P 24. CHARACTERIZING OF THE RAW MATERIALS AND UTILITIES FOR THE LABORATORY-SCALE BIODIESEL PRODUCTION

Armela Mazreku[1*], Ilirjan Malollari[2], Lorina Liçi[3]

[1]*Department of Bio-Chemistry, University of Elbasani, Albania*
[2]*Department of Industrial Chemistry, University of Tirana, Albania*
[3]*Department of Energy Resources, Polytechnic University of Tirana, Albania*

E-mail: armelamazreku@hotmail.com

ABSTRACT: Nowadays it is a well known fact that biodiesel is a renewable resource based fuel for use in diesel engines. From the most of the studies referred in the specialized literature it can be made from various oils including corn, soybean, canola, cottonseed, peanut, etc. and from animal fats, but as usually it has a more scientific term as Fatty Acid MethylEster (FAME).
The oils and fats contain triglycerides that are chemically converted into FAME by a process called "transesterification" and the fuel produced is more environmentally friendly than petroleum diesel.
Raw materials for the biodiesel production can be as follows: vegetable oils, grasses from the animal wastes and recycled; but also the waste cooking oils which has been main objective of our study. These materials all have considerable content of the triglycerides, free organic fatty acids, and other ingredients as contaminants of them, strongly depended from the way of their pretreatment before delivery.
We have considered mains olive, wheat oil, sunflower oil, soya oil, cotton oil, palm oil; as well as waste cooking oil from restaurants and fast food bars, caw and pig grease, etc.
Since biodiesel is an ester of the fatty acids it is needed also a specific catalyst for the facilitating the starting of the transesterification process, and we have used both basic and acidic chemically content of it. Also, for the biodiesel production there are necessary some utilityes and auxiliary materials , which we have characterizing them all for the study performed in the laboratory scale. The characteristics of all the raw and other needed materials we have shown in the full version of our paper.

*Keywords**:** Biodiesel, renewable resource, waste cooking oil, transesterification, catalyst*

1. INTRODUCTION

Based on the latest forecasts, the world population will grow substantially to 9 billion by 2050. This will cause further rapid growth in energy demand, significant decline in global fossil fuel reserves, and intensification of environmental challenges global ones such as global warming and climate change due to increased greenhouse gas emissions (GHG). Given the diminishing resources of fossil fuels, as well as the unstable and unstable nature of these fuels, it is necessary to find alternative energy sources. In fact, the search for renewable energy with fewer GHG emissions and the capacity of air pollution is important at the global level (*OECD, 2012*).
Among the various renewable platforms, biomass-based energy production has attracted a lot of attention due to the huge amount of biomass (eg, plants and wastes) produced globally and the potentials it has to mitigate harmful environmental impacts associated with fossil fuels.
Among biodiversity-oriented biomass fuels, biodiesel is considered to have great potential as a green and technologically feasible alternative to fossil fossil fuels. Biodiesel is derived from vegetable seed oils and animal fats and is a mixture of alkyl esters if long fatty acids, mainly produced by the method of transesterification.
The physical-chemical properties of biodiesel are very similar to those of oil, and therefore can be used as an alternative to oil in conventional diesel engines without the need for any modification.
Other biodiesel benefits include the highest number of cetane, fire point and lubrication, sulfur deficiency, and lower aromatic content compared to petroleum. *(Demirbas,2009)*
Biodiesel is mainly produced from edible oils, i e soybean, canola, palm trees, rapeseed etc. However, the application of these oil crops as a nutrient to the production of biodiesel is accompanied by adverse impacts on global food security, particularly in developing countries suffering from tangible economy

and agriculture. On the other hand, given such adverse effects on the price of food and food security, the production of biodiesel from food in the food grade can not be economically feasible.
Therefore, raw oils, animal waste greases and vegetable oils used are used for the production of biodiesel. The most important oil plants with high potential for biodiesel production include Jatropha curcas, camelina (Camelina sativa), castor beans (Ricinus communis L.), neem (Azadirachta indica A.), karanja (Pongamia pinnata L.) mahua (Madhuca spp.), simarouba (Simarouba glauca DC.) and cheura (Diploknema butyracea).
However, current oil yields from these plants are generally insufficient to meet bioenergy requirements, while the resulting oils are characterized by trace amounts of water, high water content and free fatty acid content. Thus, genetic improvements to increase oil production and properties have attracted considerable attention. *(Alaba., 2016; del Pilar Rodriguez, 2016)*

