
DIFERENCES BETWEEN BIODIESEL PRODUCTION FROM VEGETABLE OILS AND WASTE COOKING OILS

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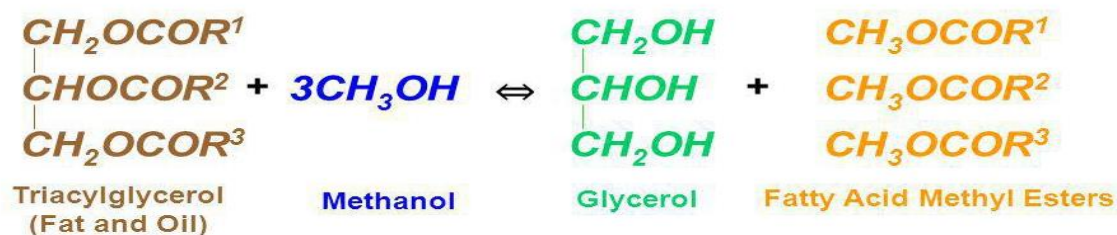
Abstract: Biodiesel has become a subject which increasingly attracts worldwide attention because of its environmental benefits, biodegradability and renewability. Negative environmental consequences of fossil fuels and concerns about petroleum supplies have spurred the search for renewable transportation biofuels. To be a viable alternative, a biofuel should provide a net energy gain, have environmental benefits, be economically competitive, and be producible in large quantities without reducing food supplies. We use these criteria to evaluate, through life-cycle accounting, ethanol from corn grain and biodiesel from soybeans. Ethanol yields 25% more energy than the energy invested in its production, whereas biodiesel yields 93% more. Compared with ethanol, biodiesel releases just 1.0%, 8.3%, and 13% of the agricultural nitrogen, phosphorus, and pesticide pollutants, respectively, per net energy gain. Relative to the fossil fuels they displace, greenhouse gas emissions are reduced 12% by the production and combustion of ethanol and 41% by biodiesel. Biodiesel also releases less air pollutants per net energy gain than ethanol. These advantages of biodiesel over ethanol come from lower agricultural inputs and more efficient conversion of feedstocks to fuel. Neither biofuel can replace much petroleum without impacting food supplies. Even dedicating all U.S. corn and soybean production to biofuels would meet only 12% of gasoline demand and 6% of diesel demand. Until recent increases in petroleum prices, high production costs made biofuels unprofitable without subsidies. Biodiesel provides sufficient environmental advantages to merit subsidy. Transportation biofuels such as synfuel hydrocarbons or cellulosic ethanol, if produced from low-input biomass grown on agriculturally marginal land or from waste biomass, could provide much greater supplies and environmental benefits than food-based biofuels. Biodiesel production typically involves the transesterification of a triglyceride feedstock with methanol or other short-chain alcohol. This paper presents a study of transesterification of various vegetable oils, sunflower, soybean, olive, and waste cooking oils, with the alkaline catalyst. Transesterification reaction plays an important role in converting vegetable oil or used oil into biodiesel. Reaction process may result in low yield, due to the conversion stage between oil and methanol takes place is not perfect and can lead to low-quality of biodiesel. In the transesterification reaction; mass of catalysts, mass of methanol, FFA value, reaction temperature, reaction time, and stirring speed is a major factor determining the quality of biodiesel produced. Reactions were carried out at 65°C temperature gives lower yield of methyl ester. Using the stirrer speed is too high will cause the saponification reaction which reduce the yield generated. Use stirring speed is too high will cause the saponification reaction which will reduce the yield generated. The results of these three variables biodiesel, has met SNI the standard and ASTM D 6751 for testing density, viscosity, cetane index, and flash point.

Keywords: biodiesel, transesterification, alkali catalyzed, vegetable oil, waste cooking oil.

