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Biorefinery approach for coconut oil valorisation: A statistical study

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ABSTRACT

The biorefinery approach, consisting in transesterification using methanol and potassium hydroxide as catalyst, has been used to assess coconut oil valorisation. Due to the fatty acid composition of coconut oil, low (LMWME) and high (HMWME) molecular weight fatty acid methyl esters were obtained. Methyl laurate (78.30 wt.%) is the major component of the low molecular weight fraction. The influence of variables such as temperature and catalyst concentration on the production of both fractions has been studied and optimized by means of factorial design and response surface methodology (RSM). Two separate optimum conditions were found to be a catalyst concentration of 0.9% and 1% and an operation temperature of 42.5 °C and 57 °C for LMWME and HMWME, respectively, obtaining conversion rates of 77.54% and 25.41%. The valuable components of LMWME may be recovered for sale as biolubricants or biosolvents, the remaining fraction could be used as biodiesel, matching the corresponding European Standard.

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1. Introduction

Due to environmental considerations concerning sustainable development and others, like their possible contribution to regional development and to support agriculture in time of surplus production, renewable resources currently attract increasing interest as raw material for industry. In this context the process of synthesis itself has a great potential to be further developed and to convert into a central tool for implementation of innovative technology. On the other hand, process integration may be used to keep costs low and thus aid these processes to compete in a market currently dominated by-products obtained via other raw materials, namely fossil fuels such as petroleum and natural gas (Narodoslawsky et al., 2008).

Research and commercial interest in converting renewable carbon into chemicals and fuels is experiencing an important increase. Biorefinery is now a recognized approach for transforming renewable raw materials into separate biobased process streams, and finally, marketable chemicals and fuels. Successful biorefinery operation has to fulfil two strategic goals: displace non renewable raw materials (environmental reasons, met by production of biofuels) and provide economic incentive to support a robust biorefining industry (economic goal, met by the production of high value chemicals, biolubricants, biosolvents, etc.). These goals can be met simultaneously by integrating chemical and fuel production within a single operation (Bozell, 2008). According to the National Renewable Energy Laboratory (NREL), “a biorefinery is a facility that integrates conversion processes and equipments to produce fuels, power, and chemicals from biomass” (National Renewable Energy Laboratory, 2005). To achieve the goals of sustainable development, biorefineries have to play a dominant role in the beginning millennia.

Fats and oils containing lauric acid (dodecanoic acid) have attracted considerable interest over recent years. Coconut oil belongs to a unique group of vegetable oils called lauric oils. The most abundant fatty acid in this group is lauric acid, most coconut oils generally contain from 46% to 49% lauric acid, although some coconut oils tested out had only 42%.

Coconut (*cocos nucifera* L.) is grown in about 93 countries in an area of 11.8 Million hectares. One of the primary natural products produced from the dry fruit (copra) is coconut oil, which has been used since immemorial times for preparation of food, pharmaceuticals and cosmetics, being modern industrial uses focused on biofuel. The Philippines is a major producer of coconut oil with a global production of 3.3 M tons for the 2006/2007 season. The three largest coconut oil importers were Europe (41%), the Asian-Pacific Area (29%) and the USA (21%) (Focus on Surfactants, 2007).

Methyl laurate, is the basis for the production of lauryl sulfate, which has emerged as the most important unbranched and therefore biodegradable surfactant in detergents (Lockemann et al., 1995). Another valuable application is to synthesize coconut estolides esters (Cermak and Isbell, 2003), which were found to be suitable as base for biodegradable lubricants. Recently, biodiesel (methyl ester) made from coconut oil has converted into a highly promising substitute for conventional fuel, in particular in the pacific countries (Cloin, 2005). However, the main drawback of this fuel is the high cost of the feedstock causing high prices of

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Nomenclature

LMWME	low molecular weight fatty acid methyl esters
HMWME	high molecular weight fatty acid methyl esters
C	catalyst concentration
T (°C)	reaction temperature
TC	temperature–catalyst concentration interaction
X_i	level of factor i
Y (%)	ester conversion
n	number of factors in a factorial design
r	correlation coefficient
t	student's t value
s	standard deviation

