negative effect to the process. However, in the supercritical alcohol method, this problem is not only being eliminated but the presence of free fatty acids and water can give a positive effect of the transesterification reaction.

Saka *et al.* [14] reported that the presence of water and free fatty acids in the starting materials gives advantage to the process. They reported that the presence of water up to a certain percentage can enhance the formation of alkyl ester, in contrast to the negative effect in many conventional transesterification processes. They also reported that with the presence of water, the separation process between the product and byproduct is easier as glycerol, which is a byproduct, is more soluble in water than in methanol. Further study by Saka *et al.* [15], reported that the free fatty acids in the oils are in fact contributing to the production of alkyl esters. In other words, free fatty acids can actually react with the supercritical alcohol to produce alkyl esters by alkyl esterification process. Thus, with the supercritical method, transesterification of triglycerides and alkyl esterifications of free fatty acids can simultaneously occur to produce alkyl esters. In common transesterification process, only the transesterification of triglycerides is the significant reaction in producing alkyl esters. This finding may be vital for consideration when dealing with oils which have high content of free fatty acids. In many conventional transesterification processes, the presence of free fatty acids in the oils resulted in the use of additional amount of catalyst (hydroxides) for neutralization. Thus to overcome this problem, supercritical method can be a viable alternative.

Demirbas [10,16] reported the advantages of supercritical method compared to the conventional way. Table 1 presents the comparisons.

Table 1: Comparisons between catalytic methanol (MeOH) process and supercritical methanol (SCM) method for biodiesel from vegetable oils by transesterification

	Catalytic MeOH Process	SCM Method
Methylating agent	Methanol	Methanol
Catalyst	Alkali	None
Reaction temperature (K)	303-338	523-573
Reaction pressure (MPa)	0.1	10-25
Reaction time (min)	60-360	7-15
Methyl ester yield (wt %)	96	98
Removal for purification	Methanol, catalyst, glycerol, soaps	Methanol
Free fatty acids	Saponified products	Methyl esters, water
Continuity easiness	Discontinue	Easy continuity

Source: [16]

One of the main challenges of using supercritical method is the requirement of very high temperature and pressure for the reaction. This condition is undesirable in industrial scale production as it would requires a lot of energy, leading to very high cost of production. The use of supercritical alcohol for the production of biodiesel is still at the initial stage of development. Since high energy requirement is one of the main challenges of this technology, perhaps a possible solution is to develop an efficient energy recovery system. Nevertheless, a lot more study has to be carried out on this technology before it can be fully commercialized. One possible way to overcome this problem is by adding of co-solvent.

Zhang *et al.* [17] have studied the use of supercritical methanol in the production of biodiesel with co-solvent. In their study, propane was used as the co-solvent. They reported that propane can be used as co-solvent as it is easy to be added into the system beforehand and to remove it from the system when the reaction is complete. They found that the method used is much simpler, environmental friendly, lower energy requirement, safer and lower production costs as compared to the conventional supercritical alcohol method. Further study by Zhang *et al.* [18] reported that apart from propane, other type of co-solvent such as CO_2 also can be used to lower the temperature and pressure requirement of the supercritical alcohol transesterification process.

CATALYTIC PRODUCTION OF BIODIESEL

Homogeneous Transesterification

Acidic Catalysts. Sulfuric acid, sulfonic acids and hydroxide acid are among some of the commonly used acids in homogenous transesterification reaction. However, acids catalysts are less favorable as compared to basic catalyst in the homogeneous transesterification because the rate of reaction is slower [12]. However, the presence of high content of free fatty acids in certain type of vegetable oils will make it more advantageous to use acid catalyst instead of basic catalyst [19]. This is because when transesterification process using homogenous basic catalyst is used on oil which contains high amount of free fatty acids and water, a significant amount of soap will be produced. The formation of soap will complicates the downstream purification step.

Low grade oils such as sulphur olive oil and waste cooking oil are the example of oils which should be transesterified using acid catalysts [20,21]. Fresh oil such as crude palm oil which is known to have high free fatty acid should also be transesterified using acid catalyzed process. Several studies that reported on acid catalyzed transesterification process includes the two-step acid-catalyzed process for the production of biodiesel from rice bran oil by Ju *et al.* [22] and on the acid-catalyzed production of biodiesel from waste frying oil by Zheng *et al.* [20]. In other studies, Crabbe *et al.* [23] reported the production of biodiesel from crude palm oil and Al-Widyan *et al.* [24] reported on the transesterification of waste palm oil using H_2SO_4 and HCl.

