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Current Status of Biodiesel Production in Baja California, Mexico

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1. Introduction

As a result of declining oil reserves in the world, the rise in fossil fuel prices and growing interest in the environment, there is considerable demand for alternative fuels. Biodiesel is recognized like the "green fuel" and has several advantages compared to diesel. It is safe, renewable, nontoxic, and biodegradable (98% biodegradable in a few weeks). Contains less sulfur compounds, and has a high-flash point (> 130°C). Biodiesel could replace diesel and can be used in any compression ignition engine without modification techniques (Leung et al., 2010). It is an alternative biofuel which has a positive energy balance in their life cycle. In terms of effective use of fossil energy resources, biodiesel yields around 3.2 units of fuel product energy for every unit of fossil energy consumed in the life cycle. By contrast, petroleum diesel's life cycle yields only 0.83 units of fuel product energy per unit of fossil energy consumed (Kiss et al., 2006).

Chemically, biodiesel is a mixture of methyl esters of long chain fatty acids and is formed from vegetable oils, animal fats or waste oils and fats through transesterification in the presence of a catalyst (Ma & Hanna, 1999). A general equation for the transesterification (where R is the remainder of the molecule of triglyceride, fatty acid R_1 and R_2 is the length of acyl acceptor) is:

$$RCOOR_1 + R_2OH \xleftrightarrow{\text{Catalyst}} RCOOR_2 + R_1OH$$

2. Regulations on biofuels in Mexico

The government of Mexico initiated a series of measures to create an internal market for biofuels in order to increase efficiency levels in end-use energy and to reduce greenhouse emissions gases. On August 22nd, 2005 was published the Law of sugarcane sustainable development, which contain guidelines for the use of sugarcane as energetic.

In early 2007, the Mexican Congress promulgated the Law of Promotion and Development of Bioenergetics, which came into force on February 1st, 2008. Its purpose was the promotion and development of bioenergetics in the Mexican agriculture without jeopardizing food security and sovereignty of the country and to ensure the reduction of pollutant emissions to the atmosphere and greenhouse gases, considering international instruments contained in the treaties that Mexico has signed.

The biofuels development in Mexico according to the law and studies of Secretaría de Energía (Secretariat of Energy) starts from two raw materials with high levels of production in the country (sugarcane and corn yellow). In Article 11 of this Law Section VIII, it is stated the granting of permits for the production of biofuels from corn by the Secretariat of Agriculture, Livestock, Rural Development, Fisheries and Food, as long as there is overproduction.

Along with the development of legislation, Mexico undertook a project to determine the feasibility of liquid biofuels called "Potential and Feasibility of using Biodiesel and Bioethanol in Mexico Transport Sector" where the test result indicates that economic production of ethanol from sugarcane or corn is suitable as long as the ethanol price is between 0.55 and 0.65 U.S. dollars. The inputs considered in this study were sugarcane, maize, cassava, sorghum and sugar beet. In the case of sugarcane, it was analyzed the production of ethanol from sugarcane bagasse.

In this project, it was assessed the production of biodiesel from rapeseed, soya, jatropha, sunflower and safflower oils, and the use of animal fat and waste vegetable oil. The results suggest that farm input costs represent between 59% and 91% of biodiesel production costs and, as a result, animal tallow and waste vegetable oil are an opportunity for biofuels production (SENER, 2006b).

As for biofuels commercialization in Mexico the first steps were taken in 2009 when Secretaría de Energía (Secretariat of Energy) gave the first 12 permits of anhydrous ethanol commercialization to participate in the tender that Petróleos Mexicanos (Mexican Petroleum) issued for the supply of anhydrous ethanol in the metropolitan area of Guadalajara (SENER, 2009).

3. Energy situation in Mexico

The primary energy production in Mexico relies mainly on oil and natural gas with a share of 61.5% and 28.2% in 2009 respectively. Renewable energy sources are next in importance, with a contribution of 6.2%, wherein the biomass stands out more than half of that value. The biomass considered by the Secretariat of Energy in the national balance sheet only includes wood and sugarcane bagasse. The remaining 4.1% is made up of coal, nuclear and condensed (see Fig 1).

The entities involved and empowered by the federal government, to ensure and guarantee the energy supply in Mexico are Petróleos Mexicanos (Mexican Petroleum) and Comisión Federal de Electricidad (Federal Electricity Commission).

3.1 Energy situation in Baja California

Baja California is located in the northwestern region of Mexico on a peninsula that bears his name, bordered on the north by the State of California, USA, on the east by the Gulf of California and the west by the Pacific Ocean. It presents dry and warm weather. Its land area is 71,576 km^2 (3.6% of the country) and has a population of 3.3 million inhabitants (3% of the total population of Mexico). Baja California is made up of 5 cities: the capital is Mexicali, Tijuana, Tecate, Ensenada and Playas de Rosarito. The GDP is above the national average. From the economic point of view, it is characterized by a high industrial growth,