In the EU Directive 2003/30 / EC, biodiesel is defined as "methyl ester" produced from vegetable or animal oils, of oil quality to be used as biofuel. "The latest EU Directive 2009 / 28 / EC has set targets for achieving by 2020, a share of 20% of energy from renewable energy sources in the EU's overall energy consumption and a 10% share of renewable energy sources in each country the consumption of transport energy. In this context, special attention is paid to the role played by the development of a sustainable and responsible biofuel production, without affecting the food chain.
Nowadays most biodiesel is produced through triglycerides transesterification of edible oils with methanol, in the presence of an alkaline catalyst *(Lotero., 2005).* The so obtained product has low viscosity and is a biofuel (fatty methyl ester) that can replace petroleum-based diesel fuel with no need of engine modifications *(Suwannakarn., 2005).* Furthermore, if compared to fossil fuel, the formed ester fuels are non-toxic, safe to handle, and biodegradable. Glycerine is also obtained as by-product as shown in Fig. 1.

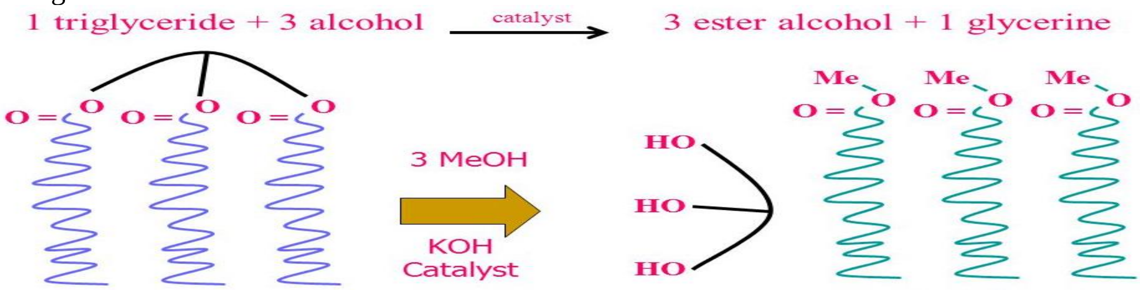

Figure.1: Transesterification of a triglyceride

Current oil production systems raise environmental concerns because the lands have been intensively cultivated, requiring high fertilizers and water inputs. These practices, intended to increase production, should be carefully reduced or regulated to prevent greenhouse gas emissions or other environmental impacts. To do this, improved agronomic practices such as the use of mixed species or crop rotation undoubtedly play a key role in mitigating negative impacts and increasing biodiversity. A profound understanding of microbial soil diversity, its effects on nutrient supply, and consequently on yield, is essential for sustainable cutting systems *(The Royal Society, 2008)*.
Energy crops for industrial destinations can represent a strategic opportunity to use land and generate revenue. However, in addition to the environmental aspects, there are economic concerns regarding the landing of land for food cultivation. In a high market tension, it may have a big impact on food / food prices, increasing inequality, especially in developing countries. In addition, increased food demand may result in slowing production of bio waste due to lower availability of raw material. This was noted in 2007 with industrial factories that use only 50% of their production capacity *(Carvoli, 2008).*

For all these reasons, it is desirable to produce biodiesel from crops specifically selected for their high productivity and characterized by low input requirements or low-cost ready-to-eat foods such as waste cooking oils (WCO), animal fats and greases *(Zhang , 2003).*
Meanwhile available food crops for biodiesel production are limited to several species (mainly palm / soybeans in the USA and palm oil / rapeseed in the EU), the purpose of using dedicated alternative

sources opens a wide choice for new species that can to be more suitable for specific conditions that result in high yield.

The WHO's high potential is also recognized by EU Directive 2009/28 / EC, where livestock or animal waste livestock is reported to save about 88% of greenhouse gas emissions, a fairly high value compared to biodiesel From ordinary vegetable oils, greenhouse gas savings range from 36 to 62%. The main issue presented by such a raw material is the need for its standardization, particularly with regard to acidity reduction. Several methods have been proposed to solve this problem. Among them, it is worth mentioning, in addition to the method of alkali refining, the addition of excess catalyst extraction with a solvent, the distillation refining process and the pre-esterification method *(Pirola, 2010; Bianchi, 2010)*.