Basic Catalysts. Compared to acid catalysts, basic catalysts are much more preferred for the homogenous transesterification process since the rate of reaction is much faster. In fact, most of the existing commercial productions of biodiesel are using basic catalysts. Another reason for favoring basic catalyst to acidic catalyst is due to the corrosive nature of acidic catalyst.

NaOH and KOH are the two most frequently used base catalyst, either in researches or commercial production of biodiesel. The other catalysts used are sodium methoxide, sodium ethoxide, sodium propoxide, sodium butoxide, potassium methoxide and carbonates [12]. However, due to the availability of many other bases, studies are still being conducted to investigate other bases for their potential of being used as catalysts in the transesterification process. In any basic catalytic production of biodiesel, the glycerides (oil) and alcohol must be substantially anhydrous because the presence of water can lead to saponification reaction, which produces soap [12,25].

Aracil *et al.* [26] investigated the performance of few basic catalysts - sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide - in the methanolysis of sunflower oil. The study was carried out under the same condition in a batch stirred reactor and the subsequent separation and purification stages in a decanter. From the study, it was found out that all the four catalysts studied gave high yield of biodiesel. However, both methoxides gave the highest yield at 98% (after the separation and purification step). The other 2 % is yield losses due to saponification of triglycerides to soap. Methyl ester dissolutions in glycerol were assumed to be negligible. However, the costs of methoxides are very much higher and difficult to manipulate since they are hygroscopic. This makes methoxide not an economically catalyst. The biodiesel yields for sodium and potassium hydroxide are lower, 85.9 and 91.67 wt %, respectively, because the yield losses to saponification reaction were more substantial.

The main disadvantages of homogeneous basic-catalytic transesterification process are the complexity of the separation process for final products and the presence of water in the raw materials. Separations steps are required to separate the product, byproduct, unreacted starting materials and also to recover the catalyst. However, since all these compounds are in the same phase, thus the separation process becomes difficult and expensive. In the common practice, washing and drying are the most common separation process used, which are probably costly and time consuming. Hence, a major challenge is to develop a special separation technology which is simple and effective to overcome the complexity of the current separation process, reducing the cost of production.

As mentioned earlier, the presence of water in the process (from the raw material), especially in the initial part of the reactions can be defective. It is known that water can lead to the formation of more soap than alkyl esters, thus significantly reduce the yield of biodiesel. Thus, it is desired that the starting materials for the transesterification process are water-free. However, even though the starting materials can be water-free at the initial point, the reaction between alcohol and catalysts especially hydroxides could still eventually produce water. As a solution to this problem, some researchers suggested the use of alkoxides instead of hydroxides. The use of alkoxides will prevent the generation of water in the reactions, thus formation of soap can be avoided. Lately it was suggested that a better alternative to overcome this problem is by using heterogeneous catalysts.

Heterogeneous Transesterification. As mentioned previously, in any conventional homogenous transesterification process, the final products i.e. alkyl ester, catalyst and unreacted starting materials are in the same phase. Separation process is required to obtain the product and to recover the catalyst. However, since the product and catalyst are in the same phase, the separation process becomes difficult. Thus, heterogeneous catalysts can be used to overcome the complexity of the separation process. Since the catalysts are in solid phase for heterogeneous reaction, thus the cost for separation can be significantly reduced.

Among the various heterogeneous catalysts used are alumina loaded with alkali metal salt [27-30], solid metal oxides (tin, magnesium, and zinc) [31-34], tungstated zirconia [32], calcium-based oxide [35], montmorillonite [36], metal complexes [37], zeolite [38,39] and ion-exchange resin [40].

The main challenges in the heterogeneous process are related to the reactivity of the solid catalysts and the mass transfer-related problems. The regenerability of the catalyst is also another important parameter because it is related to the cost of the production. It is desired to have a catalyst that is regenerable, cheap and effective.

ENZYMATIC PRODUCTION OF BIODIESEL

In a more recent development, enzyme has been used to catalyze the conversion of vegetable oil to biodiesel. The use of enzyme to catalyze the transesterification process is probably due to the specific action of enzymes that are capable to facilitate the conversion of oil to methyl ester. As compared to heterogeneous reaction, enzymatic reaction proceeds at a milder process conditions.

