Optimization of the Parameters that Affects the Solvent Extraction of Crude Rubber Seed Oil Using Response Surface Methodology (RSM)

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Abstract: **-** To avoid the major issues of fossil fuel depletion and their environmental concerns, biodiesel is one of the most feasible sources of alternative energy. Rubber seeds, due to its non-edible characteristics have a potential to be converted to biodiesel. Its utilization will help to resolve the food versus fuel controversy. Malaysia has a vast number of rubber plantations that can supply the seeds for biodiesel production. In present, work optimization of the parameters that affects the oil yield using solvent extraction technique is studied. The optimization is done via response surface methodology (RSM), using the central composite design (CCD). The parameters studied are solvent to seed ratio, temperature, extraction time and drying time for the seeds. The optimum condition is identified to be solvent to seed ratio of 37 ml/g, temperature of 60^{o}C, extraction time of 4.5 hours and drying time for the seeds of 3 hours.

Key-words: Alternative energy, biodiesel, rubber seed oil, solvent extraction, central composite design

1 Introduction

Currently the world is facing energy crisis due to the excessive demand of the fossil fuels and their limited availability. Most of the country's energy needs depend upon the ordinary fossil fuels which rise to the negative impact on their economy due to the fluctuating prices of fuels along with increasing population and industrialization [1]. Environmental concerns are also related to the fossil fuels because almost 98% of the carbon emissions in the atmosphere are due to excessive usage of these fuels [2, 3] . In order to avoid these circumstances, researchers are finding new path ways to produce an alternative and renewable energy sources. Few types of renewable energy sources include biogas, wind and solar energy. Biodiesel is carbon-neutral and can be used directly to the ordinary diesel engine without any modification [4]. Biodiesel used in any ratio with fossil based diesel fuel in the diesel engine such as B20 consist 80% fossil based diesel and 20 % biodiesel. Similarly B100 is 100 % pure biodiesel [5, 6]. At present, most of the biodiesel are produced from the edible oil resources such as rapeseed, soybean, sunflower and palm oil [7]. Biodiesel produced from this edible oil will lead to food versus fuel controversy and the prices of these oils are quiet high. To avoid this crucial situation, researchers find a way to produce biodiesel from non-edible oil sources rather than edible one. There are many non-edible oil resources such as castor oil, jatropha oil, kapok seed oil and rubber seed oil.

These non-edible oils have some toxic compounds that make them non-edible but have a potential to produce biodiesel methyl esters [8, 9].

Malaysia is the second largest producer of the palm oil and most of the biodiesel produced is from palm oil [10]. To reduce edible oil utilization in making biodiesel, the focus of the researcher's must be towards non-edible oil. Rubber seed oil (RSO) is one of the non-edible oil sources which are currently available in Malaysia.

In 2007 Association of Natural Rubber Producing countries, Kuala Lumpur, affirmed that Malaysia has an around acreage of 1,229,940 hectares of rubber plantations [11, 12]. Malaysia has a large number of un-utilized rubber seeds which will give a great contribution to produce biodiesel from rubber seed oil and overcome the "food versus fuel" controversy issue. Modhar *et al*. 2010 [13] carried out extraction and analysis of RSO using the solvent extraction technique and found the optimized conditions at which solvent extraction would give the higher percentage of yield. Badwaik *et al.* 2012 [14] optimized the extraction conditions of partially defatted peanut using the response surface methodology and studied the effects of different solvents on oil yield.

Response surface methodology (RSM) is stated as an efficient and effective way to optimize the parameters that affect the process. RSM technique is used in order to find the optimize conditions when a number of factors are involved in process and the response is affected by them. RSM has many benefits such as it reduces process cost and process time. The main objective of the RSM is to identify the response by using given process variables following experimental design such as central composite design (CCD) that fit an empirical full second order polynomial model [14, 15]. RSM is a statically technique used for the design of experiments and optimization of a complex systems. By using RSM, the number of experimental runs can be reduced in much faster and cheaper way. In previous extraction studies, RSM has been used for optimization of process parameters and gave successful optimized condition [16-18].
In the current study, the RSM is used to optimize the process parameters for the solvent extraction of RSO and to study the effect of process parameters on oil yield such as solvent to seed ratio, extraction time, drying time for seeds and process temperature. The designs of experiments were done by using CCD approach. Optimization and experimental design is employed with the help of Design Expert software version 8.0.

