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Ultrasound-assisted production of biodiesel from oils with saturated and unsaturated fatty acids

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Abstract. The reaction of biodiesel or FAME (Fatty Acid Methyl Esters) production can become especially slow because of the mass transfer between the non-polar phase (oil) and polar (alcohol) is one of the critical factors. Thus, different technologies have been developed to reduce the reaction time . One of them is ultrasound. Ultrasound is an acoustic wave with a frequency greater than the upper limit of human hearing. In the present work biodiesel from oils rich in unsaturated fatty acids (rapeseed and soybean) and saturated (coconut and palm) has been synthesized using ultrasound as auxiliary energy. For this, an ultrasonic probe at a fixed frequency of 20 kHz and 450 W of power was used. Moreover, it attempted to determine if the chemical composition affects the ultrasound assisted biodiesel synthesis... FAME yields were evaluated in the different oils. The rapeseed, soybean and palm yields achieved above 90 % wt., close to meet with European standard UNE EN 14003, but coconut oil was just over 80% wt. conversion. Thus, it was observed that the differences between the oil yields are determined by chain length of the fatty acids that form part of the triglyceride. Coconut oil has mainly short chain fatty acids opposed to rapeseed, soy and palm fatty acids having 16 carbons or higher. Regarding the reaction time, it was reduced significantly compared to conventional transesterification.

Keywords

Transesterification, fatty acid methyl esters, sonication

1. Introduction

One of the major concerns of modern society is its dependence on fossil fuels and the continued growth of pollution derived from green house gases is becoming into a serious health problem. Moreover, the continued increase in fuel prices from oil and the fact that oil is a source of invites finite energy alternatives that are viable and sustainable to provide fuel to traffic on the planet. Thus, the use of biofuels has become one of the options to consider. One is the biodiesel (BD) is synthesized by reacting the fatty acids in oils from oleaginous plants, animal fats or oils from microbial sources with a short chain alcohol (methanol or ethanol). Today, BD is marketed in many countries, including Argentina, Austria , Brazil, Czech Republic, Germany, France , Italy, Slovakia , Spain and the U.S., either in pure form or blended with diesel [1], since these fuels are stable mixtures at any concentration .

The reaction leading to BD is known as transesterification and is between two substances of very different chemical nature, oil (apolar) and the alcohol (polar), which is why you need to apply continuous agitation. Although 80 % of the cost of biodiesel is mainly due to the raw material, there are other factors that increase the total price of the product that should be taken into consideration. The reaction time is particularly high (1-2 hours depending on the oil) and the optimum temperature is normally 55-60 ° C (never exceeding the boiling point of methanol), these two factors make the energy consumption is considerably high. On the other hand, excessive use of alcohol and catalyst are also two parameters for extra charge. Thus, in recent years have sought different alternative energy sources in order to reduce the values of all the parameters involved in the reaction for biodiesel. One is the use of ultrasound (US).

1.1 Principles behind ultrasound

US is an acoustic wave with a frequency greater than the upper limit of human hearing (about 20 kHz). US is generated by a local variation of density or pressure of a continuous medium that is transmitted from one place to another through any substance, solid, liquid or gas possessing elastic properties. Table 1 shows the ranges and frequencies of US [2] and human hearing [3].

Table 1: Frequency range of US and human hearing.

Frequency range	Applications
2-10 MHz (high frequency)	Diagnostic US and medical imaging
20-100 kHz (low frequency)	Conventional US used in cleaning and Sonochemistry
16-18 kHz	Human hearing

2. Experimental procedures, materials and methods

2.1 Objectives of the study

The aim of this study is the selection of several raw materials with different chemical composition for the synthesis of BD assisted by ultrasound and tries to establish trends in FAME yields and the degree of saturation / unsaturation of fatty acids from triglycerides of each oil. It also the impact of the physical characteristics of ultrasound in the response variables specific of transesterification reaction is evaluated.

2.2 Raw materials

Vegetable oils for BD production: Soybean oil was purchased from Guinama (Alboraya, Valencia, Spain), coconut oil from Acofarma (Terrassa, Barcelona, Spain), palm oil from Químics Dalmau (Barcelona, Spain) and rapeseed oil was provided by IFAPA (Instituto de Formación Agraria y Pesquera, Córdoba, Spain).

