

# Animal Fat Wastes for Biodiesel Production

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## 1. Introduction

Our society is highly dependent on petroleum for its activities. However, petroleum is a finite source and causes several environmental problems such as rising carbon dioxide levels in the atmosphere. About 90% is used as an energy source for transportation, heat and electricity generation, being the remaining sources used as feedstocks in the chemical industry (Carlsson, 2009). As demands for energy are increasing and fossil fuels are limited, research is directed towards alternative renewable fuels (Bhatti et al., 2008). High petroleum prices and the scarcity of known petroleum reserves demand the study of other sources of energy. In this context, agroindustrial wastes (animal fats, wood, manure) play an important role as energetic materials. Oils and fats are basically triacylglycerols (TAG) composed of three long-chain fatty acids. These triacylglycerols have higher viscosity and therefore cannot be used as fuel in common diesel engines. In order to reduce viscosity, triacylglycerols are converted into esters by transesterification reaction. By this means, three smaller molecules of ester and one molecule of glycerin are obtained from one molecule of fat or oil. Glycerin is removed as by-product and esters are known as biodiesel (Fazal et al., 2011).

Biodiesel fuels are attracting increasing attention worldwide as a blending component or a direct replacement for diesel fuel in vehicle engines. Biodiesel consists of a mixture of fatty acid (chain length C<sub>14</sub>-C<sub>22</sub>) alkyl esters, derived from a renewable lipid feedstock, such as vegetable oil or animal fat. In the case when methanol or ethanol are used as reactants, it will be a mixture of fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE), respectively. However, methanol is commonly and widely used in biodiesel production due to its low cost and availability. Other alcohols such as isopropanol and butyl may also be used. A key quality factor for the primary alcohol is the water content, which interferes with the transesterification reactions and can result in poor yields and high level of soap, free fatty acids (FFA) and TAG in the final fuel (Demirbas, 2009a; Lam et al., 2010).

Biodiesel is a low-emission diesel substitute fuel made from renewable resources and waste lipid. The most common way to produce biodiesel is through transesterification, especially

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alkali-catalyzed transesterification (Leung et al, 2010). The most commonly used catalysts for converting TAG to biodiesel are sodium hydroxide, potassium hydroxide and sodium methoxide. The alkaline catalysts are highly hygroscopic and form chemical water when dissolved in the alcohol reactant. They also absorb water from the air during storage. Acid catalysts include sulfuric and phosphoric acids, being more related to directly esterification of FFA, although they are considered to be slow for industrial processing (Demirbas, 2009a). When the raw materials (oils or fats) have a high percentage of FFA or water, the alkali catalyst will react with the FFA to form soaps (Leung et al, 2010).

An alternative fuel to petrodiesel must be technically feasible, economically competitive, environmentally acceptable and easy available (Demirbas, 2009a). FAME from vegetable oils and animal fats have shown promise as biodiesel, due to improved viscosity, volatility and combustion behaviour relative to triacylglycerols, and can be used in conventional diesel engines without significant modifications (Bhatti et al., 2008). The advantages of biodiesel over diesel fuel are its portability, ready availability, renewability, higher combustion efficiency, lower sulphur and aromatic content, higher cetane number, higher biodegradability, better emission profile, safer handling, besides being non-toxic (Lapuerta et al., 2008; Demirbas, 2009a, Balat & Balat, 2010). Besides the superb lubricating property of biodiesel and its similarities in physicochemical properties to diesel, makes it an excellent fuel for compression ignition engines, revealing its potentials and practical usability for the replacement of petrodiesel in the nearest future (Atadashi et al., 2010). Moreover, biodiesel offers advantages regarding the engine wear, cost, and availability. When burned, biodiesel produces pollutants that are less detrimental to human health (Fazal et al., 2011).

Biodiesel has superior emission profile than diesel, substantially reducing emissions of unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter (Lapuerta et al., 2008). Diesel blends containing up to 20% biodiesel can be used in nearly all diesel-powered equipment, and higher level blends and pure biodiesel can be used in many engines with little or no modification. Lower-level blends are compatible with most storage and distribution equipments, but special handling is required for higher-level blends (Demirbas, 2009a).

Usage of biodiesel will allow a balance to be sought between agriculture, economic development and environment (Demirbas, 2009a). Lower cost feedstocks are needed since biodiesel from food-grade oils is not economically competitive with petroleum-based diesel fuel. Main animal fat sources are beef tallow, lard, poultry fat and fish oils. Yellow greases can be mixtures of vegetable oils and animal fats. The FFA content affects the type of biodiesel process used and the yield of fuel from that process. Other contamination present can affect the extent of feedstock preparation necessary to use a given reaction chemistry (Demirbas, 2009a). Tallow is beef fat produced by slaughterhouse, while lard is hog fat and chicken fat refers to poultry. Brown grease comes from restaurant grease traps, sewage plants, and "black grease" (sludge). The brown one is gelatinous at room temperature and has low overall oil content. Yellow and brown grease as well as tallow can be converted into biodiesel, although the costs of processing are higher and the per-gallon biodiesel yield is lower. According to the USDA, the United States produces over 1.4 billion gallons of used cooking oil and animal fat each year. In fact, around 74% of the inedible tallow and grease produced goes to animal feed, while the remainder is used to make soaps, lubricants and other products such as Biodiesel (Tickell, 2006).

Soybean oil is the major feedstock for biodiesel in the USA and in other parts of the world. Rapeseed oil is the major source of oil in Europe and it contributes about 85% of the oil for

world biodiesel production, followed by sunflower seed oil, soybean oil and palm oil. Some sources for vegetable oil extraction to be used in biodiesel production are: castor berry, palm pulp, palm kernel oil, babassu kernel, sunflower seeds, coconut kernel, cotton seed, peanut grain, canola seed (Leung et al., 2010). According to European Biodiesel Board (EBB, 2008), European production of biodiesel reached 5.7 million tons compared to US production of 1.7 billion liters in 2007. Germany is the largest producer of biodiesel among EU countries, accounting for about half of the total European biodiesel production. In the East Asian countries, palm oil is the major feedstock for biodiesel, being the annual average production expected to be about 31.4 million tons/year over the period 2006-2010 (Shrestha & Gerpen, 2010).

In 2010, about 2.4 billion liters of biodiesel were produced in Brazil, corresponding to 14% of the global participation. The country has a wide variety of feedstocks to be used in the production of oil and fatty acids. However, it is important to find new sources that don't compete with food chains. Therefore, it is necessary to invest in finding residual oils and other products (Pacheco, 2006). Sustainable alternatives for biodiesel production are being researched with the use of enzymes, which allow for mild reaction conditions and easier recovery of glycerol, preventing the drawbacks of the chemical synthesis (Rodrigues & Ayub, 2011).

## 2. Meat production around the world

In the last years, meat production has increased significantly. World meat production reached 237.7 million tons in 2010, from which 42.7%, 33.4%, 23.9% corresponds to respectively pork, poultry and beef (USDA, 2010). Consequently, a larger amount of residues from animal processing-plants has been generated in countries with intensive livestock production. Within agroindustrial residues, lipid sources may be used as feedstock to biodiesel supply, helping to solve inappropriate environmental disposal, besides contributing to energy demand.

Animal protein consumption in the world is a great well-being indicator of corporations (excluding those who decide for several reasons do not consume animal protein). As can be seen in Figure 1, consumption growth is directly related to the population income level and tends to rise as income rises, because in rich countries energy consumption is 3,470 kcal, while in poorest countries this value is 2,660 kcal (FAO, 2010). In Brazil, the studies done by Hoffmann (2000), Schlindwein (2006) and Pintos-Payeras (2009) also demonstrate income great importance in meat consumption. The percentage of meat in the diet is approximately twice the richer countries. In Brazil, it is noted that meat national consumption is already, in proportional terms, similar to consumption in rich countries, although in absolute terms the energy consumption of 3,060 kcal was below the same period.