1. INTRODUCTION

In recent years, the need for energy resources has increased with the increase of human population. Due to the depletion of world petroleum reserves and increasing environmental concerns, the interest in using renewable energy, hydroelectricity, or nuclear energy as alternative sources for petroleum-based fuels has remarkably risen (Mori, S (2009) pp 67-72). Furthermore, biodiesel is considered as one important renewable fuel (Banerjee, A. and R.Chakraborty (2009) pp 490-497). Biodiesel is a mixture of methylesters with long chain fatty acids and made from vegetable oil, animal fats, or even waste vegetable oil (WVO). Biodiesel as fatty acid methyl esters (FAMES) has many advantages such as biodegradability and non-toxicity (Leung, D.Y.C., X. Wu and M.K.H (2010)). Biodiesel also has a favorable combustion-emission profile, producing much less carbon monoxide, sulfur oxides, nitrogen hydride, particulate matter, and un burned hydrocarbons compared to the petroleum-base diesel (Zheng, S (2006) pp 267-272). Therefore, it is beneficial to reduce air pollution and minimize the emission of greenhouse gas

by using biodiesel. These properties make biodiesel a good alternative fuel to substitute the petroleum-based diesel (Patil, P.D. and S. Deng (2016) pp 1302-1306). It is believed that large-scale production of biodiesel from edible oil may bring about global imbalance in the food supply, thus increasing the prices of edible oils. Since more than 95% of the current biodiesel is made from edible oils, many problems have been arisen accordingly. Hence, the accessible utilization of WVO may be a feasible way to decrease the use of edible oils. WVO is relatively cheap and considered as a potential feedstock for biodiesel production. In addition, the improper disposal of WVO frequently causes the environmental problems. However, the use of the WVO probably leads to more complex procedure and worse fuel properties in comparison with the biodiesel produced from virgin vegetable oil (VVO) because its high content of free fatty acids (FFAs). For example, alkali catalysts are generally preferred in the conventional biodiesel industry because of their high transesterification efficiency. However, the alkali catalyst would be consumed by the FFAs to form the emulsions that make the subsequent separation process more difficult. Thus the significant saponification phenomenon results in the low biodiesel yield when the feedstock contains high FFA amount. For feedstocks with acid value higher than 2 mg KOH g⁻¹, a pre-treatment step is recommended to esterify the FFAs to generate esters (Felizardo, P., M.J.N. Correia, I. Paposo, J.F. Mendes, R. Berkemeier and J.M. Bordado (2006) pp 497-484). Therefore, WVO are usually converted into biodiesel via an esterification reaction as Eq. 2 and followed by a transesterification reaction as Eq. 1 to benefit the biodiesel yield.



The experimental conditions in the two-step procedure (esterification and transesterification reactions) includes the molar ratio of methanol to WVO (nM/nO), the reaction time (min), the stirred speed (ω , rpm), the reaction temperature (T, °C), and the catalyst dosage based on the oil weight (Wcat, wt%). Although some studies have been conducted on synthesizing the WVO biodiesel, the nature of the WVO would remarkably depend on the feedstock source. Therefore, the detailed production procedure and fuel properties using the WVO as the biodiesel feedstock in Tirana still need to be investigated. This study presents a process to convert the WVO, which was the waste collected from a restaurant in Tirana, into biodiesel via a two-step process. Moreover, the fuel properties of the WVO and VVO biodiesels including acid value, cold filter plugging point (CFPP), density, ester content, iodine value (IV), kinematic viscosity (KV), and oxidation stability were determined and compared with the biodiesel specifications of CNS 15072 in Tirana. Fuels with low CFPP values exhibit beneficial low-temperature flow properties for vehicle engines in cold-weather climates (Moser, B.R (2008) pp 4301-4306). A high IV value has been linked to poor oxidation stability, resulting in the formation of various degradation products, which can negatively affect engine operability by forming deposits on engine nozzles, piston rings, and piston-ring grooves. Note that the lower KV is the primary reason why biodiesel should be used as an alternative fuel instead of neat vegetable oils or animal fats. A fuel with a high KV can lead to undesired consequences such as engine deposits. The KV of biodiesel is approximately one order of magnitude lower than that of the parent oil or fat, leading to better atomization of the fuel in the combustion chamber of the engine. The storage of biodiesel over extended periods may lead to the oxidative degradation of the FAMES that can compromise fuel quality. The oxidation stability of biodiesel depends on the FAME composition and the quantity of natural and synthesized antioxidants in the finished fuel. Oxidation can lead to the formation of corrosive acids and deposits that may cause the increasing wear in engine fuel pumps. The oxidative instability is a major barrier to increase the acceptance of biodiesel by engine and fuel injection equipment manufacturers.

