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A Study on Castor Oil and Its Conversion into Biodiesel by Transesterification Method

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Abstract
Castor (*Ricinus communis*) beans were subjected for the extraction of oil which contained 48% yield. The refined oil contained 0.8% free fatty acid (FFA) and 76.258mg KOH/g saponification value which showed that oil was very suitable for biodiesel production. Biodiesel can be synthesized by transesterification process using acid or base catalyst. The obtained oil and biodiesel was analysed by GC/MS and characterized for its use as fuel in compression ignition motors. From GC/MS, methyl esters content (6:1 molar ratio) was found to be about 88%. The experiments were performed at variable condition such as methanol/oil molar ratio, different temperatures, types and concentration of catalysts used. The best condition for transesterification process was 9:1 methanol/oil molar ratio, 65°C and 1 weight % of KOH. Product analysis was performed by ASTM/EN standards. The obtained biodiesel provided satisfactory values of density and saponification but its viscosity was very high. This situation can be corrected by mixing other methyl esters or mineral diesel for its use as diesel fuel.

Key words: castor oil, biodiesel, viscosity, transesterification

Introduction
Energy use is the most fundamental requirement for human existence for various purposes which can easily be facilitated by solar energy, hydropower, wind energy, fossil fuels and so on, but the major source of energy is fossil fuels (petrol, diesel, kerosene, ATF, etc) which are mostly used in different sectors. Fossil fuels are highly used in industrial, agricultural, automobiles, commercial and household usage. The consumption of fossil fuels has increased to a great extent (Rafaat *et al*. 2008). The total consumption of fossil fuels globally is 10 million tons per day while Nepal consumed fossil fuels up to 11.06% in 2009 which is illustrated in Fig. 1 and this rate is tremendously increasing day by day (WBI 2010). Due to high consumption of fossil fuel, it is expected that human societies will face an extreme possibility of an energy supply collapse in near future. In few decades, the deposition of fossil fuels will be depleted so it will impact on the majority use of this energy source (Prata *et al.* 2010).

Another inconvenient of use of fossil fuel as energy is related with environmental issues. As fossil fuels emit large amount of pollutants which are harmful for the environment as well as living creatures. So, the use of fossil fuels as energy resource is seen as having major environmental impacts. The major impacts of fossil fuels occur due to their consumption which produces different toxic gases like CO_2, SO_x, CO, NO_x as well as some organic compounds such as aldehydes, monocyclic aromatic hydrocarbon (MAHs) and polycyclic aromatic hydrocarbons (PAHs). These harmful compounds damage the green house system of environment, cause global warming, pollution, acid rain and so on. Their toxicity on human health causes cancers, respiration problems, heart disease and so on. Therefore, the relevance of the search for other energy sources is noticeable as they will make possible to mitigate such problems. Hence, it is very necessary to find out other energy sources that can be obtained from biomass (from plant and animal fats). This biomass from both plants and animals absorb solar energy and store in the form of oil which can be used as fuel for

the purpose of moving machines of different types of diesel vehicles. Most of the oils obtained from biomass nowadays can be used as an alternative source of energy as biodiesel (Prata *et al.* 2010).

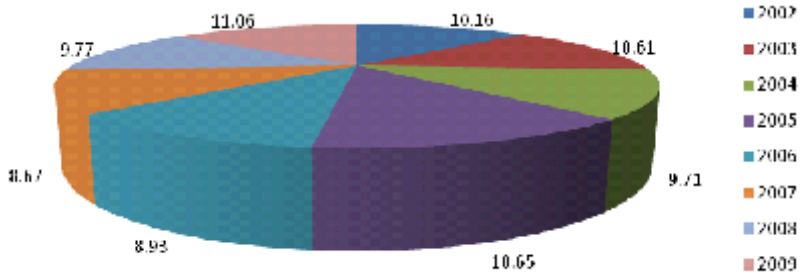
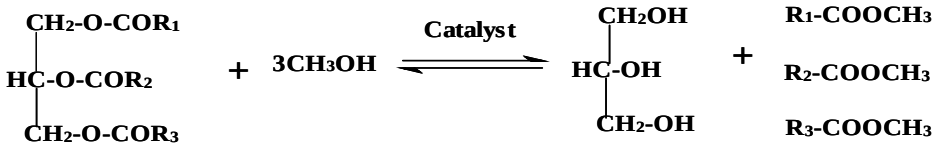


Fig. 1. Fossil fuels energy consumption (% of total) in Nepal

Biodiesel is currently the most important alternative source of energy in European Union as it contributes in reducing the external dependence on fossil fuels. Similarly, it reduces the environmental impacts as it emits substantially lower quantities of most of the regulated pollutants than mineral diesel (Morais *et al*. 2010). So, biodiesel has been gaining worldwide popularity as an alternative energy source due to its high efficiency which can overcome petroleum crisis and increasing cost of petroleum diesel (Ferero 2004).