α	distance from origin to star point in a central composite design
Y	mean response for the factorial design
Y_c	mean centre-points response
a_0	intercept
a_k	first-order model coefficient
a_{kk}	quadratic coefficient for the kth variable
a_{kj}	interaction coefficients for the interaction of variables k and j
X_k	independent variables

biodiesel. In this context we attempt to utilize coconut oil as a feedstock for an integrated process of biodiesel (from HMWME's) and laurate and myristate methyl esters (from LMWME's) production in order to overcome the economic problem, since the lauric fraction is the preferred material for the manufacture of soap and detergents due to its exceptional cleansing properties.

In this paper, the biorefinery approach has been used to evaluate the integrated process of coconut oil. The different variables affecting the alkaline methanolysis of coconut 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 unvaried approaches, allowing to evaluate interactions among experimental variables within the studied range, leading to better knowledge of the process and therefore reducing research time and costs (Box and Hunter, 1978).

2. Methods

2.1. 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 into a thermostatic bath capable of maintaining the reaction temperature to within ±0.1 °C of the set value by means of an electrical device connected to a PID controller. The impeller speed was tested between 500 and 1200 rpm and a value of 600 rpm was found appropriate to avoid external mass transfer limitation (Vicente et al., 1998; Bouaid et al., 2005).

2.2. Materials

Coconut oil was supplied by Gracomsa Alimentaria (Valencia, Spain). Free fatty acid content of the oil was determined according to the AOCS official method. The fatty acid composition and physicochemical properties of the oil are summarized in Table 1. Methanol of 99.8% purity was supplied by Panreac (Spain). The catalyst used was potassium hydroxide, pure grade, purchased from Panreac (Spain).

2.3. Procedure

Experiments were performed according to the following procedure: coconut oil was added to the reactor and the latter fitted with a reflux condenser. When the set temperature was reached, KOH catalyst diluted in methanol was introduced into the reactor. Samples were taken at regular intervals and analyzed by gas chromatography. During the experiments the pressure and impeller speed were maintained constant. The total reaction time was 60 min.

2.4. Analytical methods

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 separation program consisted of an initial oven temperature of 70 °C was increased at 4 °C/min to 160 °C for 1 min followed by a ramp of 30 °C/min to 320 °C and maintained for 20 min to complete the program. The other analysis operating conditions have been described in detail by Garcia et al. (1995) in a previous work. The internal standard technique has been used in order to quantify the amount of the chemical species.

Samples were analyzed according to the following procedures: acid value AV (AOCS Ca 5a-40), peroxide value PV (AOCS Cd 8-53), iodine value IV (AOCS Cd 1-25), moisture content (*Karl Fischer* method) and viscosity ν (ISO 3104). The oxidation stability of LMWMÉs and HMWME's were analyzed according to Rancimat method, using Metrohm 743 Rancimat (Herisau, Switzerland). The cloud point (CP) and pour point (PP) of methyl esters were measured by an Automatic analyzer (Cloud and Pour point measurements CPP 97-2), according to the ASTM D97 and ASTM D2500 methods.

2.5. Methyl esters purification

The second part of this study involved the separation of the low molecular weight methyl ester fraction. Once glycerine and methyl ester phases have been separated, the excess methanol in the

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

Characteristics	Coconut oil
Acid number (mg kOH/g)	0.08
Iodine number (I_2/100 g)	9.93
Peroxide number (meq Per/kg)	1.71
Viscosity (40 °C) (mm^2/s)	34.6
Water content (%)	0.04
Fatty acid compositions (%)	
Caprylic (C8:0)	6.05
Capric (C10:0)	4.25
Lauric (C12:0)	49.70
Myristic (C14:0)	19.30
Palmitic (C16:0)	11.10
Stearic (C18:0)	6.55
Oleic (C18:1)	2.90
Other minor components	Rest to 100

methyl ester phase was removed by simple evaporation under reduced pressure and recovered to be reused. The methyl ester 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, due to the dissolved KOH. After three successive rinses with water the washing water became clear and its pH was approximately 8.1. The washing process was continued until a pH of approximately 7 was achieved. The methyl ester phase was then distilled to remove the residual water. The final water content of the coconut methyl esters was less than 0.01%.

