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CONVERSION OF BY-PRODUCTS FROM THE VEGETABLE OIL INDUSTRY INTO BIODIESEL AND ITS USE IN INTERNAL COMBUSTION ENGINES: A REVIEW

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Abstract - Biodiesel produced from by-products and waste materials can be an economical way of reducing traditional oil consumption and environmental problems. The by-products from the vegetable oil refining industry such as soapstock, acid oil and fatty acid distillates are suitable for producing biodiesel. The present work is a survey related to the use of these by-products to obtain biodiesel, covering not only the traditional and most widely used acid/base catalysis, but also solid and enzymatic catalysis. Details of the techniques are presented and compared. The advantages and drawbacks of the different approaches are mentioned and analyzed. The synthesis and use of by-products from the vegetable oil refining industry are covered in this work. The use of the obtained biodiesel in diesel engines is also included, demonstrating the disparity between the number of papers related to biodiesel production and engine performance assessment.
Keywords: Biodiesel; Soapstock; Acid oil; Fatty acid distillate.

INTRODUCTION

Biodiesel is a well-known renewable commodity. It is composed of fatty acid methyl esters (FAMEs) and its quality and use are covered by several regulations (Lois, 2007; Demirbas, 2009; Lapuerta *et al*., 2008). The production cost for biodiesel is still high compared to diesel fuel (El Bassam, 2010; Berrios *et al*., 2010; Usta *et al*., 2005; Lam *et al*., 2010; Chongkhong *et al*., 2007; Naima and Liazid, 2013), 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 (Ramadhas *et al*., 2004; Lam *et al*., 2010; Rivera *et al*., 2009; Bao-Xiang *et al*., 2008).

Crude vegetable oil is mainly composed of triacylglycerols, but also contains numerous non-edible compounds that need to be removed by a refining process prior to human consumption. For the refining of crude vegetable oils there are two main routes, the chemical and the physical refining.

Some by-products of low commercial value are obtained from these refining processes (Ching *et al*., 2008; Haslenda and Jamaludin, 2011). 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.

On the other hand, due to the rising world population, the consumption of refined vegetable oils

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will also increase, resulting in an increase in the production of these by-products. The use of by-products for biodiesel production is a very good alternative for cost reduction of biofuel production and to solve related environmental problems (Fan and Burton, 2009; Yujaroen *et al*., 2009; Yu *et al*., 2010; Dias *et al*., 2013). This way, the ethical discussion about the competition of land use for food production against energy production (El Bassam, 2010; Balat, 2011) through biofuels can also be avoided (Budiman *et al*., 2012; El Bassam, 2010; Nigam and Singh, 2010).

The scope of this paper is to analyze the state-of-the-art for obtaining biodiesel from three less used by-products of the refining oil industry (soapstock, acid oil and fatty acid distillate) and their use in internal combustion engines. Although some previous reviews were published (Gunawan and Yi-Hsu, 2009; Dumont and Narine, 2007) these were focused only on one or two of these by-products and the analysis of reports of their use in internal combustion engines was not included, although the main task is to produce energy in a diesel engine. Another motive for including the engines test results in the study is that the biofuel physical properties strongly influence the engine's behavior (Mesquita *et al*., 2012). The updating of these topics is also necessary to cover the recent published results and trends.

VEGETABLE OIL REFINING

Chemical refining is the most widely used technique to purify vegetable oils since it successfully decreases the level of free fatty acids (FFAs), phospholipids, waxes, aldehydes, and ketones among other components; physical refining is also widely used.

Physical refining is preferred as it reduces the loss of triglycerides, minimizes chemical usage and water consumption, and enables the recovery of high quality FFAs, which leads to considerable reduction of the environmental impact. In the particular case of Malaysia, more than 95% of the crude palm oil is refined through the physical route (Haslenda and Jamaludin, 2011). The physical refining uses steam stripping in order to avoid chemical neutralization. As observed in Figure 1, physical refining is simpler for the removal 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. A detailed explanation of every process involved in the refining oil industry can be consulted in (Dumont and Narine, 2007; Haslenda and Jamaludin, 2011).

Investigation of the suitability of lower value lipids, primarily animal fats and waste greases, as feedstocks for biodiesel production has also been reported (Haas *et al*., 2001; Haas *et al*., 2003; Chongkhong *et al*., 2007; Chongkhong *et al*., 2009). In order to convert the waste by-products from the oil refining process to biofuels under good yield conditions and reasonable industrial costs, different physico-chemical techniques are modified or developed.

ESTERIFICATION AND TRANSESTERIFICATION REACTION

Most oil refining and biodiesel plants use the conventional sodium hydroxide/sodium methoxide and/or sulfuric acid based transesterification processes. This chemical esterification process would be the most convenient to use for conversion of by-products to biodiesel. The primary purpose of the transesterification is to reduce the oil viscosity (Demirbas, 2008; Ranganathan *et al*., 2008).

The technological challenge in the use of these by-products as a feedstock for biodiesel production is the same as using waste greases or other materials containing FFAs: the alkaline transesterification typically employed to synthesize esters is ineffective at esterifying FFAs. A dual reaction approach is therefore required (Haas, 2005).