These data show that income growth in peripheral countries will have a pronounced impact on meat consumption. Thus, per capita income growth in underdeveloped countries (China, India, Brazil and Russia) in the last three decades will be determinant of consumption growth and meat production. The possibility of per capita income growth in Africa will undoubtedly be a propeller of meat consumption in the near future. The surprising economic growth in China over the past 10 years and its impact on animal protein production has turned this country into a major propeller of meat dynamics in the world. In this period the gross national per capita income has grown at rates of 13.44%, and following the same line, meat consumption grew 2.3% annually (12.7 million tons in the period). In

India, increase in per capita income of 9.23% over the same period was responsible for an increase in meat consumption in the same order of 6.68% per year (2.2 million tons). In Brazil, although less intense, we can see economic growth of 5.22% from 2000 to 2009. However, it must be taken into account that the best income distribution of the Brazilian economy lead to higher meat consumption by the poorest population (+3.64% per year meaning 4.8 million tons). A similar phenomenon was observed in Russia where meat consumption grew 5.07% per year between 2000 and 2009 (3 million tons).

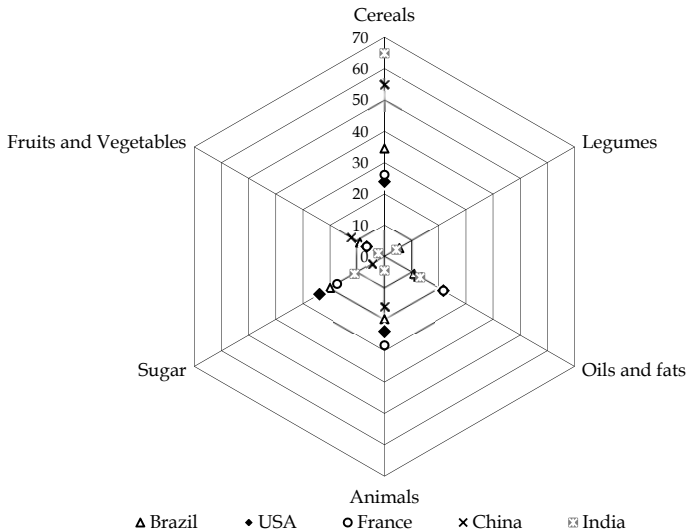


Fig. 1. Sources of per capita energy consumption from the diet as a percentage of the average period 2001-2003.

Source: FAO (2010).

The gradual effect shown in Figure 1 is a major driver of food economy, domestic and global levels, through increasing the middle class and the adoption by families who arrive there, the consumer behavior of those already there (Homem de Mello, 1990). As a result of this graduation, there would be huge demand in animal protein, legumes, fruits and vegetables. This dynamic evolution of food demand, as economic growth explains meat production growth in the world in the last two decades. Although it has been reported a large percentage increase in major meat consumption, the absolute volume consumed in India is still very low (3.8 kg) including beef, pork and poultry, when compared to 89.69, 49.9 and 57.2 kg in Brazil, China and Russia, respectively. Thus, in this country is to be expected that the continuous increase in per capita income by more than a decade will boost meat consumption to a level closer to developing countries. Worldwide, source of animal protein (except milk) most produced and consumed is pork with 29.86% (Figure 2), followed by chicken meat (22.97%), eggs (18.05%) and beef (17.56%). These four groups of sources account for 88.44% of animal protein total consumption in the world.

In a second group of sources, the following four are responsible for more than 7.00% of animal protein consumption. This group comprises the consumption of sheep (2.39%),

turkey (1.77%), eggs of other birds (1.42%) and goat (1.42%). Rounding out the meat group: duck (1.09%), buffalo (0.97%), goose and guinea fowl (0.69%), rabbits (0.53%), hunt (0.49%), other meat (0.36%), horse (0.29%), camel (0.10%), other birds (0.03%) and ostrich (0.004%). At the same group, deserves attention the consumption of buffalo that occurs almost entirely in India, where beef consumption is forbidden by Hindu religion (83% of India population). India and Pakistan are also important producers of sheep and goats. Similarly horse consumption is concentrated in Asian countries. Rabbits are produced mostly in China, Venezuela and Italy. China also concentrates the production of geese, goats, ducks and sheep.

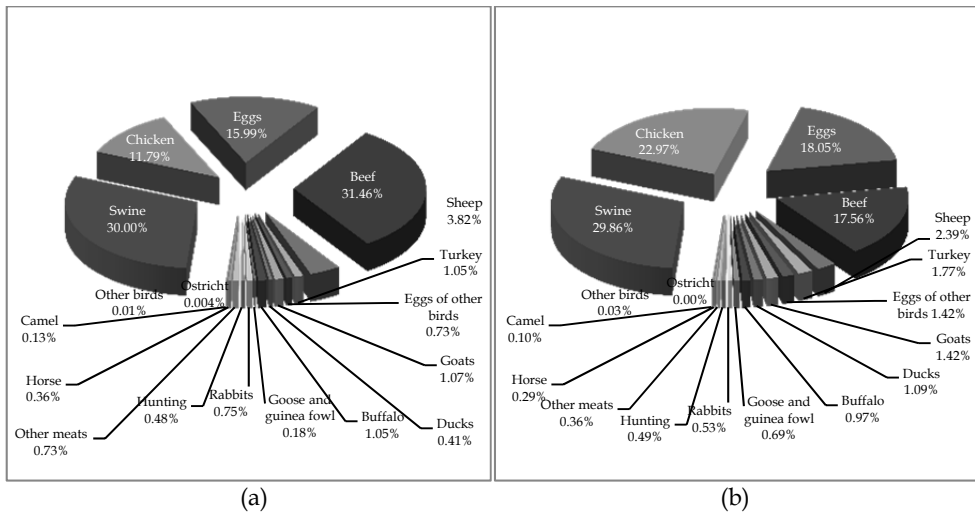


Fig. 2. Distribution of animal protein production in the world in 1975 (a) and 2008 (b) Source: FAO (2010) adapted by the authors.

Globally, a great dynamic in animal protein production can be noted. Even being less expressive regarding total production, the highest growth rates in animal protein production are focused on meat of birds. Among the most important sources, chicken may be highlighted showing an annually growth of 4.1% over the past 10 years. The negative highlight is related to beef which presented one of the lowest growth rates (1.1%). In an intermediate form, pork production increased in the order of 2.52%. Since 1975, year after year, poultry industry is consolidating itself as one of the most important animal protein sources for the population. According to data from the United States Department of Agriculture (USDA), world production of broilers grew consistently over the past 35 years, from 10.6 million tons in 1975 to 71 million tons by the end of the first decade of this century. Brazil has a different dynamic for meat production. Unlike the rest of the world, the main animal protein is chicken (41.31%), beef (36.49%), pork (12.19%), and eggs (7.38), which represent 97.37% of total produced in the country (Figure 3).

As a result of these factors one should expect a continued growth in production and consumption of meat, mainly chicken, followed by pork and beef (Figure 4).

