

RESPONSE SURFACE METHODOLOGY APPLIED IN THE BIODIESEL PRODUCTION FROM USED COOKING OIL TO REDUCE THE ENVIRONMENTAL IMPACTS CAUSED BY IMPROPER DISPOSAL

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Biodiesel is a biofuel derived from renewable sources, such as animal fat or vegetable oils. It is sulphur free, non-toxic and biodegradable; it reduces the emission of gas pollutants and global warming; it is economically competitive and may be produced by small companies. The objective of this work was to show to reduce the environmental impacts of used cooking oils through the production of biodiesel. A 22 factorial planning has been used to evaluate the influences of alcohol/oil and reaction time on the biodiesel producing yield. The optimal condition to produce the biodiesel has found by use of the response surface methodology and analysis of variance to obtain the fitting model. This study was conducted in Campinas city, Brazil, in which were collected the oil in some residences in this city. An analysis of ecological cost also has been developed. Cooking oils collected from Campinas homes were mixed with ethanol in some proportions (1:9, 1:7 and 1:5) and were transesterified at 60°C, for 30, 60 or 90 min, in order to obtain biodiesel, using NaOH as a catalyst. The results of the physical-chemical analyses demonstrated that the biodiesels obtained possessed characteristics close to those required by Brazilian standards. This fuel could be used in fleets of buses, trucks and machines, or even sold to fuel distributors; which will be able to give a solving between U\$ 0.8 and 4.5 millions. Thus, Campinas would gain environmental credits and become a sustainable city. As a proposal to collect the used cooking oils must be used the logistical planning to collect of garbage from Campinas houses, thought of one reservoir attached in garbage trucks.

Palavras-chaves: Biodiesel, Ecological Cost Accounting, Experimental Design, sustainable development

1. Introdução

Current, there are an increase in the search for sources of obtaining biofuels, as Alcohol and biodiesel, due they presented as an important option for energy supply, notably as renewable substitutes for fossil fuels. They are considered a renewable and endless resource, since they are produced from biomass, usually from an agricultural crop, reputed as renewable. Besides, it is a current belief that, by replacing oil products, their use could reduce greenhouse gases emissions (OMETTO and ROMA, 2010; PEREIRA and ORTEGA, 2010; ZAPATA and NIEUWENHUIS, 2010). Biodiesel is a biofuel derived from renewable sources, such as animal fat or vegetable oils. It is sulphur free, non-toxic and biodegradable; it reduces the emission of gas pollutants and global warming; it is economically competitive and may be produced by small companies (BENJUMEA et al., 2008; LIN and LIN, 2007).

With a trend in recent years towards US\$ 2.20/kg, as each ton of biodiesel produces over 104.4 kg of glycerol, this by-product alone adds US\$ 230 of value to each ton of biodiesel produced. The gain in carbon credits resulting from reduced CO₂ emissions by burning cleaner fuels is estimated at roughly 2.5 tons of CO₂ per ton of biodiesel. In the European market, carbon credits are sold at around US\$ 9.25/ton. Also, it can be negotiated the acquired with other nations with Clean Development Mechanism (CDM) projects, such as Canada, the Czech Republic, Denmark, France, Germany, Japan, Netherlands, Norway and Sweden; based in carbon credits market established Kyoto Protocol (GIRAÇOL et al., 2011).

The objective of this work was to show to reduce the environmental impacts of used cooking oils through the production of biodiesel. A 2² factorial planning has been used to evaluate the influences of alcohol/oil and reaction time on the biodiesel producing yield. The optimal condition to produce the biodiesel has found by use of the response surface methodology and analysis of variance to obtain the fitting model. This study was conducted in Campinas city, Brazil, in which were collected the oil in some residences in this city. An analysis of ecological cost also has been developed.