Acid catalysts are too slow to be practical for converting triglycerides to biodiesel (Canakci and Van Gerpen, 1999; Canakci and Van Gerpen, 2001); however, acid catalysts are quite effective at converting FFAs to biodiesel. Therefore, an acid-catalyzed pretreatment step to convert the FFAs to esters, followed by an alkali-catalyzed step to convert the triglycerides should provide an efficient method to convert high FFAs to biodiesel (Canakci and Van Gerpen, 2001; Bao-Xiang *et al*., 2008; Boonnoun *et al*., 2008; Usta *et al*., 2005; Kartina, 2011; Chongkhong *et al*., 2007). The more suitable alcohol for the esterification reaction is methanol (MeOH) due to economic reasons, but ethanol is also used (Marchetti, 2011).

The FFAs and water content affect the production of biodiesel (Van Gerpen, 2005). The oil acid value should be less than 1 mg KOH/g and the raw materials should be anhydrous (water content < 0.3%). If these requirements are not met, it is still possible to produce biodiesel, but the yield of the reaction is reduced due to the deactivation of the catalyst and the formation of soaps.

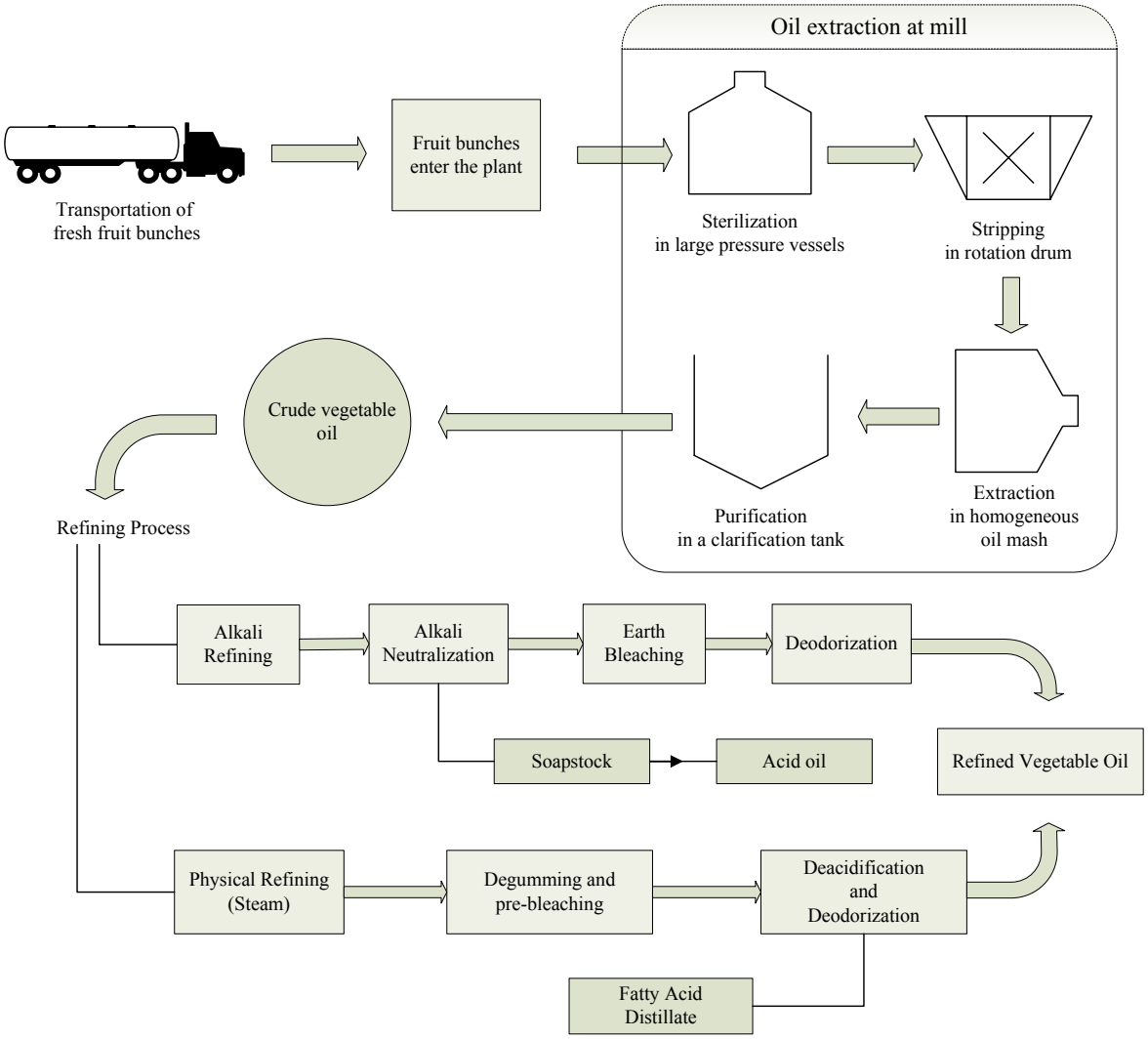

Figure 1: Full processing flow chart for a general vegetable oil refining process.