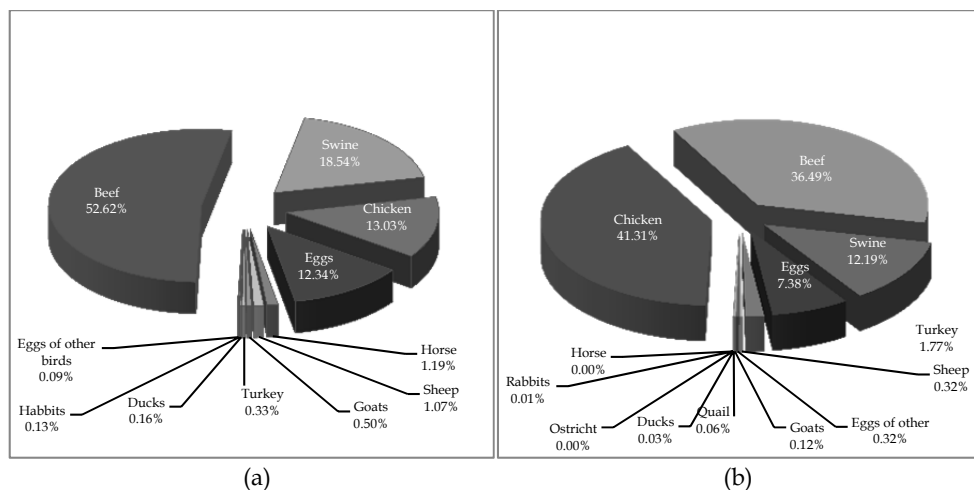


Fig. 3. Distribution of animal protein production in Brazil in 1975 (a) and 2008 (b)  
Source: FAO (2010) adapted by the authors.

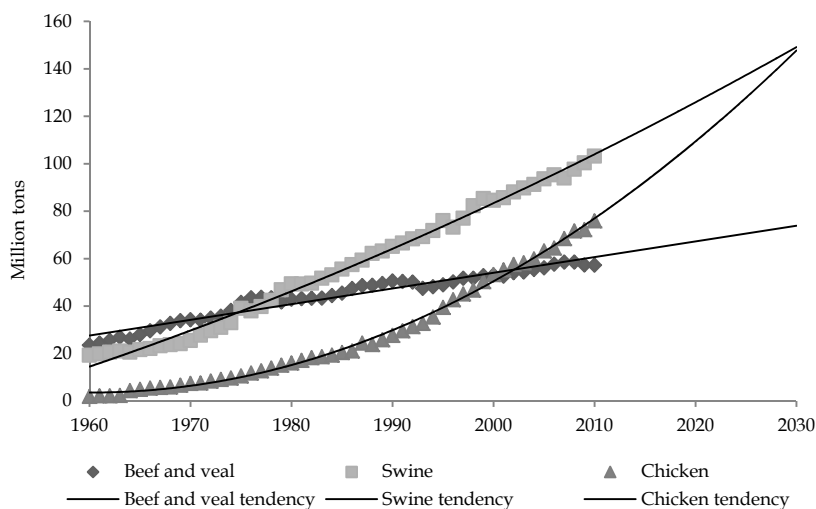


Fig. 4. Tendency of main animal protein production in the World  
Source: USDA (2010) adapted by the authors.

### 3. Characterization and generation of animal fat wastes

Oils and fats are found in living organisms, consisting essentially of fatty acid esters and glycerin mixtures, and are known as triacylglycerols (commonly called triglycerides), which are hydrolyzed during extraction processes and storage, releasing fatty acids and glycerin.

Moreover, the use of oils or fats as fuel for internal combustion engines and their derivatives have been proposed for this intention over the past 100 years, when Rudolf Diesel applied in their assays crude petroleum and peanut oil. However, the problems of petroleum supply on the world market, generated by armed conflict that began in the 30s, led to the search for viable solutions for replacing fossil fuel.

The use of greases and animal fats eliminates the need to dispose them, besides contributing to the supply of biodiesel (Janaun & Ellis, 2010). Animal fats are highly viscous and mostly in solid form at ambient temperature because of their high content of saturated fatty acids. The high viscous fuels lead to poor atomization and result in incomplete combustion. The consequences are the increased emissions of pollutants and particulate in the exhaust gas (Kerihuel et al., 2006). Animal fats are readily available because slaughter industries are generally well managed for product control and handling procedures. However, there's a biosafety issue related to animal fats that could come from the contaminated animals. The future research to ensure biodiesel quality from animal waste (cradle to grave) has been highlighted (Janaun & Ellis, 2010). Biodiesel made from used cooking oil or from animal fat is less resistant to cold weather than biodiesel made from virgin soybean oil or most other virgin oils. As additives are developed specifically for the biodiesel industry, even this distinction could soon disappear (Tickell, 2006).

Black greases are defined loosely as greases resulting from sewage or other unconventional oil sources. It has a low conversion factor to biodiesel due to its high content in FFA. Brown greases are generally defined as a combination of greases and trappings from the slaughter industry. Yellow greases comprehend the oils and greases produced in the fast food industry and collected by the rendering industry (Tickell, 2006).

In Brazilian meat chain, most animal fats are generated in slaughterhouses and rendering plants. Products of rendering industry usually have lower market value. Materials that for aesthetic or sanitary reasons are not suitable for human food are intended as feedstocks for rendering processes. Among these materials, there are fatty trimmings, bones, and offal, as well as entire carcasses of animals condemned at slaughterhouses, and those that have died on farms (deadstock) or in transit. The raw materials are collected in slaughterhouses, butcherhouses and supermarkets by trucks that take them to rendering plants. There are some industrial-scale slaughterhouses that process the residues within their own facilities. Once in the rendering plants the residues are chopped and heated in a steam-jacketed vessel to drive off the moisture and simultaneously release the fat from the fat cells using this so called "dry" method. The internal temperature of reactor reaches 1200 °C under 5-6 kg/cm<sup>2</sup> of pressure during 2 h per batch.

In Brazil, does not exists an animal fat classification, only a general designation based on the animal from which the fat originates, such as chicken fat or fish oil, tallow and lard. The greases produced in Brazil are generally described as follows:

- a. Tallow: extracted from residues of bovine slaughter and it can be filtered or not since it has guaranteed that the product contains minimum 90% total fatty acids, unsaponifiable impurities maximum 1.5% and no FFA or fat degradation products;
- b. Lard: extracted from swine slaughter residues, being its specification and quality guarantees the same as for tallow;
- c. Chicken fat: extracted from broiler slaughter residues and it can be filtered or not since it has guaranteed that the product contains minimum 90% total fatty acids, maximum 3% unsaponifiable impurities, without FFA or fat degradation products;

- d. Animal fat mix: extracted from slaughter residues of mammals or birds. It can be filtered or not since it has guaranteed that the product contains total fatty acids minimum 90%, maximum 2% unsaponifiable impurities, without FFA or products of fat degradation unless the ones generated even with good production practices implemented.

The animal species from which the fat originates must be specified. Additions of antioxidants must be informed in any of these products. The main difference between animal fat and vegetable oil is their fatty acid composition. Vegetable oils have high content of unsaturated fatty acids, mainly oleic and linoleic acid, while animal fat composition has higher proportion of saturated fatty acids (Table 1).

Oil or Fat	12:0	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:4	≥ 20
Chicken	0.1	1-1.3	17-20.7	5.4	6-12	42.7	20.7	0.7-1.3	0.1	1.6
Lard	0.1	1-2	23.6-30	2.8	12-18	40-50	7-13	0-1	1.7	1.3
Tallow	0.1	3-6	23.3-32	4.4	19-25	37-43	2-3	0.6-0.9	0.2	1.8
Fish	0.2	6.1	14.3	10.0	3.0	15.1	1.4	0.7	0.7	56.5
Butter	-	7-10	24-26	-	10-13	1-2.5	2-5	-	-	-
Soybean	-	0.1	6-10.2	-	2-5	20-30	50-60	-	-	-
Rapeseed	0.2	0.1	3.9	0.2	1.7	60.0	18.8	9.5	-	4.0
Corn	-	1-2	8-12	0.1	2-5	19-49	34-62	0.7	-	2.0
Olive	-	-	9-10	-	2-3	73-84	10-12	Traces	-	-
Cotton	-	-	20-25	-	1-2	23-35	40-50	Traces	-	-

Table 1. Average fatty acid composition of some vegetable oil and animal fat (Pearl, 2002; Rostagno et al., 2011)

Traditionally in Brazil, cleaning and toilet products industries use part of animal fat residues to produce soaps and waxes while other parts are employed in the production of lubricants and leather preservatives. Nevertheless, in Brazil, the beginning of National Program of Biodiesel Production and Use (Law #11.097) has rapidly changed this scenario and between October/2008 and March/2009 biodiesel plants consumed 43% of total tallow, which corresponds to approximately 15% of whole biodiesel produced. Although Brazil is also a major producer of chicken and swine meat, fats from these species are still not being used for biodiesel production. According to UBABEF (2009) data, Brazil produced around 23 million tons of meat, from which 3, 9 and 11 million correspond to swine, cattle and poultry, respectively. Considering the amount of residues 45% (wt/wt) cattle and 25% (wt/wt) swine and poultry contain approximately 15% fat. Thus, feedstock potential amount is 607,500, 412,500 and 112,500 tons for cattle, poultry and swine, respectively.