2. Materials and Methods

2.1. Experimental Planning

A 2² factorial design with cooking oil/ethanol volumetric rates and the reaction times as factors; as showed in Table 1 (FERREIRA et al., 2011). Solid sodium hydroxide was used as a catalyst to minimize the presence of water after the reaction. A jacketed reaction chamber was used to heat a total volume of 100 mL. The volume of reagents in the reaction chamber was 80 mL and the reaction occurred at 60° C ($\pm 2^\circ$ C) with constant agitation for one hour (Faccio, 2004; Serrão and Ocácia, 2007). The esterified materials were centrifuged to separate the glycerol. The blends were then transferred to a decanting funnel to separate the phases. After resting for 24 hours, the fractions of biodiesel were separated (BARAKOS et al., 2008; BENJUMEA et al., 2008; FACCIO, 2004; KNOTHE et al., 2006; LIN, LIN, 2007; SERRÃO, OCÁCIA, 2007).

Table 1. Conditions of manufacture of biodiesels, at 60°C and 0.1g of NaOH as a catalyzer

Factors	Levels		
	-1	0	1
Ethanol/oil rates	1/9	1/7	1/5
Reaction times	30	60	90

2.2 Biodiesel characterization

The following properties were determined: specific mass at 20° C using the ASTM-D4052 method; flash point using ASTM-D93 method; acid value using Ca 5-40 method; moisture content using the Af 2-54; and boiling point using the calorimetric method. These methods are found in AOCS (1985), Benjounea et al. (2008), Candeias et al. (2006), Faccio (2004), Lin, Lin (2007) and Sindhu et al. (2011). Yield calculations were based on Table 2, which displays the percentage of fatty acids in soybean oil, and the results obtained for residual acid value. Based on this composition, mean molecular weight was of 835 g/mol for soybean oil and 881 g/mol for the blends of ethyl esters (BARAKOS et al., 2008; BENJUMEA et al., 2008; FACCIO, 2004).

2.3 Ecological Cost Accounting Strategies

According to Fugate et al. (2009), Jüttner et al. (2010) and Whipple, Russel (2007) an operational collaboration between shippers is the best methodology for optimization of the logistical planning for the transportation of products between companies. In this work a proposal of operational collaboration will be shown to collect used cooking oil.

The considerations for the determination of the cost of biodiesel manufactured by used cooking oil were following: according to IBGE (2010), Campinas city has about 250,000 houses and; according to Giraçol et al. (2011) one liter of used cooking oil is produced for one person per month. Thus, 2.5 m³ of used cooking oil can be collected per month. The collection of used cooking oil will be made through the use of a reservoir attached to the garbage truck. Thus, the costs with logistical planning and with the collection of used cooking oil will be considered as zero net. The used cooking oil will be donated by the population and restaurants for the City Hall without taxes. The price composition for diesel currently sold, in São Paulo state, will be based on the US Dollar according to FECOMBUSTÍVEL (2009). Thus, the biodiesel costs will be associated to the diesel oil price. The biodiesel production has an associated carbon credit (BIODIESEL, 2009). Each 1 t of biodiesel is equivalent to 2.5 t carbon credit, which are sold by 9.25 US\$/t. This is a reduction of biodiesel price. The glycerine is a by-product of biodiesel manufacture (BIODIESEL, 2009). Each 1 t of biodiesel is equivalent to 104 kg of glycerol, which are sold by 2.20 US\$/kg. This also is a reduction of biodiesel price, after its sale and the biodiesel has an associated price of sale, which is greater than the price of diesel oil;

3. Results and Discussions

Table 2 shows the results of the analyses conducted on the biodiesel samples in comparison to the maximal values recommended by the Brazilian Petroleum Regulatory Agency (ANP, 2007). All the parameters analyzed fall within the regulatory standards for biodiesel in Brazil, it demonstrated the good quality of these samples.

Figure 1 shows the behavior of the yield of biodiesel manufacture according to the conditions from the experimental planning used in this work. It is noted that the yield was high to ethanol/alcohol rate of 1/9 independent of reaction time. It indicates that the ethanol reagent was in excess. The optimal condition can be observed at 1/9 of ethanol/oil for 30 min of reaction, which a yield of 94% was found.