USE OF BY-PRODUCTS OF THE OIL REFINING INDUSTRY TO PRODUCE BIODIESEL

Three main by-products from the oil refining industry are obtained, as observed in Figure1. Soapstocks, acid oil and fatty acid distillate represent 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.

The concept of reaching zero-waste with regards to utilization of by-products generated in palm oil refineries was applied to the palm oil industry (Haslenda and Jamaludin, 2011). The authors explored the capability of the oil industry to use the residual soapstock and the fatty acid distillates to produce biodiesel, but also for other industrial applications such as the production of animal feed, lubricants and soaps.

Soapstock

Soapstock emerges from the refining process when oil is treated with a dilute alkali solution separating the FFAs as soaps. This wet lipid mixture (Dumont and Narine, 2008; Haas *et al*., 2000; Dumont and Narine, 2007) 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 (Haas *et al*., 2003) and its cost represents 1/10 of the refined oil cost (Kanthavelkumaran and Seenikannan, 2012).

Soapstock is quite alkaline, with pH values between 10-11 (HaasBloomer, 2000; Haas, 2005; Young-Moo *et al*., 2010). This residual is also referred to as residual oleins (Pereda *et al*., 2003) and has poor commercial value, but can be used as an ingredient in animal feed (Haslenda and Jamaludin, 2011; Ching *et al*., 2008). It is a mixture of triglycerides of fatty acids and of the same free fatty acids.

Its physico-chemical properties tend to change with the type of vegetable oil source, seed processing, handling and storage conditions (Dumont and Narine, 2007). Soapstock can be solid (Reaney, 2002; Keskin *et al*., 2008; Haas *et al*., 2001) or liquid; it is also referred to as an emulsified aqueous mixture of glycerides and FFAs (Phillips and Leavens, 1978; Haas *et al*., 2003). The emulsion can contain about 50% of water (Haas, 2005; Young-Moo *et al*., 2010).

The first attempt at soapstocks characterization dates from 1987 (Waliszewski, 1987). The analysis of fatty acids in this matrix is not an easy procedure, because a wide polarity range can be present in it (Dumont and Narine, 2007). The first complete characterization of soapstock from cottonseed was reported in 1996 (Dowd, 1996).

The composition of the main groups of compounds suitable for obtaining biodiesel (FFAs and glycerides) found in soapstocks is not well established and is dependent of the oil source, as shown in Table 1. There is a large difference in the FFA percent in the soapstock when different feedstocks are compared, but also in reports for the same feedstock. One conclusion that emerges from Table 1 is that the FFA content in the feedstocks is strongly dependent on other factors and not only on the feedstock characteristics: climatic conditions, soil characteristics, oil processing technology, refining process, feedstock, etc.

A two-step method for the production of biodiesel from soapstock was initially presented by Haas and Scott (1996), but achieved only an 81% yield. Afterwards, Haas presented a new approach for obtaining biodiesel from soapstock (Haas *et al*., 2000) proposing a lyophilization step to remove the water content and a saponification of the soapstock before the esterification reaction. To assure the total saponification, a minimum addition of 14.6% of NaOH was needed and the reaction took 5 h. Haas reported a yield of 60% of the theoretical amount of product, which is not a good yield compared to other methods.

A three-step method was developed by Jin *et al*. (2008) for producing biodiesel from a mixture of oil sediments and soapstocks. In the first step, the mixture was extracted with ethyl ether and divided into three phases. In the second step, the soap phase was acidified with sulfuric acid to yield fatty acid. Then the acid oil was efficiently converted into methyl esters by acid-catalyzed esterification. In the third step, alkaline-catalyzed transesterification was performed to convert the triglycerides into biodiesel. Biodiesel properties such as density, kinematic viscosity, flash point, calorific value, and acid value were found to be comparable to the reference diesel fuel.

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

Feedstock	Feedstock	FFA (wt %)	Glycerides (wt %)	References
Fatty acid distillate	Cotton	85.0	Not specified	Keskin *et al*. (2008)
	Palm	93.0	Not specified	Chongkhong *et al*. (2009)
	Hazelnut	45-50	Not specified	Usta *et al*. (2005)
	Palm	70-80	20-30	Budiman *et al*. (2012)
	Soybean	40.2	Not specified	Dumont and Narine (2008)
	Soybean	45.4	23.3	Gunawan *et al*. (2008)
	Soybean	30.1	13.0	Hirota *et al*. (2003)
	Rapeseed	48.8	32.9	Liu and Wang (2009)
Soapstock	Soybean	51.6	Not specified	Dumont and Narine (2008)
	Sunflower	70.0	25.0	Garcia-Zapateiro *et al*. (2010)
	Soybean	10.0	13.9	Haas and Scott (2001)
	Cotton	85.3	Not specified	Keskin *et al*. (2008)
	Sunflower	56.0	Not specified	Pereda *et al*. (2003)
	Soybean	35.0	Not specified	Zhong-Ming *et al*. (2007)
	Cotton	60.0	Not specified	Dowd (1996)
Acid oil	Palm	88.1	Not specified	Kulkarni *et al*. (2008)
	Soybean	59.3	33.4	Haas *et al*. (2003);Haas (2005)
	Cotton	86.0	Not specified	Bao-Xiang *et al*. (2008)
	Corn	46.0	Not specified	Bao-Xiang *et al*. (2008)
	Rapeseed	77.9	10.8	Watanabe *et al*. (2007)

Several methods that have been proposed for the synthesis of biodiesel from the analyzed by-products using homogeneous acid/base catalysis are shown in Table 2. For detailed information the corresponding references should be consulted. Most of them used washing and purification processes that are not mentioned in Table 2 but that are very important to obtain adequate biodiesel yields.

