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Biodiesel Production from Babassu Oil: A Statistical Approach

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Abstract

The methyl esters synthesis from babassu oil and methanol using potassium methoxide (KOCH3) as catalyst has been developed and optimized by application of the Factorial Design of Experiments and Response Surface Methodology. The different variables affecting the alkaline methanolysis of babassu oil were studied. Temperature reaction was found to have the most significant influence on conversion. According to this study and from an economical point of view, the best conditions for overall process are catalyst concentration of 0.95% and an operation temperature of 45°C working with 6:1 methanol/oil molar ratio. With these conditions the maximum conversion obtained was 99.85%. The biodiesel produced from babassu oil has a high percentage of saturated fatty acids, 91%, mainly composed of lauric (51.8%) and myristic (22.2%) fatty acids making it particularly stable towards oxidation and resulting in good low temperature properties. The babassu oil methyl esters (BOME) could be converted in a highly promising substitute for conventional fuel possibly due to the good cold flow properties, high oxidative stability displayed and matching the European Biodiesel Standard EN 14214. These properties could make babassu oil methyl esters of a great interest.

Keywords: Biodiesel; Babassu oil; Cold flow properties; Response surface methodology (RSM)

Introduction

The current technological progress, potential reserves, and increased exploitation leads to energy insecurity and climate change by increasing greenhouse gas (GHGs) emissions due to consumption of energy at a higher rate. The use of fossil fuels is now widely accepted as unsustainable due to depleting resources and the accumulation of GHGs in the environment that have already exceeded the "dangerously high" threshold of 450 ppm CO_2 [1]. Meeting sustainable energy demand with minimum environmental impact is a major area of concern in the energy sector. Nowadays, biodiesel (fatty acid alkyl esters) is considered as an important alternative biofuel to satisfy these energy needs, due to its environmental benefits and simple production from renewable resources. The biodiesel production feedstocks vary considerably with location according to climate and availability. In United States, soybean oil is the most common biodiesel feedstock, whereas in Europe and in tropical countries, rapeseed oil and palm oil are the most common source for biodiesel respectively [2]. Nevertheless, there are no technical restrictions to the use of other types of vegetable oils. However, the main drawback of this fuel is the high cost of feedstock which leads to the high price of biodiesel. In this context babassu oil is used as an alternative and potential feed stock for biodiesel production to overcome the economic problem. Several studies have reported that the use of biodiesel has shown to be effective at reducing most regulated exhaust emissions, such as particulate matter (PM), unburned hydrocarbons (HC), and carbon monoxide (CO) [3]. In relation to the lipid feedstock, babassu oil was selected, which is extracted from Orbinya martiana, a tree whose coconuts contain in average 7 wt.% of almonds with 62 wt.% of oil. Among them, lauric acid ($C_{12}H_{24}O_2$) is the most important fatty acid. On the pragmatic point of view, babassu cannot be considered as an oleaginous species, as it contains only 4% of oil. However, considering the millions of hectares of tropical forests with a great amount of babassu palm trees and the possibilities of the integral usage of the coconut, babassu potentially constitutes an extraordinary raw material source for biodiesel production; meanwhile the other parts of the tree can be used for other purposes. In addition, it is more reasonable to use inedible oil such as babassu oil, as edible oils are not in surplus supply [4]. In this paper, the different variables affecting the alkaline methanolysis of babassu oil have been studied and optimized. The optimum values for the variables affecting the process were determined by application of factorial design and response surface methodology. Factorial design of experiments provides more information per experiment than unplanned approaches; it allows evaluating interactions among experimental variables within the range studied, leading to better knowledge of the process and therefore reducing research time and costs [5].

Materials and Methods

Equipment

Experiments were carried out in a stirred batch reactor of 500 cm^3 volume. This reactor was provided with temperature and speed control, and immersed in a thermostatic bath capable of maintaining the reaction temperature to within ±0.1°C by means of an electrical device connected to a PID controller. The impeller speed between 500 and 1200 rpm were tested; a stirring speed of 600 rpm was found appropriate to avoid external mass transfer limitation [6].

Materials

Babassu oil was supplied by Aboissa óleos vegetais (Brazil). The fatty acids composition and physicochemical properties of the oils are summarized in Table 1. Methanol, of 99.8% purity was supplied by Panreac (Spain). The catalyst used was potassium methoxide, pure grade purchased from Panreac (Spain). Samples were analyzed according to AOCS official methods. The cold flow properties (CP, PP and CFPP), of methyl esters were measured by an Automatic analyzer: Cloud and Pour point measurements CPP 97-2, according to ASTM D97 and ASTM D2500 methods.