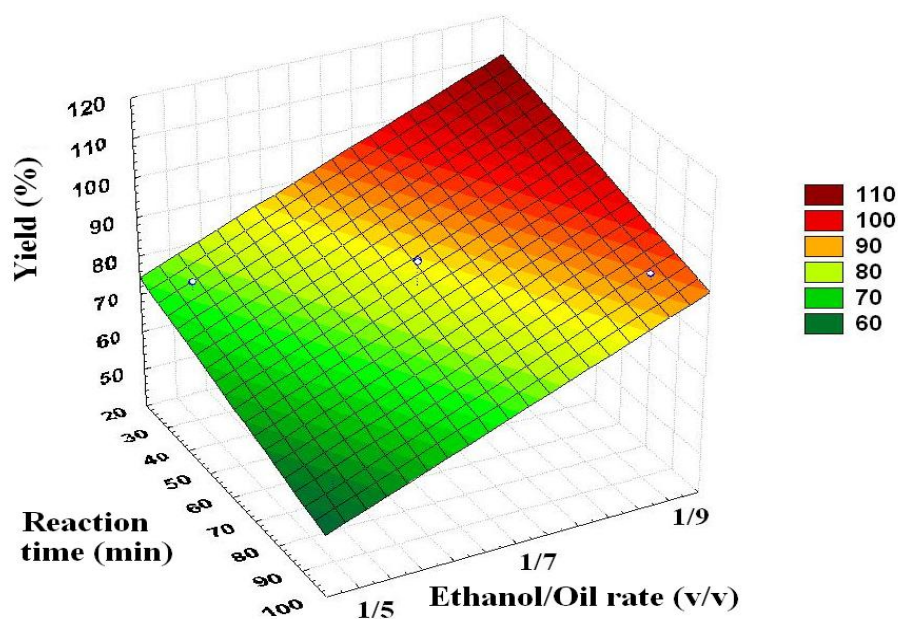
For reducing of the time and costs to collect the cooking oil used an integrating logistic were used, accordance to Fugate et al. (2009), Jüttner et al. (2010) and Whipple, Russel (2007).

Table 2. Results of quality analyzes of biodiesel samples obtained

Analysis	Biodiesel samples							ANP
	1	2	3	4	5	6	7	Standard*
Yields (%)	93,75	77,14	93,80	50,00	89,34	89,67	89,01	-
Acid value (% , m/m)	0	0	0	0	0	0	0	0,8
Moisture (% , m/m)	0	0	0	0	0	0	0	0,05
Density (kg / m ³)	891,0	895,5	895,7	887,2	745,0	825,0	836,7	875-900
Flash Point (°C)	33,5	31,0	36,0	31,0	16- 20	23- 25	37	38

*ANP Resolution (2004)

Figure 1. Response surface to optimize the best condition of biodiesel manufacture



Thus, the logistical planning used to collect of garbage from Campinas houses and restaurants must be used as a proposal to collect the used cooking oils. As beginning of the collect of used cooking oil in the Campinas homes and it use in the biodiesel production, some advantages can be observed, as cited to follow: (1) soil and water body will be no polluted for oil discard; (2) zero net of cost with the purchase of diesel oil fuel; (3) the biodiesel obtained is of low cost; (4) the environmental impacts of its discard into water bodies will be eliminated; (5) this is not topsoil erosion; (6) this is cost with fertilizers, herbicides and pesticides; (7) this is not consumption of air, CO₂ and abiotic materials; (8) it has an insignificant water consumption; (9) this is no use of agricultural area, which can prevent the expansion of the farming areas; (10) in Brazil case, reducing this expansion prevents of devastation of forest reserves, as the Amazon forest; (11) it soybean oil had use only in human food, which can prevent the augment of its price and (12) this reduces the criticism worldwide in relation to the use of oleaginous plants (CAVALETT, ORTEGA, 2010; GIRAÇOL et al., 2011; OMETTO, ROMA, 2010).