The selection of the best proposal for obtaining biodiesel from soapstock according to Table 2 is not an easy task. From a comparison starting from the reported yields (Pereda *et al*., 2003; Jin *et al*., 2008), the proposal of Jin *et al*. (2008) provided better yields at the cost of higher temperatures and reaction times, but using lower amounts of catalysts and methanol. In principle, both techniques are based on three steps.

For transformation of the soapstock into biodiesel, the esterification reaction is easily performed by acid catalysis (Benjumea *et al*., 2006) while the transesterification in this medium takes place slowly (Pereda *et al*., 2003). Alkaline catalysis cannot be applied to a material with high FFA content due to soap formation (Keskin *et al*., 2008).

Usta *et al*. (2005) obtained biodiesel from a mixture of hazelnut soapstock and waste sunflower oil in approximately equal volume proportions. The soapstock FFA composition was approximately 45-50%, but the final blend had only 20%. Even at this level of FFAs, an acid-catalyzed esterification pre-treatment at 35 °C was necessary before trans-esterifying the triglycerides with an alkaline catalyst to complete the reaction at 55 °C.

Table 2: Reaction conditions and yields for various methods used in transesterification of the by-products using homogeneous acid/base catalysis.

Feedstock	Catalyst	Temp. (°C)	MeOH/oil	Catalyst amount	Reaction time (h)	Yield (%)	Comments	References
Palm FAD	H_2SO_4	75	8.8:1 mol/mol	1.83 wt %	1	99.5	Reducing glycerides by alkaline washing	Chongkhon *et al*. (2009)
Palm FAD	Acid: H_2SO_4 Base: KOH	Acid: 60 Base: 60	Acid: 20 mol/mol Base: 8 mol/mol	Acid: 1v/ wt % Base: 0.6 wt %	Acid: 2 Base: 40 min	98.5	Intermediate neutralization	Boonnoun *et al*. (2008)
Hazelnut SS	Acid: H_2SO_4 Base: NaOH	Acid: 35 Base: 55	Acid: 8 v/v % Base: 12 % of the mixture	Acid: 1 mL of 95 wt % solution Base: 3 g/L of the mixture	Acid: 1 Base: 1 1/2	Not specified	Pre-heating to 100 °C	Usta *et al*. (2005)
Cotton SS	H_2SO_4	75	20 wt % of the SS mass	5 % of the SS mass	1 1/2	Not specified	Pre-heating to 100 °C washing with $NaHCO_3$	Keskin *et al*. (2008)
Sunflower SS	Acid: H_2SO_4 Base: NaOH	Acid: 60 Base: 60	Acid: 6 mol/mol SS Base: 6-20 mol/mol TG	Acid: 5 wt % Base: 1 wt %	Acid: 2 Base: 2	87.0	Intermediate neutralization washing with $MeOH/H_2O$	Pereda *et al*. (2003)
Soybean SS	Base: NaOH Acid: H_2SO_4	Acid: 85 Base: 65	Acid: 5 mol/mol SS Base: 6 mol/mol SS	Acid: 3 wt % Base: 1 wt %	Acid: 5 Base: 1	Acid: 90.0 Base: 94.0	Three steps	Jin *et al*. (2008)
Soybean SS	Base: NaOH Acid: H_2SO_4	85-100 55-69	Not specified 12 L/ 5 kg	8-12 wt % 1-1.7 L	Base: 4 Acid: 2	96.0	Hexane extraction, H_2O & NaCl washes	Haas and Scott (2001)
Soybean AO	H_2SO_4	80 (1 h) 95 (4 h)	2:1 mol/mol AO	Not clearly specified	3	90.0	Pressurized (4 kgf/cm^2) Distillation	Zhong-Ming *et al*. (2007)
Soybean AO	NaOH H_2SO_4	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	Haas (2005)
Soybean AO	H_2SO_4	65	1.8:1 mol/mol FFA	0.17:1 mol/mol	24	89	NaCl, $NaHCO_3$ & $Ca(OH)_2$ washing	Haas *et al*. (2003)

The ester phase was washed with pure water three times. At the end of the process, the oil was heated to 100 °C to remove any water from the oil left in the ester. Usta *et al*. (2005) found a very high viscosity compared to the standard diesel fuel for the biodiesel obtained due to the characteristics of the FAMEs and consequently it was not practicable for direct use in a diesel engine.