Lipases enzymes are the most frequently used in the study of enzymatic production of biodiesel. Among some of the lipases which have been investigated are *Pseudomonas cepacia* [41-44], *Rizopus oryzae* [45], *Candida antarctica* [42,46,47], *Candida rugosa* [43,44], *Rizhomucor meihei* [42,48], *Burkholderia cepacia* [46], *Pseudomonas fluoroscens* [43, 44], *Mucor javaniscus* [44], and *Rhizopus niveus* [44].

The biggest challenge in any enzymatic production of biodiesel is the problem of mixing enzyme with alcohol. Alcohol is one of the required starting materials in any transesterification reaction to produce biodiesel. However, it is well documented that alcohol can have some defect on the enzyme activity. As reported in the literature [49], alcohol, for example methanol can actually deactivate the enzyme activity, particularly when the ratio of methanol to enzyme is higher than 1:1. In the conventional production of biodiesel, alcohol must be supplied in excess to ensure higher yield of biodiesel. Thus, while alcohol must be supplied excessively, it will at the same time inactivate the activity of the enzyme.

In order to overcome this problem, Du *et al.* [49,50] suggested that another acyl acceptor be used as an alternative to alcohol/methanol. Du *et al.* have compared the effect of different acyl acceptor namely methyl acetate and methanol on soybean oil. They found out that higher yield of methyl ester can be obtained with the use of methyl acetate (92%) at a molar ratio of methyl acetate to soybean oil at 12:1, while lower yield when methanol is being used. Additionally, when crude soybean oil was used as the oil source and methanol as acyl acceptor, a much lower methyl ester yield was obtained compared to than that with refined soybean oil, while with methyl acetate as acyl acceptor, an equally high yield of methyl ester (92 %) was achieved for both soybean oils. They claimed that lipase loses its activity very rapidly during repeated experiments with methanol as the acyl acceptor, while there is almost no detected loss in lipase activity, even after being continuously used for 100 batches, when methyl acetate was used for biodiesel production. Moreover, the by-product triacetylglycerol is an important chemical with a higher value than glycerol, and this novel acyl acceptor seems very promising for lipase-catalyzed large-scale production of biodiesel.

EMERGING TECHNOLOGIES ON BIODIESEL

Recently, apart from developing novel catalyst for the production of biodiesel, emerging technologies for biodiesel production is the development of novel reactors. Among some of the novel development are membrane reactor [51,52] and micro-reactor [53].

The mass transfer limitations between alcohol and vegetable oil had brought some researchers to the exploration of novel reactors. As reported by Dube *et al.* [51], the immiscibility of canola oil in methanol has introduced a mass-transfer problem in the early stages of the transesterification of canola oil. Thus, as an alternative to overcome this problem, a two-phase membrane reactor has been developed to produce FAME (fatty acid methyl ester) from canola oil and methanol. In their study, the transesterification reaction was carried out via both acid- and base-catalysts. The experiments were carried out in the membrane reactor in semi-batch mode at 60, 65 and 70 °C and at different catalyst concentrations and feed flow rates. From their study, it was reported that the increases in temperature, catalyst concentration and feedstock (methanol/oil) flow rate were significantly increased the conversion of oil to biodiesel. Apart from that, they also reported that their novel reactor allows easy separation of the reaction products (FAME/glycerol in methanol) from the original canola oil feed.

In another recent development, a group of researcher from Oregon State University in association with the Oregon Nanoscience and Microtechnologies Institute (ONAMI) has developed tiny reactor to produce biodiesel [53]. With the use of this tiny reactor, several steps in conventional method can be emitted, such as the need for agitation, long period of reaction time and the need of a dissolved catalyst. The reactor, which is about half the size of a thick credit card is claimed to be able to produce biodiesel effectively. This reactor consists of a series of parallel channels, each smaller than a human hair, through which vegetable oil and alcohol are pumped simultaneously. It is claimed that at such a small scale the chemical reaction that converts the oil into biodiesel is almost instant. Although the amount of biodiesel produced from a single reactor is a trickle, the reactors can be connected and stacked in banks to dramatically increase production. Using these microreactors, biodiesel could be produced between 10 and 100 times faster than traditional methods. Apart from that, the team is also developing a method for coating the microchannels with a non-toxic metallic catalyst. This would eliminate the need for the chemical catalyst, making the production process even more simple, a key to widespread use.