Wastes from slaughterhouses are constituted by non-edible by-products and wastewater which pass through flocculation and flotation process. Non-edible animal by-products are sent for rendering plants where flours are processed and good-quality fats besides acid fats are originated. Good-quality fats are destined for drugs and cosmetics, while acidic fats (which don't attend industry acid requirements and flotation stage) have low or no commercial value, being their promising target energy or biodiesel production. Wastewater undergoes flocculation and flotation process with the aid of coagulants, being separated into solid (flotation stage) and liquids (liquid phase). The first one is destined to rendering plants, while the second one goes to treatment lagoons, as is shown in Figure 5. Animal fats are classified in three categories (low, medium and high-grade quality fat) according to the risk level, following Regulation (EC) 1774/2002 of the European Parliament and of the



Council of 3 October 2002. High-grade quality fat has below 2% of FFA, which are mainly used for drugs and cosmetics, besides pet food. Medium-grade fat presents 3-5% FFA, while low-grade fat has above 5% FFA and are destined to biofuel production.

In Brazil, according to the National Petroleum Agency (ANP 2011), raw materials of animal origin used for biodiesel production account for 14.82% of authorized nominal capacity. This value is still low compared to the raw materials of vegetable origin that account for 84.45% of biodiesel production. However, volume of animal feedstocks tends to grow since Brazil has one of the largest animal herds in the world. Brazil is currently the second largest cattle producer (over 9.1 million tons), the fourth largest pork producer (more than 3.1 million tons), and the third largest chicken meat producer, with more than 11.4 million tons. In this context, lipid by-products from slaughterhouses should become attractive, especially for economical and environmental reasons.

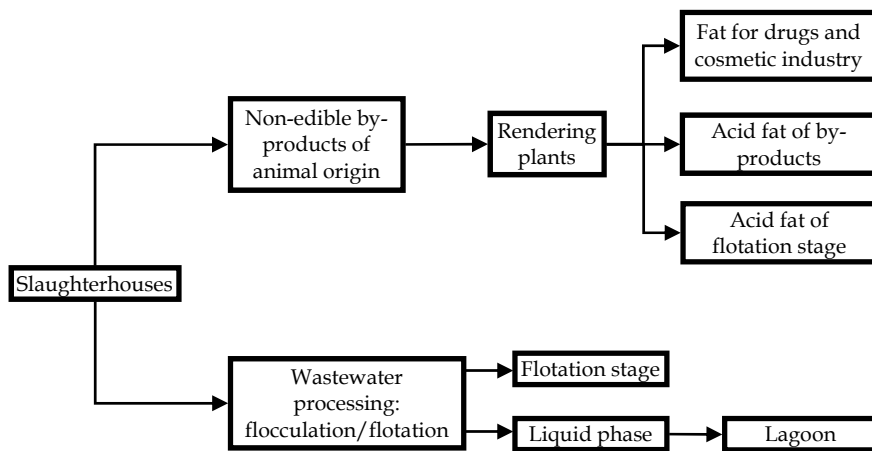


Fig. 5. Scheme of fat processing in slaughterhouses.

#### 4. Biodiesel production from animal fat wastes: technical challenges

The feedstocks issue is the critical point affecting the economic feasibility of biodiesel production, since accounts around 80% of the biofuel total cost. In this context, several efforts have been carried out in order to reduce biodiesel prices, essentially by altering lipid sources (Zhang et al., 2003a, 2003b; Canakci, 2007; Canakci & Sanli, 2008; Wang, 2009; Janaun & Ellis, 2010; Martins et al., 2011). Nowadays, edible vegetable oils are the major starting materials for biodiesel preparation. In consequence, prospection for novel feedstocks has been primarily attributed to investigations involving oleaginous species for inedible oil extraction (Nass et al., 2007). In recent, alternatively lipid residues as waste frying oil and inedible animal fats have also receiving considerable attention from biofuel sector. To take advantage of these low cost and low quality resources, a convenient action would be to reuse residues in order to integrate sustainable energy supply and waste management in food processing facilities.

To get a better understanding of challenges involved on biodiesel synthesis from animal fat wastes, a brief review regarding to fundamental reactions of carboxylic acids and esters is

presented (Formo, 1954; Carey & Sundberg, 1983; Morrison & Boyd, 1996). As illustrated in figure 6a, carboxylic acids originate their salts (soaps) by treatment with aqueous alkaline solutions (hydroxides or carbonates). Additionally, carbonyl group confers an interesting synthetic versatility to carboxylic acids since they can be converted into derivatives by nucleophilic substitution. In fact, esters are directly obtained reacting carboxylic acids using alcohols as acyl-acceptors under acidic conditions, being this process usually referred as Fisher esterification (Figure 6b). The strategy frequently employed to shift equilibrium to the right includes the use of large amounts of alcohol and water removal from the reactional medium.

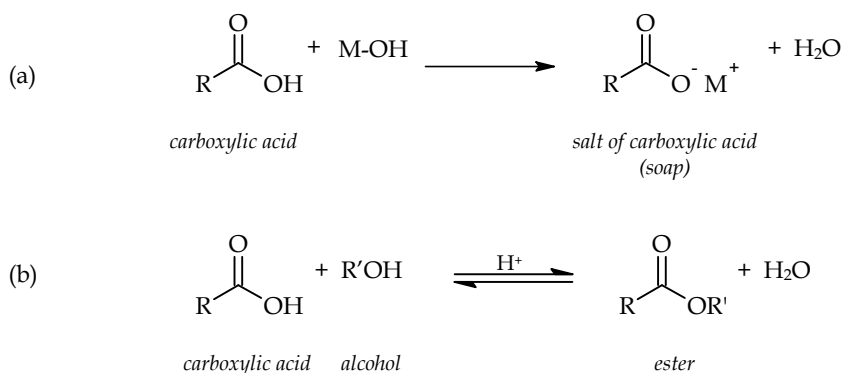


Fig. 6. Reactions of carboxylic acids: (a) acid-base neutralization (where M is Na<sup>+</sup> or K<sup>+</sup>); (b) acid-catalyzed esterification

Esters are carboxylic acid derivatives that can be hydrolyzed either in acid or basic medium. The alkali-catalyzed process is essentially irreversible (Figure 7a). On the other hand, hydrolysis in acidic solution is an equilibrium reaction, being dependent on the relative alcohol and water concentrations (Figure 7b).