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Characteristics	Babassu oil
Acid number (mg KOH/g)	0.15
Iodine number (I_2/100 g)	18
Peroxide number (meq Per/kg)	12.5
Viscosity (40°C)(mm^2/s)	38.28
Water content (%)	200
Fatty acid compositions (%)	
Caprylic (C8:0)	5.2
Capric (C10:0)	4.8
Lauric (C12:0)	51.8
Myristic (C14:0)	22.2
Palmitic (C16:0)	3.2
Stearic (C18:0)	3.3
Oleic (C18:1)	7.3
Linoleic (C18:2)	0.3
Other minor components	Rest to 100

Table 1: Characteristics of babassu oil used in this study and fatty acids composition.

Procedure

Experiments were performed according to the following procedure: Babassu oil was added to the reactor and fitted with a reflux condenser. When the set temperature was reached, the $KOCH_3$ catalyst diluted in methanol was introduced in the reactor. Samples were taken at regular intervals and analyzed by gas chromatography. The total reaction time was 60 minutes. In order to separate the two layers methyl esters and glycerol, the excess of methanol in the reaction mixture was removed by simple evaporation under vacuum pump (70 mm Hg) and recovered to be reused. This methanol evaporation step resulted in the separation of the two phases; the upper phase consisted of methyl esters, and the lower phase, glycerol.

Analytical method

Reaction products were monitored by capillary column gas chromatography, using a Hewlett-Packard 5890 series II equipped with a flame ionization detector (FID). The injection system was split-splitless. The carrier gas was helium at a flow rate of 1 ml/min. The analysis operating conditions have been described in detail by Garcia el al. [7] in a previous work.

Methyl esters purification

Once glycerine and methyl esters phases have been separated, the excess methanol in the methyl esters phase was removed by simple evaporation under reduced pressure and recovered to be reused. The methyl esters phase was purified by washing gently with water to remove residual catalyst, glycerol and soaps. The pH of washing water was initially high approximately 10.8 due to the dissolved $KOCH_3$. After 3 (successive rinses with water), the washing water became clear and its pH was approximately 8.1. The washing process was continued until the approximate pH of 7 was achieved. The methyl ester phase was distilled to remove the residual water. The final water content of the coconut methyl esters was less than 0.02%.

Statistical analysis

The synthesis of methyl esters by transesterification of babassu oil using $KOCH_3$ as catalyst was studied and optimized using the factorial design of experiments. The experimental design applied to this study was a full two-level factorial design 2^2 (two factors each at two levels) and amplified to Surface Response Methodology (RSM). Application of this method requires the adequate selection of response, factors and levels. The response selected, Y, was the yield of methyl esters. The selection of factors was made considering the chemistry of the system and the practical use of factorial design in order to optimize the process from an economic point of view. The factors chosen were reaction temperature, X_T and initial catalyst concentration, X_C. An excess of methanol is necessary to drive the equilibrium towards methyl ester formation. In this sense, initial alcohol/oil molar ratio was fixed at 6:1, working pressure was hold at 710 mm Hg and the impeller speed was set at 600 rpm. Selection of the levels was carried out considering the limits for the experimental set-up, working conditions for each chemical species and on the basis of other studies. Temperature levels were selected according to reactant properties and on the basis of other studies [8,9], hence the lower value was set at 30°C and the higher to 60°C. The levels of catalyst concentration were chosen on the basis of preliminary experiments [6]. The levels chosen were 0.8 and 1.2 wt.%, referring to the whole mass reaction. Once these values were selected, the statistical analysis was applied. The use of analysis and factorial design of experiments allowed to express the amount of methyl ester produced as a polynomial model. Hence we can display the response, which is the theoretical yield of ester, as a function of the significant factors.

Results and Discussion

Linear stage

The experimental design applied in this study was a 2^2 factorial design; to witch four central point coded (0) to evaluate the experimental error: A statistical analysis was performed on the experimental values, and then the statistically significant and interaction effects for two variables were calculated. The test for statistical significance is shown in Table 2. As observed in the statistical analysis, the concentration of the catalyst and temperature are significant factors. The statistical analysis of experimental results also indicates that there is no significant curvature effect for BOME. In order to complete the study, we consider a different design, which allows to fit the data to a second-order model.