CONCLUSION

Based on the information presented in this paper, there are many ways to produce biodiesel. The relevancy of each method for commercial use may depend on many factors. These factors may include the cost of the production, the price of vegetable oils, enzyme, catalysts and even conveniences. However, as reported in the literature, each of the method still has their limitation in which researchers now still tried to overcome.

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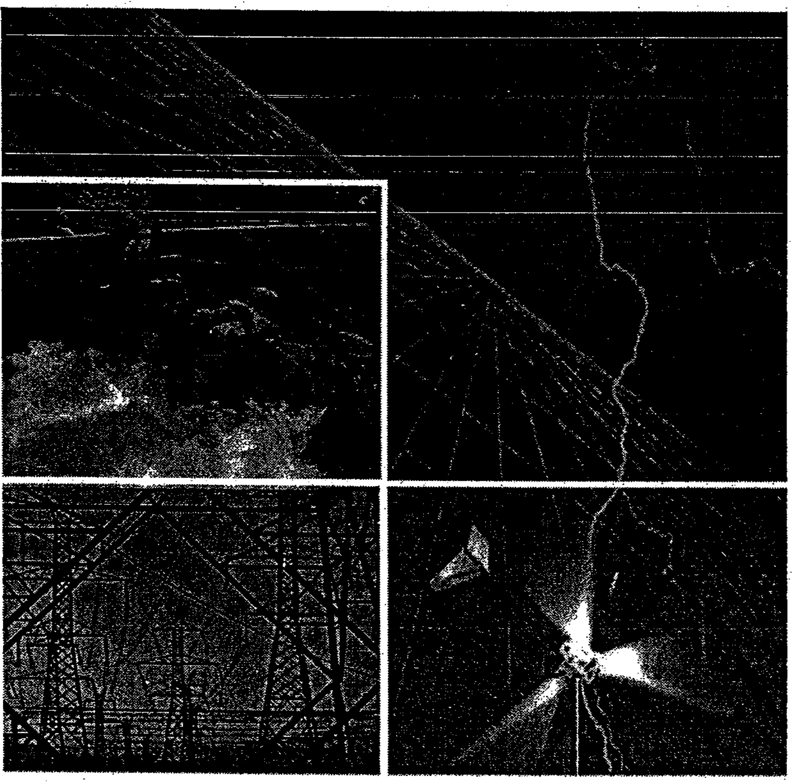

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Production of Biodiesel from Palm Oil Using Montmorillonite KSF as a Heterogeneous Catalyst

J. Kansedo, K. T. Lee, S. Bhatia

Abstract—**The production of biodiesel has become popular nowadays as a result of the increasing demand for a clean, safe and renewable energy. Biodiesel is made from natural sources such as vegetable oils and animal fats. The conventional method of producing biodiesel is by reacting vegetable oil with alcohol in the presence of homogenous catalyst (NaOH). However, this conventional method has some limitations such as the formation of soap, usage of lot wash water and complicated separation processes. On the other hand, heterogeneous process using solid catalysts has a lot of advantages over the homogenous methods. This study focused on the production of biodiesel from palm oil using montmorillonite KSF as the heterogeneous catalyst. Cooking oil and methanol were used as the raw materials. The heterogeneous transesterification process was studied using design of experiment (DOE), specifically response surface methodology (RSM) based on four-variable central composite design (CCD) with $\alpha = 2$. The transesterification process variables were reaction temperature, x_1 (50 – 190 °C), reaction period, x_2 (60 – 300 min), methanol/oil ratio, x_3 (4 – 12 mol/mol) and amount of catalyst, x_4 (1 – 5 % wt). It was found that the conversion of palm oil to biodiesel can reach up to 78.69 % using the following reaction conditions; reaction temperature of 155 °C, reaction period at 120 min, ratio of methanol/oil at 10:1 mol/mol and percentage of catalyst at 4 %. From this study, it was shown that montmorillonite KSF catalyst can be used as a solid catalyst for biodiesel production replacing the conventional homogenous process.**

Keywords: biodiesel, transesterification process, heterogeneous catalysts, montmorillonite KSF

I. INTRODUCTION

Due to increasing crude petroleum oil prices and the effect of global warming, a search for alternative fuels has gained significant attention over the years. Among the various sources of alternative energy, renewable energy such as solar, hydro and biomass present a promising alternative to replace the conventional fossil fuels. Since Malaysia is the largest producer of palm oil in the world, this commodity presents a promising alternative to be converted to bio-diesel as a source of renewable energy, replacing the petroleum-based diesel oil.