The estimated biodiesel price is US\$ 1.833/L, with B3 increasing the diesel price by US\$ 0.057 (CRAIDE, 2009; FECOMBUSTÍVEL, 2009; PONTUAL, 2009). Based on the price commercialized at refineries and using the biodiesel cost of US\$ 1.833 (which includes transportation costs), the cost of biodiesel obtained by the public authorities would be composed as follows:

- Assuming that the monthly B3 diesel consumption by the bus fleet is 2.84 million litres (EMDEC, 2009) and using the distributor's sales price (US\$ 1.122/L), the monthly cost of B3 diesel is calculated as B3 Purchase Price = 2.84 million * US\$ 1.122 = US\$ 2.653 million
- When producing B3, the city would only spend on the purchase of pure diesel from the refinery (transportation cost included), as all the other charges and prices are part of the minimal price composition that the distributor can commercialize.

$$\text{B3 cost} = 2.84 \text{ million litres} * (0.97 * \text{R}\$0.6226 + 0.03 * \text{R}\$1.833)$$

$$\text{B3 cost} = \text{US}\$ 1.871 \text{ million}$$

$$\text{Therefore, the monthly savings with B3 production} = (2.653 - 1.871) * 10^6 = \text{US}\$ 0.782 \text{ million}$$

For producing all B3 is need 85,200 litter of biodiesel is equivalent to 68.2 t of pure biodiesel (B100)l, which generates approximately 7.1 t of glycerol, the potential profit is close to US\$

15,620 from commercialising this by-product and 213 t of carbon credits which yields a profit of US\$ 1,970. Adding this to the glycerol, the profit is US\$ 19,058.

Therefore, it is possible to save US\$ 0.815 to 4.437 million with the production of B100, B3 and biodiesel derivatives using biodiesel made from used cooking oil, which reinforces the feasibility of the ecological cost accounting (ECA) proposal for the city of Campinas.

Table 2 shows a summary of suggested ecological cost accounting policy to Campinas city in which it noted an initial untenable position with bad situation to environmental, social and economical fields. However, as we'll be applying policies the situations are improving until they reach a full sustainability position and all fields.

Table 2: Evaluation of environmental costs of cooking oil disposal for city of Campinas

	Stage 1	Stage 2	Stage 3	Stage 4
Fields	Untenable	Sustainable operations		full sustainability
Environmental	Disposal of used cooking oils directly into the sewage system	Raise population awareness to store used cooking oil	Environmental officers of City hall collect the used cooking oil	Reutilization of used oil to obtain biodiesel and glycerol, acquiring carbon credits
Economical	High cost with sewage treatment and with the purchase of biodiesel	Cost with propaganda and lectures	Zero net	Solving between US\$ 0.8 and 1.4 millions/year
Social	Bad image of City	Motivation of population	Good image of City	Good life quality for the population

The following are the advantages of biodiesel production from cooking oil over soybean oil (CAVALETT, ORTEGA, 2010; GIRAÇOL et al., 2011; OMETTO, ROMA, 2010):

- The biodiesel obtained is of low cost;
- The environmental impact of discarding used cooking oil into bodies of water will be eliminated;
- There is no topsoil erosion;
- There is no cost with fertilizers, herbicides or pesticides;
- There is no consumption of air, CO₂ or abiotic materials;
- There is negligible water consumption;
- This is no use of agricultural area, thereby preventing the expansion of farm areas (in Brazil, reducing this expansion prevents the devastation of forest reserves, such as the Amazon forest);
- Soybean oil can be used for food products alone, thereby avoiding an increase in the price of this oil due to its use as a biofuel;
- There will be a reduction in criticism regarding the use of oleaginous plants for the production of biofuels.

4. Conclusions

The results of the physical-chemical analyses demonstrated that the biodiesels obtained possessed characteristics close to those required by Brazilian standards. Of accordance to response surface methodology, the best condition to obtain the biodiesel was observed at 1/9 of ethanol/oil for 30 min of reaction, which a yield of 94% has found. This fuel could be used in fleets of buses, trucks and machines, or even sold to fuel distributors; which will be able to give a saving between US\$ 0.8 and 4.5 millions. Thus, Campinas would gain environmental credits and become a sustainable city. As a proposal to collect the used cooking oils must be used the logistical planning to collect of garbage from Campinas houses, thought of one reservoir attached in garbage trucks.

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