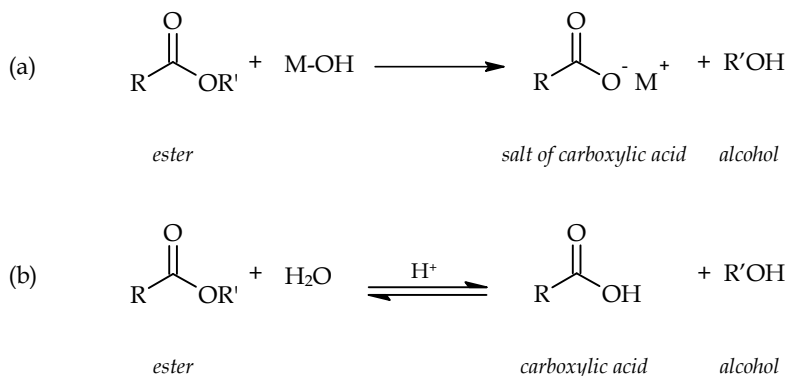


Fig. 7. Ester hydrolysis: (a) alkali-catalyzed (where M is Na<sup>+</sup> or K<sup>+</sup>); (b) acid-catalyzed

According to Xu (2003), transesterification is a general term for the reactions between an ester and a fatty acid (acidolysis), an alcohol (alcoholysis), or another ester (transesterification). Esters are converted into another by alkoxy group exchanger as exemplified in figure 8. The displacement of  $-OR'$  molecular unit is carried out when the original ester react with an alcohol to provide a new carboxylic acid derivative. Alcoholysis is usually denominated by most authors as transesterification, general term that will be used from now on to describe biodiesel production reaction. The transesterification is an equilibrium process and addition of an excessive amount of alcohol can be used in favor of products' synthesis:

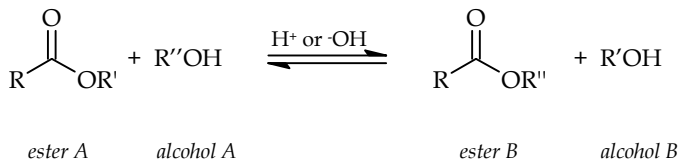


Fig. 8. Transesterification type alcoholysis

Oils and fats are complex lipids derived respectively from vegetable and animal sources. Their compositions are primarily based on triacylglycerols (TAG), which molecules consist of a glycerol backbone attached by ester bonds to three long-chain carboxylic acids (fatty acids). Reactions of ester linkages of oils and fats were recognized a long time by their technological importance (Formo, 1954). Nowadays, non-hydrolytic ester reactions (esterification and transesterification) play a fundamental role in the applied chemistry. For instance, biodiesel is a mixture of fatty acid mono-alkyl esters readily produced from TAG transesterification by using a short chain alcohol, as showed in figure 9.

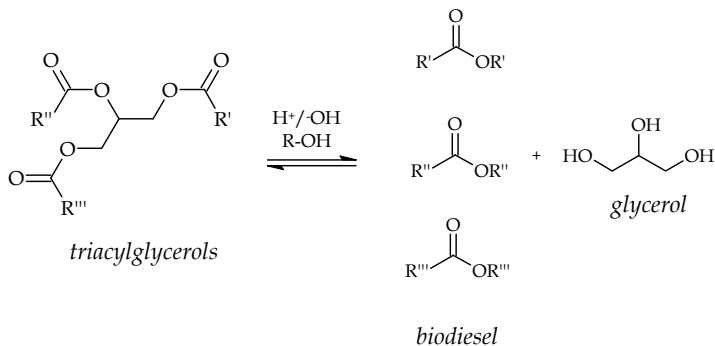


Fig. 9. Overall scheme of the TAG transesterification for biodiesel production (where R is  $-\text{CH}_3$  or  $-\text{CH}_3\text{CH}_2$ )

Transesterification of TAG is a process of three consecutive and reversible acid- or basic-catalyzed reactions. Diacylglycerols (DAG) and monoacylglycerols (MAG) are intermediates. The stoichiometry of the overall reaction requires a molar ratio of 1:3 (TAG:alcohol) to give 3 mol of ester and 1 mol of glycerol. Its course involves stepwise conversions of TAG to DAG to MAG to glycerol (GL) (Figure 10).

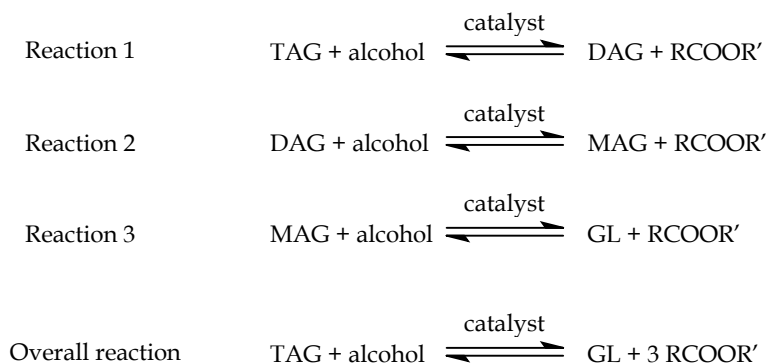


Fig. 10. Chemistry of TAG transesterification

Few studies were concerned with detailed kinetic aspects of the transesterification of vegetable oils (Freedman et al., 1986; Nouredini & Zhu, 1997; Darnoko & Cheryan, 2000; Komers et al., 2002). Freedman et al. (1986) investigated the kinetics of acid- and base-catalyzed transesterification of TAG with methanol and 1-butanol at 6:1 and 30:1 molar ratio alcohol:oil. The authors proposed pseudo first-order kinetics at high molar ratio alcohol:oil and second-order kinetics combined with a shunt-reaction at low alcohol:oil ratio. According to Nouredini & Zhu (1997), alkali-catalyzed methanolysis of oils can be described as follow: a) initially reaction is characterized by a mass transfer controlled regime (slow) that results from low miscibility of reactants; b) ester produced at beginning can act as mutual solvent and favor a kinetic controlled regime (fast) characterized by a sudden surge in products formation; c) in the final, an equilibrium regime (slow) is approached. Figure 11 shows typical distribution of reactants, intermediates and products during the course of transesterification, where a sigmoid behavior for ester production is exemplified.

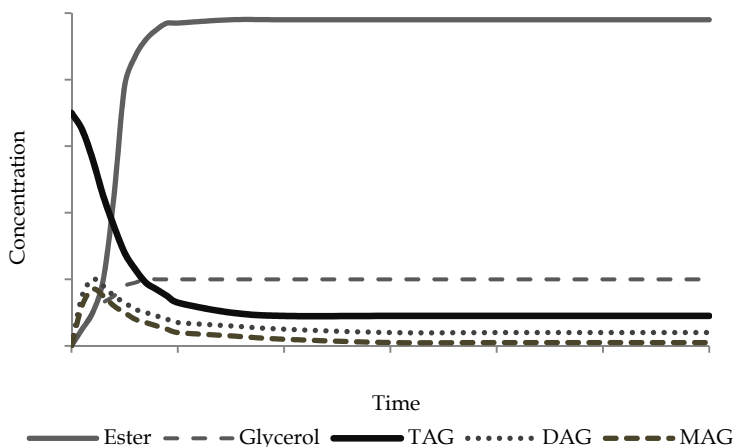


Fig. 11. Illustrative scheme of component concentration change during transesterification

Besides transesterification, reactions showed previously in this section can be involved during biodiesel preparation from lipid feedstocks depending on catalyst used. In fact, this reaction comprises a complex system. Komers and co-workers (2001b), in a fundamental research, were able to show that the reaction mixture of alkaline methanolysis of oils includes the following main components: TAG, DAG, MAG, methyl esters, methanol, soaps, KOH (in the form of  $\text{OH}^-$ ),  $\text{CH}_3\text{OK}$  (as  $\text{CH}_3\text{O}^-$ ), and water. Considering the system summarized in figure 12, the great issue is to establish appropriate conditions to minimize possible side reactions (hydrolysis and soaps formation) and, in consequence, drive the process toward ester production.

As is already well-known, transesterification may be influenced by several factors such as: feedstock composition; FFA content in raw materials, water concentration; alcohol to TAG molar ratio; catalyst type and concentration; type of alcohol; temperature; pressure; and mixing intensity. Researches have been intensively conducted to evaluate variables affecting ester yields and their respective interactions. Background about these parameters is detailed in several critical reviews (Schuchardt et al., 1998; Ma & Hanna, 1999; Fukuda et al., 2001; Van Gerpen & Knothe, 2005; Meher et al., 2006; Sharma et al., 2008; Vasudevan & Briggs, 2008; Demirbas, 2009b; Basha et al., 2009; Helwani et al., 2009; Vasudevan & Fu, 2010; Atadashi et al., 2010; Leung et al., 2010).