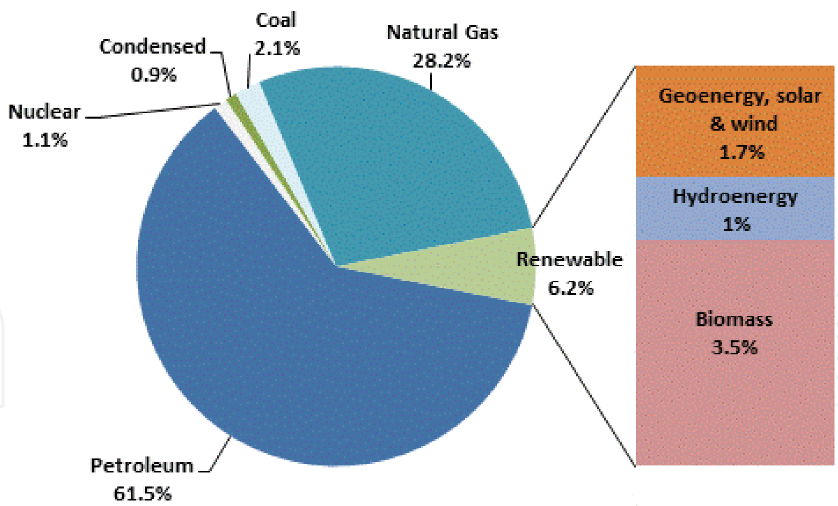

Fig. 1. Structure of primary energy production in México, 2009.

agriculture and livestock. Agriculture and livestock are intensive activities in the region, leading to the generation of large amounts of waste biomass such as animal fats and agricultural residues (wheat straw and cotton waste). Some of them are open burned *in situ*, while others are used in the production of food for livestock.

In the energy situation has primary energy sources for electricity generation, such as geothermal located in Cerro Prieto, with an installed capacity of 720 MW and wind in La Rumorosa located in the municipality of Tecate with an installed capacity of 10 MW. Besides power plants and turbo gas types exist in cities across the state and run with fuel oil and/or natural gas, its total capacity are 1,305 MW and 316 MW respectively. It is appropriate to mention that currently the Baja California's electrical system is isolated from the national grid and interconnected with the United States of America. On the other hand, it has no particular oil resources, so the fuels come the region from southern Mexico and arrive by tanker to Baja California to the Rosarito Beach, situated on the Pacific coast.

In particular may be noted that throughout the year in Mexicali weather conditions are extreme, with temperatures ranging approximately from 0°C to 50°C as shown in Fig. 2, which involve high-energy requirements to ensure physical comfort of its inhabitants.

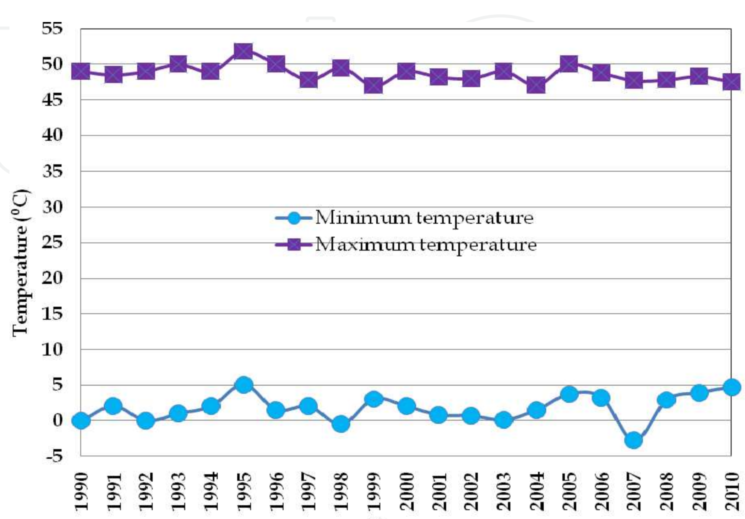

Fig. 2. Minimum and maximum temperatures of Mexicali, 1990-2010.

In 2006, the average per capita consumption of electricity in Mexico was 75% of the world average of 2,659 kWh, while Baja California and Mexicali exceeded it that by 21% and 117% respectively. As shown in Fig. 3, (adapted from Campbell et al., 2011) the annual per capita electricity consumption of Mexicali was comparable to that of Italy and was ranked ahead of countries like Brazil and Chile.

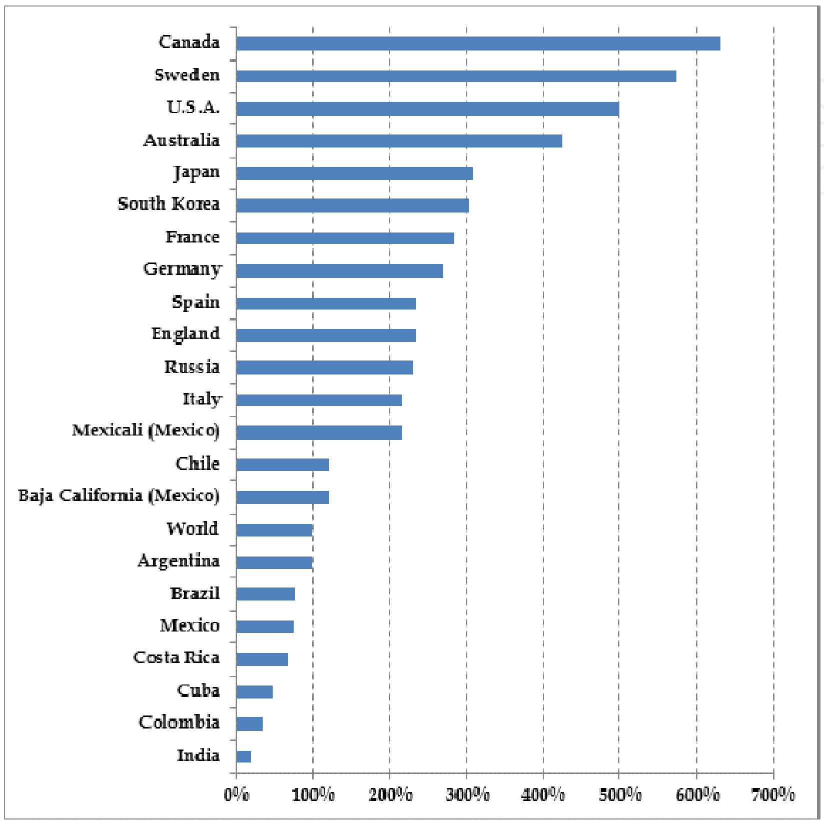

Fig. 3. Relative average annual consumption per capita 2006, World: 2,659 kWh, 100%.

