

Review

Trends in Biodiesel Production from Animal Fat Waste

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Abstract: The agro-food industry generates large amounts of waste that contribute to environmental contamination. Animal fat waste constitutes some of the most relevant waste and the treatment of such waste is quite costly because environmental regulations are quite strict. Part of such costs might be reduced through the generation of bioenergy. Biodiesel constitutes a valid renewable source of energy because it is biodegradable, non-toxic and has a good combustion emission profile and can be blended up to 20% with fossil diesel for its use in many countries. Furthermore, 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. In fact, 6% of total feedstock corresponded to animal fat in 2019. Transesterification with alkaline catalysis is still preferred at industrial plants producing biodiesel. Recent developments in heterogeneous catalysts that can be easily recovered, regenerated and reused, as well as immobilized lipases with increased stability and resistance to alcohol denaturation, are promising for future industrial use. This manuscript reviews the available processes and recent advances for biodiesel generation from animal fat waste.

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

1. Introduction

Animal byproduct production, as part of the meat and poultry processing chain, is huge. For instance, it represents nearly 17 million tons per year only in the European Union [1]. Most of the waste results from over 328 million pigs, sheep, beef, goats and dairy cattle and 6 billion chickens, turkeys and other poultry that are slaughtered every year in Europe [2]. After rendering, materials classified as edible which amount up to 12 million tons, are processed in a variety of food and feed related sectors [3]. The remaining byproducts that are considered inedible have other applications for disposal such as biofuels and biodiesel for energy generation [4,5]. It is energy generation, especially biodiesel production, that is one of the most attractive and expanding applications [6]. In this sense, the production of biodiesel guarantees a better profitability of inedible animal byproducts. Animal waste also consists of the organic matter resulting from the meat processing industry as well as from human consumption. Biodiesel consists of mono-alkyl esters of long chain fatty acids produced from oil or fat, but the use of vegetable oil adds a high price to biodiesel, and this has prompted the use of animal fats as an interesting alternative. In addition to its renewability, biodiesel also constitutes an attractive alternative because it offers better lubricating properties than fossil diesel fuel and it is biodegradable and non-toxic. It also has an improved cetane number and high flash point [7]. Biodiesel also contributes to sustainability by reducing the carbon footprint due to lower CO₂ emission compared to fossil diesel fuel [8]. CO₂ is one of the most relevant gases because it contributes up

to 72% of greenhouse gases [9]. Biodiesel from animal fat achieves nearly 80% fossil CO₂ reduction in comparison to 30% for soya [5]. In addition, the emission of polycyclic aromatic hydrocarbons is 75–90% lower than in conventional diesel, whereas total unburned hydrocarbon is 90% lower [10,11]. The emissions of sulfur and CO are also reduced [12].

The International Energy Agency reported that bioenergy must increase up to 25% until 2025 and continue to grow, and is estimated to reach 30% of the world's road transport fuel mix by 2050 [13,14]. Biodiesel is mostly produced from vegetable oils and animal fats and has been the object of research and development in recent decades. Research is directed towards the use of low grade feedstock, with the possibility of reusing catalysts and improving efficiency of reactors for transesterification [15]. In fact, oil and fat materials used as raw materials are of high relevance because they are estimated to represent 60–80% of the total cost of biodiesel production [16]. Therefore, it is important to select the best materials in each case because they are affected by the geographic location, climate and agriculture [11]. Several countries such as Malaysia, Indonesia, Argentina, USA, Brazil, and the Philippines, as well as countries in the EU, are using biodiesel as a good source of renewable and biodegradable energy [17]. A consumption of 17.4 million liters of biodiesel was reported in 2019 with 63% of this consumption by France, Germany, Spain, Sweden and Italy [18]. The total biodiesel world production in 2019 was approximately 35 to 45 million tons and is steadily increasing year by year [19]. 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 [18,20]. 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 [21,22]. Biodiesel is usually blended up to 20% with fossil diesel fuels in most countries due to its complete miscibility and the unnecessary need for engine modification at such percentage. For instance, a 20% blend is used in the United States while at least a 10% blend is used in China [23]. Blends receive the name B5, B10 or B20 when the biodiesel volume content is 5%, 10% and 20%, respectively. Today, more than 78% of diesel vehicles coming off production lines are approved for up to B20 use [21]. For biodiesel to be blended with normal fossil diesel, it must comply in Europe with EN14214 from the European Committee of Standardization (ISO) and in the US with ASTM6751 from the American Society for Testing and Materials [5].

