Biodiesel Production from Animal Fats

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Animal fats, usually found as waste from slaughterhouses, meat processing industry, and cooking facilities, constitute some of the most relevant waste with costly treatment because environmental regulations are quite strict. Part of such costs may be reduced through the generation of biodiesel that constitutes a valid renewable source of energy because it is biodegradable, non-toxic and has a good combustion emission profile. Furthermore, biodiesel can be blended up to 20% with fossil diesel for its use in many countries. Up to 70% of the total cost of biodiesel majorly depends on the cost of the raw materials used, which can be reduced using animal fat waste because they are cheaper than vegetable oil waste. Transesterification with alkaline catalysis is still preferred at industrial plants producing biodiesel. However, recent developments in technologies for process intensification like ultrasound, microwave, and different types of reactors have been successfully applied in transesterification and improved biodiesel production. Better efficiency has been achieved with new heterogeneous catalysts and nanocatalysts that can be easily recovered, regenerated and reused, and immobilized lipases with increased stability and resistance to alcohol denaturation. Also new adsorbents for increased oxidation stability of biodiesel. All these developments are promising for industrial use in near future.

Keywords: biodiesel ; fuel ; energy generation ; agricultural waste ; food waste ; animal waste ; lard ; tallow ; animal fat ; transesterification

1. Introduction

The production of biodiesel from animal fat waste requires a pretreatment that is necessary because feedstocks like animal fats usually contain large amounts of free fatty acids and water that reduce the yield of biodiesel [1] and increase production costs because of the difficulty of separation and purification [2][3]. Then, biodiesel is produced through the transesterification reaction of fat with a short-chain alcohol, usually methanol, in the presence of a catalyst that can be alkaline, acid, heterogeneous catalysts like lipases or complex catalysts like silicates, zirconias and nanocatalysts. Refining and purification are the latest steps for removal of glycerol as well as other impurities like residual catalyst, unconverted fats, and soap. The European Union is the world's largest biodiesel producer and, on an energy basis, represents nearly 75% of the total transport biofuels market. In fact, the European biodiesel industry has more than 202 plants and production in 2019 exceeded 14 million tons of biodiesel [4][5]. US production of biodiesel was more than 5.6 million tons in 2019 and came from 91 plants with a capacity of 8.3 million tons per year [6][7] . From total feedstock used for biodiesel production in 2019, 6% corresponded to animal fats. The latest advances for improving biodiesel production from animal fats are presented.

2. Developments

China has been the most active country in publishing patents in the period 1999–2018 with 647 patents on biodiesel. The US had 266 patents, with more than 50% of them focused on reactors technology and processing methods [8]. There has also been patenting activity on pretreatment methods as well as on catalysts for improving the transesterification process. Specific examples of patents for biodiesel production from animal fat waste are shown in Table 1.

Table 1. Selected patents for biodiesel production from animal fat waste.

Animal Feedstock	Particular Conditions	Catalyst	Biodiesel Characteristics	References
Lard oil, tallow oil, fish oil,	Hydrodeoxygenation and hydroisomerization of the oil in a single step	Pt and Pd and an acidic component	Mixture of C14 to C18 paraffins having a ratio of iso to normal paraffins of 2 to 8; less than 5 ppm sulfur; and acceptable lubricity	[9][10][11]

Animal Feedstock	Particular Conditions	Catalyst	Biodiesel Characteristics	References
Animal oil, fish oil, lard, rendered fats, tallow	**Unwanted water removed by cross-flow filtration**	**Immobilized lipase**	**Separation of formed crude biodiesel and crude glycerol from the second reaction medium by using a fourth cross-flow filtration cassette**	**[12]**
Animal fats	**Degumming; physical refining (heating and vacuum pulling); and glycerolysis**	**H_2SO_4, ZnO**	**Possibility of using various starting feedstocks with heat integration to minimise operating costs**	**[13]**
Animal fats incl. 10–20% free fatty acids	**Esterification in two steps**	**96% H_2SO_4**	**The amount of FFA in the mixture is reduced to <3% by weight**	**[14][15]**
Animal fats	**Esterification reaction of free fatty acids if higher than a set value**	**Alkali catalyst KOH**	**Distillation to remove byproducts like glycerol and alcohol**	**[16]**
Beef oil, pork oil, animal fats such as fish oil	**Transesterification with lower alcohol content**	**Alkali catalyst KOH**	**Reducing costs by producing glycerin and glycerin derivatives in high yield and purity**	**[17]**