In the recent years, a number of studies have shown that vegetable oil such as palm oil can be used as a source of bio-diesel fuels [1]-[4]. However, the direct utilization of vegetable oil in diesel engine can lead to a number of problems such as poor fuel atomization, poor cold engine start-up, gum and other deposit formation. Consequently, considerable efforts have been made to develop alternative bio-diesel fuels that have the properties and performance similar to the petroleum-based diesel fuels. The most promising way to overcome these problems is the transesterification of triglycerides present in vegetable oil such as palm oil to fatty acid alkyl esters.

Transesterification, also called alcoholysis, is the reaction of an oil with an alcohol to form esters and glycerol [2]-[4]. This process has been widely used to reduce the viscosity of vegetable oil. In the transesterification process, the triglycerides in the vegetable oil will react with alcohol to form mixture of fatty acid alkyl esters and glycerol [2-4]. The fatty acid alkyl esters produced from this process is known as bio-diesel which has become more attractive recently because it has almost the same properties and characteristic of petroleum-based diesel. Several studies have shown that bio-diesel produced from vegetable oil have viscosity close to petroleum-based diesel fuel [1], [5], [6]. Their volumetric heating values are a little lower compared to the petroleum-based diesel fuel, but they have high cetane and flash point values.

The transesterification process includes the reaction between oil and alcohol, with the presence of catalyst as shown in the equation (1) below.

$$\text{TG} + 3\text{R'OH} \leftrightarrow 3\text{Alkyl esters (biodiesel)} + \text{Glycerol} \qquad (1)$$

where TG is triglycerides and R'OH is alcohol.

Transesterification process is catalyzed by catalysts with both, acidic and basic sites [2]-[5]. Currently, all the

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transesterification process goes through the homogenous transesterification process by mainly using potassium hydroxide as the catalyst [2]. The Malaysian Palm Oil Board (MPOB) research centre has also successfully developed this technology [9]. In the homogeneous transesterification process, the catalysts used are in the same phase as the reactants/ products. However, homogeneous transesterification process using potassium hydroxide presents certain disadvantages. Among some of the disadvantages are [6], [7]:

a. The formation of soap in the product mixture. This has led to additional cost required for the separation of soap from the bio-diesel.
b. The separation of soap requires several steps that makes the overall process complex.
c. Since the catalyst and the reactants/products are in similar phase, the separation of products (bio-diesel) from the catalyst becomes complex.
d. The formation of soap also led to the loss of triglycerides molecules that can be used to form bio-diesel.

These disadvantages make the homogeneous transesterification process complex and uneconomical. Therefore, there is a need to develop a novel technology for the conversion of palm oil to bio-diesel using alternative route that can overcome the limitations of the homogenous transesterification process. One of the possible routes is by using heterogeneous transesterification process. In heterogeneous transesterification process, the catalysts are in different phase from the reactants/products. The advantages of heterogeneous transesterification process are as follows [5]:

a. It is a simple process whereby the products of the reaction only consist of glycerol and bio-diesel. Since glycerol and bio-diesel are essentially immiscible in each other, the separation processes are very simple. The glycerol produced has a high demand in the pharmaceutical industries.
b. Since the catalyst and the products/reactants are in different phases, separation process is simpler.
c. There is no formation of soap, and therefore there is no additional cost required for its separation.

Based on this information, it is obvious that the heterogeneous transesterification process overcomes all the limitations of the homogenous transesterification process. Recent researches have shown that there are various types of catalyst that can be used in the heterogeneous transesterification process. Jitputti *et al.* [6] studied the transesterification of coconut oil and palm kernel oil using zirconium oxide-based and zinc oxide-based catalyst, while Suppes *et al.* [10] used zeolite and metal catalyst for the conversion of soybean oil to bio-diesel. In other research, $Na/NaOH/Al_2O_3$ [8], [15] and metal complexes [12] are used as the catalyst.