2 Materials and Methodology

2.1 Materials

The rubber seeds were procured from the Vegpro Trading N. Selangor, Malaysia. The seeds were than separated from the kernel shell by using mechanical press. The average weight of the seeds was calculated to be 70% of the total weight and remaining 30% was the shell weight. The seeds were than crushed into the smaller pieces by using granulator (SG-16 series). The sizes of the pieces were further decreased by using blender. The samples were sieved to obtained the seed particles dimensions of less than 2 mm. Analytical grade of n-hexane (with purity, 99%) was purchased from Merck (Germany) and was used as the solvent for the oil extraction.

2.2 Experimental Design

Influence of the variables that affects the solvent extraction process was studied by using RSM. The variables which affect the solvent extraction are solvent to seed ratio, extraction time, process temperature and drying time of the rubber seeds. The range of process variables and actual level of independent variable are shown in the Table 1.

Table 1 Ranges for the process variables

Process Parameters	Units	Low	High
Extraction Time	hr	2	4
Solvent/Seed	volume/weight (ml/g)	22	52
Temperature	^{o}C	50	69
Drying time for seeds	hr	2	4

The response variable was selected as the oil yield which was calculated in percentage.

2.3 Experimental approach

The crushed rubber seeds were dried in an oven at ±105^{o}C to remove any moisture presence at different interval of time. 10 g of dried rubber seeds was placed onto a thimble and the thimble was put into the sohxlet extractor. N-hexane solvent was poured into three-neck- round bottom flask that is joined with the extractor and flask along with the condenser on the top to avoid any solvent losses. The whole assembly was then placed on the temperature controller heater to provide the required temperature. The temperature was measured by a thermometer that was inserted in one of the necks of the round bottom flask. After certain interval of the time the experiment was stopped and the trapped oil in the solvent was separated. The mixture of solvent and oil was separated using rotary evaporator under vacuum at temperature of 65^{o}C.

The oil obtained after evaporation was weighed and the oil yield was calculated using equation (1):

$$Oil\ yield\,(wt\%) = \frac{mass\,of\ extracted\,oil}{mass\,of\ rubber\,seed\ \ fed} \times 100 \quad (1)$$

3 Results and Discussion

The detail of the experimental outcome is shown in Table 2. The analysis of the variance (ANOVA) of the selected response surface quadratic model for the response (oil yield) is analyzed. From Table 3 the model p- value (0.0063) indicates that the conditions in the model are significant as the probability > F is less than 0.05. The Model F-value of 9.05 implies the model is significant. In the current model the factor that most influencing the response (oil yield) is the solvent/seed ratio. However, the other terms have lesser effect on the response (oil yield). A ratio greater than 4 is desirable. The ratio of signal to noise ratio of 10.10 (as shown in Table 4) indicates an adequate signal.

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The results of Table 4 show the reasonable agreement between R-Squared value model and Adjacent R-Squared value model.