2. MATERIAL AND METHODS OF WORK

Raw materials

The biodiesel production comes mostly from oils extracted oilseed plants especially sunflower, soy, rapeseed and animal fats. However, any material that contains triglycerides can be used for the biodiesel production. "In addition to the oil or fat is needed an alcohol and catalyst to convert oils and fats in alkyl esters". (Arbeláez & Rivera, 2007. pp7)

Alcohol

"Primary and secondary alcohols with string of 1-8 carbons are used for the biodiesel production, among the alcohols that can be used in this process are: methanol, ethanol" (Cujia & Bula, 2010. pp 106), propanol y butanol. "When are used alcohols such as ethanol is more complicated the recovery of pure alcohol in the process because the azeotrope that forms with water"(Cheng et al. 2008. pp 4) and the performance of ethyl esters is less compared to the methyl esters due methanol has a lower molecular weight (32.04 g/mole) compared to ethanol (46.07 g/mole)."On the other hand if you use methanol, not would contribute to environmental issues and sustainability, biodiesel would not be completely bio, by having a fossil component provided by the alcohol, because methanol is made from natural gas, which is fossil" "(Cheng et al. 2008. pp 4).To use methanol or ethanol is needed a mechanical agitation to encourage the transfer of mass"(Arbeláez & Rivera, 2007. Pp 10)."In the course of the reaction form emulsions, using methanol is easy and quickly dissolved, forming a glycerol-rich bottom layer and a higher layer in methyl esters, while using ethanol these emulsions are more stable making the process of separation and purification of ethyl esters more difficult"(Arbeláez & Rivera, 2007. pp 10).

Is preferred to use methanol in the biodiesel production because of their low viscosity (0.59 m * Pa * s at 20 °C), because using alcohols such as ethanol with high viscosity (1,074 m * Pa * s at 20 °C), the biodiesel viscosity increases and as a result a "fuel of high viscosity not will be pulverized properly by injection systems that have diesel engines. Also increase the opacity of fumes which limits their application in automotive engines"(Benjumea et al. 2007. pp 149). In the reaction performance is feasible to reach "higher conversions with methanol, ethanol using the process is more complex, expensive, requires a higher consumption of energy and time"(EREN. 2003.pp 38). "We found that it requires less reaction time when using methanol rather than ethanol, either in acid or alkaline catalysis, reaching high yields"(Giron et al. 2009.pp 18). With the above, the methanol is selected to be used in the biodiesel production due to its lower cost, better performance and less time and energy during the reaction.

Catalysts

Homogeneous, heterogeneous or enzyme catalysts are used in the biodiesel production. Homogeneous catalysts are soluble in the middle of reaction, i.e. they are in a single phase either liquid or gaseous. "One of the advantages of homogeneous catalysis is the high speed of reaction, and moderate temperature and pressure conditions" (EREN. 2003.pp 4). The catalysts can be acids or alkalis, the acid catalysts are effective but require a time interval extremely long and temperatures exceeding 100 °C for its action. "Getting conversions of 99% with a concentration of 1% sulfuric acid in relation to the amount of oil, it takes about 50 hours" "(EREN. 2003.pp 13). We can use this catalytic process when the oils have a high degree of acidity and "harm the action of alkali catalysts with acidity greater than 10 %" (EREN. 2003.pp 39). We can use sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄), among others. When is used "acid catalysts with alcohol excess is that the recovery of glycerin is more difficult as the quantities of alcohol are quite large compared to other type of catalyst" (Arbeláez & Rivera, 2007. pp13). "Using HCl are achieved yields of 61% and with H₂SO₄ we can obtain 80%"(Liu et al. 2006a pp 186), but these "catalysts are more corrosive than alkali catalysts"(Errazu et al. 2005 pp 1305). In comparison with the acidic catalysts, the basic catalysts accelerate the reaction rate, the disadvantage of basic catalysts is that produces soaps due to the high amounts of free fatty acids and water by which we must add the appropriate amount of base to neutralize fatty acids free. The most commonly used are sodium hydroxide (NaOH), potassium hydroxide (KOH) and inappropriate for industrial application (CH₃ONa) sodium methoxide since this is more expensive and "requires total absence of water" (EREN. 2003 pp 40). "The catalysts are dissolved in the reaction mixture alcohol-oil what does that not can be recovered at the end of the transesterification reaction" (Arbeláez & Rivera, 2007. pp13). "By using KOH as a catalyst we can produce potassium fertilizers such as potassium chloride, potassium sulphate and potassium nitrate if the product with phosphoric acid is neutralized" (Arbeláez & Rivera, 2007. pp14). "The maximum yield found with NaOH is 85% at a sodium hydroxide concentration of 1,0%. Adding an excess in the amount of the catalyst, it gives rise to the formation of an emulsion which increases viscosity and leads to the gel formation" "(Cheng et al. 2008. Pp 2210)."With regard to the use of catalyst as (NaOCH₃) sodium methoxide and (KOCH₃) potassium methoxide we can observe high efficiency compared with other alkalicatalysts"(Cheng et al. 2008. pp 2210). The temperature of the transesterification reaction"should not exceed the boiling point of alcohol, because it vaporizes and forms bubbles which limit the reaction in the interfaces alcohol/oil/biodiesel"(Giron et al. 2009.pp 18).