The natural resources like vegetable oils (edible and non-edible) and animal fats are good sources as alternative fuels for diesel engine but due to high viscosity, acid compositions and free fatty acids of oil create problems in diesel engines. So, various methods such as dilution, microemulsions, pyrolysis, catalytic cracking and transesterification have been considered to overcome the problem associated with direct use of oil. Of these alternatives, transesterification process has been proved to be the best option (Verma *et al.* 2007).

Transesterification is a reaction of an alcohol with an ester to form different types of alcohols and esters in the presence or absence of a catalyst. In the production of biodiesel, vegetable oil is in the form of triglyceride which reacts with a small chain alcohol (methanol, ethanol, propanol and so on) in the presence of homogeneous catalyst such as base (KOH, NaOH, CH_3OK, $(CH_3O)_2Ca$, CaO) or acid (HCl, H_2SO_4, H_3PO_4) or heterogeneous catalyst as zeolites or biocatalyst as enzymes. Hence, the process is also known as alcoholysis, for methanol methanolysis and for ethanol, ethanolysis. The esters that formed in methanolysis are called as fatty acid methyl esters (FAMEs) and esters that formed in ethanolysis are fatty acid ethyl esters (FAEEs) (Roces *et al.* 2011). The reaction of transesterification can be illustrated as given below:



Triglyceride Methanol Glycerol Methyl esters

Biodiesel has very similar physical properties just as fossil diesel fuel and even higher cetane number, which allows it to be used directly as substituted fuel in diesel engine without any modification or can be used as blending agent for diesel fuel (Bello *et al.* 2011).

Though biodiesel has many advantages as compared to petroleum diesel, its high production cost is playing the primary barrier to its commercialization. So, many researchers focused on the utilization of lower cost feedstock such as waste cooking oil, greases, soap stocks, non-edible oil like Castor oil, algae and lower cost catalysts such as dolomite, and other calcium and magnesium ores to produce biodiesel. Glycerol, which is formed as a by-product from transesterification can

be converted to promising commodity chemicals through chemo-selective catalysis such as selective oxidation, hydrogenolysis, catalytic dehydration, pyrolysis and gasification and so on. By these processes, glycerol can be converted to value- added product.

Castor oil obtained from castor beans contain about 45 -60 % of oil which can be used in production of paints, varnishes, lubricants, grease, hydraulic fluids, soaps, pharmaceuticals, cosmetics and so on. It contains 90% ricinoleic acid which is mono-unsaturated, 18- carbons fatty acid. This acid shows unusual character that it has acid group at first carbon, double bond at ninth carbon and a hydroxyl functional group on the twelfth carbon which cause unusually polar. Thus, this hydroxyl group makes the oil and ricinoleic acid highly viscous and valuable as chemical feedstock. Like any other vegetable oil, castor oil can be converted to biodiesel which can yield up to 98 % (Chakrabati *et al.* 2008).

Methodology

Collection of castor beans

The castor fruits collected from Kritipur area were shade dried and separated beans from seed shell. Then they were ground into powdered form by using a simple grinder machine and stored in cool place.

Oil extraction

The castor oil was extracted by using a soxhlet extractor. About 500 ml of hexane was poured in a round bottom flask and 100 g of ground castor beans was packed in a filter paper, placed in the thimble and fixed with a round bottom flask which was connected with a condenser. The fitted apparatus was then heated in a heating mantle to boil the solvent. When the solvent was boiled, the vapour rose through the vertical tube into condenser to the top and the vapour condensed, dripped into the thimble in the centre. The extractor seeped through the pores of the thimble and filled siphon tube where it flowed back down into the round bottom flask (Akpan *et al* .2006). The extraction prolonged to eight hours after which the resulting mixture in the round bottom flask was concentrated in rotator evaporator to recover the solvent from the extracted oil. The weight of the extracted oil was recorded.