The latter seems to be the most attractive approach and has recently received a lot of attention.

1.1 Non-edible oil crops in the Mediterranean area

A considerable amount of studies are available in major and alternative crops for the production of raw material for biodiesel. Authors made a selection of the most promising crops to be introduced into the Mediterranean area, considering that currently the Mediterranean basin includes not only mild climate, but also arid soils. Some of them have been effectively tested within the project mentioned as part of a single rotation program.

Among the oil crops, the Brassicaceae family has an extraordinary position. Rapeseed (Brassica napus) is the third-largest oil production with 12% of the world market of plant plants with the best cultivated crops in cold-hot regions *(Carlsson, 2009).*

However, the great biodiversity of Brassicaceae refers to the original species, among which Brassica juncea, Brassica nigra, Brassica rapa, Brassica carinata, Sinapis alba, Camelina sativa, Eruca sativa ssp. oleifera, etc. In addition to potentials as raw material for biodiesel, their high content of glucosinolates (GSL) makes them capable of recovering marginalized lands from terrestrial pests such as nematodes (eg nematode galling by the genus Meloidogyne and cyst nematodes from Heterodera and Globodera genera) *(Romero et al., 2009; Curto & Lazzeri, 2006).*

On the other hand, an unexpected source of oil seems to come out of tobacco culture. Pending changes in the tobacco market, new varieties for energy production are emerging. Tobacco, as drought-resistant species, appears to be a good option to deal with the shift of some early trees to dry lands caused by climate change.

1.2. Standardization of the raw materials for biodiesel production

Characterization of oil before continuing with standardization of raw materials is a very important issue. Some properties remain virtually unchanged from the initial material to the finished biodiesel, or they are, however, predetermined. It is very important to check that the values of such chemical and physical properties of oil are in the range of those required by standard regulations. The experimental procedures for obtaining such property values are also standardized and are shown in the regulations.

Table 1: European Standard specifications for biodiesel

Specification	Units	Min	Max	Methods
Ester content	% (m/m)	96.5	-	EN 14103
Density 15°C	kg/m3	860	900	EN ISO 3675 EN ISO 12185
Viscosity 40°C	mm2/s	3.50	5.00	EN ISO 3104
Sulphur	mg/kg	-	10.0	preEN ISO 20846 preEN ISO 20884
Carbon residue (10% dist.residue)	% (m/m)	-	0.30	EN ISO 10370
Cetane number		51.0		EN ISO 5165
Sulphated ash	mg/kg	-	0.02	ISO 3987
Water	mg/kg	-	500	EN ISO 12937
Total contamination	h (hours)	-	24	EN 12662

Cu corrosion max		-	-	EN ISO 2160
Oxidation stability, 110°C	h (hours)	6.0	-	EN 14112
Acid value	mg KOH/g	-	0.5	EN 14104
Iodine value	gr I2/100 gr	-	120	EN 14111
Linoleic acid ME	% (m/m)	-	12.0	EN 14103
Methanol	% (m/m)	-	0.20	EN 14110
Monoglyceride	% (m/m)	-	0.80	EN 14105
Diglyceride	% (m/m)	-	0.20	EN 14105
Triglyceride	% (m/m)	-	0.20	EN 14105
Free glycerol	% (m/m)	-	0.02	EN 14105
Total glycerol	% (m/m)	-	0.25	EN 14105
Gp I metals (Na+K)	mg/kg	-	5.0	EN 14108 EN14109
Gp II metals (Ca+Mg)	mg/kg	-	5.0	EN 14538
Phosphorous	mg/kg	-	5.0	EN 14538

The high content of sulphur and phosphorus in the available materials causes mostly engine wear and in particular shorten the life of the catalyst. Biodiesel derived from soybeans, rapeseed, sunflowers and tobacco oils are known to contain virtually no sulphur.
Soybean, sunflower, peanut and rapeseed oils contain a high percentage of the acidic linoleic acids, so they affect the properties of ester extracted with a low melting point and the cetane number.
Determination of the amount of methyl ester of linoleic acid is achieved by gas chromatography using an internal standard as the substrate is trans esterified and also allows the determination of the amount of methyl ester of other acids.

