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# Production Optimization of Biodiesel from Frying Oil Waste to Reduce the Environmental Impacts

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**Abstract:** The objective of this study was to reduce the environmental impacts of used frying oil waste through the production of biodiesel. A 2<sup>2</sup> factorial planning has been used to evaluate the influences of alcohol/oil and reaction time on the biodiesel production yield. The optimal condition to produce the biodiesel has been 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, where were collected the waste oil. An analysis of ecological cost also has been developed. Cooking oils collected from Campinas homes were mixed with ethanol in planned proportions (1:9, 1:7 and 1:5) and were transesterified at 60 °C and planned reaction times (30, 60 or 90 min), in order to obtain biodiesel, using 0.1% 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 results in a solving between US\$0.8 and US\$4.5 millions. Thus, Campinas would gain environmental credits and become a sustainable city.

Key words: Biodiesel, ecological cost accounting, factorial planning, frying oil waste.

#### 1. Introduction

Currently, there are a lot of clamor regarding the environment and its sustainability [1]. By the way, the search for sources of obtaining biofuels increased, as alcohol and biodiesel, because they presented as an important option for energy supply, notably as renewable substitutes for fossil fuels. Biodiesel can be defined as a monoalkyl ester of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat [2]. 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 [3, 4]. They are considered as 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 [5, 6].

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 CO<sub>2</sub> emissions by burning cleaner fuels is estimated at roughly 2.5 t of CO<sub>2</sub> per ton of biodiesel. In the European market, carbon credits are sold at around US\$9.25/t. Also, it can be sold to other nations with CDM (clean development mechanism) projects, such as Canada, the Czech Republic, Denmark, France, Germany, Japan, Netherlands, Norway and Sweden, based on carbon credits market established in Kyoto Protocol [7].

Thus, this work aimed to reduce the environmental impacts of used cooking oils through the production of

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biodiesel. A  $2^2$  factorial planning has been used to evaluate the influences of alcohol/oil and reaction time on the biodiesel production yield. The response surface methodology was used to obtain the optimal condition and the analysis of variance was used to obtain the fitting model. This study was conducted in Campinas city, Brazil, where were collected the waste oil. An analysis of ecological cost also has been developed.

# 2. Experiments

#### 2.1 Experimental Planning

A  $2^2$  factorial design, which had as factors: the ethanol/cooking oil volumetric rates and reaction times; as showed in Table 1. Fitting the model was performed via ANOVA (variance analysis) and the best condition can be obtained by RSM (response surface methodology), all methods are shown in Refs. [8, 9]. 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 (± 2° C) with constant agitation for 1 h. 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 1-2 h, the fractions of biodiesel were separated [2-4, 7, 10, 11].

#### 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 Refs. [3, 4, 12]. 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 835 g/mol for soybean oil and 881 g/mol for the blends of ethyl esters [3, 4, 7].

Table 1 Conditions of manufacture of biodiesels, at 60 °Cand 0.1 g of NaOH as a catalyser.

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

#### 2.3 Ecological Cost Accounting Strategies

According to Ref. [13], 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 had been presented to collect the frying oil waste.

The considerations for the determination of the cost of biodiesel manufactured by used cooking oil were following: Campinas city has about 250,000 houses and; according to Giracol et al. [7], 1 L of the used cooking oil is produced for house for mouth. Thus, 2.5  $m^3$  of the used cooking oil can be gotten by month. The collection of the used cooking oil will be made through the use of reservoir attached in the garbage truck. Thus, the costs with logistical planning and with 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 in dollar of accordance to Fecombustivel [13]. Thus, the biodiesel costs will be associated to diesel oil price. The biodiesel production had an associated carbon credit [7]. Each 1 t of biodiesel is equivalent to 2.5 t carbon credit, which are sold by US\$9.25/t. This is a reducing of biodiesel price. The glycerin is a by-product of biodiesel manufacture [7]. Each 1 t of biodiesel is equivalent to 104 kg of glycerol, which are sold by US\$2.20/kg. This also is a reducing of biodiesel price, after its sale and the biodiesel has an associated price of sale, which is greater than the price of diesel oil.