The crude oil was refined by degumming, neutralization and bleaching process. In degumming process, the crude oil was treated with hot water to remove gums, hydrates, phosphates and other impurities, then it was neutralised with 0.1N NaOH to remove FFA and soap. Finally it was bleached with activated clay to remove colour, odour, impurities and residual soap.

Transesterification

About 25 ml of oil was kept in three necked round bottom flask and heated to 65 $^{\circ}$ C. Then, calculated amount of methanol and catalyst (KOH or H_2SO_4) were added with stirring system. The experiment prolonged for three hour and then the sample was monitored by running TLC to conform the completion of reaction. After cooling, two layers were separated by separatory funnel. The upper layer was methyl ester (biodiesel) while the lower layer was glycerol. The obtained methyl ester was purified by successive rinse with 2.5% (w/w) sulphuric acid and distilled water. To avoid emulsion during washing process, NaCl solution was used. Then, the washed methyl ester was treated with anhydrous sodium sulphate to remove excess water. It was then filtered and dried by heating at low temperature (60° C) for 30 min.

Product analysis

The oil composition and methyl ester content were assayed by GC/MS (Shimadzu, Q.P.2010, Japan) from Water Engineering and Training Centre, Dillibazaar. The GC/MS used for analysis was provided with a FTD Detector, employing a silica capillary column of 30 m length, 0.32 mm ID, and 0.25 μm film thickness. Heptane was used as solvent, and the carrier gas was helium at a flow rate of 0.96 ml/min. The injector temperature was kept at 280°C; the ion source temperature was 200° C, column oven temperature 40°C and pressure 46.7 kPa.

The obtained oil and biodiesel was analyzed for characterization by ASTM method. The properties like density, specific gravity, methyl content, oil content, saponification value, acid value, FFA, refractive index were determined.

Results and Discussion

Analysis of oil

Castor beans have high yield of oil up to 48%. The gas chromatograph of castor oil has been presented in Fig. 2. The oil showed 28 compounds of them, six were major 9-tetradecenoic acid (myristoleic acid) was a major component of oil consists about 84.69%. The retention time of it was 27.776 minutes. Other fatty acids have been presented in Table 1.

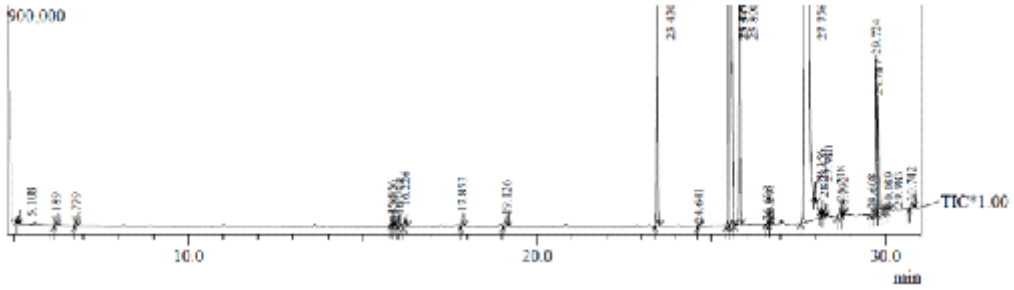


Fig. 2. Gas Chromatograph of castor oil

Table 1. Typical fatty acids in castor oil

S.N.	Fatty acids	Mol. formula	Mol Wg	RT (min)	Area %
1	Palmatic acid	$C_{16}H_{32}O_2$	256	23.43	1.43
2	Linoliec acid	$C_{18}H_{32}O_2$	280	25.5	5.18
3	Stearic acid	$C_{18}H_{36}O_2$	284	25.4	1.97
4	Oleic acid	$C_{18}H_{34}O_2$	282	25.547	4.9
5	Myristeric acid	$C_{14}H_{26}O_2$	226	27.776	84.69
6	Nonanoic acid	$C_9H_{16}O_2$	172	29.787	0.84

Myristoleic acid, which was found to be the major component in this oil, has not yet been reported in any paper so far. Moreover, ricinoleic acid which was reported as a major component of castor oil in many papers was not found in this oil. This variation may be due to change in climate, different variety of seeds or different location.