2.6. Statistical analysis

The synthesis of low and high molecular weigh methyl esters by transesterification of coconut oil using KOH 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 Response Surface Methodology (RSM). Application of this method requires the adequate selection of response, factors and levels.

The response selected, Y, was the yield of methyl ester. The selection of factors was made considering chemical and economic benchmarks of the process. 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, therefore, initial alcohol/oil molar ratio was fixed to 6:1. The working pressure was fixed at 710 mm Hg and the impeller speed was set to 600 rpm. Selection of the levels was carried out on the basis of results obtained in a preliminary study, considering limits for the experimental set-up and working conditions for each chemical species. Temperature levels were selected according to reactant properties and on the basis of other studies (Vicente et al., 1998; Bouaid et al., 2007), hence the lower value was set to 30 °C and the higher to 60 °C. The levels of catalyst concentration were equally chosen on the basis of previously published, preliminary data (Vicente et al., 2004, 2005); the amount of catalyst was progressively increased and the ester yield was monitored versus time. 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 experimental matrix for the factorial design is shown in Table 2. The first two columns of data show the "±1" coded factor levels in the dimensionless co-ordinate and the next two show the factor levels on a natural scale. All experimental runs were randomly performed. For experimental error estimation, four experiments were carried out at the central point level, coded as '0'. The use of analysis and factorial design of experiments allowed to express the amount of methyl ester produced as a polynomial model. If the levels of the factors are equally spaced, then orthogonal polynomials may be used. Hence we can display the response, which is the theoretical yield of ester, as a function of the significant factors.

Table 2
2^2 Factorial experiment matrix: experimental results.

Experiment	Coded design levels		Real values		Y_{LMWME} (%)	Y_{HMWME} (%)
	X_T	X_C	T (°C)	C (%)		
1	−1	−1	35	0.86	74.25	20.47
2	+1	−1	55	0.86	77.50	20.50
3	−1	+1	35	1.14	76.50	20.72
4	+1	+1	55	1.14	76.20	23.79
5	0	0	45	1	76.7	21.67
6	0	0	45	1	77.2	21.7
7	0	0	45	1	76.94	21.43
8	0	0	45	1	76.69	21.51

3. Results and discussion

3.1. Linear stage

The experimental design applied in this study was a 2^2 factorial design, to which four central points were added in order to evaluate the experimental error. The results obtained are shown in the first eight lines of Table 2. A statistical analysis was performed on these experimental values, then the statistically significant and interaction effects for two variables were calculated. The test for statistical significance is shown in Table 3.

Temperature (X_T), catalyst concentration (X_C) effects and their interactions (X_{TC}) were fitted by multiple regression analysis to a linear model. The response function for the main significant effects and interactions can be expressed as:

$$Y_{\mathrm{LMWME}} = 76.11 + 0.24X_C + 0.74X_T - 0.85X_{TC} \quad r = 0.99 \tag{1}$$

$$Y_{\mathrm{HMWME}} = 21.36 + 0.88X_C + 0.77X_T + 0.76X_{TC} \quad r = 0.97 \tag{2}$$

As observed in the statistical analysis, and in accordance with previous results obtained by Vicente et al. (2005) and Bouaid et al. (2009), both the catalyst concentration and the temperature are significant factors. The statistical analysis of experimental results also indicates that there is no significant curvature effect for LMWME, while it is significant for HMWME process. It was therefore necessary to consider a different design, allowing to fit the data to a second-order model.

3.2. Non-linear stage

According to the central composite design methodology and because of the significance of curvature effect found in the linear stage, a second-order model is required for HMWME. For LMWME,

Table 3
2^2 Factorial design for linear model: statistical analyses for low molecular weigh methyl esters (LMWME) and high molecular weigh methyl esters (HMWME).