In the tables below we will provide the European biodiesel standard, the oil profile for each edible oil and the main characteristics of Waste Cooking Oil (WCO) as one of the first major raw materials for Biodiesel production.

Table 2: Indicative acidic composition of some raw materials for biodiesel production

Oil	Comon Name	Fatty acid composition, wt%
Arachis hypogea	Peanut	11.9 (16:0), 3.0 (18:0), 40.0 (18:1), 40.7 (18:2), 1.2 (20:0), 3.2 (22:0)
Brassica juncea	Indian mustard	3.6 (16:0), 1.1 (18:0), 13.9 (18:1), 21.5 (18:2), 13.7 (18.3), 8.7 (20:1), 33.5 (22:1)
Brassica napus	Canola	4.7 (16:0), 0.1 (16:1), 1.6 (18:0), 66.0 (18:1), 21.2 (18:2), 5.2 (18:3), 0.9 (20:0), 0.3 (22:0)
Carthamus tinctorius	Safflower	0.1 (14:0), 6.4 (16:0), 2.2 (18:0), 14.1 (18:1), 76.6 (18:2), 0.2 (18:3), 0.2 (20:0) 0.2 (22:0)
Elaeis guineensis	Palm	0.5 (12:0), 1.0 (14:0), 38.7 (16:0), 3.3 (18:0), 45.5 (18:1), 10.8 (18:2), 0.1 (18:3), 0.1 (20:0)
Glycine max	Soybean	10.7 (16:0), 3.0 (18:0), 24.0 (18:1), 56.6 (18:2), 5.3 (18:3), 0.2 (20:0), 0.2 (22:0)
Helianthus annus	Sunflower	6.6 (16:0), 3.1 (18:0), 22.4 (18:1), 66.2 (18:2), 1.0 (18:3), 0.3 (20:0), 0.4 (22:0)
Jatropha curcas	Physic nut	0.1 (12:0), 0.2 (14:0), 14.8 (16:0), 0.8 (16:1), 4.2 (18:0), 41.0 (18:1), 38.6 (18:2), 0.3 (18:3)
Nicotiana tabacum	Tobacco	6.6 (16:0), 3.1 (18:0), 22.4 (18:1), 66.2 (18:2), 1.0 (18:3), 0.3 (20:0), 0.4 (22:0)

Lard	-	4.8 (14:0), 28.4 (16:0), 4.7 (16:1) 14.8 (18:0), 44.6 (18:1), 2.7 (18:2)
Yellow grease	-	1.0 (14:0), 23.0 (16:0), 1.0 (16:1) 10.0 (18:0), 50.0 (18:1), 15.0 (18:2)
Brown grease	-	1.7 (14:0), 23.0 (16:0), 3.1 (16:1) 12.5 (18:0), 42.5 (18:1), 12.2 (18:2), 0.8 (18:3)

Table 3 : Iodine value, viscosities and densities of WCO as alternative oas raw material for biodiesel production

Oil	Iodine value (gI2/100g oil)	Viscosity (mm2/s 40 °C)	Density (kg/m3 15° C)
WCO	54	82.2	918

1.3. Oil standardization: Free fatty acids esterification reaction

As mentioned in the introduction paragraph, the use of unrefined, unrefined oils presents the standardization problem before the trans esterification process, particularly with regard to acidity reduction. In fact, oils, in addition to triglycerides, contain acid free base facade (FFA).
The latter are able to react with the alkaline catalyst used for the trans esterification reaction that brings soaps that prevent contact between the reagents.
A FFA content lower than 0.5% wt is also required by the EN 14214.
Among the various deacidification methods listed in the introduction, the authors have been paying close attention to the pre-esterification process *(Loreto 2005; Pirola 2010; Bianchi, 2010)*.
This method is particularly suitable as it is not only able to reduce the acidity of the oils but also provides methyl esters at this stage, thus increasing the final yield on biodiesel.
A scheme of the FFA esterification reaction is given in Fig.2.