2.3 Methods and experimental procedures

2.3.1 Methods

Ultrasonic irradiation was applied by means of a Branson 450 digital sonifier (20 kHz and 450 W) equipped with a cylindrical titanium alloy probe (12.70 mm diameter) and a thermostated water bath.

Analyses performed on biodiesel samples: The determination of the water content in oil and BD was held in Karl Fischer Coulumeter DL32 from Mettler-Toledo (Schawerzenbach, Switzerland). Flash point was determined by a Seta Flash series 3 plus from Instrumentación Analítica S.A. (Madrid, Spain). Analysis were carried out following the standard UNE EN ISO 2719 [4]. HCV (high calorific value) was measured using a calorimeter bomb Optika SRL model IKA C200 from Ponteranica (Italy). Analysis were carried out following the ASTM D240 standard [5].

The conversion of oils to methyl esters was analyzed following the UNE EN 14103 standard [6] and determination of mono-, di-, triglycerides and glycerol was performed according to UNE EN 14105 [7] for rapeseed and soybean biodiesel. The equipment was a gas chromatograph with flame ionization detector (GC–FID) model Clarus 500 from Perkin-Elmer (Shelton, Connecticut, USA). The content in FAME, mono-, di-, triglycerides and glycerol in coconut and palm BD was determined by a size-exclusion chromatography (SEC) system consisted of a Waters 510 HPLC pump, a Rheodyne 7725i manual injector, a Waters model 410 differential refractive index (RI) detector, while analysis was performed with TriSEC® GPC software.

2.3.2 Experimental procedure

All experiments were carried out in batch. 20 g of each oil was weighed in a wide-mouth flask and a methanol solution with the amount of dissolved potassium hydroxide solution that contains the percentage of catalyst programmed for each experiment with respect to the molar ratio (methanol/oil) was added. Each solution was sonicated for a scheduled time for each experiment in a water bath at room temperature taking temperature after each sonication cycle at the value of the variables present for each experiment design. BD samples were subjected to centrifugation for 4 min at 4000 rpm to separate glycerol from the FAME; then, the latter were stored in refrigerator at 4 °C until chromatographic analysis. Samples of rapeseed and soybean BD were analyzed using a GC–FID instrument according to the methods specified in the Standards UNE EN 14103 and UNE EN 14105 . UNE EN 14105 excludes the analysis of mono-, di-, triglycerides and glycerol in BD from coconut and palm oils because of overlapping of chromatographic peaks between methyl esters of fatty acids (FAME) and such compounds. For this reason, samples from coconut and palm oils were analyzed using the SEC system described above.

2.3. Software for statistical analysis

Statgraphics© Centurion XVI (Statpoint Technologies, Warrenton,Virginia, USA) was used for building and analyzing the response surfaces, allowing to design the multiple response optimization and plot the graphical responses.

3. Results and discussion

3.1 First experimental design: screening step

A half fraction screening design was created and the effects of 4 experimental factors in 11 runs including 3 center points per block with 3 degrees of freedom were studied.

Table 2: First experiment design.

EXP	MR	AC	DC	A
1	4	0.2	70	60
2	5	0.2	70	40
3	5	0.2	30	60
4	4	0.8	70	40
5	4	0.2	30	40
6	4.5	0.5	50	50
7	4.5	0.5	50	50
8	4	0.8	30	60
9	5	0.8	30	40
10	4.5	0.5	50	50
11	5	0.8	70	60

Exp: Experiment, **MR:** Methanol to oil molar ratio, **AC:** Amount of catalyst (% w/w), **DC**: Duty cycle, **A:** Amplitude

The design was used to screen two chemical reaction factors (methanol-to-oil molar ratio and catalyst concentration) and two US factors (duty cycle and amplitude), all of them with potential influence on the transesterification process.
The experimental domain was defined taking into account the results obtained in preliminary studies [8-12] considering the experimental installation and the working conditions.
The most significant results of the screening were summarized in table 3.
Of the 11 experiments performed, the maximum FAME yield for each oil corresponds to **experiment 11**, where the molar ratio was 5, the amount of catalyst 0.8%, the duty cycle 70% and 60% of amplitude. In table 3, are summarized the values for each oil as weight percent for the response variables in the experiment 11.
Four response variables were analyzed in each experiment: the content of FAME (% wt.), mono-, di- and tryglicerides MG (% wt.), DG (% wt.) and TG (% wt.), aimed a maximizing the yield of content of FAME while minimizing those of glycerides.

