

# STATE OF ART OF THE FIRST AND THE SECOND GENERATION OF THE BIODIESEL SYNTHESIS

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**Abstract:** *The imminent decline of fossil fuel resources, on one hand and its high market prices and increased environmental awareness, on the other hand, made the production of alternatives fuels from renewable resources to race more and more importance. Biodiesel is a promising alternative substitute for diesel being environmental friendly due to its renewability, biodegradability and high quality exhaust emission. This paper describes the state of art of the first and second generation biodiesel produced nowadays in the world. It is also discussed different raw materials sources, technological paths of the synthesis, as well as the properties, the quality and the performance of the first and second generation biodiesel.*

**Key words:** *Biomass, Biodiesel, Transesterification, Fischer-Tropsch, Synthesis.*

## 1. Introduction

The intensive and low-efficient use of fossil fuels for supplying humans' energy needs over the past century reduced its reserves considerably, resulting in the prognosis of its exhaustion within the next decades. Climatic changes, as a result of global warming caused by greenhouse gases, mainly carbon dioxide (CO<sub>2</sub>) produced during the burning of fossil fuels, have been causing significant changes in the ecosystems and leading to nearly 150,000 additional deaths every year [11]. A solution to solve these problems is the production of biofuels. As a general conception, biofuels are products that can be used for powering internal combustion engines, being

direct replacements for the liquid fuels used in transport. Obtained from biomass (oleaginous plants, wood, wood waste, organic matter from agriculture etc.) they are renewable and can recycle the CO<sub>2</sub> from their combustion through photosynthetic ways. Nowadays, there are two main synthesis of biodiesel used in the world:

- **First generation of biodiesel** - attained out of lipids and an alcohol converted into biofuels by transesterification processes;

- **Second generation of biodiesel** - produced by gasification of different biological matter (especially wood and wood waste) for the production of synthesis gas or syngas which is further converted in biofuels through Fischer-Tropsch synthesis.

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The objective of this paper is to analyse the stages of producing biodiesel through transesterification and Fischer-Tropsch synthesis and the parameters that influence these processes. It will also be discussed the biodiesel properties, its storage stability, biodegradability and performance in engine emissions.

## 2. First Generation of Biodiesel

According to the American Society of Testing and Materials (ASTM) first generation of biodiesel is technically defined as: a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils, animal fats [11] or used cooking oil [15]. Biodiesel can be used in any mixture with petroleum diesel as it has very similar characteristics, but it has lower exhaust emissions [11], [16]. The most commonly used method to convert oils into biodiesel is the transesterification process, based on a chemical reaction between triglycerides from oils and alcohol in the presence of a catalyst. During transesterification, triglycerides are converted into fatty acid alkyl esters (FAMES) and glycerol, in a multistep synthesis.

### 2.1. Feedstock for First Generation Biodiesel

The use of vegetable oils as alternative fuels has been around for 100 years when Rudolph Diesel first tested peanut oil, in his compression ignition engine. However, the use of vegetable oils directly in diesel engines may cause many problems. First of all, vegetable oils have too high viscosities that cause incomplete combustion and carbon deposition on the injector and the valve seats, causing serious engine fouling [22]. Also, vegetable oils have low volatility and polyunsaturated character. To overcome these problems, vegetable oils can be used as feedstock for biodiesel production. The

most commonly used oils as raw materials for biodiesel production are soybean, especially in United States, rapeseed and sunflower in Europe, while canola, palm and coconut oil are used in Asia. Table 1 shows physical and chemical characteristics of vegetable oils and biodiesel obtained from those vegetable oils, as well as the cetane number and the yield of biodiesel production under different conditions [15].

However, the price of biodiesel is much higher than the price of traditional diesel due to the high prices of edible vegetable oils. 70-95% from the price of biodiesel represents the feedstock cost. For this reason, many researchers are more and more interested to investigate biodiesel synthesis with non edible oils, like waste cooking oils. Leung and Guo [16] compared the transesterification reaction conditions of neat canola oil with used cooking oil. The results showed that for waste cooking oil was needed a higher temperature (333 K), higher molar ratio methanol : oil (7:1) and more catalyst (1.1% NaOH) comparative with edible canola oil (315-318 K, 6:1 methanol : oil and 1% NaOH). But in the same time, the reaction was completed in less time (20 min) in case of waste oil, comparative with canola oil where reaction finished after 60 min. Also, Dias et al. [7] made a comparison of different homogeneous alkali catalysts used for transesterification of virgin and waste oils and showed that transesterification of waste cooking oils could reach high yields of conversion (92%) close to those of virgin oils (97%).