Nonlinear stage

For BOME, the experiments have been amplified using a Response Surface Methodology. Additional experimental points (star points) [7] were incorporated in the two level factorial design for the two significant factors, reaction temperature and catalyst concentration. The corresponding model is the complete quadratic surface between the response and the factors, as shown by Equation 1:

$$Y = a_0 + \sum_{k=1}^{2} a_k X_k + \sum_{k=1}^{2} a_{kk} X_k^2 + \sum_{k \neq j}^{2} a_{kj} X_k X_j \quad (1)$$

The coefficients of Equation (1) were determined by multiple regression analysis. This analysis includes all the independent variables and their interactions, regardless of their significance levels. The best-fitting response surfaces can be expressed by the following statistical model: (r=0.97)

$$Y_{BOME} = 99.47 + 0.60\, X_T + 0.51\, X_C - 0.12\, X_T^2 - 0.07 X_C^2 - 0.79\, X_{TC} \quad (2)$$

The statistical model was obtained from coded levels. Equation (2) can be represented as dimensional surfaces plot see (Figure 1), revealing the predicted yield for BOME, within the investigated range of temperature and initial catalyst concentration.

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ME yield (%wt)
Main effects and interactions:
I_T=1.76, I_C=1.6, I_{TC}=-1.58
Significance test (Confidence level: 95%)
Mean responses
Y=99.01
Standard deviation
S=0.306 t=3.182
Confidence interval:
±0.49
Signifiant variables:
T(+),*C*(+),*TC*(-)
Signifiance of curvature
$C=Y-Y_C$=0.46
Confidence Curvature interval: ±0.68 Significance: NO
Response equation
$Y=99.01+0.88\ X_T+0.8\ X_C-0.79\ X_{TC}$ r=0.96

Table 2: 2^2 Factorial design for linear model: statistical analyses for babassu oil methyl esters (BOME).

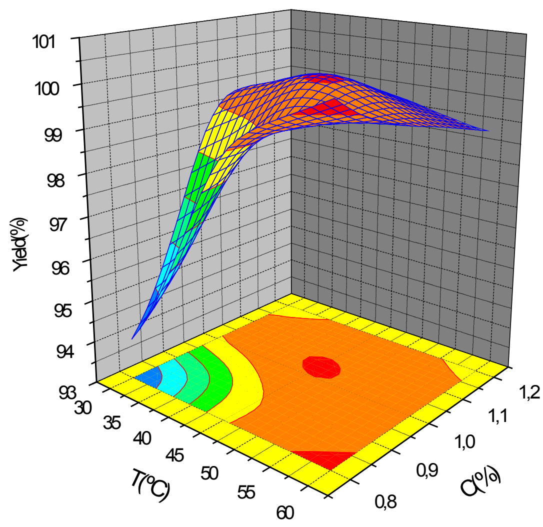

Figure 1: Response surface and contour plot of ester yield us temperature and catalyst concentration for BOME. Reaction time, t=1 h.

Discussion

From the statistical analysis, it can be concluded that within the experimental range, the temperature reaction is a significant factor in the range studied (30-60°C) affecting the process of BOME esters production. It has a positive influence on the response. The effect of temperature is greater than that of the catalyst concentration. The initial catalyst concentration influence is statistically significant in the range studied (0.8-1.2%). This effect has a positive influence in the process. Interaction of the main significant effects temperature and catalyst concentration (T-C) is significant and negatively affects the transesterification process of BOME production, possibly due to the formation of emulsions and by-products, such as soaps.

Analysis of response: Yield of ester

The ester yield generally increases with increasing catalyst concentration and temperature, but it progressively decrease at high levels of these factors. This finding may be explained by the formation of by-products, possibly due to saponification processes, side reactions which are favoured at high catalyst concentrations and temperatures. This side reaction produces potassium soaps and thus, decreases the ester yield. The free fatty acids neutralization could not be substantial since the acid value for the babassu oil was only 0.15 mg KOH/g. Consequently, triglyceride saponification must be the only possible side reaction. This is due to the presence of the metoxide group that originated soaps by triglyceride saponification. Owing to their polarity, the soaps dissolved into the glycerol phase during the separation stage after the reaction. In addition, the dissolved soaps increased the solubility of methyl ester in the glycerol phase and this involved an additional loss of methyl ester yield. The surface and the contour plot of BOME yield versus temperature and catalyst concentration obtained when individual experimental data are plotted and shown in Figure 1. Lower temperature and insufficient amount of catalyst resulted in an incomplete conversion of triglycerides into esters. While higher temperature would lead to methanol losses and catalyst concentrations larger than 1.2 wt.% are not recommended, since undesirable soap formation occurs leading to product loss and purification problems. However from an economic point of view the best conditions for the process BOME is a catalyst concentration of 0.95% and an operation temperature of 45°C, working with 6:1 methanol/oil molar ratio. According to these conditions the maximum conversion obtained was 99.86%.