Biodiesel can be used in existing diesel engines without the need for substantial modification. Biodiesel has a higher oxygen content than conventional diesel and the carbon to hydrogen ratio is also lower. This explains the major advantages of biodiesel such as lower emission of particulate matter, but also a lesser content of sulfur, hydrocarbon and carbon monoxide [24,25]. The major challenge nowadays is the production of environmentally and economically viable biodiesel [23] and the use of animal fat waste could contribute towards achieving this goal. This review is highlighting the latest advances in the available processes for biodiesel production from animal fat waste.

To elaborate on the present review, the literature search was performed in Web of Science (WoS) database from 1 January 2010 to 28 February 2020. The terms "biodiesel production," "animal fat" and "transesterification" were used for the survey of published papers. In total, 1602 publications were found, 1594 of them in English, with most found over the last three years. Of these, 1541 manuscripts were research articles, 141 were reviews, 210 corresponded to meetings, 27 corresponded to books, and the rest fell under another category. Eligibility criteria were established as: (a) full-text with English language article; (b) articles selected were published in scientific journals that apply a peer review system; (c) books, workshops, conference reports, theses and case reports were excluded due to lack of peer review; (d) articles with other feedstocks like vegetable oils; and (e) articles that only analyzed the overall performance of the process and did not provide specific parameters for comparison or evaluation were not included. Titles and abstracts of manuscripts were further evaluated for selection of manuscripts and those selected were used for the current review. Some relevant publications published before 2010 were also considered as well as websites of producers and international

agencies with current data and updated information on industrial use of feedstocks, animal fats and biodiesel production.

2. Animal Fats as Feedstock

About 328 million animals (cattle, sheep, pigs and goats) and 6 billion poultry (mainly chickens and turkeys) were slaughtered in 2014 in the European Union [2]. Such a high number of slaughtered animals produces enormous amounts of waste animal residue including fats that need to be treated to reduce pollution or recycled to give them some added value [26,27]. Such fats include beef tallow extracted from rendering fatty tissue of cattle, mutton tallow from rendering sheep, pork lard from rendering pigs and chicken fat from rendering feathers, blood, skin, offal and trims [28,29]. The wet rendering process includes the presence of water and fats heated below 49 °C. The goal is separation of the fat from the protein fraction. Other fats are those resulting from meat and the meat processing industry and those from recycling of the industrial cooking business. Such recycled greases that are produced from heated animal fats collected from commercial and industrial cooking can be classified as yellow grease and brown grease depending on the content of free fatty acids (FFA). Yellow grease is considered if FFA < 15% by weight and brown grease when FFA > 15% [30].

Typical fatty acid composition of pork lard, beef tallow, mutton tallow and poultry fats are shown in Table 1. There is a wide variety depending on the animal species [31] but in general, they contain common types of fatty acids, most of them having 16 to 18 carbons. Most relevant fatty acids are palmitic (16:0) and stearic (18:0) acids as saturated fatty acids (SFA); oleic acid (18:1) as monounsaturated fatty acids (MUFA); and linoleic (18:2) and arachidonic (20:4) acids as polyunsaturated fatty acids (PUFA) [32]. Due to their high content of saturated fatty acids (near 40% SFA), ruminant and pig fats are predominantly solid while those from chicken fat (nearly 30–33% of saturated fatty acids) are almost liquid or in semi-solid form [33]. Therefore, it must be taken into account that raw animal fats are mostly in a solid state at ambient temperature and therefore, preheating at 45 °C is required for their use as fuel for diesel engine [14]. Further, such high content in saturated fatty acids generally results in more stable biodiesel with high cetane numbers (more than 50 for lard and tallow).