### 2.2. Transesterification Mechanism

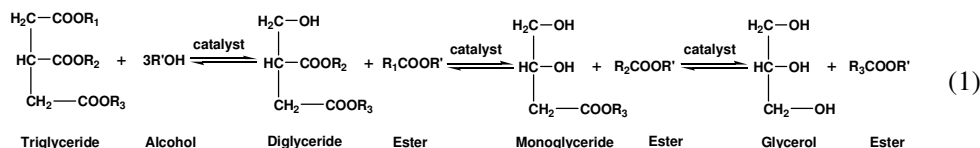
The transesterification mechanism is represented by the general equation (1) and consists of a sequence of three reversible reactions. On the first sequence, triglyceride reacts with the alcohol resulting diglyceride and fatty alkyl ester.

Characteristics of vegetable oils and their corresponding biodiesel Table 1

Vegetable oil and the corresponding biodiesel	Density [g/cm <sup>3</sup> ]	Viscosity [cst, at 40 °C]	Acid value [mg KOH/g]	Heating value [MJ/kg]	Cetane number	Yield [%]
Soybean oil Biodiesel from soybean	0.91 0.885	32.9 4.08	0.2 0.15	39.6 40	52	>95
Rapeseed oil Biodiesel from rapeseed	0.91 0.88	35.1 4.3-5.83	2.92 0.25-0.45	39.7 45	49-50	95-96
Sunflower oil Biodiesel from sunflower	0.92 0.88	32.6 4.9	- 0.24	39.6 45.3	49	97.1
Palm oil Biodiesel from palm	0.92 0.86-0.9	39.6 4.42	0.1 0.08	- 34	62	89.23
Canola oil Biodiesel from canola	- 0.88-0.9	38.2 3.53	0.4 -	- 45	56	80-95

Second step, diglyceride is converted to monoglyceride and in the last step, monoglyceride is converted to glycerol. Fatty alkyl esters are formed also in the second and the last step. Stoichiometrically, the reaction requires 1 mol of a triglyceride and 3 mol of the alcohol which means that is needed a

3:1 molar ratio of alcohol to triglycerides. But because the reactions are reversible, it is necessary a little excess of alcohol to shift the equilibrium towards the formation of alkyl esters. Moreover, a catalyst is needed to improve the reaction rate and yield [10]:



#### • Alcohols used in transesterification reaction

The alcohols that can be used in transesterification are methanol, ethanol, propanol, butanol, isopropanol, amyl alcohols [1], [5], [15], [21], [22]. Among these alcohols, methanol and ethanol are used most frequently and between these two, methanol is the most used due to its cheapest price and physical and chemical advantages. Leung and Wu [15] reported that methanol is more reactive with triglycerides and the catalysts are easily dissolved in it. Also, the fatty acid methyl esters are more volatile than those of the fatty acid ethyl esters. However, methanol is more toxic than ethanol, with a high risk of explosion due to its low boiling point, colourless and odourless. It is also obtained

from non-renewable fossil sources, like natural gas. In contrast, ethanol is less toxic and can be obtained from renewable sources by fermentation.

#### • Catalysts used in transesterification reaction

The catalysts used in transesterification reaction can be divided into three categories, called homogenous catalysts:

- **alkali catalysts** (NaOH, KOH, CH<sub>3</sub>ONa, CH<sub>3</sub>OK) are the most widely used with a higher activity, lower process temperature required and good rate of conversion; however, these catalysts produce soaps, being necessary a purification of biodiesel and glycerol by important amount of water. Also, alkali catalysts are hygroscopic and form water when are dissolved in alcohol,

affecting the yield. They are very sensitive to free fatty acids, being necessary pretreatment steps for raw materials, especially used oils which have a high amount of free fatty acids. Many researchers reduced the free fatty acids content using acid catalyst followed by alkaline transesterification. Leung and Guo [16] tested NaOH, KOH and CH<sub>3</sub>ONa as catalysts for biodiesel synthesis. The lowest amount required was found in case of NaOH (1.1%, comparative with CH<sub>3</sub>ONa 1.3% and KOH 1.5%). However, CH<sub>3</sub>ONa had the highest yield because it didn't form water as side product.