Besides the high-electricity consumption, the fuel requirements of different services sectors should be meet which are supplied with fuel from Southern Mexico, as is the case of diesel.

3.2 Consumption of diesel in Baja California

Baja California has 3 diesel outlets in the cities of Mexicali, Ensenada and Rosarito Beach catering to other locations in the region. The average sales volume of diesel was 717,211 m^3 in the period 2000-2010, as presented in Fig. 4.

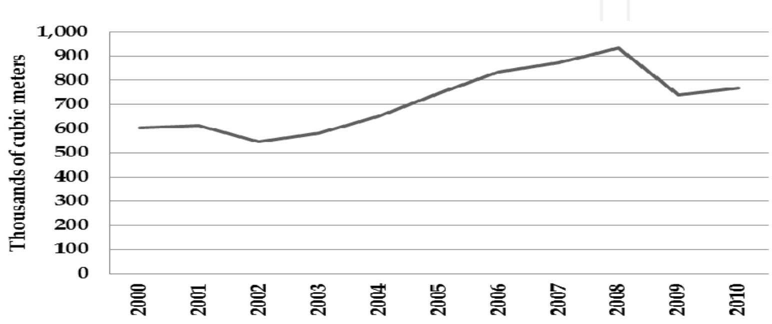

Fig. 4. Diesel sales volume of Baja California, period 2000-2010.

It can be seen that the volumes of diesel are high, and for that reason, it is proposed its replacement with biodiesel obtained from different raw materials available in the state.
With respect to biofuels such as biodiesel, currently its production is inexistent in commercial scale, in North Mexico and incipient in the rest of the country, as shown in the map of Fig 5, which presents the current state of production facilities of biodiesel in Mexico. In Baja California are only reported biogas projects. (Adapted from REMBIO, 2011).

Fig. 5. Bioenergy projects in Mexico.

4. Feedstocks availability in Baja California

In order to evaluate the resources available in the state of Baja California for processing and use as biofuels, Biofuels Group of the Institute of Engineering of the Universidad Autónoma de Baja California, started from 2008, a series studies to identify the biomass resources and determine their potential use as feedstock for the production of biofuels. The materials considered were animal fats, waste vegetable oil (WVO), castor oil, *jatropha curcas* and agricultural waste.

4.1 Waste vegetable oil

The Waste Vegetable Oil (WVO) is highly available resource in the state, as well as in the rest of the country, and its amount varies depending on the demand for edible vegetable oil. Its generation is closely linked to the food preparation processes in various sectors: a) the restaurateur, b) food industrial and c) domestic. Traditionally, the WVO has an inadequate disposal and it is directly discharged to the sewage system and illegal dumping. This creates problems of clogging of the sewage system, soil and water pollution and increased maintenance costs and wastewater treatment.
The WVO is that oil that has been altered physical-chemical properties due to its use in a batch or continuous processes of food preparation. Mexican standard NOM-052-SEMARNAT-2005

establishes the characteristics, the procedure of identification, classification and listing of hazardous waste and does not include the WVO as hazardous waste.

The WVO for its high energy content, about 30 MJ/kg (Talens et al., 2006), is likely to be reused as raw material for bioenergy production or other manufacturing processes such as production of soap. Currently a fraction of the WVO generated in Baja California is collected by companies certified from the appropriate authorities, and sell the residues to their end use as food for beef cattle. Other companies choose to export the WVO to the United States, where it is used as feedstock in biodiesel production and eventually that biodiesel is acquired by Mexico for use in vehicles, machinery and equipment of the Comisión Estatal de Servicios Públicos de Tijuana (State Public Services Commission of Tijuana). So then, it is presented a scenario where a valuable resource from the energy standpoint, it is not processed locally, and instead is exported as raw material and imported as a finished product, missing the economic, environmental and social development in the region.

There are several reasons why it is appropriate to promote the development of biodiesel from WVO, among which it can be mention, the following (Canacki & Gerpen, 2001; Gerpen et al., 2006):

- Represents a sustainable method where is revalued and reused a resource with a high-energy content, to produce a cleaner fuel. This will no longer discard a valuable resource from the energy standpoint, and at the same time is greatly benefited the environment and society in general.
- Avoid the use of edible oil crops in the production of biodiesel, so it does not risk food security because it is the reuse of a waste.
- It is an opportunity to mitigate the environmental impact caused by emissions of greenhouse gases responsible of global warming.
- It is an opportunity to diversify the energy matrix, traditionally based on fossil fuels.
- Reduces dependence on fossil fuels.
- Emissions of carbon dioxide are integrated to the carbon cycle of plants from which oils are extracted.
- It has excellent lubricating properties for the diesel engines motors.
- They come from a renewable resource.
- They are biodegradable.

In 2008, was estimated a generation of 2.1 million liters of WVO in the restaurant sector of Mexicali city, capital of Baja California (Coronado, 2010). The results indicate that the types of foods that have greater participation in this generation are: fast food, international food, mexican and china food.

The Fig. 6 shows that 100% of oil used in food preparation 41% is consumed in food or disposed of in cookware, while the remaining 59% becomes WVO. Also, shows that 59% of WVO has different destinations: 33% are collected by companies engaged in such activity, private collectors 16%, 8% were discharged to municipal sewage system and 2% are donated to be reused in food preparation.