One of the main applications of inedible animal fat byproducts is the production of biodiesel [6,34]. Inedible animal byproducts are structured into three categories within the EU that are defined according to their risk to human or animal health. Category 1 has the highest risk, Category 2 still offers a high risk, while Category 3 offers the lowest risk and is fit for human consumption although generally not used for human food because of its non-edible content or for commercial reasons. Major uses for Category 3 byproducts are as feed and pet food. In any case, fats from all three categories can be destined to biodiesel production and some stakeholders have reported that Category 3 provides better quality for biodiesel production [35]. Nearly 81% of caul and lung fat and 26% of cod and kidney, knob and channel fat from cattle are destined for biodiesel production. In the case of sheep fats, 88% of caul fat, 43.3% of lung fat and 67.1% of knob and channel fat are destined for biodiesel production [36]. In 2019, the total amount of vegetable oil and animal fat used as feedstock for biodiesel exceeded 13 million tons in the EU. From them, 800 thousand tons (6% of total feedstock) corresponded to animal fats, and such amount has remained fairly constant since 2014 [18,19]. In the case of the US, animal fats represented 8.4% of total feedstock and were poultry fat, tallow and white grease with amounts of 74, 132 and 243 thousand tons, respectively [21].

Table 1. Typical composition in major fatty acids (as % of total fatty acids) of pork, beef, mutton and chicken fats.

Fatty Acid		Pork Lard	Beef Tallow	Mutton Tallow	Poultry Fat
		[37]	[38]	[39]	[40]
Myristic	C14:0	1.6	1.6	2.2	0.4
Palmitic	C16:0	25.1	21.6	21.1	21.6
Stearic	C18:0	12.6	17.7	11.6	6.3
Palmitoleic	C16:1	2.8	2.5	2.1	3.2
Oleic	C18:1	36.5	31.5	38.7	30.0
Linoleic	C18:2	16.5	3.3	10.2	28.4
Linolenic	C18:3	1.1	1.3	0.6	2.4
Arachidonic	C20:4	0.3	-	-	3.4
Docosapentaenoic	C22:5	0.2	-	-	0.3
Docosahexaenoic	C22:6	-	-	-	0.8
Total saturated	SFA	39.4	49.1	40.4	29.1
Total monounsaturated	MUFA	39.7	41.0	47.1	33.2
Total polyunsaturated	PUFA	20.9	10.0	12.5	37.6

3. Transesterification for Producing Biodiesel from Animal Fats

The major steps in the production of biodiesel from animal fat waste are shown in Figure 1. A pretreatment is needed because feedstocks like animal fats usually contain a high amount of free fatty acids (FFA) and water which reduces the yield of biodiesel [41] and increases production costs because of the difficulty of separation and purification [42,43]. Biodiesel is produced through the transesterification reaction of a fat with a short-chain alcohol in the presence of a catalyst. Different catalysts are available to be used for biodiesel production. Those most typically used in transesterification reactions are alkalis (sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide, sodium amide, sodium hydride, potassium amide and potassium hydride), acids (sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid), heterogeneous catalysts like enzymes (lipases) and complex catalysts like silicates, zirconias, nanocatalysts, etc. [44]. A faster reaction rate of animal fats transesterification is obtained using alkali catalysts in comparison to acid catalysts [45,46] which are 4000 times faster [47] as well as less expensive and readily available [48]. Sodium and potassium hydroxides run quite well, and methoxides perform better but are more expensive [47]. Polyol-derived alkoxide base catalysts were prepared by heating aqueous sodium hydroxide solution and polyols under vacuum pressure [49] and potassium glyceroxide catalysts were produced from potassium hydroxide and non-volatile, non-toxic polyols like byproduct glycerol by heating and drying, making it cheap to produce. Furthermore, the rate of transesterification reactions in methanol was reported to be comparable to those observed for the conventional potassium methoxide catalyst under the same reaction conditions [50]. On the other hand, the use of acid catalysts for a transesterification reaction results in slower reaction rates and requires a higher alcohol to fat molar ratio and a larger reactor that may be subject to corrosion [51]. Acid catalysts are mainly used for reducing the free fatty acids content before its transesterification with alkaline catalysts [47].

