

## By-products from the vegetable oil industry as a feasible source for biofuels production and pollution reduction

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**Abstract.** Biodiesel produced from by-products and waste materials can be an economical way for reducing the traditional oil consumption and environmental problems. The by-products from the refining vegetable oil industry such as soapstock, acid oil and fatty acid distillates are suitable for producing biodiesel. The present work is an approach to the use of these by-products to obtain biodiesel covering the traditional and most widely used acid/base catalysis. The advantages and drawbacks of the different methods are mentioned and analysed. The synthesis and use of by-products from the vegetable oil refining industry are covered in this work.

### Key words

Biodiesel, soapstock, acid oil, fatty acid distillate

## 1. Introduction

Biodiesel is a well-known renewable commodity. It is composed of fatty acid methyl esters (FAMES) [1-3]. The production cost for biodiesel is still higher compared to diesel fuel but this can be expected to decrease in the future. More than 75 % of the production costs of biodiesel are due to the costs of the raw materials.

Some by-products of low commercial value are obtained from these refining processes. Important amounts of by-products such as soapstocks (SS), deodorizer fatty acid distillates (FAD) and acid oil (AO) are produced from the oil refining processes. These by-products are harmful to the environment if they cannot be used for any beneficial or industrial activity. The use of by-products for biodiesel production is a very good alternative for cost reduction of biofuels production and to solve related environmental problems.

The scope of this paper is to demonstrate the feasibility of the biodiesel obtaining from three less used by-products of the refining oil industry (soapstock, acid oil and fatty acid distillate) and the industrial residuals reduction associated to this treatment proposal. An approach to their use in internal combustion engines is also included.

### Vegetable oil refining

Chemical refining is the most widely used technique to purify the vegetable oils since it successfully decreases the level of free fatty acids (FFAs), phospholipids, waxes,

aldehydes, ketones among other components, but also the physical refining is widely used.

Soapstock emerges from the refining process when oil is treated with a dilute alkali solution separating the FFAs as is more simplified for the removing of FFAs than the chemical process and also reduces the amount of oil loss, but cannot avoid the production of a by-product in important amounts.

### Use of by-products of the refining oil industry to produce biodiesel

Three main by-products from the refining oil industry are obtained, as is observed in Fig.1. Soapstocks, acid oil and fatty acid distillate represents low value by-products but according to the composition, they are suitable for the production of biodiesel, adding value to them and a higher efficiency to the vegetable oil refineries.

Soapstock emerges from the refining process when oil is treated with a dilute alkali solution separating the FFAs as soaps. This wet lipid mixture is separated from the crude oil by centrifugation. It is generated at a rate of about 6 % of the input of oil entering the refining operation and its cost represents 1/10 of the refined oil cost. Soapstock is quite alkaline, with pH values between 10-11. This residual is also referred to as residual oleins [5] and has poor commercial value; therefore its use to produce biofuels generates a second generation biofuel.

Several methods proposed for the synthesis of biodiesel from the analysed by-products using the homogeneous acid/base catalysis are published. Most of them used washing and purification processes.

In the field of patents several are registered. Some of them cover methods for biodiesel production from soapstock, recovering of products from soapstock, obtaining of biodiesel from soapstock using enzymatic esterification or acidulation.

One of the potential raw materials for biodiesel production is the Fatty Acid Distillate (FAD) that contains high amounts of FFAs. It is also a by-product obtained through the final deodorization stage of the refining process [6].

The unsaponifiable materials of FAD have been considered a potential source of highly valuable phytochemicals.