On the other hand, it was realized the spatial distribution of restaurants in Mexicali by using a satellite Geo positioning obtaining the geographic coordinates in UTM Zone 11 N of each food preparation facility and place them on a satellite image that is illustrated in Fig. 7.

Usually there is a greater density of restaurants in commercial areas and main avenues. It was confirmed the existence of a relationship between the density of restaurants with a higher incidence of the problem of clogging in the sewage system of the city, due to the discharge of the WVO.

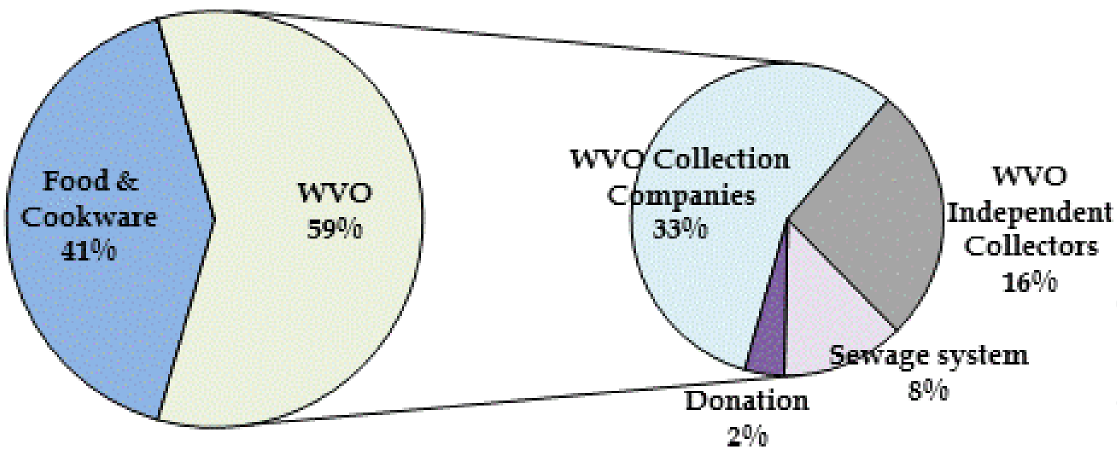

Fig. 6. Waste vegetable oil disposal.

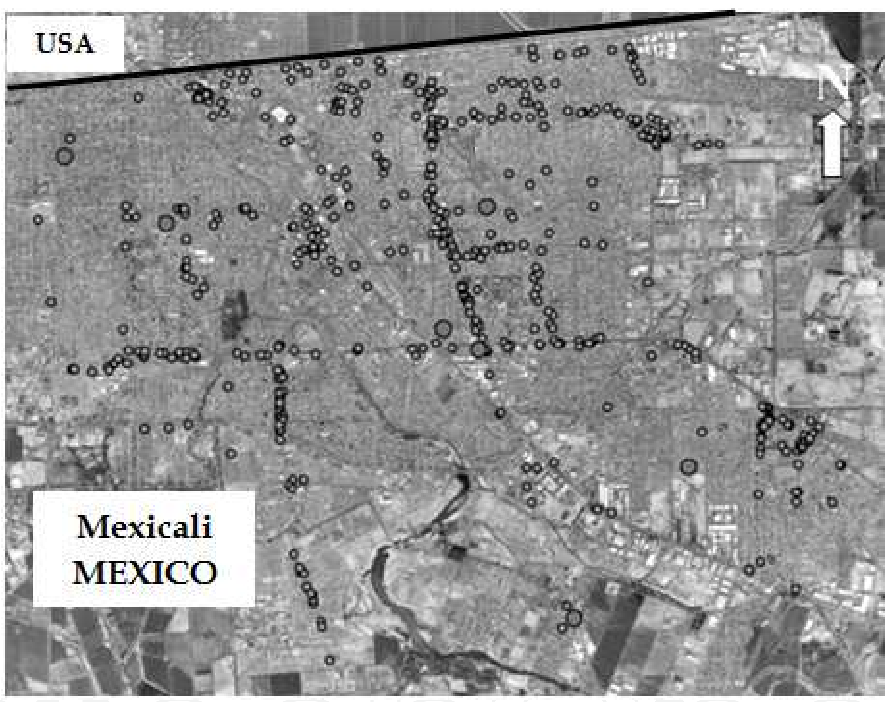

Fig. 7. Spatial distribution of Mexicali restaurants.

Finally, it was performed a dynamic model that helped to predict the WVO generation for a period of 10 years, from 2008 to 2017. The results showed an average generation rate of 3 million liters of WVO, or 3.4 L per capita/year.
In order to determine the WVO availability of the restaurant industry in Baja California, the results were extrapolated from the survey conducted in Mexicali. The volume of WVO estimated was 8 million liters per year. From this value, it would be feasible to produce 6.4 million liters of biodiesel annually, assuming a conversion efficiency of 80%, obtained experimentally.

4.2 Animal fat

According to the report of the Mexican Service of Information, Food, Agriculture, and Fishery (SIAP, 2009), in 2008 Baja California holds the 6th national rank in beef carcass production. In that year, 695,000 fowls and 259,000 heads of cattle (beef, pigs, goats, and sheep) were processed to produce meat. The number of the standing head of cattle in Baja California in 2008 is shown in Fig. 8.