The most commercially used short-chain alcohol for the transesterification reaction is methanol because of its cheap price, but other alcohols such as ethanol, propanol and butanol may also be used [52]. Transesterification consists of the conversion of triacylglycerols to diacylglycerols, releasing one fatty acid. Then, diacylglycerols are converted to monoacylglycerols, releasing a second fatty acid and, finally, monoacylglycerols are converted to glycerol, releasing a third fatty acid. In general, transesterification has a high conversion efficiency and low cost [53]. However, once a pretreatment has been performed [54], the efficiency of the transesterification reaction depends on many variables like the time and temperature of the reaction, type and molar ratio of alcohol, type and amount of catalyst used, the amount of water present in the reaction media, the composition of fatty acids and the release of free fatty acids to the reaction media. In industrial processing plants, approximately 100 kg of fat react with 10 kg of a short-chain alcohol (usually methanol) in the presence of an alkaline

catalyst, either sodium hydroxide or potassium hydroxide, to generate 100 kg of biodiesel and 10 kg of glycerin [55].

Examples of operating conditions during the transesterification step for production of biodiesel from animal fats are shown in Table 2. The optimum alcohol to oil molar ratio to get a biodiesel yield higher than 90% in alkaline catalyzed transesterification is reported to be around 6:1 which gives enough alcohol the capability to break the fatty acid–glycerol linkages. The use of a ratio greater than 6:1 gives a better yield in some cases but could hinder the glycerol separation process [56].

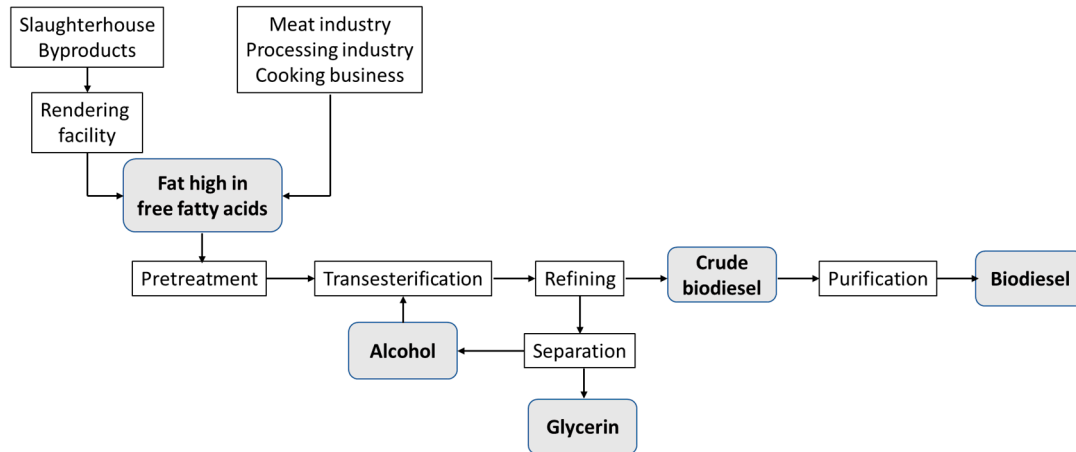


Figure 1. Major steps in the production of biodiesel from animal fat waste. Adapted from [46,47,53].

Table 2. Examples of operating conditions during the transesterification step for the production of biodiesel from animal fat waste.