Pereda *et al*. (2003) reported biodiesel obtained from soapstock with 56% of FFAs (expressed as oleic acid). They reported the use of three steps: esterification in acid medium, transesterification in alkaline medium and neutralization. The transesterification of the esterified olein without neutralization of the residual FFAs yields a product in which no phase separation is observed due to the emulsifier properties of the soaps formed (Pereda *et al*., 2003; Haas *et al*., 2006). This can be avoided by neutralizing the FFAs before the transesterification. Using this treatment, the reaction conversion can be increased from 56% to 72-73% (Pereda *et al*., 2003).

The water content is critical for the transesterification reaction since it competes with the alcohol reactant, transforming the desired esterification reaction into ester hydrolysis and generating FFAs (Haas, 2005).

In the field of patents several are registered. Some of them cover methods for biodiesel production from soapstock (Stern *et al*., 1996; Basu and Norris, 1996), recovering of fatty acid products from soapstock (Phillips and Leavens, 1978), obtaining biodiesel from soapstock using enzymatic esterification (Araujo and Almeida, 2009) or soapstock acidulation (Reaney, 2002).

Fatty Acid Distillate

One of the potential raw materials for biodiesel production is Fatty Acid Distillate (FAD) (Budiman *et al*., 2012; Kartina, 2011; Nang *et al*., 2009), which contains high amounts of FFAs. It is also a by-product obtained in the final deodorization stage of the refining process (Yang *et al*., 2010).

It is also called deodorizer distillate and contains compounds similar to soapstocks (Dumont and Narine, 2008; Dumont and Narine, 2007). Additionally, it contains material with some commercial value (Dumont and Narine, 2008; Garcia-Zapateiro *et al*., 2010; Verleyen *et al*., 2001; El-Mallah *et al*., 2006) as animal feed ingredient (Nang *et al*., 2009; Haslenda and Jamaludin, 2011). Several methods have been proposed to recover phytosterols from the deodorizer distillate (Yan *et al*., 2010; VerleyenVerhe, 2001; Kasim *et al*., 2010; Fabian *et al*., 2009). The by-product obtained through physical refining has a higher FFA content than that obtained by chemical refining (El-Mallah *et al*., 2006).

The unsaponifiable materials of FAD have been considered to be a potential source of highly valuable phytochemicals (Gapor, 2000; Naz *et al*., 2012) such as vitamin E, phytosterols, and squalene among others (Verleyen *et al*., 2001; Gunawan *et al*., 2008; Fabian *et al*., 2009; El-Mallah *et al*., 2006). The vitamin E profile of Malaysian FAD is 10.3 wt% of α-tocopherol, 18.7 wt% of α-tocotrienol, 49.8 wt% of γ-tocotrienol, and 14.6 wt% of δ-tocotrienol (Bonnie and Mohtar, 2009).

A process to obtain biodiesel from FAD through two simultaneous chemical reactions has been reported (Budiman *et al*., 2012; Kartina, 2011) and referred to as reactive distillation. This procedure can improve the conversion and reduces the catalyst requirement. Biodiesel is produced from FAD in two steps (esterification and transesterification). Both reactions are well described in (Budiman *et al*., 2012).

Chongkhong *et al*. (2007) studied the conversion of FAD from palm oil into biodiesel. The study covered variations in the methanol/FAD molar ratios and the purification and reaction conditions. The quality of the biodiesel obtained showed properties near to those specified in ASTM D6751-02. The technique and yield are indicated in Table 2. The authors went deep into their process in a further paper (Chongkhong *et al*., 2009). In the second paper they proposed a one-step method but also needing an alkaline washing step.

A method using a column reactor packed with a cation exchange resin was reported for biodiesel synthesis from rapeseed oil deodorizer distillate (Liu and Wang, 2009). Under the optimal conditions, biodiesel production from FAD afforded a methyl ester yield of over 96%. The resin showed good operational stability and the same efficient activity as conventional sulfuric acid catalyst.

Both techniques proposed in Table 2 for the synthesis of biodiesel from FAD are quite similar. Only small differences in yield, reaction temperatures and amount of catalyst are observed. The yield starting from FAD is higher than that reported from soapstocks.

Acid Oil

Biodiesel can be obtained from the acid oil (Haas *et al*., 2003; Feng *et al*., 2012b) that results from the treatment of soapstock with sulfuric acid (Zhong-Ming *et al*., 2007; Dumont and Narine, 2007; Yan

et al., 2010a; Young-Moo *et al*., 2010; Moulay *et al*., 2005; YuLi, 2010). 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 (Cherng-Yuan and Yi-Wei, 2012), consists of a long chain FFA mixture along with small amounts of mineral acids, glyceride, phospholipids and sterols (Kulkarni *et al*., 2008; Zhong-Ming *et al*., 2007) and is contaminated with fatty matter (Dumont and Narine, 2007). Acid oil characterization is reported in Johansen *et al*. (1996), Mag (1983) and Zhong-Ming *et al*. (2007).

Compared to the two previously analyzed by-products, acid oil has almost no economic value (Dumont and Narine, 2007). Acidulation of soapstock is one of the least desirable processes in an integrated facility because it is difficult to perform effectively and its cost has no significant return (Zhong-Ming *et al*., 2007).