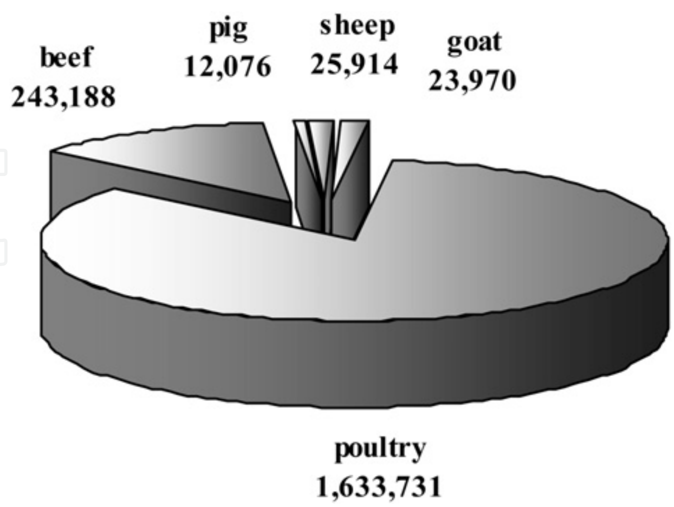

Fig. 8. Standing cattle in Baja California in 2008.

Some portions of the cow mass (49%), of the pig (44%), and of the fowl ((37%) are not suitable for human consumption (Clottey, 1985), so a considerable amount of organic residues are generated by the slaughter processes. Before the rendering process, their average composition is 60% water, 20% proteins/minerals, and 20% fat. These residues could be used to produce biodiesel, due to the fat content. These organic materials with microorganisms potentially pathogens for humans and animals are processed by rendering, which fulfills all of the basic requirements for environmental quality and disease control (Meeker & Hamilton, 2006).
The basic rendering of the materials generated in the beef processing systems is presented in Fig. 9 (Toscano et al., 2011).

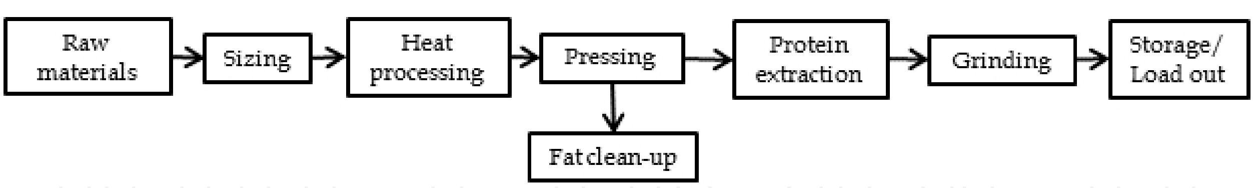

Fig. 9. Scheme of the basic rendering of the materials generated in the beef processing system.

In order to determine the potential of producing biodiesel from yellow grease, it was considered the fat fraction generated in the beef rendering process "in Baja California". The result for 2008 was 1,380 t of fat (Toscano et al., 2011). Assuming conversion efficiency of fat into biodiesel it is stated in 95% (Bhatti et al., 2008), it was estimated that the potential for producing biodiesel in 2008 was 1,311,000 L.
In addition to the residues presented previously, Baja California has oil crops, which represent potential raw material for biodiesel production. Such crops include castor oil plant (*Ricinus communis*) and *jatropha curcas* that are characterized by their high oil content and because it is not edible, so do not compete with food. In the case of the *jatropha curcas*,

experimental plantings were conducted in Mexicali Valley, to determine their adaptation to soil conditions and climate. The results highlighted that the growth of the plant was not successful. However, in the coast of Baja California, south of Ensenada with Mediterranean climate, this plant grows successfully.

The castor oil plant (*Ricinus communis*) is a Baja California endemic plant and has made significant progress in the modernization of such cultivation for mass production in order to obtain oil for its transformation in biodiesel.

Given the raw materials constituted of waste biomass as well as those derived from oilseed plants endemic from Baja California; Institute of Engineering of the Universidad Autónoma de Baja California (Autonomous University of Baja California) is developing research to adapt processes and technologies to achieve the highest conversion yields in the process of biodiesel production. This has been used in different catalytic pathways are described below.

5. Transesterification process

The transesterification reaction can be catalyzed by alkalis, acids (Canacki & Gerpen, 1999) or enzymes (Vyas et al., 2010). Several studies have been performed using different oils as raw material, alcohols, as well catalysts, including homogeneous catalysts such as sodium hydroxide, potassium hydroxide and sulfuric acid and heterogeneous catalysts such as lipase (Nielsen et al., 2008), CaO (Lim et al., 2009) and MgO (Refaat, 2010).

5.1 Transesterification by acid catalyst

The transesterification process is catalyzed by Bronsted acids, preferably sulfuric and hydrochloric acids. These catalysts show high yields, but the reactions are slow. The molar ratio alcohol/vegetable oil is one of the main factors affecting transesterification. An excess of alcohol promotes the formation of alkyl esters. On the other hand, an excessive amount of alcohol impairs the recovery of glycerol, so the ideal ratio of alcohol/oil must be established empirically, considering each individual process (Demirbas, 2009). It has been observed that the use of an acid catalyst is more effective than an alkaline catalyst when the concentration of free fatty acids is high, above 1%. These reactions require washing, because the acids involved a large amount of salts produced during the reaction which can be corrosive. The mechanism of acid catalyzed transesterification of vegetable oil is shown in Fig. 10, for a monoglyceride. However, this can be extended to di- and triglycerides. Protonation of the ester carbonyl group produces one carbon cation II which after a nucleophilic attack of alcohol causes the tetrahedral intermediate III and removes the glycerol to form the new ester IV and regenerate the catalyst H^+.

According to the mechanism, carboxylic acids can be formed by the reaction of the carbon cation II when water is present in the reaction mixture. This suggests that transesterification by acid catalyst should be done in the absence of water to avoid the formation of carboxylic acids, which reduces the yield of alkyl esters (Schuchardt et al., 1998).