Animal Fat	Catalyst	Weight (% to Fat)	Reaction Yield (%)	Alcohol:Oil Ratio	Operating Conditions	References
Beef tallow	KOH	0.8	90.8	6:1	60 °C, 2 h	[57,58]
Pork Lard	KOH	0.8	91.4	6:1	60 °C, 2 h	[57,58]
Poultry fat	KOH	0.8	76.8	6:1	60 °C, 2 h	[57,58]
Chicken waste	KOH	1	-	6:1	60 °C, 2 h	[59]
Duck tallow	KOH	1	97.1	3:1	65 °C, 3 h	[60]
Pork fat	KOH	0.5	97.3	6:1	65 °C, 2 h	[61]
Catfish fat	KOH	0.8	92.7	6:1	50 °C, 0.75 h	[62]
Chicken fat	KOH	0.8	82.0	8:1	60 °C, 1 h	[63]
Swine lard	KOH	1.1	98.0	7.4:1	65 °C, 3 h	[64]
Mutton fat	MgO-KOH	20	98.0	22:1	65 °C, 20 min	[65]
Chicken fat	H ₂ SO ₄	1.25	99.0	1:30	50 °C, 24 h,	[24]
Mutton tallow	H ₂ SO ₄	1.25	93.2	1:30	60 °C, 24 h	[24]
Chicken fat	NaOMe	1	88.5	6:1	60 °C, 4 h	[66]
Chicken fat	Nano CaO	1	88.5	9:1	60 °C, 5 h	[67]
Chicken fat	Composite membrane & NaOMe	1	98.1	1:1	70 °C, 3 h	[68]
Chicken fat	CaO/CuFe ₂ O ₄	3	94.5	15:1	70 °C, 4 h	[69]
Lard	35%CaO/zeolite	8	90.9	30:1	65 °C, 1.25 h	[15]
Chicken fat	AC/CuFe ₂ O ₄ encapsulated with CaO	3	95.6	12:1	65 °C, 4 h	[70]
Brown grease	Mesoporous silica diphenylammonium triflate	15	98.0	15:1	95 °C, 2 h	[71]
Brown grease	ZnO/ZrO ₂	0.8	78.0	1:1.5	200 °C, 2 h	[72]
Lard	Supercritical methanol	-	89.9	45:1	335 °C, 20 MPa, 15 min Agitation 500 rpm	[73]
Waste lard	Immobilized lipase from <i>Candida antarctica</i>	6	96.8	6:1	50 °C, 30 min Ultrasound assisted	[74]

Table 2. Cont.

Animal Fat	Catalyst	Weight	Reaction	Alcohol:Oil	Operating	References
		(% to Fat)	Yield (%)	Ratio	Conditions	
Beef tallow	Immobilized lipase from <i>Burkholderia cepacia</i>	20	89.7	12:1	50 °C, 48 h	[75]
Animal fat	Immobilized lipase from <i>Candida antarctica</i>	10	79	50:6	40 °C, 6 h	[76]
Lard	Lipase from <i>Candida</i> sp	20	87.4	3:1	40 °C, 30 h	[77]
Lard	Lipase from <i>Candida antarctica</i>	10	74	1:1	30 °C, 72 h	[78]
Lard	Lipase from <i>Candida antarctica</i>	2–6	97.2	5:1	50 °C, 20 h	[79]

