BIODIESEL PRODUCTION USING HETEROGENEOUS CATALYSIS WITH ULTRASOUND IRRADIATION

Alex Nogueira Brasil, brasil@uit.br
Programa de Pós-Graduação em Engenharia Mecânica-UFMG / FAEN-Universidade de Itaúna

Leandro Soares de Oliveira, leandro@demec.ufmg.br
Adriana Silva França, adriana@demec.ufmg.br
Departamento de Engenharia Mecânica-UFMG

Abstract. *Worldwide, many studies have been undertaken in the pursuit of renewable forms of energy, biofuels, which are efficient in their production processes, present positive energy balance and are environmentally friendly. Brazil, like other nations of the world, is engaged in this type of research and, among the mitigating actions that have already been taken in regard to environmental issues, is the formulation and implementation of public policies to encourage use of biofuels towards a gradual reduction in fossil fuel use. The industrial processes of biodiesel production most commonly employed are based on the transesterification of vegetable oils and animal fats with methanol or ethanol as esterification agent and homogeneous catalysts, especially the strongly alkaline such as sodium or potassium hydroxide and sodium methoxide. Among the recent advances in the transesterification processes, those employing ultrasound stand out for effective improvement in the process, both in terms of degrees of conversions and reducing reaction time and energy consumption. Moreover, the production units tend to be more compact, especially if continuous production processes are developed and become viable, allowing the construction of small-scale units for production at low cost. Other advances in biodiesel production are related to the development and implementation of alternative catalysts, mainly targeting processes in heterogeneous catalysis. This reaction medium has advantages over the homogeneous, which are: ease of use in continuous processes; the possibility of obtaining a cleaner glycerol; absence of a neutralization step of the catalyst and of its continuous addition in the process. In view of the aforementioned, this work aimed at contributing to sustainable development of the biodiesel production process by developing innovative technologies, involving the utilization of new heterogeneous catalysts and the development of technology for biodiesel production using ultrasound irradiation. The developed system allowed for a greater interaction between the phases, resulting in increases in ester yield, reduced reaction times and reduced reagent consumption and therefore saving energy. The catalysts were successfully developed based on carbonaceous materials.*

Keywords*: Biodiesel, ultrasound, transesterification, heterogeneous catalysts.*

1. INTRODUCTION

Biodiesel is a biofuel derived from renewable biomass for use in internal combustion engines with compression ignition or as means for generating other types of energy, and can partially or totally substitute fossil fuels. It is a clean-burning alternative fuel produced from domestic resources, and it is renewable. Biodiesel contains no petroleum, is biodegradable, nontoxic and essentially free of sulfur and aromatic compounds.

Biodiesel is chemically defined as the alkyl monoesters of long chain fatty acids (FAs) derived from renewable feedstocks such as vegetable oils, animal fats and recycled cooking oil. The most widely known process consists of a chemical reaction in which the triacylglycerides (TAGs) found in these fatty materials (e.g., soybean oil) combine with an alcohol (methanol or ethanol) in the presence of an alkaline catalyst (usually NaOH, KOH and their alkoxides) to produce alkyl monoesters (biodiesel) and glycerin. As a co-product, glycerin has little or no fuel value but it presents several industrial applications that are critical to support the economics of the process (Brasil and Oliveira, 2010).

The process for producing biodiesel from oil, methanol (or ethanol) and catalyst, is quite simple. However, due to its slow reaction kinetics, the conversion of the triglycerides to fatty methyl esters (FAME) and glycerin is usually not complete, i.e., during the transesterification process, not all fatty acid molecules are turned into their respective alkyl esters (biodiesel). This reduces biodiesel quality and yield significantly. Biodiesel is commonly produced in batch reactors using heat and mechanical mixing as energy input. Ultrasonic cavitation is an effective alternative means to achieve a better conversion of FAs into their alkyl esters in commercial biodiesel processing. Ultrasonic cavitation provides the necessary activation energy for the transesterification of oils to occur in shorter periods of time.

Manufacturing biodiesel from vegetable oils (e.g. soy, canola, jatropha, sunflower seed or algae) or animal fats, involves the base-catalyzed transesterification of fatty acids with methanol or ethanol to give the corresponding methyl esters or ethyl esters. Glycerin is an inevitable byproduct of this reaction.