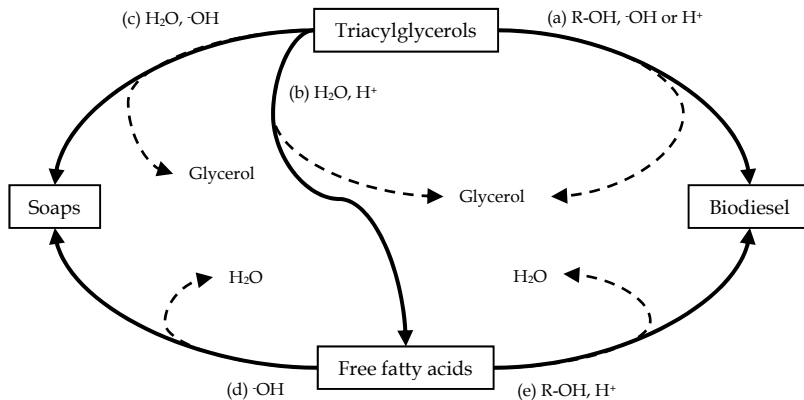


Fig. 12. Reactions involved in conventional biodiesel production: (a) alkali-catalyzed transesterification (expected route); (b) acid-catalyzed hydrolysis; (c) alkali-catalyzed hydrolysis; (d) acid-base neutralization; (e) acid-catalyzed esterification (expected route)

Homogeneous alkali-catalyzed transesterification is the most widely employed industrial process for biodiesel production (Helwani et al., 2009; Atadashi et al., 2010; Leung et al., 2010). This fact is because the base-catalyzed reaction is faster than the acid one under mild conditions (Formo, 1954) resulting in a fuel-grade biodiesel. Alkaline catalysts are furthermore less corrosive than acidic compounds. Batch reactors are used for transesterification of refined vegetable oils with alcohol (molar ratio alcohol to oil 6:1) under anhydrous conditions. In summary, high esters conversion rates (>95%) are obtained in short times (after 1 h) at atmospheric pressure in temperatures ranged from 40 to 70 °C.

Metal hydroxides (NaOH and KOH) and methoxides (NaOCH<sub>3</sub> and KOCH<sub>3</sub>) are generally applied as catalysts in concentrations ranging from 0.5 to 2% wt/wt of oil (Vicent et al., 2004; Dias et al., 2008). The most common acyl-receptor is methanol owing to its low cost. However, ethanol can be successfully used as well (Feuge & Gros, 1949; Wu et al., 1999; Encinar et al., 2002; Ghassan et al., 2004; Ferrari et al., 2005; Bouaid et al. 2007). Ethylic route is particularly interesting in countries with consolidated sugarcane industry like Brazil (Nass et al., 2007), allowing biodiesel production entirely based on biomass resources. Afterwards reaction achievement, spontaneous separation of biodiesel and rich-glycerol phases occurs by gravitational settling. In some cases, a centrifugation step may be used to speed up the separation of phases. Then biodiesel is isolated and purified by removal alcohol excess, water washing, drying, and vacuum distillation.

Rendered animal fats are attractive raw materials for biodiesel industry once they are immediately available and found in huge amounts at relative low-prices in regions with intensive livestock. The mentioned lipid sources are generated in meat-processing plants with different quality degrees. Often, inedible residual fats don't present specific requirements for direct application in conventional biodiesel approach mediated by alkalis. According to system showed in figure 12, feedstocks and reactants necessarily should meet suitable quality with respect to FFA and moisture. For that reason, refined vegetable oils are favored instead of lipid wastes.

The main technical restrictions with processing animal fat wastes are their relative high FFA (ranging from 5% to 30%) and water content. These two factors are key parameters for determining viability of transesterification process, because they may cause catalyst effectiveness and promote soaps formation. In fact, alkaline catalysts are consumed by neutralization with FFA in the reactional medium, leading to soaps and water formation. As a result of catalyst deactivation, ester yield is significantly reduced. In addition, post-treatment of the final mixture is more difficult by the occurrence of soaps, which prevents phase separation between esters and glycerol, promoting stable emulsion establishment in washing operations. Kusdiana & Saka (2004) were able to demonstrate this effect on TAG methanolysis using 1.5% NaOH (wt/wt) as illustrated in figure 13a. Restrictive limits of FFA ranging from <1% to <3%, as recently reported (Atadashi et al., 2010). According to reports involving fat residues, starting materials for basic-catalyzed transesterification should not exceed values beyond 0.5% FFA, which corresponds to an acid number of 1 mg KOH/g of oil (Ma et al., 1998; Canakci & Van Gerpen, 2001). For vegetable oils, a FFA value lower than 3% (6 mg KOH/g of oil) is recommended for good conversion efficiency (Dorado et al., 2002; Tamasevic & Siler-Marinkovic, 2003; Phan & Phan, 2008). In both cases, transesterification rate can be enhanced with bases if FFA is around 5%, although further quantity of catalyst must be added to compensate higher acidity and loss due soap formation (Van Gerpen, 2005). Particularly, this procedure involving excessive amount of catalyst is not recommended since it gives rise to the formation of gels that interfere in the reaction, hinder glycerol separation, and contribute to emulsification during water washing.

It's well-established that TAG transesterification with basic catalysis is also sensitive to water content. Water is one of the main causes for side reactions besides alcoholysis. The effective catalyzing agents in the alkaline catalyzed transesterification are alkoxide ions (RO<sup>-</sup>). According to equilibrium study reported by Komers et al. (2001a), initial concentration of alkolate (RO<sup>-</sup>) decreases with an increasing amount of water in methanol and KOH. This effect can also occur by water presence in oils and fats. Then, transesterification doesn't occur without catalyst

generation and besides hydrolysis may take place as competitive reaction follow-on to soaps production. For the alkaline-catalyzed methanolysis of oils, ester conversion was slightly reduced when water concentration increased in reaction system, as showed in figures 13b and 14a (Canakci & Van Gerpen, 1999; Kusdiana & Saka, 2004). The effects of FFA and water content on alkali-transesterification of beef tallow were investigated by Ma and co-workers (1998). A significant interaction between two factors was clearly observed, characterizing synergistic negative effect on the reaction, according to data showed in figure 15b. With respect to the single effect, the apparent yield of beef tallow methyl esters (BTME) was the highest without addition of FFA and water. The apparent yield decreased with the increase of the water amount without addition of FFA. A similar behavior was noted without water addition when FFA level increased. Water generally can be removed from raw materials by drying, gravitational settling or with desiccant agents before processing transesterification.

The FFA content turn waste lipids unsuitable for conventional biodiesel route. Transesterification via acid catalysis is an alternative process claimed as more tolerant to high FFA levels (Lotero et al., 2005). The homogeneous acid-catalyzed transesterification is slower than alkaline process. Generally, this reaction is performed at high molar ratios of alcohol:oil (50:1) at 80°C, and high catalyst concentrations (3% by weight of lipid feedstock). Besides, strong mineral acids (HCl and H<sub>2</sub>SO<sub>4</sub>) are corrosives, causing damages to reactors. As can be see in figure 13b, water is the major obstacle to this reaction, being more critical than in base catalysis. According to Canakci and Van Gerpen (1999), in order to achieve good ester conversion, the acid catalyst also requires water content lower than 0.5%, which is around the same for alkaline reaction. Only 0.1% of water in reaction medium is enough to result in some reduction of the methyl ester yield (Kusdiana & Saka, 2004). In acid-catalyzed transesterification mechanism, the key-step is the protonation of the carbonyl oxygen. This increases the electrophilicity of the carbonyl carbon, making it more prone to nucleophilic attack. When present in reactional medium, water can form clusters around protons with less acid strength than alcohol-only proton complexes. Therefore, the catalytic species (H<sup>+</sup>) are deactivated by hydration, and don't allow TAG and their intermediates susceptible to alcohol attack (Helwani et al., 2009). On the other hand, acids are able to simultaneously catalyze both transesterification and esterification. Acid catalysts are effective at converting FFA to ester quickly. The integrated process is convenient to produce biodiesel from feedstocks having high FFA levels (Canakci & Van Gerpen, 2001; Zhang et al., 2003a, 2003b). The two-step approach includes an acid-catalyzed pre-treatment to esterification of FFA prior to alkali-catalyzed transesterification of TAG.