Table 2 Experiment design for the rubber seed oil extraction

Run	Extraction Time (Hour)	Solvent/Seed (v/w)	Temperature (^oC)	Drying Time for Seeds (Hour)	Response (Oil Yield) (Percentage)
1	4.00	52.00	50.00	2.00	32.22
2	3.00	37.00	60.00	3.00	32.96
3	2.00	22.00	50.00	2.00	27.53
4	3.00	62.00	60.00	3.00	33.17
5	4.00	22.00	69.00	4.00	32.97
6	3.00	12.00	60.00	3.00	26.98
7	3.00	37.00	60.00	3.00	32.97
8	2.00	52.00	50.00	4.00	30.52
9	2.00	22.00	69.00	2.00	27.61
10	3.00	37.00	60.00	4.50	32.12
11	3.00	37.00	60.00	3.00	32.98
12	3.00	37.00	60.00	1.30	30.11
13	3.00	37.00	60.00	3.00	33.11
14	3.00	37.00	45.00	3.00	29.65
15	3.00	37.00	60.00	3.00	32.64
16	1.30	37.00	60.00	3.00	28.54
17	4.00	22.00	50.00	4.00	32.61
18	4.50	37.00	60.00	3.00	33.56
19	4.00	52.00	69.00	2.00	32.25
20	2.00	52.00	69.00	4.00	32.97
21	3.00	37.00	75.00	3.00	31.98

Table 3 ANOVA (Analysis of Variance) Analysis for the results

Source	Sum of Squares	df	Mean square	F-Value	P-Value Prob.>F
Model	86.75	14	6.20	9.05	0.0063
A-Extraction time	12.60	1	12.60	18.39	0.0052
B- Solvent/seed	19.16	1	19.16	27.97	0.0019
C-Temperature	3.42	1	3.42	5.00	0.0667
D-Drying time for seeds	2.02	1	2.02	2.95	0.1367

To identify the statistical properties of the model, the CCD normal probability plot of the residuals shows the normality of the model. Fig. 1 shows the diagnostic graph for this model. The data points should be approximately linear. A non-linear pattern indicates abnormality in the error term which may be corrected by transformation. From Fig. 1 there is no sign of any abnormality in this model.

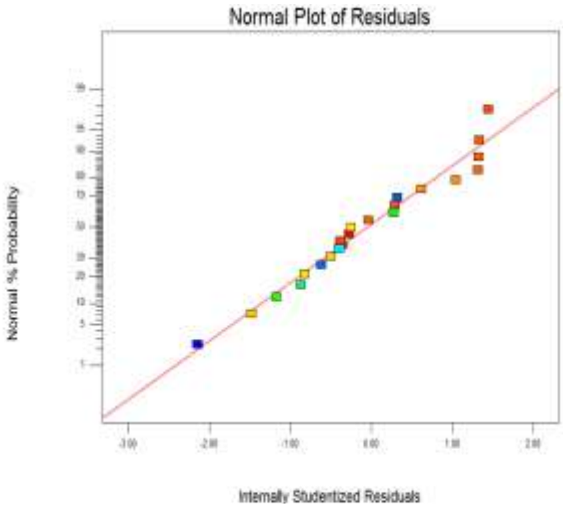

Fig. 1 Dignostic graph for the model

The perturbation plot for the model is shown in Fig. 2. Perturbation provides the outline views of the response. For the response surface designs, perturbation plot shows how the response changes as any of the parameters moves from the reference point, with all other factors held constant at the reference value.

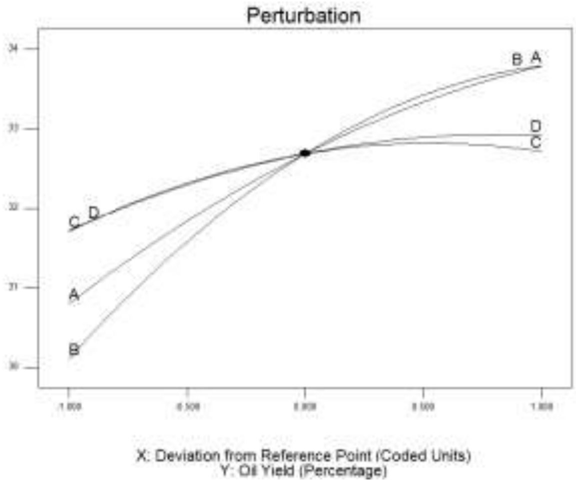

Fig. 2 Perturbation plot for model

In Fig. 2, it is shown that factor A (extraction time) and B (Solvent to seed ratio) produces higher affect on the response as compared to C (temperature) and D (drying time for seeds) because factors A and B show higher slope than Factors C and D. The perturbation chart shows that the factor B has more influence and affects the response compared to others because of its steep slope. The response surface quadratic model equation for the weight percentage of oil yield for coded factors and with actual factors is shown in equation (2) and (3).

