COMPARISON OF BIODIESEL YIELDS FROM WASTE COOKING OIL AND EXTRACTED OILS FROM CASTOR AND SESAME SEED

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ABSTRACT: Petroleum product exhaustion and natural debasement are twin crises through which the world is defied. Waste cooking oil, castor and sesame oil were taken into consideration and their physio-chemical properties were observed. Biodiesel as produced via alkali trans-esterification and monitored by varying types of lye (KOH/NaOH) concentration i.e., 0.5, 1, and 1.5%.The ratio of methanol to oil was from 4:1, 3:1, 2:1 and 1:1with reaction time of 30 minutes and temperature of 60°C. Under optimized conditions maximum biodiesel was produced from waste cooking oil, castor oil with 1% KOH and sesame oil with 1% NaOH. The maximum biodiesel yield calculated for waste cooking oil and sesame oil was 98.78% and 82.19% for castor oil. HPLC was used to confirm the conversion of triglycerides into fatty acids methyl esters. Utilization of low cost feed stocks and further study of Physico-chemical properties of biodiesel will contribute in producing eco-friendly biodiesel for engines.

Key words: Trans-esterification, Biodiesel yield, Fatty acid methyl esters, free fatty acids, Triglycerides.

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INTRODUCTION

In a few decades the crude oil reserves are expected to last therefore it is a dire need to discover alternative source to make biodiesel. As the quantity of petro diesel is decreasing, it is creating an economical imbalance in the world oil prices. Fossil fuels are at a decline phase and cannot fulfill the current demand. Their consumption has harmful effects like global warming and ozone layer depletion (Ramadhas *et al.*, 2004). The yearly exhaustion from claiming diesel may be 934 million tons, for which Canada and United States devour 2.14 and 19.06 respectively. Biodiesel derived from the bio resources are the most promising alternate to the crude fossil fuel and obtained from green sources as well as free of aromatics and sulphur (Shay, 1993). It is biodegradable, non-toxic and it can eliminate toxic gases from the environment. Therefore, biodiesel might become a good alternative for sustainable environmental development as well as used in the transportation sector, almost providing 82% of biodiesel required for EU. Ease in production and environmental credentials such as biodegradability and reduced pollutant emission makes it an attractive alternative of petro-diesel (Cervero *et al.*,

2008). Biodiesel is a synthesis of mono-alkyl esters of long chain unsaturated fats derived from the trans esterification of various oils, for example, Waste cooking oil (WCO),Castor oil (CO), Sesame oil (SO) and oil from coconut, jatropha, karanja, palm, sunflower and blended lake green growth. To the world extent, the sulfur substance of vegetable oil is near zero, high fiery remains point, and safe stockpiling is preferred standpoint of biodiesel. A base catalyzed trans-esterification process is used for the commercial preparation of biodiesel whereas acid catalysis and enzyme trans-esterification is also used (Goering *et al.*, 1982). The state of Pakistan is not as good as any other developing country to meet the crises of renewable energy resources. Therefore Waste vegetable oils, plant based oils and animal fats can be used as an alternate source. In the present research, a comparative study is being conducted on castor, sesame and waste cooking oil to observe maximum biodiesel production capability. The study is being conducted to find out differences between the various renewable resources in terms of biodiesel production by varying NaOH/KOH concentration through the process of base trans-esterification. The result can be specified by the HPLC. This process is economically feasible than the other methods and thus the diesel produced require more washing.

MATERIALS AND METHODS

The biodiesel fuels in principle are acceptable, economically affordable, easily available and synchronize with the environment. Waste cooking oil was collected from a local restaurant in Lahore whereas Castor and sesame seeds were purchased from local market, Castor and Sesame seeds were first washed, sterilized and grounded. After that the oil was extracted by milling and pressing. Physico-chemical Characterization of the Extracted oils was obtained by using standard methods, such as color, odor, pH, density, specific gravity, acid value, Peroxide Value and Saponification value. After that, the oil was processed for biodiesel production. As feedstock cannot be used directly because they have high viscosity, low volatility, poor atomization and incomplete combustion, it is chemically modified before processing for biodiesel. Pyrolysis, micro emulsification and trans-esterification are the three most recognized method for biodiesel production. Chemical trans-esterification is the most simplest and efficient method of production using various vegetable oils. The process was carried out for both types of lye NaOH and KOH under different concentrations and their molar ratios with respect to oil. After that the trans-esterified mixture is poured to a separating funnel and left overnight. Two layers are separated in this procedure, the upper layer is biodiesel and the lower layer is glycerin. After collecting the glycerin, the upper layer was washed several times with distilled water. Biodiesel was recovered, washed, purified and dried by adding magnesium anhydrous sulphate. The effect of various reaction parameters such as types of catalysts, different catalyst concentration and oil to molar ratios at a fixed temperature of 60 °C for 30 minutes at fixed 350 rpm were taken into consideration and the yield of biodiesel was calculated. The formula used for calculation is as follows:

Fatty Acid Methyl Esters (FAME's) (%Y) =Methyl esters produced in g/g of oil used during trans-esterification reaction ×100.