Additional drawbacks for conversion of acid oil to biodiesel are: addition of an excess of methanol and acid catalyst is required; a complete hydrolysis of the acylglycerols to fatty acids prior to FAME production is required in order to avoid the methanol and acid excess (Watanabe *et al*., 2007).

Nevertheless, several studies covering the conversion of acid oil to biodiesel have been reported. A kinetic study of the acid catalyst used in the reaction was reported (Marchetti *et al*., 2010). Zhong-Ming (Zhong-Ming *et al*., 2007) presented a technology for the production of biodiesel from acid oil after transformation of the soapstock.

Haas *et al*. (2003) proposed a method for obtaining biodiesel from acid oil. The process did not achieve efficient esterification of the fatty acids in the acid oil, but avoids the substantial amount of solid sodium sulfate generated as a by-product verified by Haas *et al*. in a previous approach (Haas *et al*., 2000). The optimal reaction occurred at 1:1.8:0.17 acid/methanol/sulfuric acid, with a reaction time of 14 h at 65 °C. The authors also found that the accumulation of water released by the esterification prevented the complete esterification.

The process developed by Haas has been criticized (Zhong-Ming *et al*., 2007; Yan *et al*., 2010b; Yan *et al*., 2010a) due to the high temperature required to recover acid oil from soapstock, low efficiency, the additional process required in the technology and mainly for the long esterification reaction time.

Cherng-Yuan and Yi-Wei (2012) used the high-acid oil from soybean soapstock as the feedstock for biodiesel production using supercritical-methanol transesterification. The authors analyzed and compared the fuel properties of biodiesel produced using various molar ratios of methanol to high-acid oil.

HETEROGENEOUS AND ENZYMATIC CATALYSTS

The development of heterogeneous catalysts has been a relatively recent area of research in the synthesis of biodiesel (Sharma *et al*., 2011; Trakarnpruk, 2012). Their use has a great potential not only technologically but also economically (Marchetti, 2012; Joon *et al*., 2011). The aim of the development of heterogeneous catalysts is related to the drawbacks of homogeneous catalysts: washing of biodiesel with water to remove the catalyst present, which results in wastewater and loss of biodiesel as a result of water washing.

Heterogeneous catalysts have the benefit of easy separation from the product without washing requirement (Jiang *et al*., 2010). Reuse of the catalyst is another advantage (Sharma *et al*., 2011; Oliveira *et al*., 2010; Bournay *et al*., 2005; Jiang *et al*., 2010). They are categorized as solid acid and solid base catalysts. Solid base catalysts show higher yields of biodiesel; however, they are sensitive to the presence of FFAs and thus solid acids are more recommended.

There are reports of the use of heterogeneous acid catalysis for biodiesel production (Meher *et al*., 2004; Melero *et al*., 2009a; Melero *et al*., 2009b; Semwal *et al*., 2011; Lotero *et al*., 2005; Puna *et al*., 2010; Baig and Flora, 2010). Solid acid catalysts (Chavan *et al*., 2001; Feng *et al*., 2010; Feng *et al*., 2012a; Helwani *et al*., 2009b) and zeolites (Sasidharan and Kumar, 2004) used for triglyceride transesterification showed high catalytic activities. Sulfated zirconia, sulfated tin oxide and sulfated titanium oxide are some of the catalysts that hare shown good catalytic activities (Kiss *et al*., 2006; Furuta *et al*., 2004; Muthu *et al*., 2010). The use of anionic ion-exchange resins as heterogeneous catalyst is also reported (Shibasaki-Kitakawa *et al*., 2007). Much interest has been shown in CaO among other heterogeneous base catalysts due to its economic advantage, lower solubility and easy handling (Peng-Lim *et al*., 2012).

A growing number of papers have appeared in this field, including several reviews (Sharma *et al*, 2011; Helwani *et al*., 2009a; Lam *et al*., 2010; Zabeti *et al*., 2009; Kiss *et al*, 2006; Leung *et al*., 2010; Melero *et al*., 2009b; Joon *et al*., 2011). In our paper we focus on the use of these catalysts for biodiesel production from the studied by-products.

Yan *et al*. (2010b) used a solid catalyst for obtaining

biodiesel from acid oil that can be used five times without any treatment in a reaction at 200 °C for 2 h. Feng *et al*. (2012b) used a lignin-derived carbonaceous catalyst (LCC) for obtaining biodiesel from the acidulated soapstock, reaching a yield of 97.2 %, but the process takes 5 h. Additional features of both methods are presented in Table 3.

Yan *et al*. (2010a) proposed a hybrid of both the traditional chemical method and solid acid catalyst for obtaining biodiesel from acid oil. A first distillation process for the acid oil in order to separate the FFAs from the triglycerides is necessary. Afterwards, they applied conventional alkali catalysis for the triglycerides and super acid catalysis for the FFAs, reaching high conversion into FAMEs.