The long conversion time and the inferior biodiesel yield can be attributed to a large part to the use of inappropriate mixing systems. In principle, oil and methanol are immiscible. Therefore, there is a need for a methanol-in-oil emulsion to be formed. This requires emulsification equipment rather than conventional mixers or stirrers. Ultrasonic cavitation is one of the most advanced processes to form fine-size emulsions at large processing scale. Excess methanol and catalyst

are significant cost factors in biodiesel production. Ultrasonic reactors add cavitational shear to the mixing process, allowing for smaller methanol droplets to be formed, thus resulting in improved methanol and catalyst utilization, i.e., less methanol and catalyst are required. In addition, the ultrasonic cavitation enhances the reaction kinetics, leading to faster and more complete transesterification.

Making use of the Biodiesel Didactic Plant and the Ultrasound Module, it becomes possible to perform scheduling of experimental studies of biodiesel production and it can easily vary the types of oils, alcohols and catalysts used in the process. Both the Didactic Plant and Ultrasound Module were constructed in the same spirit of using equipment with easy operation, transportation, installation and maintenance. The above equipments allow to perform experiments for the biodiesel synthesis by using conventional mechanical mixing and basic catalysts (Didactic Plant, Fig. 1), and ultrasonic cavitation using heterogeneous catalysts (Ultrasound Module, Fig. 2).

Figure 1. Biodiesel didactic plant and industrial simulation.

Figura 2. Biodiesel ultrasound module.

Therefore, this paper aims to disseminate information about the design, construction and operation of an ultrasound biodiesel plant and its use with heterogeneous catalysts. This module is design to be used in conjunction with the Biodiesel Didactic Plant and Industrial Simulation. Able to produce six (6) liters of biodiesel per batch by transesterification process, using any type of vegetable oil or animal fat through the methyl or ethyl routes in the presence of basic or heterogeneous catalysts. This prototype aims to carry out experiments for the biodiesel synthesis by ultrasound irradiation in the presence of heterogeneous catalysts and comparison with conventional process.

The proposal to design and build a plant to produce biodiesel on a small scale follows the philosophy of having to use a low equipment cost, relative to those industrial domestic or imported, easy to use and easy to be transported. Mobility and ease of use were primary factors for the development of the project.

2. MATERIALS AND METHODS

Tests for transesterification of soybean oil “in nature” were initially performed in a borosilicate glass reactor, heated, under stirring and capacity of 8 liters, as shown in Figs. 1 and 4. The main parameters that influence the yield of the transesterification reaction are temperature, reaction time, type and amount of catalyst used, type of alcohol and its molar ratio.

The temperatures to be tested will be in the range 25 to 60°C (just below the boiling temperature of alcohol, methanol and ethanol, respectively), to ensure maximum yield. The masses of catalysts will be varied in order to verify their effect on the yield and conversion of the transesterification. The molar ratios between alcohol and oil will be varied in the range of 3:1 (stoichiometric) to 6:1. After completion of tests in mechanically agitated glass reactor, tests will be performed in a reactor with ultrasonic irradiation, the maximum power of 1000W and frequency of 20 kHz (Kubota et al., 1996 and Marshall et al., 1999). The same parameters for the glass reactor will be assessed to the ultrasonic reactor, the power will be a variable parameter to be studied in order to optimize the reaction conditions. The analysis that characterize the quality of biodiesel produced will be made in accordance with auditing standards and optimized methodologies described in the literature.

For the experiments with ultrasound irradiation a test bench was designed for installation of a Hielscher ultrasound transducer, UIP1000hd model (20kHz, 1000W). Figure 1 shows the schematic drawing of the test bench for biodiesel production using heterogeneous catalysts by ultrasound irradiation.