Properties of oil

The properties of the oil were slightly changed from the reported values. The oil was highly acidic and viscous. The saponification value was lower value than reported value. The GCMS report and saponification value showed that the molecular weight of the oil was extremely high from the expected value 180.33 mg KOH-gsample^{-1} (Akpan *et al.* 2006). The FFA value was 0.8064% while reported value is 3.4% (Jumat *et al*. 2010).

Table 2. Castor oil properties

S.N.	Properties	Crude oil	Refined oil	Reported value
1	Density(kg/m^3) at 15°C	917.3	917.3	961.20
2	Specific gravity	0.92	0.92	0.96
3	Viscosity(cSt)	326.08	282.61	258.01at 40°C
4	Moisture content	1.75%	1.003%	0.2%
5	Oil content	48%	48%	45-60%
6	Acid value (mgKOH-gsample^{-1})	2.629	1.566	1.09
7	Free fatty acid %	1.354	0.8064	3.4
8	Saponification value (mgKOH-gsample^{-1})	79.159	76.258	180.33
9	P_H	4	3.96	6.34
10.	Refractive index	1.479	1.476	1.476-1.479
12.	Colour	yellow	yellow	yellow

Analysis of biodiesel

The experiment for production of biodiesel was done with two types of catalysts such as H_2SO4 as acid catalyst and KOH as base catalyst. Different operations were done with variations such as types and concentration of catalysts, methanol/oil ratio and temperature influence.

The reaction time and agitation rates (high speed) were fixed as common parameters in all experiments.

Types and concentration of catalyst influence

Different concentrations of H_2SO4 and KOH were subjected in the experiment to analyze the influence on methyl esters content.

Table 3. Methyl ester content as function of catalyst type and concentration catalyst.
(Reaction conditions: methanol/oil molar ratio, 9:1; temperature, 65 °C; time, 3hrs)

Type of catalyst	Concentration of catalyst (w/w %)	Methyl Ester content (w/w %)
H_2SO_4	2	6.28
	3	8.29
	4	6.78
KOH	0.5	91.05
	1	92.01
	1.5	87.56

Table 3 showed that the transesterification reaction of castor oil under the study was more favourable with basic catalyst than acidic. Because the oil has low value of FFA so the use of acidic catalyst shows insignificant improvement of the process. The methyl ester content increased from concentration of basic catalyst from 0.5 to 1% (w/w) but slight decrease from 1 to 1.5% (w/w). In general, as the catalyst concentration increased, the conversion of triglyceride also increased (Leung *et al.* 2010). Because an insufficient catalyst concentration results in an incomplete conversion of triglyceride into methyl ester to participate in the production of more soap and so reduction in production of ester (Eevera *et al.* 2009). In acidic catalyst, the production of ester was nearly negligible.

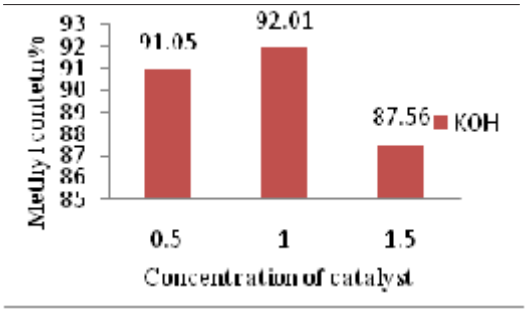


Fig. 3. Concentration of base catalyst influence in the production of biodiesel

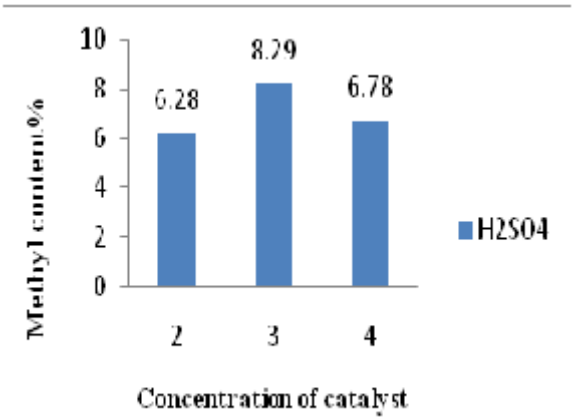


Fig. 4. Concentration of acid catalyst influence in the production of biodiesel

Figures 3 and 4 of methyl ester % vs concentration of catalyst showed the reaction was extremely enhanced with base catalyst compared to acid.