Other researches have investigated various heterogeneous catalysts such as zeolites [10], [28], metal oxides [11], [19], [21], [22], [25], [29]-[32], metal complexes [12], tungstated zirconia [13], resins (acid and basic) [14, 16], NaOH-alumina catalyst [15], sulfonic-acid functionalized [17], activated calcium oxide [19], anionic ion-exchange resin [20], solid super acid [21], amorphous zirconia [20,22], calcium based compounds [23,31,32], alumina-supported potassium iodide [24], KF-ZnO [25], Mg-Al hydroalcites [26], potassium loaded on alumina [27], zinc modified with alkali earth metals [31], vanadyl phosphate [18], enzymes and etc. These researches have used various natural oils such as soybean oil, rapeseed oil, sunflower oil and etc.

However only limited that use palm oil as the feed stock. Since palm oil is the cheapest vegetable oil in the world, therefore the aim of this study is to convert palm oil to biodiesel using montmorillonite KSF as the heterogeneous catalyst.

II. METHODS

a. Materials

Purified palm oil was purchased from Yee Lee Edible Oils Sdn Bhd, Malaysia and methanol from R & M Chemicals, UK. Montmorillonite KSF, methyl myristate, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate (as standard references) and methyl heptadecanoate (internal standard) was obtained from Fluka Chemie, GmbH, Riedstr Germany. These methyl esters were used for the analysis of the product.

b. Experimental Design

The design of experiment (DOE) for the transesterification processes was developed using Design-Expert software, in which response surface methodology (RSM) was applied. The RSM was based on four-variable central composite design (CCD) with $\alpha = 2$. The variables were reaction temperature x_1 (50-190 °C), reaction period x_2 (60-300 min), ratio of oil/methanol x_3 (4-12 mol/mol) and amount of catalyst x_4 (1-5 % wt). Table 1 shows the complete DOE matrix with experimental results for the transesterification processes. Table 2 shows the actual values of coded experimental variables used in Table 1.

c. Experimental Procedure

The transesterification processes were carried out in a low pressure batch reactor with a magnetic stirrer, as shown in the Figure 1. Mixture of palm oil, catalyst and methanol was charged into the reactor. The mixing intensity of the magnetic stirrer was set at 190-200 rpm. The reaction temperature, duration, ratio of oil/methanol and amount of catalyst (montmorillonite KSF) were set according to the values as proposed in the DOE.

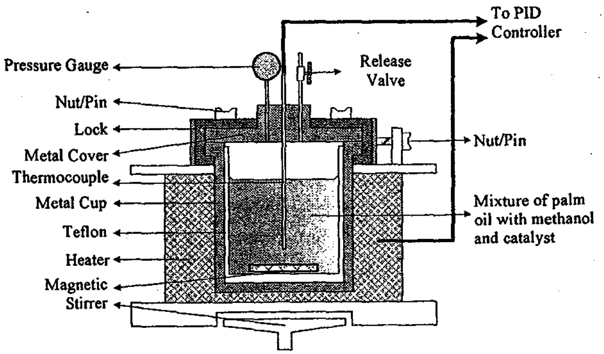

Figure 1. Schematic diagram of the low pressure batch reactor for the transesterification process

d. Analytical Method

The resulting products from the transesterification processes were analyzed using Gas Chromatography (GC) to identify the presence of methyl esters (biodiesel) in the sample. Methyl heptadecanoate was used as internal standard for the calculation of the conversion. The conversion of the transesterification processes were calculated as mol ratio of methyl esters produced to palm oil used.

III. RESULTS AND DISCUSSION

The experimental result (conversion) of the transesterification processes is shown in Table 1. Apart from that, the conversion values predicted using the model developed by the DOE software is also shown in Table 1.

Table 1: The DOE experimental matrix and results for the transesterification processes