$$Oil\ yield\ (wt\%) = +32.69 + 1.49 \times A + 1.84 \times B + 0.50 \times C + 0.60 \times D - 0.58 \times A \times B \quad (2)$$

$$Oil\ yield\ (wt\%) = -1.4 = 4.15 \times ExtractionTime + 0.36 \times Solvent/SeedRatio + 0.59 \times Temperature - 2.26 \times DryingTimeForSeeds - 0.03 ExtractionTime \times Solvent/SeedRatio \quad (3)$$

Table 4 Response of the model

Standard Deviation	0.83	R-Squared	0.96
Mean	31.40	Adjacent R-Squared	0.85
(Co-efficeint of variation) C.V. %	2.64	Adeq. Precision(Signal to Noise Ratio)	10.10

Fig. 3-6 shows the 3D plots of the factors with respect to the response. From Fig. 3 and 4, the extraction time is shown to be the most important factor that affects the response with respect to solvent to seed ratio and drying time for the seeds. The increase in the extraction time results in more oil yield. The gum formation around the flask results in difficult gum removal when the process is operated for 5 hours. The drying time for the seeds is also an important factor, as the moisture and volatile content in the seeds are reduced by drying the seeds at different intervals of time and results in higher oil yield. This drying time for seeds also affects the whole process economy as by lowering the moisture and volatile content in the oil will reduce the amount of solvent used.

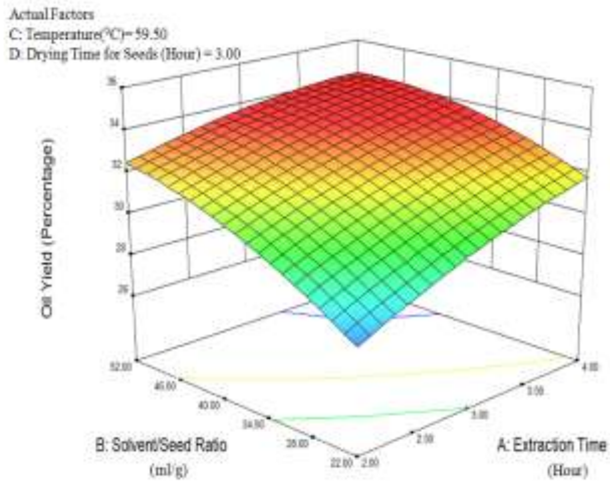

Fig. 3, 3-D plot of respond with respect to extraction time and solvent to seed ratio

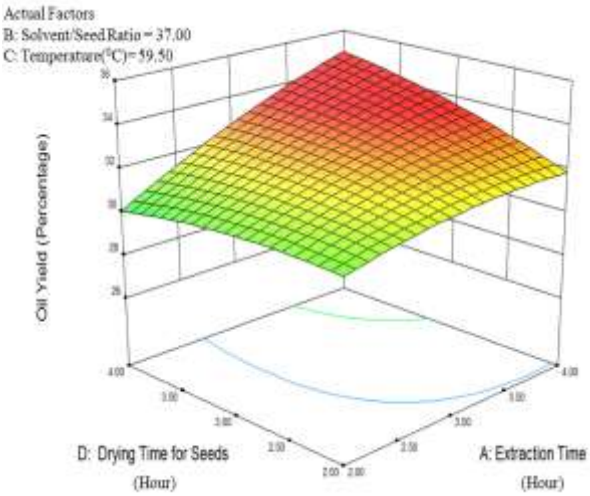

Fig. 4, 3-D plot of response with respect to extraction time and drying time for the seeds

Fig. 5 shows the affect of the solvent to seed ratio on the yield. Solvent to seed ratio has the highest affect on the oil yield. At lower solvent to seed ratio the oil yield obtained is lesser, due to lower solubility of the oil in solvent. As the solvent to seed ratio increased, the oil yield also increased because the amount of vapour contacted with the seeds increased.