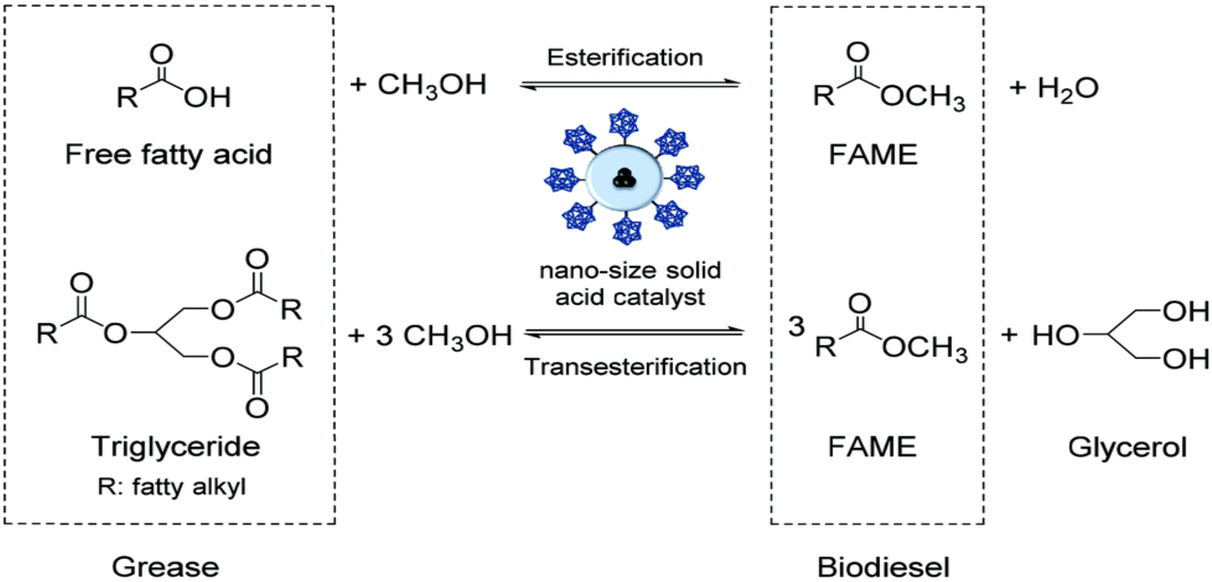

Fig. 2. Scheme of the Free Fatty Acid Esterification Reaction.

Using heterogeneous catalysts is usually preferred for use homogeneous catalysts, as it prevents neutralization and separation costs, except that they are not corrosive, thus avoiding the use of expensive building materials. Another important advantage is that recovered catalysts can be used potentially for a long time and / or multiple reaction cycles.

2. RESULTS AND DISCUSSION

The use of oil crops derived from alternative crops or residual oils as raw material for the production of biodegradable is a very convenient way to reduce the production costs of this biofuels.

From a chemical point of view, the high concentration of FFA that contains these raw materials (residues or alternative culture) leading to the formation of soaps during the final phase of transesterification can easily be overcome by performing a pre-esterification reaction.
This treatment allows lowering of the raw material content below the limit required by the biodiesel standard, while also avoiding the formation of soaps during the transesterification phase. FFA fragmentation is also beneficial in increasing final biodiesel productivity as it produces methyl esters.
The cooking oil (WCO) at first sight does not seem to represent a raw material of good potential for the production of biodiesel due to its properties that hardly match the required standards. But it has been proven that it is possible to use this kind of nutrient from its use in blends with other oils characterized by lower viscosity.
The authors have successfully deacidified WCO and then also receiving an increase in the reaction rate. t should be noted that in Albania the only low cost alternative and the substantial amount of raw material is considered only WCO because we do not have a developed industry of edible or non-edible oil production. The cost of importing edible or non-edible oil is very high and WCO remains the best alternative to Biodiesel production in Albania.

REFERENCES

A. S. Ramadhas, S. Jayaraj, and C. Muraleedharan, (2004) *"Use of vegetable oils as I.C. engine fuels—A review," Renew. Energy, vol. 29, no. 5, pp. 727–742.*

Alaba, P.A., Sani, Y.M., Daud, W.M.A.W(2016). *Efficient biodiesel production via solid superacid catalysis: a critical review on recent breakthrough. RSC Adv. 82, 78351-78368.*

Aspen Technology, Inc. (2009). Beginning building and running a procedure model

Carvoli, G., Ragaini, V. & Soave, C. (2008) *Il futuro è dietro l'angolo. La Chimica e l'Industria,* Vol. 1, pp. 38-41

Carlsson, A. S. (2009). *Plant Oils as Feedstock Alternatives to Petroleum - A Short Survey of Potential Oil Crop Platforms. Biochimie,* Vol. 91, (June 2009), pp. 665–670, ISSN 0300-9084

Curto, G. & Lazzeri, L. (2006). *Brassicacee, un Baluardo Sotterraneo Contro i Nematodi. Agricoltura,* Vol. 34, No. 5, (May 2006), pp.110-112

del Pilar Rodriguez, M., Brzezinski, R., Faucheux, N., Heitz, M., (2016.) *Enzymatic transesterification of lipids from microalgae into biodiesel: a review. AIMS Energy.* 4(6), 817-855.