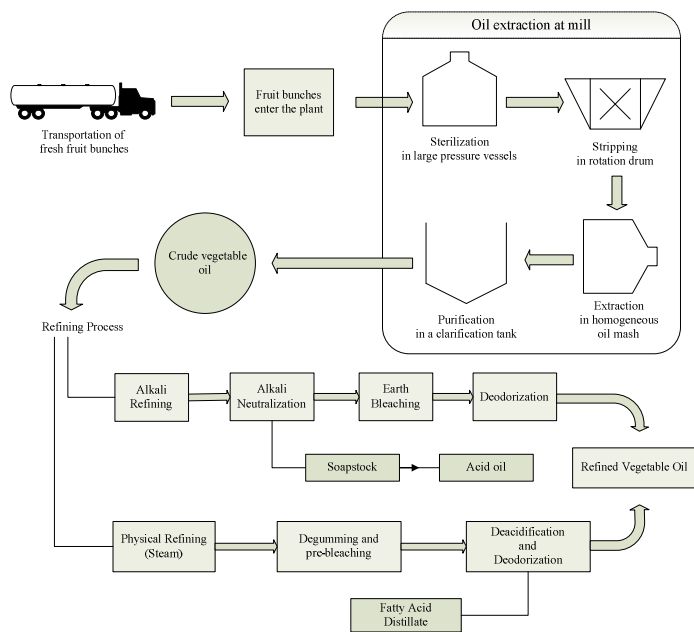


Fig.1 Full processing flow chart for a general vegetable oil refining process

Biodiesel can be obtained from the acid oil that results from the soapstock treatment with sulphuric acid. Its use for biodiesel production can also improve the economic feasibility of the biodiesel process. The acid oil (AO) also known as high-acid oil [7] consists of a long chain FFA mixture along with small amounts of mineral acids, glyceride, phospholipids and sterols and is contaminated with fatty matter. Acidulation of soapstock is one of the least desirable processes in an integrated facility because it is difficult to perform it effectively and its cost has no significant return [8]. The obtaining of biodiesel from AO is reported and under regular conditions can produce biodiesel or a biofuel but the influence of their use in internal combustion engines is still under studies.

### Heterogeneous and enzymatic catalysts

The development of heterogeneous catalysts has been a relatively recent area of research in the synthesis of biodiesel. Their use has a great potential not only technologically but economically [9, 10]. The aim for the development of heterogeneous catalysts is related to the homogeneous catalysts drawbacks: washing of biodiesel with water to remove the catalyst present, which results in wastewater and loss of biodiesel as a result of water washing.

Next to the heterogeneous catalysis based synthesis, the use of enzymes has also been reported. Biodiesel production using enzyme catalysts is a more environmentally friendly process and reaches adequate or even higher yields than the previously analysed processes [10-12], but these processes involving enzymes are costly.

Table 1. FFA and glyceride content in by-products from different feedstocks

Feedstock	Feedstock	FFA (wt %)	Glycerides (wt %)
Fatty acid distillate	Cotton	85.0	Not specified
	Palm	93.0	Not specified
	Hazelnut	45-50	Not specified
	Palm	70-80	20-30
	Soybean	40.2	Not specified
	Soybean	45.4	23.3
	Soybean	30.1	13.0
Soapstock	Rapeseed	48.8	32.9
	Soybean	51.6	Not specified
	Sunflower	70.0	25.0
	Soybean	10.0	13.9
	Cotton	85.3	Not specified
	Sunflower	56.0	Not specified
	Soybean	35.0	Not specified
Acid oil	Cotton	60.0	Not specified
	Palm	88.1	Not specified
	Soybean	59.3	33.4
	Cotton	86.0	Not specified
	Corn	46.0	Not specified
	Rapeseed	77.9	10.8

Using enzymes, conversion efficiency between 70-90 % for the transesterification reaction can be obtained. Using lipase, 63 % of esterification conversion is reported [13] with an overall efficiency of 81 %.

### Use in Internal Combustion Engines

A direct injection single cylinder Petter engine TD111 with a compression ratio 17:1 and fuel injection timing 24-33° (before top dead center) was used to test blends of biodiesel obtained from cotton oil soapstock and diesel fuel increasing the percent of biodiesel in the blend up to 60 % [14].

A Ford XLD four cylinder, four stroke, water cooled, 21.5:1 compression ratio, turbocharged, indirect injection diesel engine was used to test blends of biodiesel-diesel fuel [15]. The volume percent was up to 25 % of biodiesel in the blends. Although the heating value of the biodiesel is lower than diesel fuel, they found for biodiesel blends a slightly higher torque and power output at full load and partial loads. At partial loads, it was found that the blend did not cause significant changes in the CO and CO<sub>2</sub> emissions.

Haas et al. [13] conducted tests in a heavy-duty truck engine. It was a six-cylinder four-stroke, direct injection, turbocharged, intercooled and nominally rated at 257 kW at 1800 rpm. As fuel 100 % soapstock based biodiesel, commercial biodiesel prepared from soybean and a reference diesel fuel were tested. For HC emissions they

Table 2. Conditions and yields in esterification of the by-products using the homogeneous acid/base catalysis