However, the heterogeneous catalysts have not been widely used in industry because of the high catalyst cost and difficulty in filtering the small catalyst particles. Bao-Xiang *et al*. (2008) evaluated large particles of the SO_4^{2-} /TiO_2-SiO_2 solid acid catalyst for its catalytic activity in biodiesel production.

Next to the heterogeneous catalyst-based synthesis, the use of enzymes (Watanabe *et al*., 2000; Watanabe *et al*., 2007; Demirbas, 2008; Ranganathan *et al*., 2008) 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 analyzed processes (Rivera *et al*., 2009; Yujaroen *et al*., 2009; Joon *et al*., 2011). Although these processes involving enzymes are costly (Chongkhong *et al*., 2009; Haas, 2005; Yujaroen *et al*., 2009; Yan *et al*., 2010b; Liu and Wang, 2009; Helwani *et al*., 2009b; Wang *et al*., 2007), the enzyme-based processes reduce energy cost as well as tend to have lower waste treatment costs (Dos Santos Correa *et al*., 2011).

Using enzymes, conversion efficiencies between 70-90% for the transesterification reaction can be obtained (Rivera *et al*., 2009; Haas, 2005; Dos Santos Correa *et al*., 2011; Juan *et al*., 2011; Modi *et al*., 2006). Using lipase, 63% esterification conversion was reported (Haas, 2005) with an overall efficiency of 81%. A combination of enzymes and supercritical fluid extraction/reaction for obtaining biodiesel from soapstocks was also reported (King *et al*., 1998; Cherng-Yuan and Yi-Wei, 2012; Yujaroen *et al*., 2009). Supercritical extraction also has drawbacks, mainly related to the high pressures required and excessive energy costs (Chen *et al*., 2009; Helwani *et al*., 2009b).

Shao *et al*. (2008) proposed the use of *C. rugosa* lipase as catalyst starting from rapeseed soapstock. A conversion of 63.6% was obtained with a methanol molar ratio of 4:1, an enzyme amount of 8%, a water content of 6% and 45 °C. The methyl ester content was above 95% after molecular distillation.

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	References
Soybean AO	LCC	70	9:1 mol/mol	7 wt % of AO	5	97.2	-	Feng *et al*., 2012b
Cotton & Corn AO	SO_4^{2-} /TiO_2-SiO_2	200	9 mol/mol SS	3 wt %	6	94.0	Continuous process	Bao-Xiang *et al*., 2008
Palm FAD	$H_3PW_{12}O_{40}/SiO_2$ $Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$	85	12 mol/mol	15 wt %	15	96.7	Complex catalyst preparation	Trakarnpruk, 2012
AO source not specified	Acid: $SO_4^{2-}/ZrO_2/La^{3+}$ Base: sodium methoxide	Acid: 60 Base: 55	Acid: 15 mol/mol Base: 5 mol/mol	Acid: 5 wt % Base: 0.6 wt %	Acid: 4 Base: 0.5	Acid: 98.0 Base: 97.2	Previous distillation	Yan *et al*., 2010a
AO source not specified	WO_3/ZrO_2	150	9 mol/mol	20 wt %	0.4 g/mL (oil)	96.0	-	Young-Moo *et al*., 2010
Rapeseed FAD	-	60	6-15 mol/mol	-	4	93-97	cation exchange resins D002 and 002CR, flow rate 1 mL/min	Liu and Wang, 2009
Rapeseed FAD	H_2SO_4	60	12:1 mol/mol	5 wt %	4	96.8	-	Liu and Wang, 2009

Watanabe *et al*. (2007) achieved 98% of FAME for acid oil conversion into biodiesel using a two-step enzymatic method. The enzyme used was lipase at 0.5 wt. % for the first step and 6 wt. % for the second step, with the possibility of reusing lipase several times. As an alternative procedure, a non-catalytic supercritical methanol process was proposed (Yujaroen *et al*., 2009). The effect of water content in the feed on the yield of FAMEs was investigated, and also the yield of FAMEs from the non-catalytic esterification was compared to the conventional acid-catalyzed esterification and transesterification in supercritical methanol. The most suitable conditions were FAD to methanol molar ratio of 1:6 and a reaction temperature of 300 °C during 30 min, in which 95% of FAMEs was produced. Compared to the conventional acid-catalyzed esterification of FAD using a similar molar ratio, they found that only a 75% yield was obtained in 5 h.

Silva *et al*. (2012) obtained biodiesel from beef tallow with ethanol, reaching reaction times between 24-48 hours at 45 °C. The authors used an enzymatic route with two different lipases.

The main information regarding the use of heterogeneous catalysts for biodiesel production from soapstock, fatty acid distillates or acid oil is presented in Table 3. Even when the solid catalyst avoids waste and the use of acid/alkali chemicals, the amount of methanol used is higher compared to the processes indicated in Table 2. The yield of biodiesel obtained is significantly higher compared to the methods in Table 2, meaning that the use of these catalysts is a good choice, but still has to be improved in order to optimize the reaction parameters and mainly to reduce costs; this is still the main drawback of this technology (Marchetti, 2012; Bajaj *et al*., 2010).