Responses		
LMWME yield (%wt)		
Main effects and interactions	$I_T = 1.48$, $I_C = 0.48$, $I_{TC} = -1.7$	
Significance test (confidence level: 95%)		
Mean responses	$Y = 76.11$	
Standard deviation	$S = 0.24$	$t = 3.182$
Confidence interval	±0.38	
Signifiant variables	$C(+)$, $T(+)$, $TC(-)$	
Signifiance of curvature		
Curvature	$C = Y - Y_C = 0.77$	
Confidence curvature interval	±1.08	
Significance	Yes	
Response equation		
$Y = 76.11 + 0.24\ X_C + 0.74\ X_T - 0.85\ X_{TC}$		$r = 0.99$
HMWME yield (%wt)		
Main effects and interactions	$I_T = 1.55$, $I_C = 1.77$, $I_{TC} = 1.52$	
Significance test (confidence level: 95%)		
Mean responses	$Y = 21.36$	
Standard deviation	$S = 0.075$	$t = 3.182$
Confidence interval	±0.12	
Signifiant variables	$C(+)$, $T(+)$, $TC(+)$	
Signifiance of curvature		
Curvature	$C = Y - Y_C = 0.4$	
Confidence curvature interval	±0.34	
Significance	Yes	
Response equation		
$Y = 21.36 + 0.88X_C + 0.77\ X_T + 0.76\ X_{TC}$		$r = 0.97$

the experiments have been amplified using a Response Surface Methodology. Additional experimental points (star points) had to be incorporated in the two-level factorial design for the two significant factors, reaction temperature and catalyst concentration. The full central composite design, adapted from Box and Wilson (1951), includes factorial points, centre-points and star points and is also shown in Table 2 and Table 4. The corresponding model is the complete quadratic surface between the response and the factors, as shown by Eq. (3):

$$Y = a_0 + \sum_k = 1^2 a_k X_k + \sum_k = 1^2 a_k k X_k^2 + \sum_k \neq j^2 a_k j X_k X_j \qquad (3)$$

Four additional runs, called star points and coded ±α, were added to the 2^2 factorial plus centre-points to form a central composite design and are summarized in Table 4, where α, the distance from the origin to the star point, is given by $\alpha = 2^{n/4}$, in the design, $\alpha = 1.414$. The coefficients of Eq. (3) 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:

Table 4
Experimental results of the star points.

Experiment	Coded design levels		Real values		Y_{LMWME} (%)	Y_{HMWME} (%)
	X_T	X_C	T (°C)	C (%)		
9	+α	0	60	1	75	25
10	−α	0	30	1	76.25	21.44
11	0	+α	45	1.2	77.16	20.5
12	0	−α	45	0.8	76.2	20.98

$$Y_{LMWME} = 76.88 + 0.28X_C + 0.14X_T - 0.88X_TX_C - 0.63X_T^2 - 0.11X_C^2 \quad r = 0.97 \qquad (4)$$

$$Y_{HMWME} = 21.4 + 0.35X_C + 1.01X_T - 0.76X_TX_C - 0.75X_T^2 - 0.48X_C^2 \quad r = 0.98 \qquad (5)$$

The statistical model was obtained from coded levels. Eqs. (4) and (5) can be represented as dimensional surface plots (see Fig. 1a and b), revealing the predicted yields for HMWMÉs and LMWMÉs within the investigated range of temperature and initial catalyst concentration.

In the following, the influence of the variables reaction temperature and catalyst concentration on low and high molecular weight methyl ester yields will be discussed. The influence of the main factors and interactions will be discussed from statistical models.