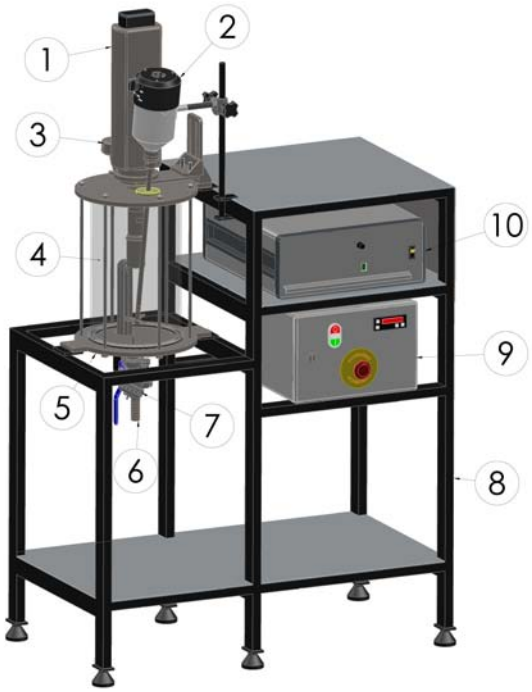

Figure 3. Technical drawing of the ultrasound module.

Below are presented the information used in the equipment mechanical design:

(1) Hielscher ultrasound transducer: with a frequency of 20kHz and power of 1000W, UIP1000hd model used for biodiesel synthesis;

(2) Mechanical mixing for semi-viscous products: microprocessor adjustable rotation between 120 and 2000 rpm to maintain a constant speed. It has a naval propeller made of stainless steel that allows the realization of the mixture of reagents: alcohol, oil and catalyst for further realization of the transesterification reaction by ultrasonic irradiation;

(3) Filling nozzle: made of stainless steel, threaded SMS and Viton® O-ring. Allows the addition the vegetable oil mass, alcohol and catalyst;

(4) Reactor: a cylindrical body made of borosilicate glass of high resistance, with support flanges of stainless steel and Viton® seals. The mixture of alcohol (ethanol or methanol), catalyst (sodium methoxide or heterogeneous catalysts) and vegetable oil is performed with the aid of a mechanical stirrer. The heating is accomplished by encapsulated electrical resistance and temperature control via thermocouple connected to microprocessor temperature controller. The transesterification reaction is carried out by ultrasonic irradiation;

(5) Bottom flange: stainless steel construction with Viton® Seal, allows the coupling of encapsulated electrical resistance with 1000W power for process reagents heating;

(6) Spigot attached to the tripartite ball valve, stainless steel construction: it allows the removal of biodiesel produced and forwarded to the next steps of distillation, decanting and purification to be held at Biodiesel Didactic Plant and Industrial Simulation;

(7) Thermo element 3F (PT100): sensor for the reagents temperature measurement inside the reactor;

(8) Modular construction: built in carbon steel, equipped with vibration dampers;

(9) Electric central control panel: offering buttonhole to drive the heating system, microprocessor temperature controller that allows adjustment and control the temperature of reagents during the reaction step. In order to protect the equipment from crash, has an emergency button which, when activated, disables all electrical equipments;

(10) Hielscher ultrasound generator: with a frequency of 20kHz and power of 1000W, UIP1000hd model used for biodiesel synthesis.

The reaction parameters presented in Tab. 1, were derived from the higher content of ester obtained by soybean oil transesterification in Biodiesel Didactic Plant and Industrial Simulation.

Table 1. Parameters used in the methyl transesterification of soybean oil.

Basic Homogeneous Catalysis	
Soybean oil mass	4126g
Catalyst percentage	2%
Molar ratio	(7:1)
Reaction temperature	60°C
Reaction time	90 minutes
Distillation temperature	90°C
Distillation time	40 minutes
1st decanting time	60 minutes
1nd decanting time	60 minutes

Soybean oil, anhydrous methyl alcohol and sodium methoxide were used as reagents in the process and after defining the reaction parameters, describe the procedure for biodiesel production.

In natura vegetable soybean oil is poured into the reactor (3) where it is heated to 60°C and mixed with anhydrous methyl alcohol - molar ratio (7:1) - and sodium methoxide, 2% on the mass of oil. Under strong agitation, the mixture lasts for 90 minutes. The mixture is pumped to the first decanter (7) to separate the phases, where it stays for 60 minutes; and from there, the lower phase is directed by gravity to the tanking of glycerin (8). The light phase (ester), also by gravity is directed to the distiller (9), where the alcohol excess is evaporated by heating to 90°C for 40 minutes with the aid of vacuum. The alcohol vapor passes through heat exchanger, condenses and is then recovered in the tank of alcohol (10). The retained in the distiller (9) is pumped into the second decanter (13) with the objective of a new phase separation, and allowed to rest for 60 minutes. Again the heavy phase is directed by gravity to the glycerin tank (8) and light phase, fatty esters, directed with continuous flow of 8 liters per hour, with the help of compressed air pump

for the purification columns (15 and 16) where biodiesel percolate through ion exchange polymer resin that holds all the waste glycerin, the catalyst and salts. Even in continuous flow, the purified biodiesel is stored in its storage tank (18).