USE IN INTERNAL COMBUSTION ENGINES

A direct injection single cylinder Petter engine TD111 with a compression ratio of 17:1 and fuel injection timing of 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% (Keskin *et al*., 2008). No differences were found in the measured engine power output between diesel fuel and the blends at lower speeds. However, at higher engine speeds, a nearly 6% decrease in power output of the engine was observed, depending on the amount of biodiesel in the blend and the engine speeds. The authors related this behavior to the lower heating value of the blend compared to diesel fuel. An increase of the specific fuel consumption up to 10.5% was observed using blends compared to diesel fuel, depending on the amount of biodiesel in the blend. For the blends, decreases of 46% in particulate matter in the exhaust emissions were also observed.

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 (Usta *et al*., 2005). 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 a slightly higher torque and power output at full load and partial loads for biodiesel blends. At full load, the CO emissions for the blend were higher at low speed and lower at high speeds than those of diesel fuel, while higher CO_2 emissions in the speed range were found for the blend. At partial loads, it was found that the blend did not cause significant changes in the CO and CO_2 emissions. They also reported a significant SO_2 reduction with the blends due to the lower sulfur content of the biodiesel. NOx emissions slightly increased, attributed to the higher combustion temperature and the presence of oxygen with the blend at full load.

Haas (2005) conducted tests in a heavy-duty truck engine, a six-cylinder four-stroke, direct injection, turbocharged, intercooled engine 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 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. When methyl esters obtained from a soapstock were tested in a diesel engine, reductions of particulate matter near 70% and increases in NOx emissions up to 10% compared to diesel fuel were observed (Haas *et al*., 2001; Haas, 2005), but also 40% reductions in CO emissions (Haas, 2005).

Graboski *et al*. (2003) performed tests in a six-cylinder, four-stroke diesel engine, nominally rated at 257 kW and 1800 rpm, direct injected, turbocharged, intercooled and electronically controlled. They tested soapstock methyl esters for exhaust emissions and compared the results with a reference diesel fuel. Important reductions in some pollutants such as total hydrocarbons (80%), CO (66%) and particulate matter (58%) compared to diesel fuel were observed, but also increases in the NOx (10.5%) and CO_2 (2.7%) were reported.

Avoiding the chemical transesterification reaction in order to obtain the FAMEs, one solution could be to use these by-products with a preheating system.

The problem is that a higher viscosity and cloud point compared to standard diesel fuel should be expected. Could present long term engine operation durability problems, but also changes in injection, fuel spray characteristics, droplet size and spray penetration. The main problem is that the direct use of these by-products after preheating in a diesel engine will cause serious corrosion problems due to the high acidity of the by-products; therefore this approach should be avoided.

Galle *et al*. (2012) 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. In the deposits, amounts of carbon, sodium, magnesium and iron were found. As the authors concluded, most of the damage in the injectors was induced by the fuel characteristics. Heavy erosion produced by particles in the fuel facilitates the start of microcracks, producing fatigue loads and the failure of fuel injectors. The problems encountered during the testing of the engine were related to the fuel composition, mainly related to its contamination content, the water present and the alkali.

Another possibility is the use of an emulsion or microemulsion (Ranganathan *et al*., 2008). As was analyzed in this paper, during biodiesel production, the lack of elimination of the water from these by-products can cause, in the second step of the synthesis, an emulsion between the oil phase and the water promoted by the soap content. According to the analyzed papers, this should be avoided, but it will be interesting to take into account the possibility of the oil-water emulsion in order to test in engines.

Another topic that enhances de microemulsification is that the water can be generated (even when water-free reactants are used) during the reaction of the hydroxide ion with the alcohol used (Andreani and Rocha, 2012). Therefore, the removal of the residual waste water produced is crucial, leading to more costly processes, which is not necessary if the microemulsification route is followed.

There are a large number of studies and evidence that, in relation to the efficiency of the combustion process, the use of emulsions is favorable for the engine performance and exhaust emissions (Abu-Zaid, 2004; Cherng-Yuan and Li-Wei, 2009; Husnawan *et al*., 2009; Kannan and Anand, 2011; Lif *et al*., 2010; Subramanian, 2011; Demirbas, 2003), although there are also drawbacks (Abbaszaadeh *et al*., 2012). Alcohol-oil microemulsions for use in diesel engines have been suggested (Yusuf *et al*., 2011). If the use of an emulsion of this nature is feasible, it can also reduce the number of steps in the biodiesel synthesis.

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

CONCLUSIONS

The feasibility of the use of by-products from the oil refining industry to produce biodiesel is clear. There is currently 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 for the extraction or isolation of several industrially useful compounds in a wide range of applications. There is a huge disparity in the amount of papers published on this topic comparing the synthesis of biodiesel and the performance of the biodiesel produced in diesel engines.

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NOMENCLATURE

AO	Acid oil
FAMEs	Fatty acid methyl esters
FAD	Fatty acid distillate
FFAs	Free fatty acids
FFB	Fresh fruit bunches
LCC	Lignin-derived carbonaceous catalyst
MeOH	Methanol
RBD	Refined, bleached and deodorized
SS	Soapstock
wt %	Weight percent

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