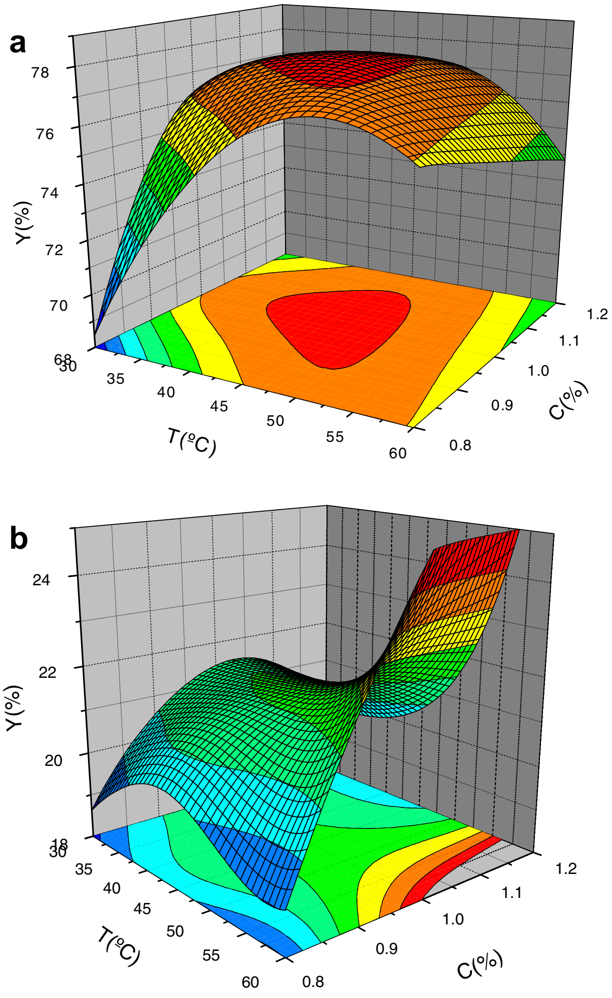

Fig. 1. Response surface and contour plot of ester yield us temperature and catalyst concentration for LMWME (a) and HMWME (b). Reaction time, $t = 1$ h.

3.3. Influence of the initial catalyst concentration

From the statistical analysis can be concluded that within the experimental range, initial catalyst concentration is a significant factor affecting the transesterification process for both LMW and HMW methyl ester production. The effect of catalyst concentration is greater for HMWME than for LMWME. It has a positive influence on the response; in other words, the ester yield generally increases with increasing catalyst concentration. Insufficient amount of catalyst resulted in incomplete conversion of triglycerides into esters, as indicated by a lower ester content Fig. 1(a and b).

3.4. Influence of temperature

For both the linear and non-linear model, the influence of temperature is statistically significant in the studied range (30–60 °C). This effect has a positive influence in the process. Increasing temperature increases the solubility of the alcohol in the oil (melting point around 30 °C), which may explain a positive effect on the conversion. When the temperature increase above 55 °C, the product yield (LMWME) started to decrease Fig. 1(a and b), which is possibly due that higher temperatures accelerate a side reaction by saponification, mainly affecting the short and medium chain fatty acids.

3.5. Influence of (T–C) interaction

The non-linear model (Central Composite Design) yields binary influences of all the factors used in the design. Interaction of the main significant effects temperature and catalyst concentration (*T*–*C*) is significant and negatively affects the process in the case of LMWME production, possibly due to the formation of by-products, such as soaps. It should be noted that the LMWME fraction is mainly composed of caprylic (C8:0), lauric (C12:0) and myristic (C14:0) fatty acids, which are more reactive.

3.6. Analysis of response: ester yield

The ester yield was defined as the weight percentage of methyl ester with respect to the amount of vegetable oil (coconut oil) poured into the reactor. For HMWME and LMWME, corresponding yields refer to the HMWME and LMWME concentration (wt.%) in the overall methyl ester fraction; corresponding numerical values were determined by capillary gas chromatography.

The ester yield generally increases with increasing catalyst concentration and temperature, but it progressively decreases at high levels of these factors in the case of LMWME. This finding may be explained by the formation of by-products, possibly due to saponification processes, favoured at high catalyst concentrations and temperatures. This side reaction produces potassium soaps and thus, decreases the ester yield.