Methanol/Oil molar ratio

The methanol/oil molar ratio is very important parameter for the production of methyl ester both in catalytic and non- catalytic reaction. Normally, transesterification requires 3 moles of alcohol for one mole of triglyceride to form three moles of fatty acid esters and one mole of glycerol (Mathiyazhagan *et al.* 2011). In alkaline catalysed process, the yield of methyl ester increases with an increase in alcohol/oil ratio as the equilibrium shift towards the product (Verma *et al.* 2007). Methanol/ oil molar ratio is also associated with the type of catalyst used. In general acid catalysed process requires high molar ratio than base catalysed process as shown in Table 4.

Table 4. Methanol/Oil molar ratio influence
(Reaction conditions: temperature, 65°C; time, 3hrs)

Methanol/oil ratio (mol:mol)	Catalyst	Methyl Ester content (w/w %)
6:1	H_2SO_4,	3.58
9:1	3 *w/w* %	6.29
12:1		6.21
6:1	KOH,	88.09
9:1	1 *w/w* %	92.01
12:1		90.31

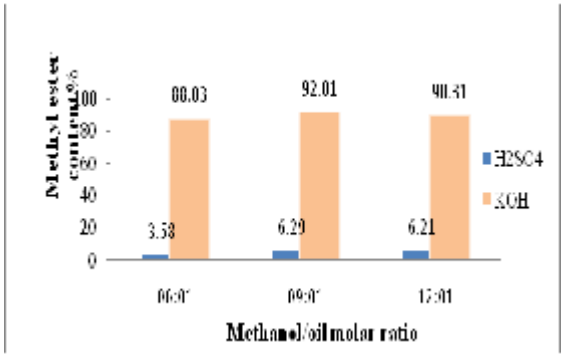


Fig. 5. Molar ratio influence in the production of biodiesel

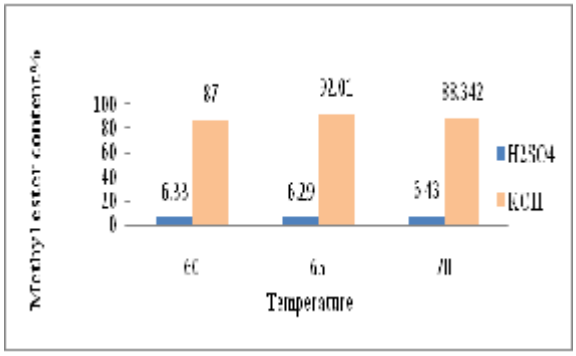


Fig. 6. Temperature influence in the production of biodiesel

Figure 5 and Table 4 showed that when the molar ratio increased from 6:1 to 9:1 in both catalysts, the methyl ester content also increased but on increasing molar ratio 12:1, there was no significant change was shown by acidic catalysis while it slightly decreased in methyl esters content in basic catalysis. Because the higher alcohol molar ratio interfered in the separation of glycerol due to high solubility. Again on excess use of alcohol, it seemed to favour conversion of di- to mono-glyceride but there was also slight recombination of esters and glycerol to mono-glycerides as their concentration kept on increasing on the course of the reaction than in the reaction of lower molar ratio. In basic catalysis, this effect can be seen because the reaction was fast while in acidic catalysis, the effect was no apparently seen due to the low rate of reaction (Encinar *et al*. 2005).

Temperature influence

The transesterification of castor oil with methanol was carried out at 60, 65, 70ºC in order to determine the temperature influence on the methyl ester production.

Table 5. Temperature influence (Reaction conditions: temperature, 65ºC; time, 3hrs)

Temperature (˚C)	Catalyst	Methyl Ester content (w/w %)
60	H_2SO_4,	6.33
65	3 w/w %	6.29
70		6.43
60	KOH,	87.00
65	1 w/w %	92.01
70		88.342

The optimized temperature for transesterification was 65º C (the boiling point of methanol is 64.7^{O}C). Below and above this temperature, the yield of methyl ester was low. Because at lower temperature, the reaction was not completed and at high temperature, methanol vaporizes and burn. So, decomposition of solvent results in ineffective conversion of oil to methyl ester. The higher temperature may also cause deactivation of catalyst so incompletion of reaction might occur.