5.2 Transesterification by alkali catalyst

Transesterification of vegetable oils by alkali catalyst proceeds faster than the reaction by acid catalyst. The first step is the reaction of the base with the alcohol, producing an alkoxide and a catalyst protonated. The nucleophilic attack of the alkoxide to the carbonyl group of the triglyceride generates a tetrahedral intermediate from which form the alkyl

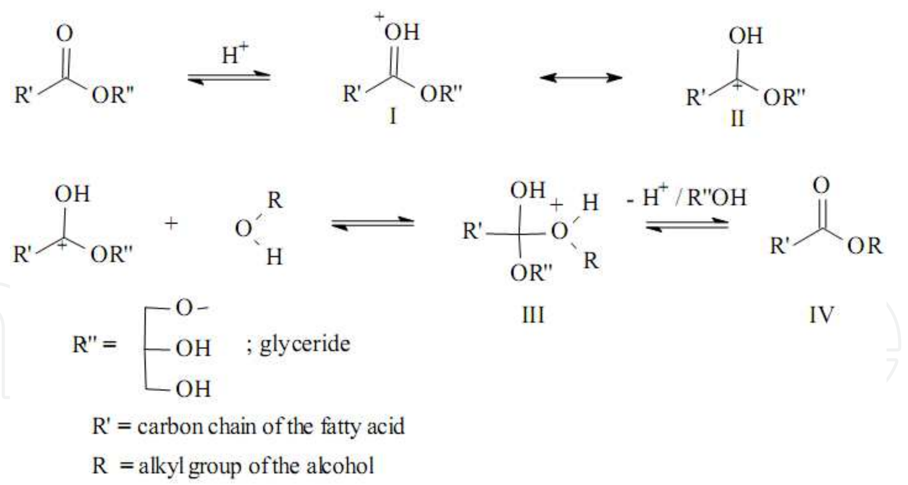

Fig. 10. Mechanism of the acid-catalyzed transesterification of vegetable oils.

ester and the corresponding anion of the diglyceride. Diglycerides and monoglycerides are converted by the same mechanism. The alkali metal alkoxides (CH_3ONa for methanolysis) are the most active catalysts which offer high yields in short reaction times (30 min). However, the reaction requires no water (Demirbas, 2009). The reaction mechanism for catalysis of transesterification is displayed in Fig.11.

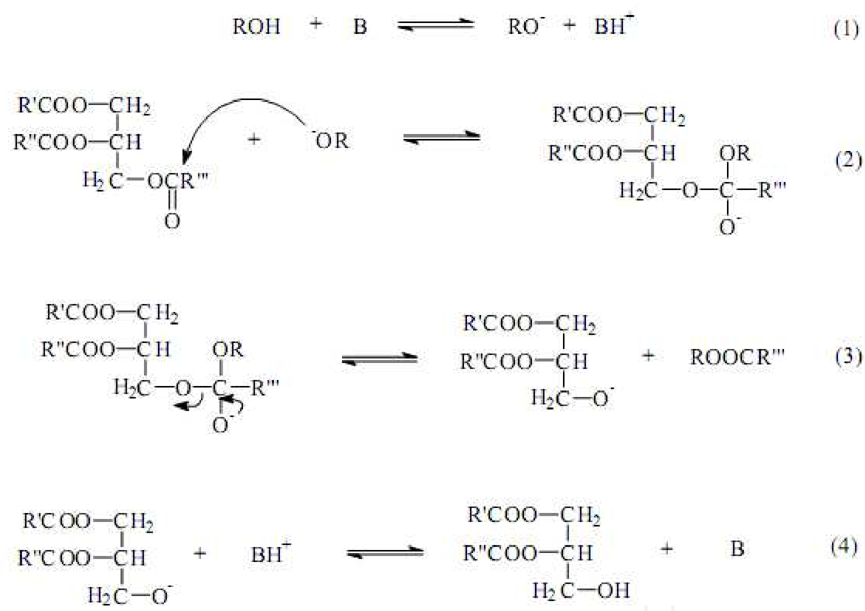

Fig. 11. Mechanism of the base-catalyzed transesterification of vegetable oils.

The transesterification process by alkali catalyst is 100% in the commercial sector, because the chemicals used have proved to be the cheapest for their high level of conversion to esters at low temperature and atmospheric pressure. The main inconvenient of this technology is the sensitivity of alkaline catalysts with the purity of the raw material. The presence of free fatty acids and water in the raw materials has a significant impact on the transesterification reaction (Marchetti et al., 2008). Besides the complex purification of the final products of reaction, this method requires treatment of waste water produced during the process. The amount of wastewater produced is about 200 kg/t of biodiesel produced which increases the costs of this technology and makes it unfriendly to the environment (Ghaly et al., 2010). Fig. 12 depicts the process of transesterification by alkali catalyst (Bacovsky et al., 2007).