Quality control of babassu oil methyl esters

The biodiesel produced from babassu oil can be used as a diesel fuel substitute since it meets the European Biodiesel Standard EN14214. Some of the important quality parameters of biodiesel viscosity, acid value, ester contents, cloud point, pour point and oxidative stability for the optimum reaction conditions are shown in Table 3. The measured values were in agreement with European Union Standard EN14214. The kinematics viscosity was 2.98 mm^2/s at 40°C and is within the range specified in EN 14214. The acid value was 0.24 mg KOH/g, within the maximum 0.5 mg KOH/g set in EN14214.

Cold flow: BOME displayed a cloud point (CP) of -4, a pour point (PP) of -6 and a cold filter plugging point (CFPP) of -8, these values are relatively low. This results may be justified due to the lower melting points of babasu methyl esters components such as methyl caprylate (C8:0), and methyl caprate (C10:0) with a melting point of (-37.3°C) and (-13.1°C) respectively [10]. The BOME is suitable to be used as biodiesel either in hot and cold weather. It may be noted that the cloud point CP is the parameter contained in the biodiesel standard ASTM D6751, while the European standard EN 14214 prescribes the cold filter plugging point (CFPP). The CP can be correlated with tests such as the CFPP and is more stringent as it relates to the temperature at which the first solids form in the liquid fuel [11]. Oxidative stability of BOME was determined by the Rancimat method EN14214, the average of two tests was 8.32 h. Thus, BOME met the oxidative stability requirements in the EN14214 standard. Although BOME contain only a low amount of unsaturated esters compared to saturated ones, the oxidative stability of BOME is influenced by these unsaturated esters. This observation has been predicted in the literature [12]. However, the nature and physicochemical properties of the BOME composition, and the presence of mono-, diglycerides (intermediates in the transesterification reaction) and/or glycerol, may play a major role in oxidative stability and cold flow properties. According to the biodiesel standard EN 14214, the monoglycerides content should be lower than 0.8 wt.%, diglycerides and triglycerides contents each lower than 0.2 wt.%. In addition, the ester content should be greater than or equal to 96.5 wt.%. For BOME the contents of ester was 99.85% and individual

Properties	BOME	EU standard, EN 14214
Viscosity at 40°C	2.98	Max. 5.00 mm^2/s
Acid value (mg KOH/g)	0.24	Max. 0.50 mg KOH/gr
Iodine value (mg I_2/g)	13	Max. 120
Water content	200	Max. 500 mg/kg
Ester contents (wt.%)	99.85	Min. 96.5% (m/m)
Monoglyceride content (wt.%)	0.00	Max. 0.80% (m/m)
Diglyceride content (wt.%)	0.15	Max. 0.20% (m/m)
Triglyceride content (wt.%)	0.00	Max. 0.20% (m/m)
Free glycerol (wt.%)	0.013	Max. 0.02% (m/m)
Oxidative stability (h)	8.32	Min. 6 h
Cloud point (°C)	-4.00	-[a]
Pour point (°C)	-6.00	-[a]
Cloud filter plugging point (CFPP)	-8.00	Depending on the country

[a]Not specified. EN 14214 uses time and location dependent values for the cold filter plugging point (CFPP) instead.

Table 3: Quality control of babassu oil methyl esters compared to EN 14214.

glyceride (MG, DG and TG) were within the three specifications, which implies that the transesterification reaction was complete

Conclusions

The study of the factors affecting the response shows that, within, the experimental range considered, the most important factor is the temperature reaction. Under optimum condition, and from an economic point of view, the maximum yield of ester (99.85%) can be obtained. It has been found that biodiesel, produced by transesterification of babassu oil using methanol as alcohol could improve biodiesel operability in cold weather. The biodiesel sample shows a high oxidative stability and displays physical-chemical properties suitable for use as diesel car fuel. As a sustainable fuel, babassu oil is promising because it is only harvested in the wild from tropical rain forests so it does not contribute to de-forestation. The shells of the fruits can also be used as biomass for fuel after the oil plant has been harvested.

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