Product Analysis

Gas chromatogram of biodiesel is given in Fig. 7. The biodiesel consists of 88% methyl ester (6:1) with 6 compounds in Fig. 7.

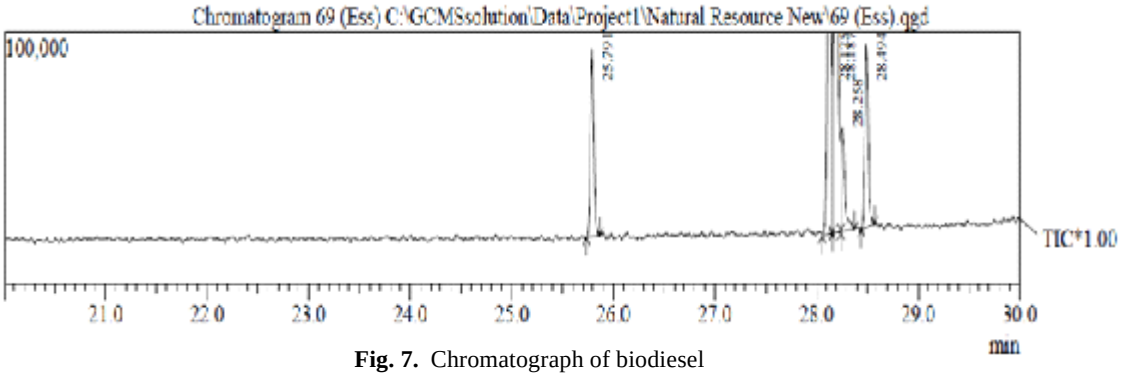


Fig. 7. Chromatograph of biodiesel

Table 6. Composition of methyl ester

S.N	Methyl ester	Molecular formula	Molecular weight	Retention time	Area%
1	Methyl palmitate	$C_{17}H_{34}O_2$	270	9.86	9.86
2	Methyl linoleate	$C_{19}H_{34}O_2$	294	30.25	30.25
3	Methyl octa-9-enoate	$C_{19}H_{34}O_2$	296	32.76	32.76
4	Methyl 9,10 methylenthexadecanoate	$C_{18}H_2O_2$	282	5.38	5.38
5	Methyl stereate	$C_{19}H_{38}O_2$	298	9.78	9.78
6	2 pentanone,4-hydroxy-40 methyl diacetone alcohol	$C_{10}H_{18}O_3$	116	11.97	11.97

Properties of biodiesel

The properties of biodiesel were analyzed according to ASTM Standards presented in Table 7.

Table 7. Properties of biodiesel

S.N.	Properties	Biodiesel	Mineral Diesel	ASTM Std.
1	Methyl ester content %	88 (6:1), 92 (9:1)	-	97
2	Density(kg/m^3) at 15°C	900	850	860-890
3	Specific gravity	0.9	0.85	0.86-0.89
4	Viscosity (cSt) @ 40°C	20.62	3.2	1.9-6.0
5	Moisture content %	0.37	-	0.05
6	Saponification value (mgKOH- gsample^{-1})	88.878	-	-
7	Refractive index	1.461	-	-

Methyl ester content at 6:1 ratio was 88% while for 9:1 ratio it was 92% which are near to ASTM limits. The density and specific gravity were key properties of fuel which directly affect the engine performance. The denser fuel has greater mass which influences in the engine output. The density and specific gravity of the biodiesel found to be within the limits.

Viscosity is another parameter of the fuel which depends on the flow of its liquid. Higher viscosity is a major problem of biodiesel in diesel engines (Akpan *et al.* 2006). The high value of viscosity of fuel causes depositions on engine which effect on its function. Though the viscosity of oil has been decreased up to 93% after conversion to biodiesel but this value is still high as compared to reported value. Thus, the biodiesel cannot be directly used in diesel engine. To minimize the viscosity of fuel, it can be used by blending with other methyl ester or mineral diesel up to 10 to 20%.

Moisture content can cause microbial growth that leads to tank corrosion. The water content is out of limit.

Saponification value shows average molecular weight of a sample. This value slightly increases from the value of oil due to formation of methyl ester.

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