To be used as catalyst NaOH with methanol, has been found that the optimum temperature to achieve high yields was 60 °C, while using KOH to this same temperature not achieved such high yields and higher catalyst concentrations should be used to using NaOH” (Liu et al. 2006b pp 110). "In an alkali catalyzed process is reached high purity and yields in short periods of time ranging between 30 - 60 minutes” (Liu et al. 2006a pp 186). Heterogeneous catalysts are found in two phases and a contact area, "the use of these catalysts simplifies and makes more economical the purification process due the easy separation of the products and reactants. The disadvantage is the difficulty to temperature control for very exothermic reactions, limitations on mass transfer of reactants and products, as well as high mechanical resistance to the catalyst” (Arbeláez & Rivera, 2007. pp12). Among the most common catalysts are the metal oxides (MgO, CaO), acids of Lewis (SnCl₂), etc. For example, by using zinc oxide are obtained yields of 50.7%, when using Al₂O₃ is obtained 57.5% and using CaO yield of 65%”(Rojas & Torres. 2009 pp 15). “These catalysts have limitations on transfer of mass of reactants and products” (Arbeláez & Rivera, 2007. pp12), but they have the advantage that they are not corrosive to the reactor”(Guan et al. 2009 pp 520).The easy separation of the products generates a "simplification of the manufacturing process since the catalyst can be separate from the products of reaction with a simple filtration process”(Lles et al. 2008 pp 63). “Don't generate byproduct of soap by reaction with free fatty acids (AGL)". (Bournay et al. 2005.pp 191). “Using CaO is achieved a yield of 65% and by using MgO a yield of 64%”(Bournay et al. 2005. pp 192). To achieve high yields the reaction must be carried out "to a higher temperature increasing energy costs” (Bournay et al. 2005. pp 191).Reported high reaction times, because the "speed of transesterification reaction with these catalysts is lower in comparison with homogeneous catalysts, due to the mass transfer resistance” (Guan et al. 2009 pp 522). Finally, the lipases being effective for the transesterification reaction can be used between the enzyme catalysts. "This type of catalysis has the advantage of allowing the use of alcohol with high content of water (more than 3%), low temperatures, which is an energy-saving and high degrees of acidity in oils” (EREN. 2003. pp 41).

Waste cooking oil

The waste cooking oil is generated from the fried food, which need large amounts of oil because it requires the full immersion of food at temperatures greater than 180 °C. Accordingly to the high temperatures are generated changes in its chemical and physical composition, as well as in its organoleptic properties which affect both the food and oil quality. Reuse of domestic oil has a high risk to the health of consumers as depending on the type of food subjected to frying, “this absorbs between 5% and 20% of the used oil, which can increase significantly the amount of hazardous compounds that provide degraded oil to food” (EREN. 2003. pp 31).“In an alkali catalyzed process is reached high purity and high yields in short periods of time ranging between 30 - 60 minutes”(Liu et al. 2006 pp 186).

3. MATERIALS

Refined safflower oil, soybean oil, corn oil and Waste cooking sunflower oil , methanol, KOH,

Process Conditions

Pre- heating of oil: 46-50-65°C

Pressure: 1 atmosphere

The mixture of reaction time: 60 min

Transesterification method: the method applied is basic transesterification with KOH as catalyst.