The produced biodiesel was monitored with the help of HPLC analysis. HPLC monitoring of chemical trans-esterification method was carried out by applying definite amount of sample from reaction mixture to a reverse phase C-18 column. Hexane, isopropanol and methanol were used as mobile phase. The detection was performed using UV detector at wavelength of 205 nm. The FAME and TG peaks were observed in HPLC chromatogram.

RESULTS

The results of physio-chemical characteristics of oils (WCO, Castor oil and sesame oil) were calculated for this research (Table 1) which revealed that the density of WCO was 933kg/dm3, for castor oil 976kg/dm3 and sesame oil was 937kg/dm3.Whereas specific gravity for WCO was 0.933, 0.976 for CO, and 0.937 for SO respectively (Table 1). After that, the oil was processed for biodiesel production. The biodiesel yield was observed with two types of lye (NaOH/KOH) and different concentrations of lye. The biodiesel yield of Waste Cooking Oil with lye concentrations of 0.5%, 1%, and 1.5% found was 84.86%, 82.11%, 83.24% with NaOH and 94.44%, 98.78%, 98.30% with KOH respectively. The biodiesel yield with castor oil under 0.5% ,1%,1.5% concentration of lye was 83.87% , 68.67 % ,72.45 % for NaOH and 80.48%,82.19%80.70% for KOH. The sesame oil gave biodiesel yield of 96.97%, 98.78%, 89.13% for NaOH and 94.13%, 96.34%, 91.19% for KOH under 0.5%, 1%, 1.5% concentrations respectively (Table 2 & 3). The produced biodiesel was monitored with the help of HPLC analysis. The result of high performance liquid chromatography revealed that the peaks converted FAME was obtained from 3 to 5 minutes. The peaks obtained from 0 to 1 minutes represented by FFA. The peaks from 1 to 3 minutes denoted by MAG. The peaks from5 to 7 minutes were showed by DAG. The small peaks from 7 to 8 minutes were represented by TAG (Fig-1).

The biodiesel densities were measured by two types and different concentrations of lye [NaOH/KOH]. The densities of biodiesel from Waste Cooking Oil with concentrations of 0.5%, 1%, and 1.5% were found 0.85mg/g, 0.90mg/g, and 0.88mg/g with NaOH and 0.90mg/g,0.85mg/g, 0.88mg/g with KOH respectively. The densities of biodiesel produced from castor oil under 0.5% ,1%,1.5% concentration of lye was 0.95, 0.95mg/g, 0.92mg/g for NaOH and 0.95mg/g, 0.81mg/g, 0.92mg/g for KOH. The sesame oil gave biodiesel yield of 0.87mg/g, 0.88mg/g, 0.89mg/g for NaOH and 0.88mg/g, 0.89mg/g, 0.90mg/g for KOH under 0.5%, 1%, 1.5% concentration respectively.

The biodiesel acid values were measured with two types of lye (NaOH/KOH) and different concentrations of lye. The acid values of biodiesel yielded from Waste Cooking Oil with concentrations of 0.5%, 1%, and 1.5% were found 0.55mg/g, 0.58 mg/g, 0.59 mg/g with NaOH and 0.50 mg/g, 0.53 mg/g and 0.56 mg/g with KOH respectively. The acid value of biodiesel produced from castor oil under 0.5%,1%,1.5% concentration of lye was 0.52g/mg,0.54mg/g, and 0.59mg/g of biodiesel for NaOH and 0.58mg/g, 0.51mg/g, and 0.56mg/g of biodiesel for KOH. The observed acid values for sesame oil based biodiesel were 0.50mg/g, 0.53mg/g and 0.56mg/g for NaOH and 0.55mg/g, 0.52mg/g, and 0.53mg/g for KOH under 0.5%, 1%, 1.5% concentration respectively (Table-4).