Run	Level				#Exp. Conv. (%)	*Pre. Conv. (%)
	x_1	x_2	x_3	x_4		
KSF 01	+1	+1	+1	-1	71.63	74.29
KSF 02	+1	+1	-1	-1	59.1	62.73
KSF 03	+1	-1	+1	+1	78.69	81.35
KSF 04	-1	+1	-1	+1	5.07	8.70
KSF 05	+1	-1	-1	+1	55.1	58.73
KSF 06	-1	-1	+1	-1	3.92	6.58
KSF 07	-1	+1	+1	+1	5.43	8.09
KSF 08	-1	-1	-1	-1	2.9	6.53
KSF 09	-2	0	0	0	0.79	0.00
KSF 10	+2	0	0	0	74.34	71.20
KSF 11	0	-2	0	0	14.49	11.35
KSF 12	0	+2	0	0	60.05	56.91
KSF 13	0	0	-2	0	36.52	32.41
KSF 14	0	0	+2	0	51.39	49.22
KSF 15	0	0	0	-2	32.54	29.40
KSF 16	0	0	0	+2	61.98	58.84
KSF 17	0	0	0	0	55.07	54.50
KSF 18	0	0	0	0	50.88	54.50
KSF 19	0	0	0	0	55.75	54.50
KSF 20	0	0	0	0	55.07	54.50
KSF 21	0	0	0	0	55.75	54.50

\# Experimental conversion in percentage

* Predicted conversion in percentage

Table 2. The actual values of the parameters for each level

Variables	-2	-1	0	+1	+2
Reaction temperature, x_1	50	80	120	155	190
Reaction period, x_2	60	120	180	240	300
Ratio oil/methanol, x_3	1:4	1:6	1:8	1:10	1:12
Amount of catalyst, x_4	1	2	3	4	5

Units – x_1 (°C), x_2 (min), x_3 (mol/mol), x_4 (% g)

Based on Table 1 above, the highest conversion was achieved at a reaction temperature of 155 °C, reaction period of 240 min or 4 hr, oil/methanol ratio of 1:10 and % catalyst of 4 % wt of oil. Whereas the lowest conversion was obtained at a reaction temperature of 50 °C, reaction period of 3 hr, oil/methanol ratio of 1:8 and % catalyst of 3 % wt of oil.

Visual inspection of the data trend shown in Table 1 indicates that the maximum conversion occurs at the border of the experimental variables selected for this study. This finding was also supported by the model developed using the DOE software whereby no maximum conversion was located within the experimental domain examined. Therefore, optimum experimental conditions to obtain the highest conversion cannot be derived (except for the experimental conditions at the border of the design variables). Thus, the model developed by the DOE software was used to facilitate a straight forward examination of the effects of the variables and their interaction towards the conversion of the transesterification process. Figure 2, 3 and 4 show the interactions between the parameters/variables used in the transesterification processes.

Referring to figure 2, both oil/methanol ratios showed increasing conversion of palm oil to biodiesel with increasing reaction temperature. Apart from that, higher ratio of oil/methanol, 1:10, gives higher conversion whereas lower ratio of oil/methanol, 1:6, gives lower conversion of palm oil to biodiesel. This behavior is in agreement with those reported in the literature Technically, the equilibrium of the reaction will shift to the right (equation 1), with the additions of more heat or when more methanol is used in the reaction.

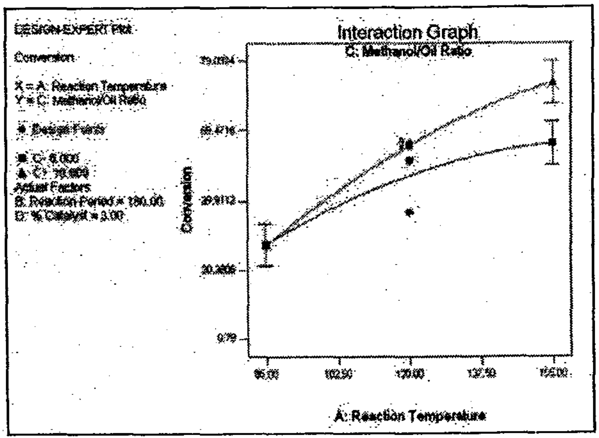

Figure 2. Interaction between the reaction temperature and methanol/oil ratio towards conversion

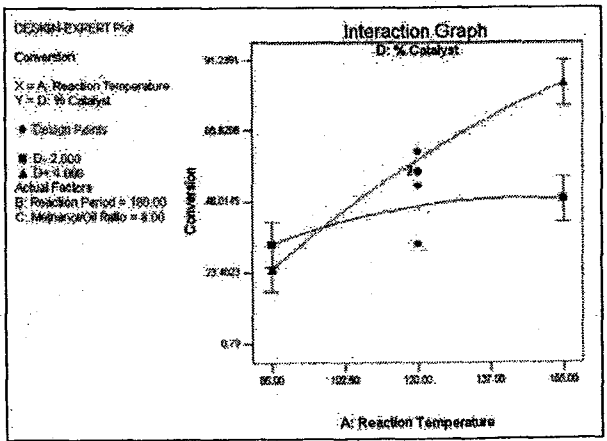

Figure 3. Interaction between reaction temperature and % of catalyst towards conversion