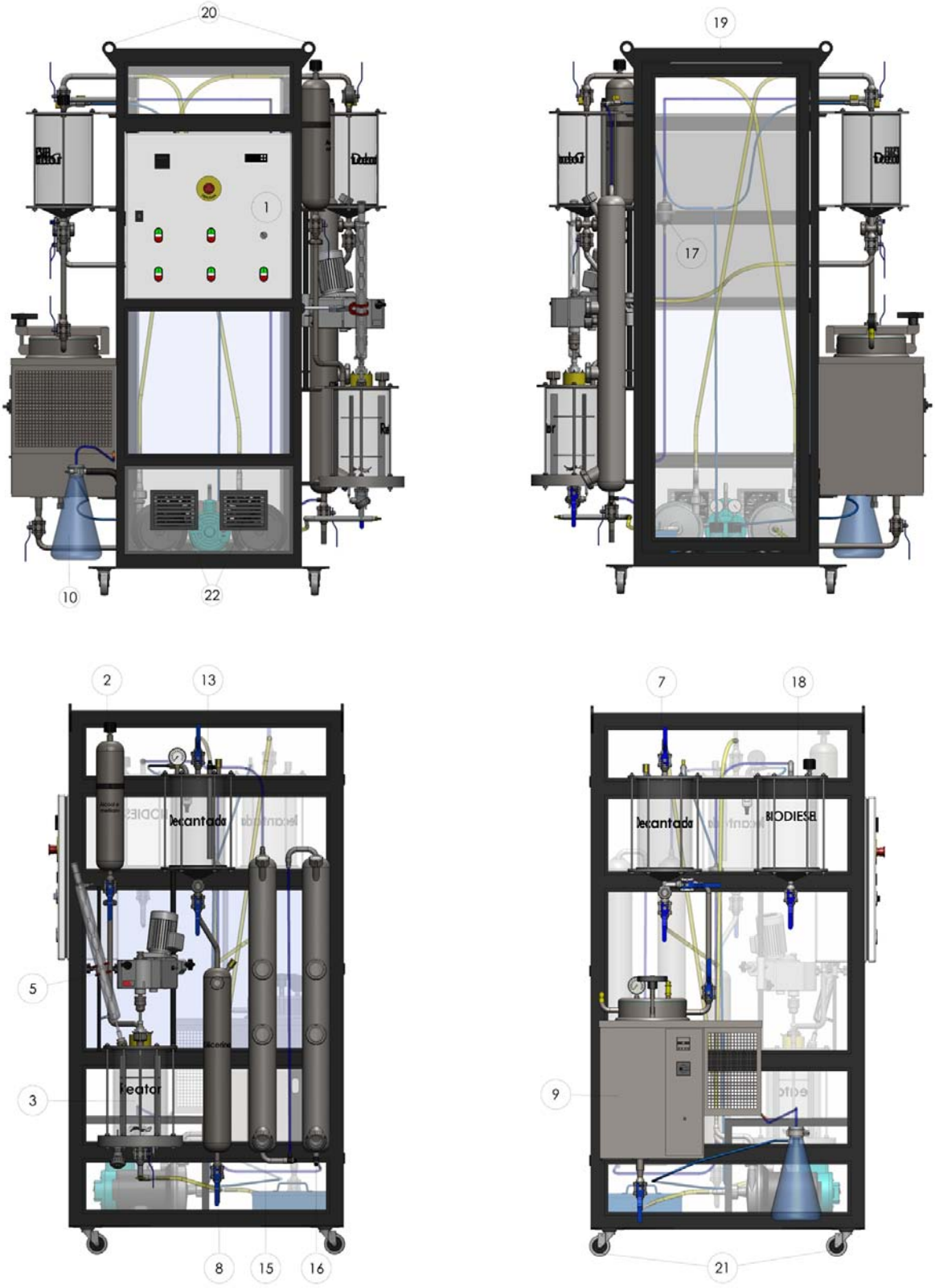

Figure 4. Technical drawing of the didactic biodiesel plant.