- **acid catalysts** (H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, HCl, sulfonic acid) are used in order to reduce the formation of soaps. Enweremadu and Mbarawa [10] reported that acid catalysts are better than alkali catalysts in case of oils with higher amount of free fatty acids than 1%. At a molar ratio 3.6:1 ethanol : oil, temperature 73 °C and 0.1% H<sub>2</sub>SO<sub>4</sub> the yield of conversion was 66.9%, while at temperature 50 °C and with 0.4% KOH the yield was only 28.9%. However, acid catalysts require higher temperature and alcohol amount; these catalysts are rarely used in industrial scale because are more corrosive and need long time to achieve high yield.

- **enzyme catalysts** (lipases) have become attractive because they avoid soap formation and purification steps, however they are not used in larger scale because of the longer reaction time and higher prices [23], [26-27].

Homogeneous catalysts require neutralization, separation from the final products, high temperature and important amount of alcohol. The biggest issue of homogeneous catalyst is the purification step of biodiesel for removing soaps, glycerine, unreacted catalyst. A highly demand of water and energy are required. Moreover, they cannot be regenerated or reused. Thus, heterogeneous catalysts are becoming more attractive for the researchers because they can be easily separated by filtration, they can be regenerated and have

a less corrosive character, leading to safer, cheaper and more environment friendly operations [13]. Nowadays, for heterogeneous catalysis, the following catalysts are tested: CaO, SrO, ZnO, Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>/KNO<sub>3</sub>, TiO<sub>2</sub>/SO<sub>4</sub><sup>-</sup>, Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>/ZnO. Sharma et al. [22] reported the activity of CaO as heterogeneous catalyst and confirmed that CaO could be used in biodiesel synthesis without deactivation up to 8 times. Nevertheless, the experiments carried out with heterogeneous catalysts showed a limitation in case of yield of conversion, that is why is necessary for the future to establish the optimum conditions for transesterification reaction with this kind of catalysts.

### 2.3. Main Factors Affecting Transesterification Reaction

• **Molar ratio of alcohol to oil** - theoretically the molar ratio alcohol to oil is 3:1, however since the reaction is reversible, excess of alcohol is needed; a minimum molar ratio 6:1 should be used [13], [15], [22], [24].

• **Reaction time** - the yield of conversion increases with the increase of the reaction time between 30 to 60 min, after that the yield remains constant or even decreases due to the backward reaction [15], [24], [26].

• **Reaction temperature** - the optimal temperature range is between 50 °C and 60 °C, after this level the temperature accelerates soap formation [15], [22], [26].

• **Catalyst amount** - determines the reaction time and saponification; the optimum catalyst amount is 0.5-1 wt% [6], [15], [24], [26], otherwise, catalyst excess rises soaps and emulsion formation.

• **Free fatty acids and moisture** - are responsible for the soap formation, consumption and effectiveness of catalysts and because of that two-step esterification process is required for the vegetable oils with more than 2% fatty acids content.

### 3. Second Generation of Biodiesel

Biofuels produced from biomass have the potential to cut CO<sub>2</sub> emission because the plants use CO<sub>2</sub> in photosynthesis [25]. First generation biodiesel can offer some CO<sub>2</sub> benefits and can help to improve domestic energy security [18]. But concerns exist about the sourcing of feedstock, including the impact it may have on biodiversity and land use and competition with food crops. It must not forget that transesterification reaction has important issues unsolved until now: necessity of using large amounts of toxic compounds (CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, NaOH, H<sub>2</sub>SO<sub>4</sub>), pre-treatment, separation and purification steps, obtaining secondary products (glycerol, soaps, polymers) difficult to separate from biodiesel, higher price of biodiesel due to oils. In these circumstances, production of biodiesel by Fischer-Tropsch synthesis is a good alternative for obtaining biofuels, using non-edible lignocellulosic raw materials, many of them considered to be residues and, therefore not competing with food production. Also, their available volume is much higher. Fischer-Tropsch fuel production started in Germany, in 1935, consist in converting synthesis gas (CO and H<sub>2</sub>) into hydrocarbon products by highly exothermic reaction in the presence of a catalyst. Depending on the temperature, it is distinguished high temperature FT (HTFT, 300-350 °C) and low temperature FT (LTFT, 200-240 °C) [9].