It is generally perceived that higher percentage of catalyst used will results in higher conversion of triglycerides to biodiesel because of higher availability of active sites. However, this perception may not always be true. Referring to figure 3, the conversion of oil to biodiesel was found to be lower at 4% catalyst as compared to 2% catalyst when the reaction temperature was lower than 95°C. This may suggest the real interactions between the supplied energy (heat) and the active site on the catalyst itself. The active sites on the catalysts may require a certain amount of energy to be activated. At lower temperature, smaller percentage of catalyst, 2 %, will reach the activation energy more quickly than the 4 % catalyst because the ratio of active site to energy (heat) is smaller. In other words, the total energy required to activate the whole active sites on the 2 % catalyst is much smaller than those for 4 % catalyst. Thus, lower temperature (small energy) may just be enough to activate the whole active site on the 2 % catalyst but not for the 4 % catalyst because of the assumption of fair distribution of energy to all active sites. Thus, the transesterification reactions by 2 % catalysts will commence sooner, while the 4 % catalyst will show delay in transesterification reactions. However, as activation energy for all catalyst in the 4 % is fully achieved at higher temperature, the reactions will proceed rapidly and subsequently exceeds to that of 2 % catalyst. Thus, only when the reaction temperature is sufficient to activate all the active sites of the catalyst, then only the perception that high amount of catalyst will results in higher conversion applies.

As in figure 4, at shorter reaction period, 2 % catalyst showed a significant lower conversion of palm oil to biodiesel compared to that of 4 % catalyst. However, the conversion by 2 % catalyst continues to steadily increase until it subsequently exceeds to that of 4 % catalyst after 210 minutes of reaction. The 4 % catalyst showed a fairly constant conversion for most of the time and slightly dropped when the reaction period is beyond 210 minutes. From this behavior, it can be said that the equilibrium of the reactions is reached rapidly with 4 % catalyst, and after reaching the equilibrium, the transesterification reactions may become stagnant or start to reverse. The equilibrium of transesterification reactions by 2 % catalyst may only reached after longer reaction time because of smaller active site availability, thus defines the staging increment of conversion by 2 % catalyst from 120 min to 240 min. After all, the total rate of reactions, be it transesterification or reversed reaction, may directly be influenced by the total active sites of the catalyst, whereby higher active sites will accelerate both reactions.

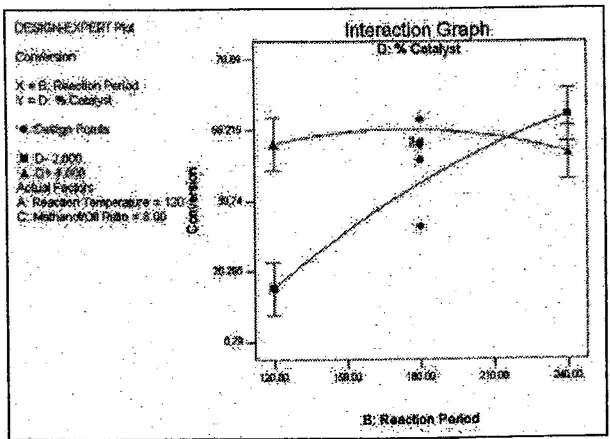

Figure 4. Interaction between reaction period and % of catalyst towards conversion

The ability of montmorillonite KSF to catalyze the transesterification reactions, at any rate, is due to the acidic properties of the catalyst itself. Montmorillonite KSF has free acid of 8-12 %, and its surface partially laid with H_2SO_4. H_2SO_4 is known as a typical strong acid, and since the transesterification reactions can be catalyzed with acid or base, therefore the strong acidity of this montmorillonite KSF will definitely contribute to the high conversion of palm oil to biodiesel.

IV. CONCLUSIONS

Based on the experimental result obtained, it can be concluded that montmorillonite KSF could be used as an effective catalyst for the conversion of palm oil to biodiesel. However, future research on this catalyst is still needed to investigate wider range of the parameters, and also new possible parameters which can be included in the reaction process such as the mixing intensity, reaction pressure and so forth.

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