Another possible side reaction, the neutralization of free fatty acids, also produces potassium soaps and may be considered partly responsible for the decrease in the reaction yield. Anyhow, this reaction cannot be very important since the free fatty acids content for the coconut oil was only 0.08 mg KOH/g. Consequently, triglyceride saponification must be the predominant possible side reaction. After the reaction and during the separation stage, these soaps are, due to their polarity, dissolved into the glycerol phase, causing here increase of the solubility of LMWME, involving an additional loss of LMWME yield.

The surface and the contour plot of LMWME and HMWME yields versus temperature and catalyst concentration obtained when individual experimental data was used are shown in Fig. 1(a) and (b). The comparison of these plots shows that the maximum ester yield (Y_{LMWME} = 77.54%) is achieved at a medium level for both catalyst concentration and operation temperature in the case of LMWME. While for HMWME, (Y_{HMWME} = 25.41%) a maximum level of temperature and a medium level of catalyst concentration have to be applied.

Fig. 2 presents a plot of the residual distribution, defined as the difference between calculated and observed values, over the observed values for the two responses studied, LMWME and HMWME yields. In both cases, the quality of the fit is good because the residual distribution does not follow any trend with respect to the predicted variables. All the residuals are smaller than 0.9% and 1.3% for LMWME and HMWME yields, respectively, which indicate that the models adequately represent the methyl ester yield over the experimental range studied.

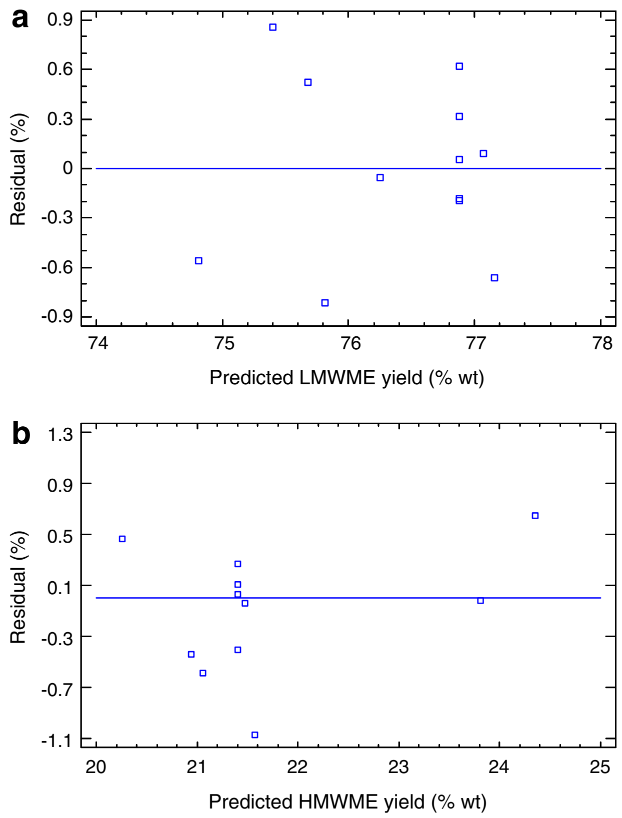

Fig. 2. Residual plots of methyl esters yield for the second-order model. (a) LMWME and (b) HMWME.

Lower temperature and insufficient amount of catalyst resulted in incomplete conversion of triglycerides into esters. Higher temperature would lead to methanol losses, causing catalyst concentrations larger than 1.2 wt.%, which is not recommendable because undesirable soap formation may occur, leading to product loss and purification problems.

However from an economic point of view, the highest possible yield for the more valuable LMWME fraction should be targeted, consequently a catalyst concentration of 0.9% and an operation temperature of 42.5 °C should be chosen. According to these conditions and working with 6:1 methanol/oil molar ratio, conversion rates of 77.54% and 20.63% for LMWME and HMWME, respectively, could be obtained.

The purified methyl ester layers obtained under the optimized working conditions predicted by the quadratic model were subjected to a vacuum distillation using a thermally stable silicone oil bath, applying a temperature of 140 °C and a vacuum maintained at 4 mm Hg for 2 h. The distillate composition was then determined by gas chromatography, results are shown in Table 5. Fig. 3 presents different liquid processing steps in a typical biorefinery based on coconut oil.