Table 3: Optimal values for FAME, MG, DG and TG (% wt.) in screening step.

OIL	FAME	MG	DG	TG
Rapeseed	79.84	1.62	3.20	7.07
Soybean	79.47	1.34	3.36	9.41
Coconut	74.92	1.77	2.73	16.85
Palm	79.99	2.15	5.43	8.91

3.2 Second experiment design: surface response step

Table 4: Second experiment design.

EXPERIMENT	AC	US CYCLE
1	1	2
2	0.8	2
3	1.2	2
4	1.2	1
5	1	1
6	1	2
7	0.8	1
8	1.2	3
9	1	2
10	1	2
11	1	3
12	0.8	3

AC: Amount of catalyst (% wt.)

Because the amount of catalyst was the only parameter with a positive and significant impact at 95% confidence level on the four response variables, it was the only parameter of the first screening design that was included in the second experimental design. The second design also included a second parameter: the insertion of stop intervals between sonication cycles (US cycles). A response surface design experiment was performed. A 3-level factorial design was created to study the effects of 2 factors (amount of catalyst and US cycle) in 12 runs including 3 center points per block and 6 degrees of freedom. The response variables were 4: MG (% wt.), DG (% wt.), TG (% wt.) and FAME (% wt.). Design 2 is outlined in Table 4.

BD samples were analyzed using the same methods as in the previous experiment design. The optimum values obtained were analyzed following the UNE EN 14214 standard, the results are summarized in table 5.

Table 5: Physical and chemical properties of optimal biodiesel for each raw material (DOE II) according to standard 14214.

PROP	RB	SO	CB	PB
MG	0.55	0.42	4.11	1.31
DG	0.61	0.69	1.57	1.62
TG	2.15	6.03	10.37	3.21
Gly	0.66	0.88	0.22	0.84
FAME	95.03	94.66	81.37	93.08
FP (°C)	175.5	169	108	131
HCV (J/s)	39786	39683	38064	38338
WC (ppm)	303.21	412.2	485.17	463.32
μ (mm/s^2)	4.62	4.7	3.2	5.63
ρ (kg/m^3)	882	883	5.63	874

FP: Flash point. **HCV:** High calorific value.
WC: Water content. **μ:** Kinematic viscosity. **ρ:**Density.
PROP: property. **Gly:** Glycerol

Considering FAME yields and the weight percentages of the glycerides, two groups of oils in terms of reactivity can be distinguished. Rapeseed, soybean and palm oils whose average length of chain are higher than 17 carbon atoms exhibit maximum of FAME yields above 90%. However, coconut oil whose length of chain is 13 carbon atoms hardly presents maximum yields exceeding 80%.

In this case, it is observed that there is very pronounced chain of length effect.

The physical and chemical properties for each optimal value were analyzed as well as the chemical composition of biodiesel. Table 5 summarizes the results obtained. It can be observed the chemical composition of the optimal values of each biodiesel. FAME yields of biodiesel from rapeseed, soybean and palm are above 90% wt., coconut biodiesel reaches only 81.3% wt.. Table 5 allows conclude that the density data for the four types of biodiesel are in agreement with the standard, all of them are below 900 kg/m3. The standard water content is also satisfied because the four values are below 500 ppm. Kinematic viscosity of biodiesel from rapeseed, soybean and coconut oils are between the standard values indicated (3.5–5.0 mm/s^2). Only palm oil has a value of 5.6 mm/s^2, that exceeds the standard. UNE EN 14214 [13] establishes the flash point in a minimum of 120 °C. The only BD that does not reach this value is coconut, with a flash point of 108 °C. HCV values are around 39000 J/s.