#### 3.1. Feedstock for Second Generation Biodiesel

Nowadays, the most economic way to produce liquid fuel is to use natural gas for syngas generation (Gas To Liquid, GTL). Already existing and under construction large-scale industrial FT complexes will increase the worldwide capacity for fossil base FT fuels to about 30 Mt/year in 2010.

In addition to GTL the coal liquefaction (Coal To Liquid, CTL) via FT synthesis is becoming a significant technological alternative for fuel production especially in the USA and China due to their enormous coal reserves. However, CTL and GTL bring along additional CO<sub>2</sub> emissions during the entire fuel production which is a result of the deficient hydrogen content. An alternative to this unsustainable fuel production is the use of biomass as raw material for the syngas production. FT synthesis based on biomass is based on a new technology and therefore it requires progressing research and development. The main products obtained after gasification of biomass at CHP Güssing plant reported by Rauch [20] are: 35-45% H<sub>2</sub>, 19-32% CO, 20-24% CO<sub>2</sub>, 7-10% CH<sub>4</sub>. Minor compounds were ethene (2-3%), nitrogen (0.7-2%) and as toxic compounds: NH<sub>3</sub>, H<sub>2</sub>S, benzene, organic sulphide, particulate matter. The process occurred at temperatures of 800-1000 °C in a particular reactor, called gasifier, where raw materials reacted with steam as gasifying agent in order to gain a nearly nitrogen free product gas. As gasifying agent it can also be used air, O<sub>2</sub>, H<sub>2</sub> or CO<sub>2</sub>.

#### 3.2. Fischer-Tropsch Mechanism

FTS is a catalytic process that converts synthesis gas (CO and H<sub>2</sub>) into a mixture of hydrocarbons (synthetic fuel). The FTS consists on carbon monoxide hydrogenation and is expressed as follows [3], [8]:



There are also other reactions taking place in the FT reactor, but the detailed mechanism of the reactions is not well known. Several possible reactions are listed in Table 2 [14]. These reactions determine obtaining of desirable (paraffins, olefins and alcohols) and undesired products (aldehydes, ketones, acids, esters, carbon etc.).

Table 2  
Reactions occurring in FT reactor

Reaction	$\Delta H_{300\text{ K}}$ [kJ/mol]
$\text{CO} + 2\text{H}_2 \rightarrow -\text{CH}_2- + \text{H}_2\text{O}$	-165.0
$2\text{CO} + \text{H}_2 \rightarrow -\text{CH}_2- + \text{CO}_2$	-204.7
$\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$	-39.8
$3\text{CO} + \text{H}_2 \rightarrow -\text{CH}_2- + 2\text{CO}_2$	-244.5
$\text{CO}_2 + 3\text{H}_2 \rightarrow -\text{CH}_2- + 2\text{H}_2\text{O}$	-125.2

Because these reactions are highly exothermic, cooling of the reactor is very important to secure stable reaction conditions. The total heat of reaction corresponds to 25% of the heat of combustion of synthesis gas [8], leading to a limitation on the maximum efficiency of FT process.

#### • Catalysts used in Fischer-Tropsch synthesis

Different supported and unsupported catalysts such as Fe, Co, Ni, Ru and Rh have been used in mainly three different reactions systems such as fixed-bed, slurry and bubbling fluid bed with an aim to improve syngas (e.g.,  $\text{CO} + \text{H}_2$ ) conversion to the liquid fuels [3]. Ruthenium is the most active catalyst but is very expensive and quantitatively limited. Nickel is also very active but produces a high quantity of  $\text{CH}_4$  and volatile carbonyls.

The most used catalysts in industrial scale are iron and cobalt. Iron catalyst is attractive because of its lowest price, high selectivity and activity, being used with metal promoters, especially alkali metal (Na, K, Ba, Ca), also metal oxides ( $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ). Moreover, iron catalyst has high reactivity for water-gas shift (WGS) reaction (eq. 3):



However, iron catalyst deactivates faster due to its possible oxidation and coke deposition on its surface.

Cobalt catalyst is commonly used at low temperature because at higher temperature

excess of  $\text{CH}_4$  is formed. Cobalt catalysts provide best compromise between reduced costs, high CO conversion, but in the same time, in comparison with iron catalyst has a lower WGS reactivity.