It should be noted that 78.3 wt.% of the distillate consisted in methyl laurate, which has lower toxicity, higher biodegradability and excellent lubricating properties compared to similar petroleum based products. Due to its exceptional properties (Cermak and Isbell, 2009; Woodcock et al., 2008), the lauric fraction has potential to be used by the chemical industry for manufacturing of detergents, surfactants, biolubricants, biosolvents and other products. Cermak and Isbell (2002) reported that the lauric (C12:0) and myristic (C14:0) fatty acids could be used as excellent low temperature estolides.

The LMWME fraction displayed a cloud point of −6 C and a pour point of −9 °C, possibly due to the low melting points of particular LMWME components such as methyl caprylate (C8:0, melting point −37.3 °C) and methyl caprate (C10:0, melting point −13.1 °C) (Rashid et al., 2008), which are below the cloud point of LMWME. Another point is that the simple vacuum distillation decreases the amount of higher melting saturated fatty esters such as methyl palmitate (C16:0, melting point around 30 °C) in the LMWME fraction. These good cold flow properties could make from the low molecular weigh methyl esters fraction a material of great interest. Both CP and PP should be closely monitored by the user to ensure trouble-free operation in cold climates.

Table 5
Composition of the distillate and some properties.

Component	Methyl esters composition (wt.%)
Methyl caprylate C8	10.09
Methyl caprate C10	0.99
Methyl laurate C12	78.30
Methyl myristate C14	8.45
Methyl palmitate C16	1.20
Methyl oleate, methyl stearate, C18:0, C18:1	0.29
Methyl linoleate C18:2	–
Physicochemical properties	
Viscosity (40 °C) (mm^2/s)	2.56
Oxidative stability (h)	>24
Cloud point (°C)	−6
Pour point (°C)	−9

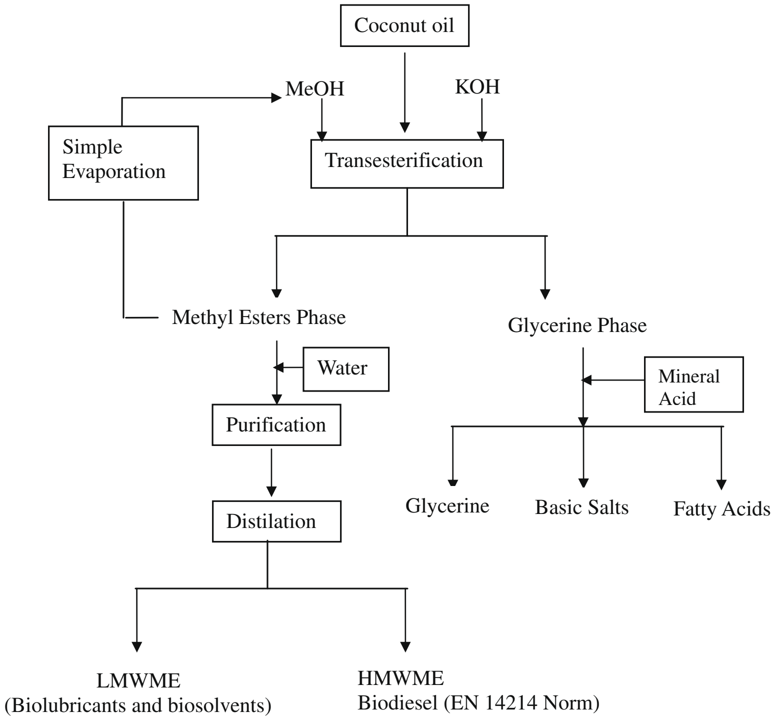

Fig. 3. A conceptual biorefinery based on coconut oil.