3. RESULTS AND DISCUSSION

The plant has production capacity of 6 liters of biodiesel per batch, thus, a 3-liter sample was taken and sent to the Bioagri, laboratory accredited by the ANP (National Agency of Petroleum, Natural Gas and Biofuels). Table 2 presents the results according to the specifications of the ANP.

Table 2. Results of biodiesel analysis according to the ANP standards.

Certificate N° 184579 Sample identification: Soybean methyl ester			
Parameters	Limit	Result	Unit
Aspect	LII	LII*	-
Density at 20°C	850-900	881.5**	kg/m³
Kinematic viscosity at 40° C	3.0-6.0	4.01	mm²/s
Water content (maximum)	500	484	mg/kg
Total contamination (maximum)	24	8	mg/kg
Flash Point (minimum)	100	153.6	°C
Ester (minimum)	96.5	96.8	%(m/m)
Carbon Residue (maximum)	0.05	0.02	%(m/m)
Sulfated Ash (maximum)	0.02	0.002	%(m/m)
Total Sulfur (maximum)	50	10.3	mg/kg
Sodium + Potassium (maximum)	5	0.5	mg/kg
Calcium + Magnesium (maximum)	5	<0.5	mg/kg
Phosphorus (maximum)	10	<0.5	mg/kg
Copper Corrosion, 3h a 50°C (maximum)	1	1	corrosion degree
Cetane Number	Note	51.5	-
Cold Filter Plug Point	19	-9	°C
Acid Value (maximum)	0.5	0.09	mg KOH/g
Free Glycerin (maximum)	0.02	0.002	%(m/m)
Mono-glycerides	Note	0.697	%(m/m)
Di-glycerides	Note	0.160	%(m/m)
Triglycerides	Note	0.045	%(m/m)
Total Glycerin (maximum)	0.25	0.207	%(m/m)
Methanol (maximum)	0.2	<0.01	%(m/m)
Iodine Value	Note	131	g/100g
Oxidation Stability 110°C (minimum)	6.0	25.33	h

* Clear and free of impurities at 26.0°C
** Test temperature = 26.0°C

When you make biodiesel, slow reaction kinetics and poor mass transfer are lowering your biodiesel plant capacity and your biodiesel yield and quality. Ultrasonic reactors improve the transesterification kinetics significantly. Therefore lower excess methanol and less catalyst are required for biodiesel processing.

Excess methanol does not react during the conversion process. It is added to support the chemical reaction kinetics only and it needs to be recovered at the end of the process. Recovered methanol is of inferior quality, only. That is why methanol recovery increases your processing costs. The use of ultrasonic reactors reduces the required amount excess methanol by up to 50%. A molar ratio between 1:4 or 1:4.5 (oil : methanol) is sufficient for most feedstock, when using ultrasonic mixing.

This leads to a better distribution and increased catalyst efficiency. In addition to that, the ultrasonic cavitation improves the mass-transfer. As a consequence, up to 50% catalyst can be saved when compared with shear mixers or stirrers.

Glycerin is a byproduct of biodiesel production. A higher conversion rate and lower excess methanol lead to a much faster chemical conversion and to a sharper separation of the glycerin. For the reasons described above, the glycerin contains less catalyst or mono-glycerides, leading to lower refining costs.

Proposals for transposition of a laboratory scale to production scale in industrial plants will be made to the system (type of catalyst / reactor type) that give the best performance for the conversion of oils into fatty acid alkyl esters and also the best return. The transposition of scale in case the step of removing impurities from the biodiesel will follow the basic rules of design of adsorption units, based on data obtained in batch tests.

Preliminary tests were conducted with the ultrasonic reactor, using dehydrated barium hydroxide as a heterogeneous catalyst. Reaction times were set to about 1 hour to be able to verify its performance compared to that of the batch mechanically agitated reactor. The results obtained indicated a conversion of the order of 85%. The catalyst was easily separated from the reacted mixture by filtration.

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