Nevertheless, as mentioned previously in this section, acid-catalyzed esterification is an equilibrium reaction, and hydrolysis occurs as inverse process. Water is produced in reactional medium when FFA react with alcohol to give esters. Canakci & Van Gerpen (1999), simulating FFA content in oil with palmitic acid, showed that water formed during acid-catalyzed esterification has similar negative effect on transesterification than when water was deliberately added to reaction mixture. This fact is noted in figure 15a by coincident lines of acid-catalyzed transesterification (3% H<sub>2</sub>SO<sub>4</sub>, molar ratio 6:1, at 60°C) with water from reaction of palmitic acid and only with water addition. Then, water formed in the esterification limited FFA levels in the lipid source to 5%.

Even with all the above mentioned details regarding to raw materials' properties, several researches have stated that animal fat wastes are really important sources for biodiesel production. In Table 2, reactional conditions for biodiesel preparation from different animal fats are summarized.

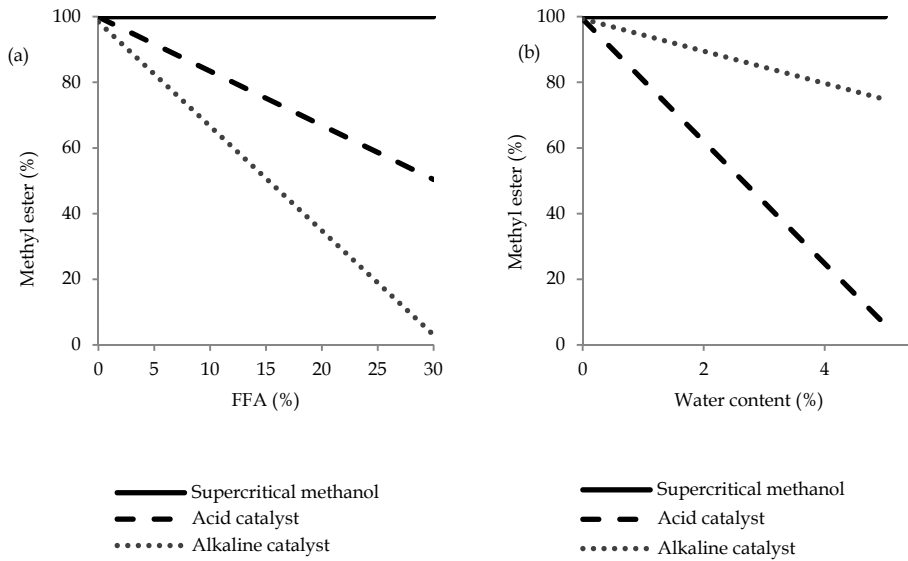


Fig. 13. Effects of FFA (a) and water (b) contents on the transesterification reaction of oils (adapted from Kusdiana & Saka, 2004).

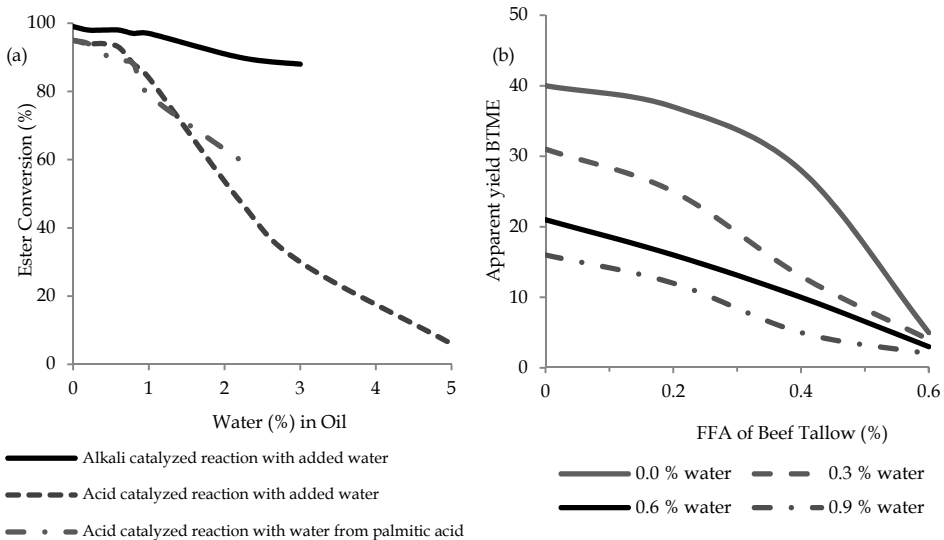


Fig. 14. (a) Water effect on transesterification of oils (adapted from Canakci & Van Gerpen, 2001); (b) FFA and water effects on alkali-catalyzed transesterification of beef tallow (adapted from Ma et al., 1998)



Feedstock	Catalyst (wt/wt of fat)	Alcohol	Molar ratio	T (°C)	Time (h)	Conv. (%)	Reference
Beef tallow	Step 1: NaOH 1% Step 2: NaOH 0.2%	MeOH	6:1 20%	70	0.5	-	Zheng & Hanna, 1996
	60			1			
Beef tallow	H <sub>2</sub> SO <sub>4</sub> 1%	MeOH	6:1	60	48	13.0	Alcantara et al., 2000
	NaOCH <sub>3</sub> 1%						
Beef tallow	KOH 2%	MeOH	-	65	1.5	>95	Moraes et al., 2008
Beef tallow	KOH 1.50%	MeOH	6:1	65	3	Quantitative	da Cunha et al., 2009
Beef tallow	Sulfonated polystyrene 20 mol%	MeOH	100:1	64	18	70.0	Soldi et al., 2009
Beef tallow: sunflower oil blends	NaOH 1%	MeOH	6:1	60	1	-	Taravus et al., 2009
Chicken tallow	H <sub>2</sub> SO <sub>4</sub> 25%	MeOH	30:1	50	24	Quantitative 88.1	Bhatti et al., 2008
	NaOH 1.5%	MeOH	-	30	1		
Feather meal fat	KOH 1%	MeOH	9:1	70	1/4	Quantitative	Kondamudi et al., 2009
Mutton tallow	H <sub>2</sub> SO <sub>4</sub> 25%	MeOH	30:1	60	24	93.2	Bhatti et al., 2008
	NaOH 1.5%	MeOH	-	30	1	78.3	
	KOH 1%	MeOH	6:1	65	3	79.7	
Duck tallow	NaOH 1%	MeOH	6:1	65	3	62.3	Chung et al., 2009
	NaOCH <sub>3</sub> 1%	MeOH	6:1	65	3	79.3	
Lard:soybean oil blends	NaOH 0.8%	MeOH	6:1	65	1	81.7-88.6	Dias et al., 2008
Lard:waste frying oil blends	NaOH 0.8%	MeOH	6:1	65	1	81.7-88.0	Dias et al., 2008
Lard	Step 1: H <sub>2</sub> SO <sub>4</sub> 2% Step 2: NaOH 1%	MeOH	6:1	65	Step 1: 5 Step 2: 1	66.2	Dias et al., 2009
Lard:soybean oil blend (25:75 wt/wt)	Step 1: H <sub>2</sub> SO <sub>4</sub> 2% Step 2: NaOH 1%	MeOH	6:1	65	Step 1: 5 Step 2: 1	64.4	Dias et al., 2009
Lard:soybean oil blend (25:75 wt/wt)	NaOH 1%	MeOH	6:1	65	1	77.8	Dias et al., 2009
Lard	Immobilized-lipase ( <i>Candida</i> sp. 99-125)	MeOH	1:1(3x)	40	1/2	87.4	Lu et al., 2007
Lard	KOH 1.26%	MeOH	7.5:1	65	1/3	98.6	Jeong et al., 2009
Lard	KOH 0.9%	MeOH	6:1	60	1/3	89.2	Berrios et al., 2009
Leather	KOH 0.75%	MeOH	6:1	50	1/4	Quantitative	Ísler et al., 2010
Poultry fat	Mg-Al hydrocalcite 10%	MeOH	30:1	120	8	93.0	Liu et al., 2007
Tallow	NaOH 0.5%	MeOH	6:1	60	3	-	Öner & Altun, 2009
Waste animal fat	H <sub>2</sub> SO <sub>4</sub> 2.25 M	EtOH	-	50	2	78.0	Ghassan et al., 2004
Waste animal fat	Step 1: H <sub>2</sub> SO <sub>4</sub> 0.08% Step 2: NaOH 0.01%	MeOH	-	62	2	89.0	Gürü et al., 2009