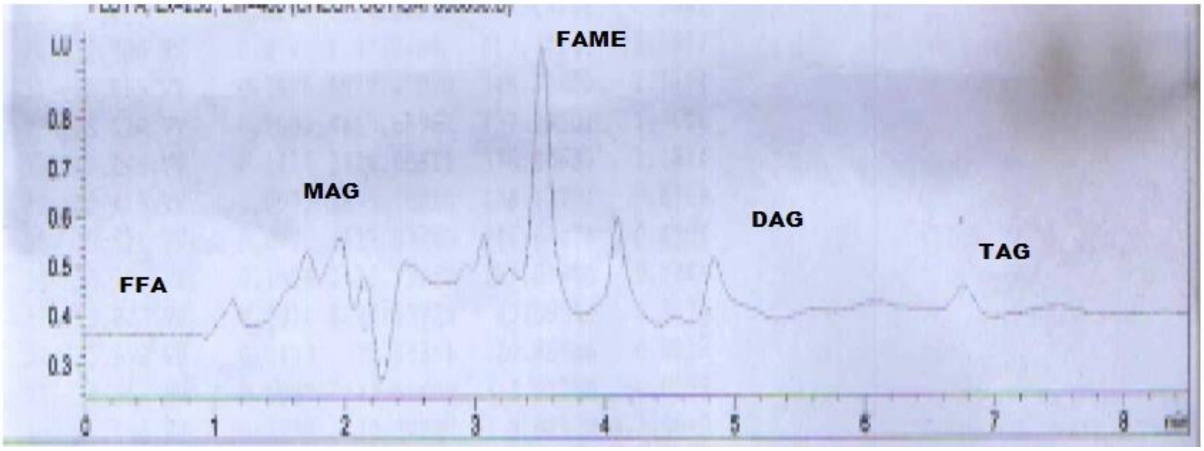

Figure-1: HPLC chromatogram showing peak of FFA conversion into FAME.
FFA: Free fatty acids, MAG: Monoacylglycerol, FAME: Fatty Acid Methyl Esters, DAG: Diacylglycerol, TAG: Triacylglycerol

Table-1: Physical and Chemical characteristics of WCO, CO and SO.

Properties	WCO	CO	SO
Density [Kg/dm^3]	933 ± 0.4	976 ± 0.46	937 ±0.23
Specific gravity	0.933 ± 0.4	0.976 ± 0.46	0.937± 0.23
Acid value [mg/g of oil]	0.52± 0.30	1.29± 0.61	1.4±0.51
Peroxide value	10.0± 0.85	15.6± 2.007	21± 1.13
Saponification value [mg/g of oil]	197.65 ±0.55	176.54 ±0.78	212.51±0.56

Waste Cooking Oil (WCO), Caster oil (CO), Sesame oil (SO)

Table-2: Comparison of Biodiesel Yield (%) at different molar ratios of Methanol to Oil by different feed stocks with NaOH and KOH as Catalysts (0.5%) at 60 ºC for 30 minutes.

Feed Stock	NaOH				KOH			
	4:1	3:1	2:1	1:1	4:1	3:1	2:1	1:1
WVO	69.19 ± 0.907	72.35 ± 0.581	80.75 ± 0.622	84.86 ± 0.89	73.6 ± 0.655	80.79 ± 0.772	85.54 ± 1.117	94.44 ± 2.06
CO	68.8 ± 1.196	76.64 ± 0.643	81.89 ± 0.907	83.87 ± .191	70.35 ± 0.647	77.63 ± 0.89	79.56 ±1.161	80.48 ± 1.845
SO	68.53 ± 1.057	78.65 ± 1.117	83.56 ± 1.496	96.97 ± 0.352	70.54 ± 1.481	75.48 ± 1.102	82.75 ±1.179	94.13 ±0.525

WVO: waste vegetable oil, CO: cooking oil, SO: sesame oil, NaOH: Sodium hydroxide, KOH: Potassium hydroxide.

Table-3: Biodiesel Yield from different feed stocks through base catalyzed trans-esterification.

Feed stock	Catalyst	Catalyst Concentration	Biodiesel Yield (%)
Waste Cooking Oil	NaOH	**0.5 %**	**84.86**
		1%	82.11
		1.5%	83.24
	KOH	0.5 %	94.44
		1%	**98.78**
		1.5%	98.30
Castor Oil	NaOH	0.5 %	**83.87**
		1%	68.67
		1.5%	72.45
	KOH	0.5 %	80.48
		1%	**82.19**

		1.5%	81.70
Sesame Oil	NaOH	0.5 %	96.97
		1%	**98.78**
		1.5%	89.13
	KOH	0.5 %	94.13
		1%	**96.34**
		1.5%	91.19

Table-4: Biodiesel densities and acid values observed under different Lye Concentrations.