3.7. Quality control of HMWME

The leftover after distillation can be used as a diesel fuel substitute, since it matches the European Biodiesel Standard EN14214. Some of the important quality parameters of biodiesel listed herein (viscosity, acid value, ester content, cloud point, pour point and oxidative stability for optimum reaction conditions) are shown in Table 6. The experimentally determined values were in agreement with EN14214 requirements. The kinematic viscosity of HMWME was 4.4 mm^2/s at 40 °C, which is within the specified range and the acid value was 0.09 mg KOH/g, substantially under the maximum of 0.5 mg KOH/g set in the normative. The HMWME fraction displayed a cloud point of 5 °C and a pour point of 2 °C, being these values relatively high. However, the material is suitable to be directly used as biodiesel in hot clima zones, like those where coconut is grown. Even for use at lower temperatures, the cold flow properties could easily be improved by a variety of treatments, as described by Dunn et al. (1996) and Nestor et al. (2006). It is noteworthy that the cloud point (CP) is the parameter contained in American biodiesel standard (ASTM D6751), while the European standard (EN14214) prescribes the cold filter plugging point (CFPP). The CP can be correlated to the CFPP, but is more stringent as it relates to the temperature at which the first solids form in the liquid fuel (Knothe et al., 2009). The oxidative stability of the HMWME fraction was determined by the Rancimat method EN14214, the average of two tests was 6.14 h, thus matching the oxidative stability requirements of the EN14214 standard. Although HMWME generally contain only a low amount of unsaturated esters, it is thought that the oxidative stability of HMWME basically depends on them (Imahara et al., 2006). However, the nature and physicochemical properties of the HMWME components and the presence of mono-, diglycerides (intermediates in the transesterification reaction) and/or glycerol may also play a major role in oxidative stability and cold flow properties. According to EN 14214, the monoglyceride (MG) content should be lower than 0.8 wt.%, and the content of diglycerides (DG) and triglycerides (TG) lower than 0.2 wt.%, each. In addition, the ester content should be greater than or equal to 96.5 wt.%. For the HMWME fraction the latter value was 98.7% and individual glyceride (MG, DG and TG) concentrations were also matching the specifications, which implies that the transesterification reaction was complete.

Table 6
Quality control of high molecular weight methyl ester (HMWME) compared to EN 14214.

Properties	HMWME	EU Standard EN 14214
Viscosity at 40 °C	4.40	Max. 5.00 mm^2/s
Acid value (mg KOH/g)	0.09	Max. 0.50 mg KOH/gr
Water content	100	Max. 500 mg/kg
Ester contents (wt.%)	98.7	Min. 96.5% (m/m)
Monoglyceride content (wt.%)	0.08	Max. 0.80% (m/m)
Diglyceride content (wt.%)	0.10	Max. 0.20% (m/m)
Triglyceride content (wt.%)	0.00	Max. 0.20% (m/m)
Free glycerol (wt.%)	0.01	Max. 0.02% (m/m)
Total glycerol (wt.%)	0.12	Max. 0.25% (m/m)
Cloud point (°C)	5.00	[a]
Pour point (°C)	2.00	[a]
Oxidative stability (h)	6.14	Min. 6 h

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

3.8. Glycerine purification

The glycerine by-products contain unused catalyst and soaps, which were neutralized with phosphoric acid. The fatty acids formed hereby could be recovered as a valuable additional product, while the basic salts formed in this step were recovered to be used as fertilizer. The obtained glycerol could be used for a variety of recently developed applications, such as automotive fuel (Fernando et al., 2007) and in the fields of animal feed, carbon feedstock in fermentation processes, polymer production, intermediates and lubricants (da silva et al., 2009).

4. Conclusions

This study has established an integrated process for coconut oil as raw material, focussing on production of the valuable low molecular weight methyl ester fraction (methyl caprylate, methyl laurate and methyl myristate). Under optimum conditions, a yield of 77.54% could be obtained. The resulting higher molecular weight fraction (20.63%) directly matched the European requirements to be used as biodiesel; from other by-products additional valuable components could be recovered. Hence, the use of this raw material as a renewable feedstock in an upgraded industrial process could help to successfully develop a self sustained biorefinery.

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