In order to improve the catalytic performance, current researches consist in investigation of bimetallic catalysts containing Fe, Co, Ni and Ru. Das et al. [23] reported that bimetallic catalysts are more active towards CO conversion and improve selectivity for olefins and heavier hydrocarbons, as compared to single metal catalysts. It was investigated the hydrogenation of CO over pure Fe, Co, Ni and bimetallic Fe-CO, Co-Ni, Ni-Fe catalysts supported on  $\text{SiO}_2$ . The results showed that all bimetallic catalysts exhibited higher activities for CO conversion and higher selectivity for heavier hydrocarbons.

#### 3.3. Main Factors Affecting Fischer-Tropsch Synthesis

The Fischer-Tropsch process is preferentially conducted at 473-573 K and at 1.01-6.06 MPa for high liquid product selectivity [22]; however, many factors are involved in the Fischer-Tropsch process, including the catalytic material and its support, their synthesis procedure, choice of reactor, and process conditions (e.g., syngas composition, the residence time of the feed in the reactor, reactor pressure and temperature).

• **Temperature** - increase of the temperature determines the selectivity to move towards lower carbon number products ( $\text{CH}_4$ ) and the probability of chain growth decreases.

• **Feed gas composition** - for the cobalt catalyst a  $\text{H}_2/\text{CO}$  usage ratio of about 2.15 is necessary, while when an iron based catalyst is used, the water-gas shift reaction changes the overall ratio; dependent on the temperature, the  $\text{H}_2/\text{CO}$  usage ratio lies at an iron based catalyst between 1.05 and 1.7 [9].

• **Water effect** - Water is a primary oxygen-containing product in the FTS as oxygen atoms in CO are predominantly removed. The water may affect the syngas conversion, hydrocarbon selectivity, FT product distribution and catalyst longevity due to its influence on the degree of syngas adsorption on the catalyst, chain initiation, chain growth, hydrogenation to paraffins and dehydrogenation to olefins [3].

#### 4. Quality Control of First and Second Generation Biodiesel

For commercial fuel, biodiesel synthesized must be analyzed in order to ensure it meets international standards. The most commonly used standards are ASTM D 6751 and EN 14214 [6]. Generally, biodiesel standards identify the parameters that pure biodiesel must meet before being used as a pure fuel or being blended with distillate fuels. Biodiesel is safe to store and the properties of biodiesel should be conform to respective standards after it has been stored for a long time. Table 3 shows the limits for biodiesel parameters conforming to the international standards.

Table 3  
*Specifications for the quality of biodiesel*

Parameter	Unit	Limits	
		ASTM D6751	EN 14214
Flash point	°C	130 min	101 min
Viscosity at 40 °C	mm <sup>2</sup> /s	1.9-6.0	3.5-5.0
Cetane number	-	47 min	51 min
Carbon residue	% [m/m]	0.06 max	0.3 max
Density	kg/m <sup>3</sup>	-	860-900
Sulphur content	ppm	0.0015 max	-
Water and sediment	%vol	0.05 max	-

Phan et al. [19] analyzed biodiesel and its blends with diesel by their physical properties. Biodiesel was obtained by alkali-catalyzed transesterification of waste cooking oils. The results showed that most of the physical properties of the biodiesel were within EN 14214 standards: density (at 15 °C) - 880 kg/m<sup>3</sup>, viscosity (at 40 °C) - 4.89 mm<sup>2</sup>/s, flash point - 130 °C, acid value - 0.43 mg KOH/g, water content - in trace. However, the carbon residue was much higher in the biodiesel than in diesel. The carbon residue was 4 wt% for biodiesel and only 0.05 % for diesel. The formation of a much higher amount of residue could be explained by the polymerisation of unsaturated alkyl chains and the degradation of glycerides and free fatty acid remained in the biodiesel at a high temperature. Mixing biodiesel with traditional diesel decreased significantly the carbon deposits at a percentage of biodiesel in the blends below 50 wt%.

Another main criterion for the quality of biodiesel is the storage stability. Vegetable oil derivatives and paraffines tend to deteriorate because of the oxidation and hydrolytic reactions. Their degree of unsaturation makes them susceptible to thermal and oxidative polymerization, leading to the formation of insoluble products that cause problems within the fuel system, especially in the injection pump [17].