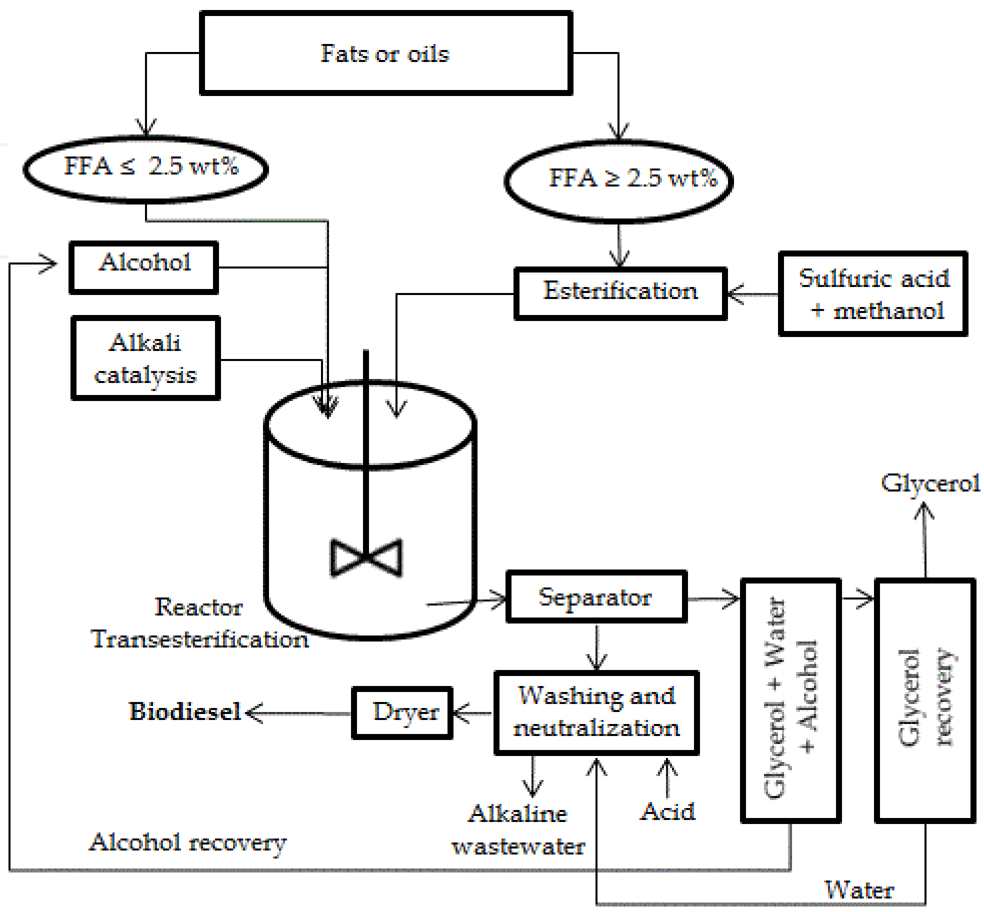

Fig. 12. Process diagram of biodiesel production by alkali catalyst.

5.3 Transesterification by enzymatic catalyst

Biological enzymes, including lipases, can be used as catalysts instead of acids or bases. The use of such enzymes in the production of biodiesel has several advantages (Hass et al., 2002):

- Requires little or no heating.
- The presence of free fatty acids (FFA) in the raw material increases performance, without the production of soap, creating a source of opportunities for the use of low-quality raw materials and low cost.
- It works even in the presence of water.
- Required less alcohol and do not produce salts.

A large number of lipases have been explored as catalysts in biodiesel production. Researchers in China have tested a wide variety of lipases, obtaining yields of up to 94%. Italian researchers tested different lipases and found that the lipase produced by *Pseudomonas cepacia* had a yield of 100% in six hours.

Similar studies were performed in the United States (Jin & Bierma, 2010). Unfortunately, lipases and other enzymes tend to be expensive due to the purification process, which increases the costs of biodiesel production (Gerpen et al., 2004).

In order to increase the duration of the activity of lipase, thereby reducing costs, research has been developed in the immobilization of lipases using physical structures to stabilize the enzyme and allow its reuse. Lipases have been covalently attached to activated polyvinyl chloride, nylon or silica gel. They have also been immobilized by entrapment in alginate gels. Adsorption on hydrophobic or hydrophilic media is some of the techniques used to lipase immobilization (Minovska et al., 2005). Although the enzymatic process is not commercially developed, a large number of publications have shown that enzymes are promising catalysts. These studies consist mainly on the optimization of reaction conditions (temperature, ratio alcohol/oil, type of microorganisms that produce lipase, lipase amount, time, etc.) to establish the characteristics of industrial application.
Fig. 13 shows the enzymatic production of biodiesel using immobilized lipase (Du et al., 2008).

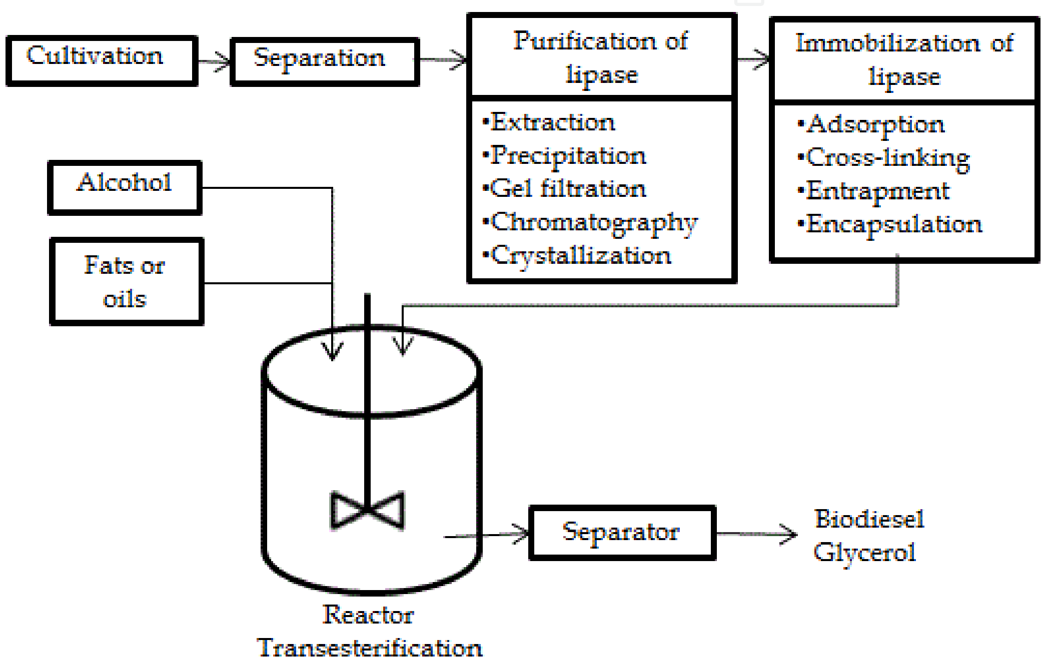

Fig. 13. Enzymatic biodiesel production by immobilized lipase.