2.1. Technology

Transesterification with alkaline catalysis is still preferred at industrial plants producing biodiesel but innovative technologies for process intensification, like ultrasound and microwave, have been developed to be applied in transesterification and improve biodiesel production. The goal is to improve the miscibility of oils and methanol and thus increase the yield of the transesterification [18][19]. Immiscible liquids can be emulsified at an industrial scale through the use of low frequency ultrasonic irradiation. In the case of microwave irradiation, reactants can be efficiently and rapidly heated to the target temperature [20]. Other process intensification technologies like static mixers [21], capillary reactors [22], microreactors [23][24], or oscillatory flow reactors [25] are also intended to accelerate the reaction rate and enhance biodiesel production.The use of microwave heating for animal fats containing up to 20% free fatty acids allowed for a decrease in the required time for free fatty acid reduction and increased the final yield [26]. Another alternative was the use of supercritical methanol with temperatures of 300–400 °C, pressures up to 41.1 MPa, alcohol to fat ratios of 3:1 and 6:1, and short time (between 2–6 min) that gave 88% conversion for chicken fat [27]. The yield of biodiesel obtained with refined lard could also be obtained with waste lard containing fatty acids and water with no need for pretreatment [28]. Supercritical processes give faster reaction rates with no catalyst and avoid the need for pretreatment even in the presence of free fatty acids and water associated with the use of animal fats [29]. Neste renewable diesel is produced through the hydrogen catalyzed conversion of triglycerides into the corresponding alkanes and propane. Nearly 3 million tons are produced in five plants and mixed with fossil diesel for its use in aviation, turbines, generators and ships [30].

2.2. Catalysts

New heterogeneous catalysts that can be easily recovered, regenerated and reused have been developed for biodiesel production. Such catalysts include alkaline earth metal oxides such as CaO and MgO, hydrotalcite, acid zirconia and alumina-based catalysts and immobilized lipase [3]. The use of a new nano catalyst consisting of $CaO/CuFe_2O_4$ during the transesterification process was successfully assayed for biodiesel production from chicken fat [31]. A sodium silicate catalyst that does not saponify with free fatty acids during transesterification was recently assayed to produce biodiesel that could be blended up to 30% with diesel, giving good performance. The brake specific fuel was 26% higher than diesel and the brake thermal efficiency was 4% lower while CO was reduced by 24.4% and hydrocarbons by 22.9%. However, no emission was increased by 11% at full load [32]. Shells of *Mytilus galloprovincialis*—waste from fish industry—containing CaO that can be used as a catalyst, were used for transesterification of jojoba oil. As CaO could be contaminated with CO_2 and H_2O, it was calcined immediately before use [33]. Calcined scallop shell was also reported as a very active catalyst for transesterification of rapeseed oil [34]. Recently, a cheap and safe catalyst consisting of metal hydrated salts was proposed for the pretreatment of animal fats with a high content of free fatty acids that could be esterified up to 99% with alcohol under mild conditions [35]. The methyl esters remained in the oily phase and could be used for transesterification directly with alkaline catalysts. On the other hand, a biorefining strategy for animal fat waste was proposed for the conversion of free fatty acids into triglycerides that could be blended with fossil diesel and be used in engine combustion systems [36].

A variety of lipases from diverse microorganisms such as *Candida antarctica*, *Candida rugosa*, *Pseudomonas cepacia*, *Pseudomonas* spp. and *Rhizomucor miehei*, and immobilized lipases, have been reported as effective for biodiesel production [9]. The use of lipases requires lower energy consumption and absence of soaps; another advantage is that lipases are specific and selective reducing the possibility of undesired reactions [37]. However, the costs of the enzyme are high, the enzyme can be denatured by alcohol and can be used only once. Immobilisation of the enzyme increases its stability and allows its reuse although some denaturation by alcohol may still exist [38]. Transesterification with immobilised lipase in supercritical CO_2 reduced the interaction between methanol and enzyme, and its toxicity with an immediate separation of CO_2 from the product [39] Other authors have assayed the coimmobilisation of lipases on the same surface [40] or layer by layer [41] in order to get better global activity.

2.3. Adsorbents

Recently, adsorbents like magnesium aluminum hydroxycarbonate and 1,3,5-trimethyl-2,4,6-tris(3,5-ditert-butyl-4-hydroxybenzyl) benzene were proposed to enhance the oxidative stability of biodiesel and its blends and therefore retard their degradation. The acid value could be reduced up to 9%. In this way, the adsorbents can remove the precursors of the aging of biodiesel by stabilizing the generated free radicals and preventing them from starting new oxidation chains [42]. Precipitates of steryl glucosides are found in biodiesel produced from vegetable oils and may produce filter blockage. Their removal is achieved through adsorption with 3% silica at 112 °C for 72 min [43].

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