Table 2. Conditions of animal fats transesterification for biodiesel preparation

Figure 15 presents the raw materials employed for biodiesel production in Brazil from March 2010 until March 2011. As can be seen, soybean oil is the major feedstock. Additionally, beef tallow also plays an important role in this economic segment. The application of animal lipid sources in the Brazilian bioenergy sector is likely to increase because of accessibility to others profitable raw materials such as chicken and swine fat wastes. Recently, the simulation of investment in an industrial plant, made by Santos Filho et al. 2010, with processing capacity of 10,000 liters per day presented results that attest to the profitability of the enterprise.

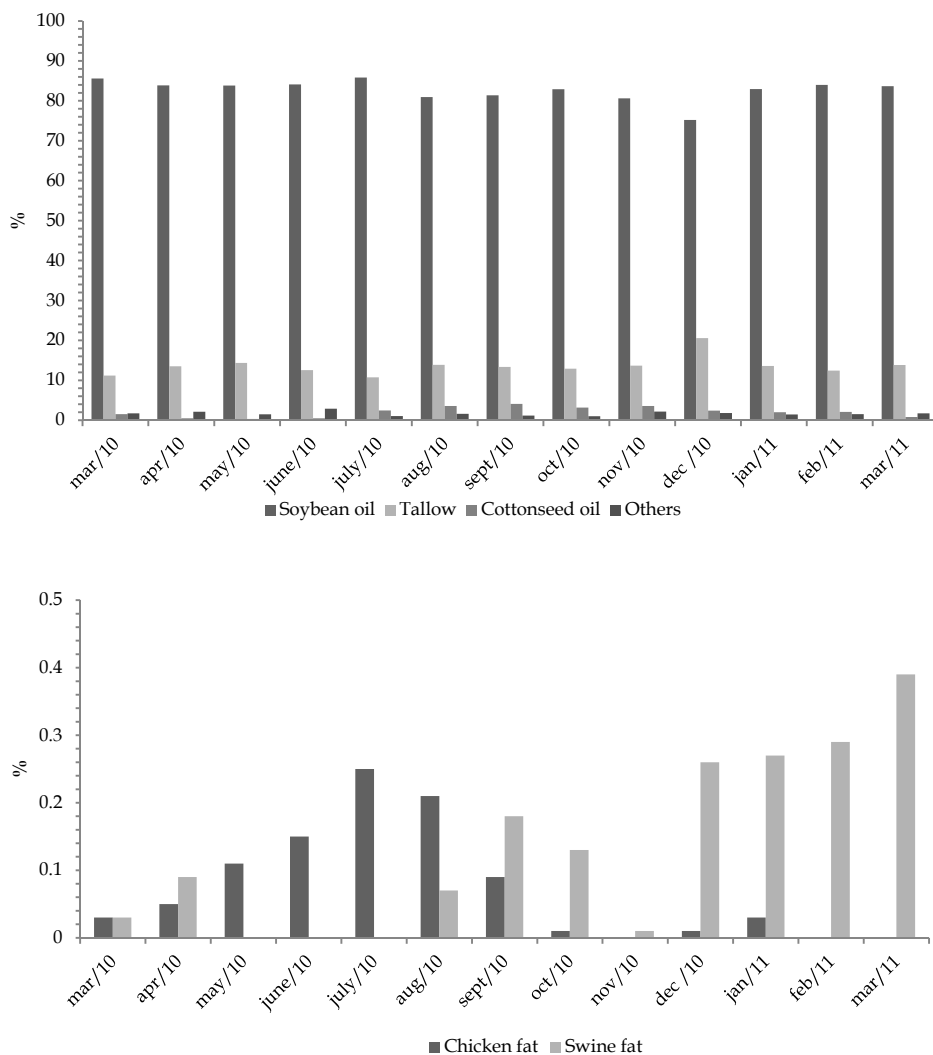


Fig. 15. Raw materials used for biodiesel production in Brazil  
Source: (ANP, 2011)

The internal rate of return for an undertaking was 191%, the payback time was 1.51 years and the minimum price that enables the project was R\$ 1,57, about US\$ 1.00 (currency exchange August, 3<sup>rd</sup>, 2011), which is lower than the worst market since 2005. According to the authors, the results indicate that the use of acid fat from the slaughter of pigs and poultry for biodiesel production is technically and economically feasible, because there is high supply of raw material in different states of the country, facilitating logistics and providing a low cost transport of products. Increased demand for biofuels, especially for biodiesel, which year after year has been more requested for blending with diesel fuel, rising from 2% (2008) to 5% (2010) representing a consistent demand for production. Therefore, conversion of swine and poultry fats into biodiesel is advantageous for meat-processing industries that use this waste for burning and heat generation for boilers. Its use allows an increase in income and the chain will also be promoting an increase in the competitiveness of pork and poultry, turning a product with virtually no value into an income generator.

## 5. Conclusion

Worldwide vegetable oils are preferred as the main lipid starting materials for biodiesel production. However, animal fats have a great potential as feedstocks for biofuel segments, because they are not commodities, having a lower market value. Over the last years, meat production has increased significantly attaining 237.7 million tons in 2010, from which 42.7%, 33.4%, 23.9% corresponds respectively to pork, poultry and beef. Then a larger amount of residues from animal processing-plants has been generated in countries with intensive livestock production. Within agroindustrial residues, lipid sources may be used to solve inappropriate environmental disposal, besides contributing to energy supply. Brazilian government demands increasing addition of biodiesel into fossil diesel, taking place in 2010 a novel regulatory mark which raised the level up to 5%. Therefore, it has been encouraged the search for other renewable raw materials for application in the biofuel industry, such as non-edible oils and waste animal fats. Brazil is one of the main meat producers account to 9.1 beef, 3.2 pork, and 12.3 poultry million tons, dominating the world market together with the USA. In Brazil there is a broad range of residual lipid sources from slaughterhouse and rendering establishments ready available for application in biodiesel synthesis, including tallow, lard, poultry fat, mixed animal fat (mammal and poultry fat), and floating material from wastewater treatment plants. In a couple of years, researches focusing on fat residues should be accomplished mainly in order to improve feedstocks standardization process, because FFA and water content are decisive factors determining economic viability and biodiesel quality. Besides, researches in the field of prominent process such as heterogeneous catalysis (Di Serio et al., 2008; Cordeiro et al., 2011), enzyme-based process (Shimada et al., 2002), and supercritical fluids (Demirbas, 2006) should be carried out using animal fat wastes turning these raw materials more and more attractive.

## 6. Acknowledges

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