As previously mentioned, if an alkaline catalyst is used for transesterification and there is a high content of free fatty acids, the reaction efficiency is drastically reduced because of the reaction of such free fatty acids with the catalyst resulting in soap formation [80,81]. This causes a loss of catalyst and ester product [82] and reduces the biodiesel yield to low levels, and therefore, the production costs increase [83]. The soap formation also makes glycerol separation and biodiesel purification difficult, which increases the cost of the resulting alkaline wastewater treatment [84]. The quality can also be affected due to side reactions producing unwanted products [85]. The free fatty acid content in animal fats is within the range of 5–30%, making a pretreatment necessary [26]. For an effective transesterification reaction, it is recommended that a limit in free fatty acids be equivalent to 1.0–1.5% [86], or an acid value below 2 mg KOH/g of oil [87]. There are different strategies in order to get such reduction in free fatty acids. For instance, waste pork fats containing free fatty acids within the range 4.9–13.5% were esterified for 4 h at 65 °C with 0.5 wt.% H₂SO₄ or 1.0 wt.% p-toluene sulfonic acid, keeping a 6:1 methanol to fat molar ratio, and the acid value was reduced below 2 mg KOH/g [61]. Furthermore, the waste fat of rendered pork was reported to have a high acid value of 4.3 mg KOH/g, but it could be reduced down to 0.75 mg KOH/g through a standard titration pretreatment method using sulfuric acid, even though it can be corrosive [23]. A continuous esterification process that reduced the reactor cost and reaction time, was designed for pretreatment deacidification using an ion exchange resin reaching an acid value reduced to 0.89 mg KOH/g and a conversion rate as high as 99.26% [80].

Thus, pretreatments are necessary to remove the excess of water, free fatty acids and suspended solids of animal fats before transesterification. Some of such pretreatments for moisture reduction are heat drying, silica gel, calcium chloride or anhydrous sodium sulfate [88–90]. The excess of free fatty acids may be removed by neutralization and separation [78]. Finally, the suspended matter may be removed by filtration under vacuum or through cellulose filters [88,90]. However, although the quality and yield of biodiesel are better, pretreatment steps result in additional costs [91].

An alternative process would be a two-step transesterification being the first step—an acid-catalyzed pretreatment to esterify the free fatty acids and thus, reducing their content—and the second step, where triacylglycerols undergo transesterification with the alkaline catalyst [52]. Other alternatives to consider are heterogeneous acid and base catalysts that have better tolerance to high water content and free fatty acids and can be re-used [82].

Heterogeneous catalysts offer the possibility of recycling and reducing the biodiesel production steps. Basic zeolites, alkaline earth metal oxides and hydrotalcites constitute some of the most used in recent literature. CaO is one of the most used catalysts and it has been loaded onto zeolite that offers a large surface area [15]. However, CaO can be poisoned when contacting water and carbon dioxide, making it not so attractive for industrial operation [92]. This catalyst could be recycled but the biodiesel yield is rapidly decreased down to 37.5% after its third use. Several nanocatalysts like nano CaO [48], activated carbon/CuFe₂O₄ encapsulated with CaO [69] and KF/CaO nanocatalysts [93] have been reported at the laboratory scale. Such nanocatalysts show a higher catalytic efficiency, better rigidity, larger specific surface area and better resistance to saponification [69].

Heterogeneous solid acid catalysts are reported to give lower yields. However, they have some advantages in the case of animal fats because they are insensitive to the problem of

contents in free fatty acids and can perform esterification and transesterification simultaneously. Furthermore, the purification of biodiesel is avoided, and another advantage is the easier separation of the catalyst from the reaction products [94].

In cases where there is a high content of moisture and free fatty acids (e.g., animal fats), the enzymatically catalyzed transesterification is more attractive. Lipase converts both free fatty acids and triglycerides into biodiesel in the presence of an acyl acceptor. The main advantages are the mild reaction conditions, high selectivity and specificity of transesterification, broader substrate range, no soap formation, lower alcohol to oil ratio, lower requirements for purification and higher yields [95]. However, the major cost is due to the enzyme itself and its poor stability and longer reaction time, and the slow conversion rate because of the diffusion caused by its byproduct [96]. These troubles can be partly overcome through enzyme immobilization on an inert support that increases the enzyme stability, avoids the need for enzyme separation and improves process efficiency [97,98]. Other costs are derived from the deactivation of the enzyme at high molar ratios of alcohol to fat [96]. Three solutions have been proposed, which are using methanol stepwise addition, replacing methanol with an acyl acceptor like methyl acetate or ethyl acetate or using a solvent like t-butanol to get an improved solubility of methanol [99]. A variety of lipases from diverse microorganisms such as *Candida antarctica*, *Candida rugosa*, *Pseudomonas cepacia*, *Pseudomonas* spp. and *Rhizomucor miehei*, and immobilized lipases (i.e., Lipozyme[®] RMIM from *Rhizomucor miehei* or Novozym[®] 435 from *Candida antarctica*), have been reported in the literature [100]. It must be pointed out that transesterification with alkaline catalysis is still preferred at industrial plants producing biodiesel. In spite of much research on heterogeneous and enzyme catalysis, biodiesel producers have not yet adopted these technologies [101].