Feedstock	Catalyst	Temp. (°C)	MeOH/oil	Catalyst amount	Reaction time (h)	Yield (%)	Comments
Palm FAD	H <sub>2</sub> SO <sub>4</sub>	75	8.8:1 mol/mol	1.83 wt %	1	99.5	Reducing glycerides by alkaline washing
	Acid: H <sub>2</sub> SO <sub>4</sub> Base: KOH	Acid: 60 Base: 60	Acid: 20mol/mol Base: 8 mol/mol	Acid: 1v/ wt % Base: 0.6 wt %	Acid: 2 Base: 40 min	98.5	Intermediate neutralization
Cotton SS	H <sub>2</sub> SO <sub>4</sub>	75	20 wt % of the SS mass	5 % of the SS mass	1 1/2	Not specified	Pre-heating to 100 °C washing with NaHCO <sub>3</sub>
Sunflower SS	Acid: H <sub>2</sub> SO <sub>4</sub> Base: NaOH	Acid: 60 Base: 60	Acid: 6mol/mol SS Base: 6-20mol/mol TG	Acid: 5 wt % Base: 1 wt %	Acid: 2 Base: 2	87.0	Intermediate neutralization washing with MeOH/H <sub>2</sub> O
Soybean SS	Base: NaOH Acid: H <sub>2</sub> SO <sub>4</sub>	Acid: 85 Base: 65	Acid: 5mol/mol SS Base: 6mol/mol SS	Acid: 3 wt % Base: 1 wt %	Acid: 5 Base: 1	Acid: 90.0 Base: 94.0	Three steps
Soybean AO	H <sub>2</sub> SO <sub>4</sub>	80 (1 h) 95 (4 h)	2:1 mol/mol AO	Not clearly specified	3	90.0	Pressurized (4 kgf/cm <sup>2</sup> ) Distillation
	NaOH H <sub>2</sub> SO <sub>4</sub>	100 35	15:1 30:1	15:1 mol/mol 5:1 mol/mol	2-4 2	- 99	unesterified FFA residual is removed by washing

reported between 25-50 % reductions compared to diesel fuel. They found an increase in the brake specific fuel consumption around 18 %, related to the lower energy density of the biodiesel.

Jonas et al. [16] tested fatty acid distillates in a medium speed diesel engine. The by-product was heated to 110 °C in order to decrease the viscosity to 8 mPas. During the investigation, dark deposits were detected on the piston crown, the rings, the combustion chamber and the injector.

A lack of papers about the use of biodiesel obtained from these by-products was found, meaning that this is a widely open field for research. Most research is focused on obtaining better yields of biodiesel, more efficient chemical processes and cost reductions.

According to the approach and the scope of this paper, a number of tables were omitted. All the information related to a more complete approach to the use of industrial residuals for biofuels or biodiesel production for their use in internal combustion engines can be consulted in an accepted paper soon published in the Brazilian Journal of Chemical Engineering entitled: Conversion of by-products from the vegetable oil industry into biodiesel and its use in Internal Combustion Engines: A Review.

Table 3 Reaction conditions and yields for various methods used in transesterification of the by-products using heterogeneous catalysis

Feedstock	Catalyst	Temp. (°C)	MeOH/oil	Catalyst amount	Reaction time (h)	Yield (%)	Comments
Soybean AO	LCC	70	9:1 mol/mol	7 wt % of AO	5	97.2	-
Cotton & Corn AO	SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub> -SiO <sub>2</sub>	200	9 mol/mol SS	3 wt %	6	94.0	Continuous process
Palm FAD	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /SiO <sub>2</sub> Cs <sub>1.5</sub> H <sub>1.5</sub> PW <sub>12</sub> O <sub>40</sub> /SiO <sub>2</sub>	85	12mol/mol	15 wt %	15	96.7	Complex catalyst preparation
AO source not specified	Acid: SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> /La <sup>3+</sup> Base: sodium methoxide	Acid: 60 Base: 55	Acid: 15mol/mol Base: 5mol/mol	Acid: 5 wt % Base: 0.6 wt %	Acid: 4 Base: 0.5	Acid: 98.0 Base: 97.2	Previous distillation
AO source not specified	WO <sub>3</sub> /ZrO <sub>2</sub>	150	9mol/mol	20 wt %	0.4 g/mL (oil)	96.0	-
Rapeseed FAD	-	60	6-15 mol/mol	-	4	93-97	cation exchange resins D002 and 002CR, flow rate 1 mL/min
Rapeseed FAD	H <sub>2</sub> SO <sub>4</sub>	60	12:1 mol/mol	5 wt %	4	96.8	-

## Conclusions

The feasibility of the use of by-products from the refining oil industry to produce biodiesel across the amount of papers published is clear. There currently is a trend to change from the traditional acid/base catalyst to heterogeneous or enzymatic catalysts in order to eliminate the traditional drawbacks. The so called low commercial value by-products are really suitable to extraction or isolation of several industrially useful compounds in a wide range of applications. A huge disparity in the amount of papers published in this topic is found comparing the synthesis of biodiesel and the performance of the biodiesel produced in diesel engines.

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