3.2.1 Desirability study of surface response

A second study of desirability was applied to know the trends of the two variables together, thus trying to establish their optimal values. Table 6 shows that the maximum number of US cycles for the four biofuels is 3. Therefore, it is possible to increase this variable to achieve higher performance in FAME. In the case of the amount of catalyst, for BD from rapeseed and palm, the maximum is 1.2%, thereby also could further increase this variable. Coconut and soybean have maxima of 1.13 and 1.06%, respectively; so, this variable would be optimized. Making a general analysis, oils with predominance of unsaturated FFAA (rapeseed and soybean) have better performance than those with predominance of saturated FA (coconut and palm), being the coconut that giving a lower yield.

Table 6: Effects of each reaction parameter on each response variable for four kinds of BD.

Rapeseed BD	
Factor	***Optimum***
Catalyst	1.2
US cycle	3.0
Soybean BD	
Factor	***Optimum***
Catalyst	1.06
US cycle	3.0

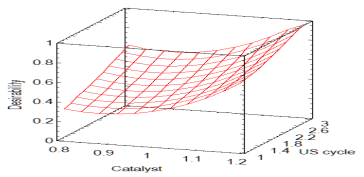
Coconut BD	
Factor	***Optimum***
Catalyst	1.13
US cycle	3.0

Palm BD	
Factor	***Optimum***
Catalyst	1.2
US cycle	3.0

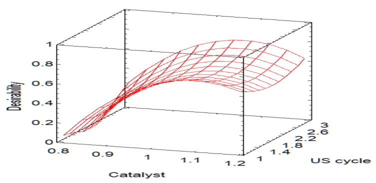
On the other hand, if cycles of US are observed, they are not statistically significant, so it could increase the values of US in order to increase FAME values. However, US cycles are definitely the reaction time and this study attempts to reduce reaction time and save energy.

Trends in each response variable in the response surface study are shown in Figure 1.

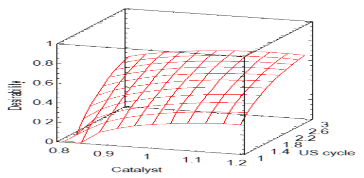
Rapeseed BD



Soybean biodiesel



Coconut biodiesel



Palm biodiesel

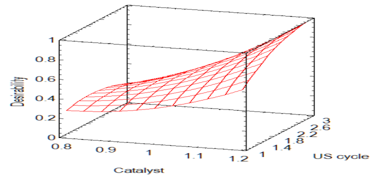


Figure 1: Response surfaces

4. CONCLUSIONS

The main objective of this study was to try to establish significant differences between FAME yield and properties of BD synthesized by US assistance from oils with a composition rich in unsaturated FA (rapeseed and soybean) as compared to others rich in saturated FA (coconut and palm). The study was also aimed at evaluating the effect of US characteristics on the response variables (MG, DG, TG and FAME yields).

In terms of conversion to FAME, rapeseed oil, soybean oil (mainly with unsaturated FFAA) and palm oil (mainly with saturated FFAA) provide similar yields (93-95%). Coconut oil has a particularly low yield (> 80%), far from that of other saturated oil (palm oil). Therefore, significant differences cannot be established between BD from oils rich in saturated FFAA as compared to that obtained with oils rich in unsaturated FFAA when US are used as auxiliary energy to facilitate–accelerate the process.

Although the chemical composition of the oils seems to exert no significant effect on FAME conversion, the length of the FFAA chain has a significant impact, as shown by the behavior of coconut oil, with a 75% of saturated FFAA with 14-carbon chains or shorter. Conversions are higher for oils with FFAA of 16-carbon atoms chains or longer.

Regarding US, it can be concluded that none of US characteristic variables (viz. power and duty cycle) has a significant impact on FAME yield for any of the studied oils. The only response variable that had a notable effect on yield was the amount of catalyst in both experimental designs. Also, application of sonication cycles has not a significant effect on any of the factors, except a negative effect on DG synthesis in soybean oil.

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