Bondioli et al [2] studied the storage stability of eleven different biodiesel samples, prepared from different feedstock and using different synthesis technologies. The samples were stored in 200 L drums and periodically monitored during the complete storage by analysis of fifteen different properties. The results showed that several properties did not show significant changes during storage, while others like viscosity, peroxide value showed changes related to the nature of starting product. Also it was made a

parallel test carried out in simulated wrong storage conditions. The test lead to strong changes in biodiesel composition and can be used as a guide for devising biodiesel production set-up, storage and distribution chain.

### 5. Performance of Biodiesel in Engine Emissions

Comparative with petroleum diesel, biodiesel has better properties, such as renewability [1], [6], [10], [26], non-toxicity [15], [16], lower sulphur and aromatics content [12], [15], [16], higher combustion efficiency [6], [22]. Also, biodiesel is biodegradable in freshwater, as well as soil. 90-98% of biodiesel can be mineralized in 21-28 days under aerobic or anaerobic conditions [12], [17]. Sharma et al. [7] reported the degradation of more than 98% of biodiesel after 28 days, comparative with 50% diesel fuel and 56% gasoline. Moreover, biodiesel had reduced exhaust emissions, like CO, CO<sub>2</sub>, SO<sub>2</sub>, particulate matter and unburned hydrocarbons. Only oxides of nitrogen (NO<sub>x</sub>) were reported to increase due to oxygen content in the biodiesel. The emission impact of 20 vol% for soybean based biodiesel added to an average base diesel fuel showed a significant reduction in hydrocarbons (21%), particulate matter (11%), CO (10%) and 2% increase in NO<sub>x</sub> emission.

### 6. Conclusions

In recent years, biodiesel has become more attractive as an alternative fuel for diesel engines because of its environmental benefits and the fact that it is made from renewable resources.

Both methods for producing biodiesel - transesterification reaction for the first generation of biodiesel and Fischer-Tropsch synthesis for the second generation of biodiesel - can provide high qualitative

biodiesel. For this reason, further research and developments must be done so that these methods could play a more important role within the high competitive fuel industry.

In case of transesterification reaction, future developments are based on testing new solid heterogeneous catalysts as ZnO, MgO, SrO, Al<sub>2</sub>O<sub>3</sub>/KI, Al<sub>2</sub>O<sub>3</sub>/KNO<sub>3</sub>, ZrO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>/ZnO, in order to overcome disadvantages of use of homogeneous catalysts and to reduce the cost of biodiesel production by operating in continuous processes.

For Fisher-Tropsch synthesis, new approaches consist in:

- improving the process using biomass as feedstock for syngas, in order to replace natural gas or charcoal;
- new technologies for syngas purification, using bioscrubbers, membranes, sludge or different catalysts based on zeolites;
- using new types of catalysts for syngas conversion to hydrocarbons: metallic and bimetallic catalysts (Fe, Co, Ni, Ru, Fe-Ni, Co-Ni) supported by SiO<sub>2</sub>, TiO<sub>2</sub>, MnO, of different zeolites (HZSM5, SBA-15, MCM-41).

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### References

1. Escobar, J.C, Venturini, O.J., Castillo, E.F.: *Biofuels: Environment, Technology and Food Security*. In: *Renewable and Sustainable Energy Reviews* **13** (2009), p. 1275-1287.
2. Leung, D., Wu, X.: *A Review on Biodiesel Production Using Catalyzed Transesterification*. In: *Appl. En.* (2009), p. 1083-1095.