Demirbas, A. (2009). *Production of biodiesel fuels from linseed oil using methanol and ethanol in non-catalytic SCF conditions. Biomass Bioenergy, 33(1), 113–118.*

G. Knothe, (2005) "Dependence of Biodiesel fuel properties on the structure of fatty acid alkyl esters," Fuel Processng Technology, vol. 10, no. 86, pp. 1059-1070.

K. S. Tyson, (2001) "*Biodiesel: Handling and Use Guidelines," Golden*,

L. Brennan and P. Owende, Feb. (2010) "*Biofuels from microalgae—A review of technologies for production, processing, and extractions of biofuels and co-products," Renew. Sustain. Energy Rev., vol. 14, no. 2, pp. 557–577.*

M. K. Lam, K. T. Lee, and A. R. Mohamed, Jul. (2010)*"Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review," Biotechnol. Adv., vol. 28, no. 4, pp. 500–518*

M. Zabeti, W. M. A. Wan Daud, and M. K. Aroua,(2009) *"Activity of solid catalysts for biodiesel production: A review," Fuel Process. Technol., vol. 90, no. 6, pp. 770–777.*

Morais, S. et al. (2010). *Simulation and life cycle assessment of process design alternatives for biodiesel production from waste vegetable oils. J. Cleaner Prod., 18(3), 1251–1259.*

OECD,(2012). OECD Environmental Outlook to 2050: the Consequences of Inaction.

Palmer, C.E., Warwick, S. & Keller, W. (2001). *Brassicaceae (Cruciferae) Family, Plant Biotechnology, and Phytoremediation. International Journal of Phytoremediation,* Vol. 3, No. 3, pp. 245–287, ISSN: 1549-7879

P. M. Ejikeme et al. (2010), *"Catalysis in Biodiesel Production by Tra9nsesterification Processes-An Insight,"*

E-Journal ofChemistry, vol. 7, no. 4, pp. *1120-1132,* Pirola, C., Bianchi, C.L., Boffito, D.C., Carvoli, G. & Ragaini, V. (2010) *Vegetable oil deacidification by Amberlyst : study of catalyst lifetime and a suitable reactor configuration. Industrial & Engineering Chemistry Research, Vol. 49 (2010)*, pp. 4601- 4606

Romero, E., Barrau, C. & Romero, F. (2009). *Plant Metabolites Derived from Brassica spp. Tissues as Biofumigant to Control Soil Borne Fungi Pathogens. Proceedings of the 7th International Symposium on Chemical and non- Chemical Soil and Substrate Disinfestation*, ISBN 9789066056237, Leuven, Belgium, September 2009

United States Department of Agriculture Foreign Agricultural Service. 2012). Table 19: *World: Palm Oil, Coconut Oil, and Fish Meal Supply and Distribution*. http://www.fas.usda.gov/. Accessed on May 10, 2012

Wolfram, C., Shelef, O. & Gertler, P. J. (2012). *How will energy demand develop in the developing world? Working paper, National Bureau of Economic Research, Massachusetts, U.S. Retrieved 15 May 2013, http://www.nber.org/papers/w17747*.

Yan, S., Dimaggio, C., Mohan, S., et al.(2010.) *Advancements in heterogeneous catalysis for biodiesel synthesis. Top. Catal. 53, 721-736*

Zhang, Y. et al. (2003). *Biodiesel production from waste cooking oil: 1. Process design and technological assessment. Biores. Technol., 89(1), 1–16*.

Zhang, Y. et al. (2003). *Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. Biores. Technol., 90(3), 229–240.*

Zhang, Y., Dube, M.A., McLean, D.D. & Kates, M. (2003). *Biodiesel production from waste cooking oil: 1. Process design and technological assessment. Bioresource Technology*, Vol. 90, pp. 229-240.