Table 2 shows the results of the analyses conducted on the biodiesel samples in comparison to the maximal values recommended by the Brazilian Petroleum

Analain	Biodiesel samples						AND star 1 st <sup>*</sup>		
Analysis	1	2	3	4 5 6		6	7	ANP standard <sup>*</sup>	
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 <sup>3</sup> )	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	

Table 2 Results of quality analyses of biodiesel samples obtained.

\*ANP resolution [13].

Regulatory Agency (ANP) [13]. All the parameters analyzed fall within the regulatory standards for biodiesel in Brazil, which demonstrated the good quality of these samples.

# 3. Results and Discussion

Fig. 1 shows the behavior of the yield of biodiesel manufacture according to the conditions from the experimental planning used in this work. It correlation was of 0.98, which, according to the methodology of variance analysis, indicated that the model had a good fit [8, 9]. It has been noted that the yield was higher in 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 observed a yield of 94%.

For reducing of the time and costs to collect the

cooking oil used an integrating logistic were used, according to Ref. [13]. Thus, the logistic of the collection of garbage from Campinas houses could be used as a proposal to collect the used cooking oils. With collecting of oil and biodiesel production, some advantages can be observed, as follows: (1) Soil and water body will not be 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 not cost with fertilizers, herbicides and pesticides; (7) This is not consumption  $CO_2$  and abiotic materials; (8) It has an insignificant water consumption; (9) This is not use of agricultural area, which can prevent the expansion of the farming areas; (10) In Brazil case, prevents of devastation of forest reserves,

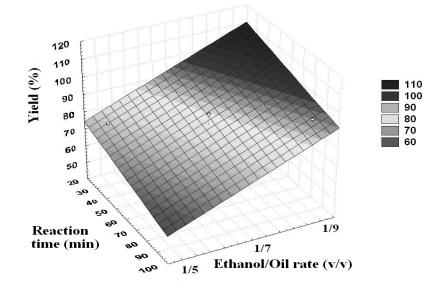


Fig. 1 Response surface methodology to optimize the best condition of biodiesel manufacture.

as the Amazon forest; (11) As the soybean oil is use only in human food, thus, it is possible prevent the augment of its price and (12) this reduces the criticism worldwide in relation to the use of oleaginous plants [5-7].

The estimated biodiesel price is US\$1.83/L, with B3 increasing the diesel price by US\$0.057 [13]. Based on the price commercialized at refineries and using the biodiesel cost of US\$1.83 (which includes transportation costs), the cost of biodiesel obtained by the public authorities would be composed as follows:

(1) Assuming that the monthly B3 diesel consumption by the bus fleet is 2.84 million L [7] and using the distributor's sales price (US1.122/L), the monthly cost of B3 diesel is calculated as B3 Purchase Price = 2.84 million × US1.122 = US2.653 million;

(2) 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 parts of the minimal price composition that the distributor can be commercialized.

B3 Cost =  $2.83 \times 10^{6}$  (L) × (0.97 × 0.62 (US\$) + 0.03 × 1.83 (US\$)) = US\$1.863 millions

Therefore, the monthly savings with B3 production =  $(2.653 - 1.871) \times 10^6$  = US\$ 0.782 millions

For producing of B3 is need 85,200 L of biodiesel is equivalent to 68.2 t of pure biodiesel (B100), which give a profit of 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 US\$4.437 million with the production of B100, B3 and biodiesel derivates using biodiesel made from used cooking oil, which reinforces the feasibility of the ECA (ecological cost accounting) proposal for the city of Campinas.

Table 3 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 will be applying polices, the situations are improving until they reach a full sustainability position and all fields.