Feedstock: vegetable oil (soybean, corn and sunflower), waste cooking oil .

Transesterification process

The transesterification reaction was carried out using 100% technical grade methanol. The alcohol used was 160ml per liter of vegetable oil. First the alcohol and catalyst mix to form methoxide. Then oil were poured into the reactor vessel in which the reaction was to be carried out. When the temperature was 50°C we put into the vessel methoxide. Transesterification was carried out using a heating plate and a magnetic stirrer.

4. RESULTS AND DISCUSSION

Table 1 summarizes the physic-chemicals indicators of biodiesel producing by different raw materials. And figure one shows us the different appearance of biodiesel.

Table 1: Physic-chemical characteristic of process of transesterification basic and qualitative indicators biodiesel

	Physic-chemical indicators	Biodiesel from WCO	Biodiesel from soya	Biodiesel from sunflower	Biodiesel from corn
1	Density of biodiesel; ($t=24\text{ }^{\circ}\text{C}$)	0.891	0.893	0.874	0.893
2	Density of biodiesel; (d_4^{20}); (gr/cm^3)	0.8925	0.8946	0.876	0.8946
3	Angle of refraction; (n_D^{24})	1.471	1.473	1.458	1.473
4	Flash point; ($^{\circ}\text{C}$)	222 $^{\circ}\text{C}$	238 $^{\circ}\text{C}$	108 $^{\circ}\text{C}$	238 $^{\circ}\text{C}$



Fig 1 : Biodiesel from soya, from wco, from corn and from sunflower oil

5. CONCLUSIONS

Thus Biodiesel was prepared from used vegetable oil, the properties resembled closely to that of commercial Diesel. Hence it can be used as an alternate for diesel. It is relatively economic than diesel and emits less pollutants. It can be used for Vehicular use, Railway usage, as heating oil when blended with other fuel oil in proportion. The experimental work carried out in this project shows that bio-diesel of acceptable quality can be produced on a small scale from a number of low-cost raw materials. However, the search for alternative feed-stocks needs to be continued. More research on the esterification of used vegetable oil is needed, to establish process requirements for high yield and quality, and to find ways of improving its low-temperature properties so that a higher proportion could be included in bio-diesel blends. The ester yields obtained from all the oils used in these trials have been low in comparison with those obtained from refined vegetable oils in existing large-scale plants. Rising of yields has a significant effect on the economics of bio-diesel production. Modern technology is giving very high yields; it needs to be demonstrated that the same can be achieved with other raw materials, whereas more information is required on alternative uses for small amounts of glycerol. On this scale, the investment required to produce pharmaceutical grade glycerine could not be warranted. Uses that require a minimum amount of additional plant investment, but add maximum value to the produce, need to be examined. When a use for the glycerol has been decided a plant for the removal of methanol and any further processing of the glycerol can be specified. In this work, biodiesel was prepared using alkali catalyzed method where the raw material used was waste sunflower oil used for cooking. Biodiesel can also be manufactured using non-edible oil such as pongamia oil as raw material. Further studies can also be carried out by modifying the catalysis. i.e. by using either acid-base or algae as the catalyst. Increased utilization of renewable bio fuels results in significant microeconomic benefits to both the urban and rural sectors, and the balance of trade. The chief advantage of Biodiesel for agriculture is cost minimisation. The expression "oil well on your farm" means in fact a higher local value added. Oil plants renew themselves every year. In any event, the focus is not only on providing emergency supplies but also to a large extent on reducing the pollution load produced by day-to-day operations. The flexibility of Biodiesel plants is also a response to another energy target: the

creation of manageable regional supply systems. The production of biodiesel is relevant for developing countries where the demand of transport fuels is going to increase to a great extent. A high-quality research is promoted in support of a sustainable development of society covering subjects of strategic importance to economic and social development and aiming a greater energy self-sufficiency and security in addition to environmental (decreasing the air pollution from transportation and mitigating greenhouse gas emissions) benefits. The biodiesel fuel production has gained importance for its ability to replace fossil fuels, its environmental benefits and the fact that it is a renewable source of energy. Since the direct usage of vegetable oils as biodiesel is impractical, many processes have been developed to convert them into a suitable form.

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