3. Leung, D.Y.C., Guo, Y.: *Transesterification of Neat and Used Frying Oil: Optimization for Biodiesel Production*. In: *Fuel Processing Technology* **87** (2006), p. 883-890.
4. Sharma, Y.C., Singh, B., Upadhyay, S.N.: *Advancements in Development and Characterize of Biodiesel: A Review*. In: *Fuel* **87** (2008), p. 2355-2373.
5. Dias, J.M., Alvim-Ferraz, M.C.M., Almeida, M.F.: *Comparison of the Performance of Different Homogeneous Alkali Catalysts during Transesterification of Waste and Virgin Oils and Evaluation of Biodiesel Quality*. In: *Fuel* **87** (2008), p. 3572-3578.
6. Enweremadu, C.C., Mbarawa, M.M.: *Technical Aspects of Production and Analysis of Biodiesel from Used Cooking Oil - A Review*. In: *Renewable and Sustain. Energy Reviews* **13** (2009), p. 2205-2224.
7. Robles-Medina, A., González-Moreno, P.A.: *Biocatalysis: Towards ever Greener Biodiesel Production*. In: *Biotech. Advan.* **27** (2009), p. 398-408.
8. Demirbas, A.: *Comparison of Transesterification Methods for Production of Biodiesel from Vegetable Oils and Fats*. In: *Energy Conversion and Management* **49** (2008), p. 125-130.
9. Asakuma, Y.: *Theoretical Study of the Transesterification of Triglycerides to Biodiesel Fuel*. In: *Fuel* **88** (2009), p. 786-791.
10. Xiangmei, M.: *Biodiesel Production from Waste Cooking Oil Via Alkali Catalyst and Its Engine Test*. In: *Fuel Process in Tech.* **9** (2008), p. 851-857.
11. Sinha, S.: *Biodiesel Development from Rice Bran Oil: Transesterification Process Optimization and Fuel Characterization*. In: *Energy Conv. and Management* **49** (2008), p. 1248-1257.
12. Shay, E.G.: *Diesel Fuel from Vegetable Oil: Status and Opportunities*. In: *Biomass Bio-energy* **4** (1993) No. 4, p. 227-42.
13. Zabeti, M.: *Activity of Solid Catalysts for Biodiesel Production: A Review*. In: *Fuel Processing Technology* **90** (2009), p. 770-777.
14. Georgogianni, K.G.: *Transesterification of Rapeseed Oil for the Production of Biodiesel Using Homogeneous and Heterogeneous Catalysis*. In: *Fuel Processing Technology* **90** (2009), p. 1016-1022.
15. Demirbas, A.: *Progress and Recent Trends in Biodiesel Fuels*. In: *Energy Conversion and Management* **50** (2009), p. 14-34.
16. Stevens, C.V., Verhe, R.: *Renewable Bioresources Scope and Modification for Nonfood Application*. In: England. John Wiley and Sons Ltd., 2004.
17. Naik, S.N.: *Production of First and Second Generation Biofuels: A Comprehensive Review*. In: *Renewable and Sustainable Energy Reviews* (2009), p. 578-597.
18. Dry, M.E.: *The Fischer-Tropsch Process: 1950-2000*. In: *Catalysis Today* **71** (2002), p. 227-241.
19. Rauch, R.: *Results of the Iron Based FT Catalyst at the Biomass CHP Güssing*. Institute of Chemical Engineering, Technical University of Vienna, (2009), p. 4-17.
20. Kim, Y.: *A Simulation Study on Gas-To-Liquid (Natural Gas to Fischer-Tropsch Synthetic Fuel) Process Optimization*. In: *Chemical Engineering Journal* **155** (2009), p. 427-432.
21. Dry, M.E.: *Chemical Concepts Used for Engineering Purposes*. In: *Stud. Surf. Sci. Catal.* **152** (2004), p. 196-257.
22. Dalai, A.K., Davis. B.H.: *Fischer-Tropsch Synthesis: A Review of Water Effects on the Performances of Unsupported and Supported Co*

- Catalysts*. In: *Applied Catalysis A: General* **348** (2008), p. 1-15.
23. Das, P.C., Pradhan, N.C., Dalai, A.K., Bakhshi, N.N: *Carbon Monoxide Hydrogenation over Various Titania-Supported Ru-Ni Bimetallic Catalysts*. In: *Fuel Processing Technology* **85** (2004), p. 1487-1501.
24. Phan, A., Phan, T.M.: *Biodiesel Production from Waste Cooking Oils*. In: *Fuel* **87** (2008), p. 3490-3496.
25. Meher, L.C., Vidya Sagar, D., Naik, S.N.: *Technical Aspects of Biodiesel Production by Transesterification - A Review*. In: *Renewable and Sustainable Energy Reviews* **10** (2006), p. 248-268.
26. Bondioli, P., Gasparoli, A., Bella, L.D., Silvia, T.: *Evaluation of Biodiesel Storage Stability Using Reference Methods*. In: *European Journal of Lipid Science and Technology* **104** (2002), p. 777-784.
27. Ferella, F.: *Optimization of the Transesterification Reaction in Biodiesel Production*. In: *Fuel* **89** (2010), p. 36-42.