The following are the advantages of biodiesel production from cooking oil over soybean oil [1, 7]:

(1) The biodiesel obtained is of low cost;

(2) The environmental impact of discarding used cooking oil into bodies of water will be eliminated;

(3) There is no topsoil erosion;

(4) There is no cost with fertilizers, herbicides or pesticides;

(5) There is no consumption of air,  $CO_2$  or abiotic materials;

(6) There is negligible water consumption;

(7) 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);

(8) 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;

(9) There will be a reduction in criticism regarding

Table 3	<b>Evaluation</b> of	environmental	costs of	cooking	oil dis	posal for	city of Can	npinas.

Fields	Stage 1	Stage 2	Stage 3	Stage 4		
	Untenable	Sustainable	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 US\$1.4 millions/year		
Social	Bad image of city	Motivation of population	Good image of city	Good life quality for the population		

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. According 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 observed a yield of 94%. 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 US\$0.8 and US\$4.5 millions. Thus, Campinas would gain environmental credits and become a sustainable city. As a proposal to collection the used cooking oils must be used the logistic of the collect of garbage from Campinas houses, thought of one reservoir attached in garbage trucks.

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### References

- Passarini, K. C.; Pereira, M. A.; Faria, T. M. B.; Calarge, F. A.; Santana, C. C. Assessment of the Viability and Sustainability of an Integrated Waste Management System for City of Campinas (Brazil), by Means of Ecological Cost Account. J. Clean. Prod. 2014, 65, 479-488.
- [2] Diyauddeen, B. H.; Aziz, A. R. A.; Daud, W. M. A. W.;

Chakrabarti, M. H. Performance Evaluation of Biodiesel from Used Domestic Waste Oils: A Review. *Process Saf. Environ. Prot.* **2012**, *90*, 164-179.

- [3] Benjumea, P.; Agudelo, J.; Agudelo, A. Basic Properties of Palm Oil Biodiesel-Diesel Blends. *Fuel* 2008, *87*, 2069-2075.
- [4] Lin, C.Y.; Lin, H. A. Engine Performance and Emission Characteristics of a Three-Phase Emulsion of Biodiesel Produced by Peroxidation. *Fuel Processes Technol.* 2007, 88, 35-41.
- [5] Cavalett, O.; Ortega, E. Integrated Environmental Assessment of Biodiesel Production from Soybean in Brazil. J. Clean. Prod. 2010, 18, 55-70.
- [6] Pereira, C. L. F.; Ortega, E. Sustainability Assessment of Large-Scale Ethanol Production from Sugarcane. J. Clean. Prod. 2010, 18, 77-82.
- [7] Giraçol, J.; Passarini, K. C.; Silva, F. S. C.; Calarge, F. A.; Tambourgi, E. B.; Santana, J. C. C. Reduction in Ecological Cost through Biofuel Production from Cooking Oils: An Ecological Solution for the City of Campinas, Brazil. *J. Clean. Prod.* **2011**, *12*, 1324-1329.
- [8] Ferreira, J. F.; Santana, J. C. C.; Tambourgi, E. B. The Effect of pH on Bromelain Partition from *Ananas comosus* by PEG4000/Phosphate ATPS. *Braz. Arch. Bio. Technol.* 2011, 54, 125-132.
- [9] Santana, J. C. C.; Ehrhardt, D. D.; Tambourgi, E. B. Optimizing of Alcohol Production from Manioe Starch. *Ciênc. Tecnol. Aliment.* **2010**, *30*, 613-617.
- [10] Official and Tentative Methods; AOCS (American Oil Chemists Society); Chicago: EUA, 1985.
- [11] Jüttner, U.; Christopher, M.; Godsell, J. A Strategic Framework for Integrating Marketing and Supply Chain Strategies. *Int. J. Logist. Managem.* 2010, *21*, 104-126.
- [12] Fecombustivel (National Federation of Fuel and Lubricant)
  [online]. *Economy*. http://www.fecombustiveis.org.
  br/economia (accessed Sept. 2013).
- [13] ANP (Brazilian Regulatory Agency for Petroleum). 2004 ANP Resolution [online] http://www.anp.gov.br/petro/ legis\_biodiesel (accessed Aug. 2012).