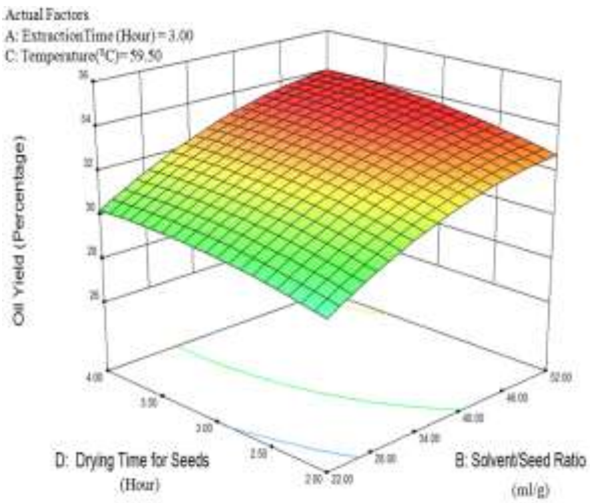

Fig. 5, 3-D plot of response with respect to solvent to seed ratio and drying time for the seeds

Fig. 6 shows the affect of the temperature on the oil yield. From the plot it shows that by increasing the process temperature the oil yield increase and gave maximum oil yield on 69^{0}C which is the boiling point of the n-hexane solvent. The same affect of the temperature has been discussed by researchers [13] [19].

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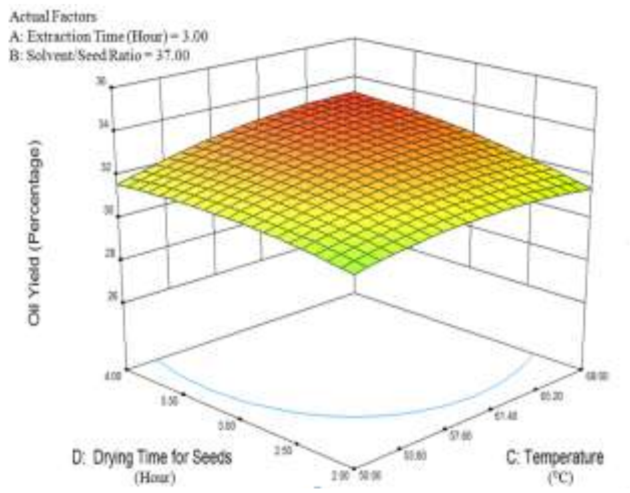

Fig. 6, 3-D plot of Response w.r.t Temperature and Drying time for the seeds

The optimized process parameters for the maximum oil yield obtained are listed in Table 5. The optimized process parameters is comparable approximately to the data published by other researchers. [12,13]

Table 5 Optimized process parameters for the maximum oil yield by solvent extraction technique using response surface methodology

Process Parameters	Units	Optimized Value
Extraction Time	Hour	4.5
Solvent/Seed	Volume/weight (ml/g)	37
Temperature	^{o}C	60
Drying time for seeds	Hour	3

4 Conclusions

Rubber seed oil has the potential to be utilized as the source of biodiesel thus reduced dependency on using edible oil feedstock. The optimized oil yield using the solvent extraction of rubber seeds was found to be 33.56% (weight basis) at the operating parameters of temperature 60^{o}C, solvent to seed ratio of 37ml/g, extraction time of 4.5 hour and drying time for the seeds of 3 hours. It has been observed that the solvent to seed ratio and extraction time is the most crucial parameters that affect the oil yield.

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