4. Quality of Biodiesel Produced from Animal Fat Waste

Biodiesel has to comply with regulations EN14214 from the European Committee of Standardization (ISO) and the ASTM6751-3 from the American Society for Testing and Materials (ASTM). There are relevant benefits in the use of biodiesel produced from animal fats, such as the emission of polycyclic aromatic hydrocarbons being reduced by 75–90% and total unburned hydrocarbon by 90% when using biodiesel produced from animal fats when compared to conventional diesel [10,11]. The emissions of sulfur dioxide and CO are also reduced [12] as well as the particulate matter and nitrous oxides at part loads [18,66]. The properties of biodiesel produced from animal fats are compiled in Table 3. The cetane number reflects the ignition characteristics of the fuel. A high number is associated with better ignition quality [47]. The cetane number of biodiesels produced from animal fats is >50 and higher than that produced from vegetable oils due to their content of saturated fats (higher than 40%) and lower content of carbon and higher content of oxygen in comparison to conventional diesel [14]. The acid value is associated with the content in free fatty acids which, at high concentrations, can cause corrosion of the fuel supply system of the engine [66]. The cold filter plugging point (CFPP) represents the lowest temperature that a volume of liquid fuel will still flow through a given filter in a determined period of time when the fuel components start to gel or crystallize [102]. It is especially important for cold weather conditions. CFPP of biodiesel from animal fats is higher than 2 °C due to a higher content of saturated fatty acids. Flash point is the temperature at which the biodiesel exposed to a flame will ignite. Biodiesel from animal fats has a flash point higher than 150 °C and this provides better safety during transport and storage [47]. Biodiesel provides good lubricity that helps for a longer engine life [103]. However, the viscosity is higher than 3.5 mm²/s due to the saturated fats that give higher amounts of CH₂ in the fatty acid methyl esters [104] which might create problems in pumping and combustion [11]. Finally, the percentage of free glycerin reflects the amount of glycerol remaining in the final biodiesel and, if the content is high, it could result in coking of the injector and damage to the fuel injection [47].

The cost of the obtained biodiesel from animal fat waste depends on several parameters such as the cost of the feedstock, the amount of free fatty acids and the type of necessary pretreatment, the type of catalyst, the operational maintenance and the type of purification for the biodiesel [105]. The refining of

crude biodiesel obtained from animal waste is more costly than that from vegetable oils. Large amounts of glycerine (glycerol) are produced during transesterification which need to be removed because they influence the quality of the fuel and reduce the engine durability. The purification process (see Figure 1) usually consists of either wet washing based on water, dry washing based on adsorption and ion exchange, or novel methods based on liquid–liquid extraction, deep eutectic solvents or membranes. The purification step will thus remove glycerol as well as other impurities like residual catalyst, unconverted fats, and soap, and provides a better quality of biodiesel fuel [106]. About 1 kg of glycerol is produced for each 10 kg of biodiesel [107]. The recovered glycerol may be used for pharmaceutical, food, personal care biopolymers, or fuel additive applications although the value is low due to the large worldwide production of glycerol [92,105].

Table 3. Properties of biodiesel produced from animal fat waste.