Currently in the Institute of Engineering is being developed a project that aims to identify a microorganisms that produces a high yield of lipase, with the necessary characteristics to be used in the synthesis of biodiesel. So it was analyzed the production of lipase from 6 different fungi (*Aspergillus niger, Aspergillus oryzae, Aspergillus Awamory, Trichoderma sp, Trichoderma reesei* and *Penicillium chrysogenum*).
The advantage of this methodology is based on the fact that extracellular lipases can be produced in large quantities under standard laboratory conditions. This could be successful by using the appropriate media and the optimal process parameters.

6. Economic analysis of biodiesel production from WVO and yellow fat in Mexicali, Baja California

Mexicali has a motor vehicle fleet of diesel estimated at 14,000 units and cargo transport. The transport cargo sector with 11,861 units consumes about 169 million liters of diesel. The diesel used in Baja California comes from southern Mexico and is one of the causes of CO_2 emissions that affect air quality in Mexicali, it is therefore necessary to explore options for replacing it with biodiesel, which produces less CO_2 and can be obtained from waste material. Thus, in this analysis, was considered the use of waste vegetable oil from the Mexicali restaurant industry as a raw material for the production of 4.78 million liters of biodiesel energy equivalent to 4.45 million liters of diesel.

The environmental benefit involving the replacement of such a volume of diesel with biodiesel is to reduce emissions by about 9,700 t of CO_2, 22 t of SO_x and 11 t of PM_{10}.

To determine the economic feasibility of producing biodiesel, were applied the methodologies of net present value and internal rate of return. The results indicate that the production of biodiesel is profitable. However, the recovery time of investment, coupled with the uncertainty presented by the biofuels market, make necessary a policy that implements local tax resources to support the promotion, production and use of biodiesel for the transport sector. Therefore, under the circumstances considered in this analysis, the production of biodiesel is feasible if it is developed synergy among the productive sectors, education and government.

The profitability indicators are set at the discretion of the financial analysis methodology. The final report of economical evaluation of this project is supported with the following results:

a. The net present value with a bank interest rate of 17%, meets the acceptance criteria to generate 423,747 USD, however, the magnitude of the indicator does not provide the certainty to accept conditions of project implementation.
b. The internal rate of return is calculated based on cash flow net present value, resulting in the profitability of 23.5%; therefore the project is considered financially viable, however, an acceptance criterion is to get 10 points above the discount rate.
c. The Benefit/Cost Ratio result is 1.05, therefore, is slightly positive, meets the criteria of acceptance, but does not provide the necessary clearance to run the project within the evaluation period.
d. The Profitability Index of the project is 0.227, which does not meet the acceptance criteria for the project.

Based on the evidence derived from cost-benefit analysis it may be concluded that carrying out the project to produce biodiesel from WVO in Mexicali is profitable. However, the return time of investment and the uncertainty presented by the biofuels market, make necessary a policy that implements local tax resources to support the promotion, production and use of biodiesel for the transport sector (Vazquez et al., 2011).

7. Conclusion

Baja California has significant potential for the development of biodiesel production projects, taking into account residual material such as yellow fat or others that are not currently used as vegetable oils, which are discarded mostly. It has also been encouraged by the government of Mexico the planting of bioenergy crops such as castor and *jatropha curcas*.

The promotion for these projects, in areas without oil resources such as Baja California, will slightly shift the use of fossil fuels, and thereby avoid the emission of sulfur compounds.

The current state of biofuel development in Baja California largely reflects the current situation of production, operation and sales of biofuels, including biodiesel, in Mexico.

From an economic standpoint, the production of biodiesel in Baja California will be successful as long as the support from the productive sectors, education and government.

8. Acknowledgment

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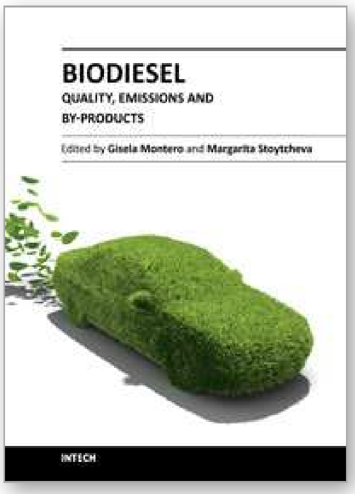

Biodiesel- Quality, Emissions and By-Products

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This book entitled "Biodiesel: Quality, Emissions and By-products" covers topics related to biodiesel quality, performance of combustion engines that use biodiesel and the emissions they generate. New routes to determinate biodiesel properties are proposed and the process how the raw material source, impurities and production practices can affect the quality of the biodiesel is analyzed. In relation to the utilization of biofuel, the performance of combustion engines fuelled by biodiesel and biodiesels blends are evaluated. The applications of glycerol, a byproduct of the biodiesel production process as a feedstock for biotechnological processes, and a key compound of the biorefinery of the future is also emphasized.

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