Properties	EN14214 Limits	Poultry Fat [47]	Poultry Fat [58]	Chicken Fat [29]	Chicken Fat [108]	Chicken Fat [66]	Pork Lard [58]	Pork Lard [61]	Mutton Tallow [24]	Beef Tallow [47]	Beef Tallow [58]
Density at 15 °C (kg/m ³)	860–900	-	877	830	870	883	873	870	856	-	870
Viscosity at 40 °C (mm ² /s)	3.50–5.00	4.50	6.86	3.5	5.4	4.94	5.08	4.74	-	4.82	5.35
Cetane number	>51.0	-	-	50	58.4	-	-	56.9	59.0	-	-
Acid value (mg KOH/g)	<0.50	0.044	0.55	-	0.8	0.22	0.22	0.23	0.65	0.147	0.20
Iodine value (g/100 g)	<120	-	78.8	-	-	-	75.6	66.7	126	-	44.4
Water content (mg/kg)			1201			200	184	500	200		374
Flash point (°C)	>120	>160	172	50	174	171.8	147	175	-	>160	171
Pour point (°C)	-	-	-	-6	-	-6	-	-	-5	-	10
Cloud point (°C)	-	6.1	-	-	-	-5	-	-	-4	16	-
Free glycerin (%)	-	0.002	-	-	-	0.19	-	-	-	0.008	-
Cold filter plugging point (°C)	8	2	3	-	-	-	5	-20 to 5	-	14	10

5. Developments in Improving Biodiesel Production from Animal Fats

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 [11]. 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 4.

Table 4. 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	[100,109,110]
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	[111]
Animal fats	Degumming; physical refining (heating and vacuum pulling); and glycerolysis	H ₂ SO ₄ , ZnO	Possibility of using various starting feed stocks with heat integration to minimize operating costs	[112]
Animal fats incl. 10–20% free fatty acids	Esterification in two steps	96% H ₂ SO ₄	The amount of FFA in the mixture is reduced to <3% by weight	[113,114]
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	[115]
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	[116]

Technologies for process intensification like ultrasonic 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 [73,117]. 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 [118]. Other process intensification technologies like static mixers [119], capillary reactors [120,121], microreactors [122,123] or oscillatory flow reactors [124] 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 [66]. Another alternative was the use of supercritical methanol with temperatures of 300 °C–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 [125]. 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 [72]. 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 [30]. Other authors have assayed the transesterification with immobilized lipase in supercritical CO₂ and reported its contribution in reducing the interaction between methanol and enzyme, reducing its toxicity [75] and immediately separating CO₂ from the product.

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 [20]. The use of a new nano catalyst consisting of CaO/CuFe₂O₄ during the transesterification process was successfully assayed for biodiesel production from chicken fat [69]. 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 [25]. 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 CO₂ and H₂O, it was calcined immediately before use [126]. Calcined scallop shell was also reported as a very active catalyst for transesterification of rapeseed oil [127].

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 [128]. 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 [129]. 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 [130]. 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 [131]. Finally, it is important to mention that 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 [132].

6. Conclusions

Biodiesel produced from agricultural waste has been rapidly expanded around the world due to its relevant advantages such as being biodegradable, renewable and sulphur-free. The cost of biodiesel majorly depends on the cost of the raw materials being used, with animal fat waste being cheaper than vegetable oil waste. Animal fats, usually found as waste from slaughterhouses, the meat processing industry, and cooking facilities, can be used as feedstock for biodiesel production. As reported in this manuscript, there are numerous processes already available for the production of biodiesel from animal fats and operating conditions during transesterification. There are also alternative solutions for pretreatment which mainly depend on the moisture and FFA content of such residues. Alkaline catalysis is still preferred at industrial plants producing biodiesel because it is faster than acid catalysis and cheaper than most alternative catalysts including acid catalysts and lipases. Although much research has been published on heterogeneous and acid and enzyme catalysts which avoid the challenges of water and FFA in animal fats, biodiesel producers have not yet adopted these technologies. However, there are recent developments that are promising for future industrial use. This is the case with heterogeneous catalysts that can be easily recovered, regenerated and reused, and immobilized lipases that improve efficiency and reduce costs by increasing enzyme stability and making the enzyme more resistant to denaturation by alcohol.

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