Feed Stock	Catalyst	Catalyst Concentration	Density mg/g of biodiesel	Acid Value mg/g of biodiesel
Waste Vegetable Oil	NaOH	0.5 %	0.85	0.55
		1%	0.90	0.58
		1.5%	0.88	0.59
	KOH	0.5 %	0.90	0.50
		1%	0.85	0.53
		1.5%	0.88	0.56
Castor Oil	NaOH	0.5 %	0.95	0.52
		1%	0.95	0.54
		1.5%	0.92	0.59
	KOH	0.5 %	0.95	0.58
		1%	0.81	0.51
		1.5%	0.92	0.56
Sesame Oil	NaOH	0.5 %	0.87	0.50
		1%	0.88	0.53
		1.5%	0.89	0.56
	KOH	0.5 %	0.89	0.55
		1%	0.83	0.52
		1.5%	0.90	0.53

DISCUSSION

The quality evaluation of feed stocks used for the synthesis of biodiesel is very important. Therefore, the feed stocks under study were subjected to physical and chemical characteristics for the evaluation of initial parameters (Table 1) The degree of rancidity due to free fatty acid contents of fats and oils is embodied by their acid values as upon rancidification the resultant fatty acids and glycerol increases level of acids values. The acid values measured during research study were close to the standard values. The liberated free fatty acid radicles from unsaturated fatty acids during oxidative reactions converts into peroxide free radicals, which then reacts with molecular oxygen generates toxic unwanted products with violent smell, thus reduces the quality of oils regarding their nutritional and safety values (Sherwin, 1978, Checke, 1991, Frankel *et al.,* 1996*).* The peroxide values observed for Castor oil was higher than the other feed stocks as represented in Table 1. The density of oil is represented by their mass per unit volume (Gunstone, 1994). It was observed that the differences in the density values for different oils from WCO, Castor and Sesame oil was quite low. Saponification value is inversely associated with molecular weight of oil's fatty acid content (Nasir *et al*., 2009). The high saponification values also ascertained by the intactness of oil or fat molecules (Denniston *et al*., 2004).In current study conducted sesame oil exhibited the highest saponification value than the other oil (Table 1). According to the results it can be seen that oil to methanol ratio of 1:1 gave the highest biodiesel (methyl esters) production compared with 4:1, 3:1, and 2:1, whereas the lowest yield was obtained with 4:1ratio (Table 2). The aim behind the increase in molar ratio of oil to methanol was to observe its impact on yield of FAME. For obtaining enhanced fatty ester produce, it is required to have comprehensive trans-esterification reaction in terms of products like ester and glycerin. Many researchers found that alcohol in low quantity causes the trans-esterification to be incomplete. During various researches done it was found that the oil to methanol ratio of 1:6 would be optimum. However, increase in molar ratio of alcohol to vegetable oil interferes with the separation of glycerin due to increase in its solubility. The soluble remains of glycerin in solution, drives the equilibrium in back ward direction, thus reducing the esters yield. In the current study, the optimum molar ratio was found 1:1, which is in accordance with the study conducted by Hossain *et al*., 2010 and Murugesan *et al*., 2009 that reported highest biodiesel production at1:1 ratio of oil to methanol during trans-esterification of waste vegetable oil.

According the results KOH gave the slightly better yield of fatty ester than NaOH, except in Sesame oil. No clear reason is there to elucidate why KOH is better catalyst, nor NaOH. But in several of researches done it was found that performance of various kinds of catalyst is highly dependent on feedstock used. The finding of research conducted was similar to studies of Refaat *et al*., 2008 that 95.15% biodiesel yield was obtained during KOH catalyzed trans-esterification of Waste cooking oil.

The obtained results revealed that 1 % (wt. %) catalyst, i.e., NaOH and KOH, gave best yield of biodiesel among the tested ratios of 0.5%, 1.0% and 1.5%. It was observed that fatty ester yield was increased with the increase of catalyst concentration (irrespective of type) until 1.0%. Later the yield started to decline above that value. These findings were in accordance with the results obtained by Hossain *et al*. (2010). As a rule when there is an increase in the catalyst amount, it will help to faster the reaction and gave better yield. However, it is known that like all other chemical reactions, there is an optimum catalyst concentration, beyond that a decrease will be seen in the rate of reaction (Dorado *et al.*, 2004).

The biodiesel yield from Castor oil is comparatively low in current research (82.19%) as compare to the 95% reported by Gosawami *et al.*, 2011. The differences between the two researches revealed that crude oil was used in current research as compare to refined and neutralized version of Castor oil by Gosawami *et al.*, 2011). Biodiesel from castor oil is not suitable for use in diesel engine due to its high viscosity value. There is an alternative method to use castor oil and petroleum biodiesel blends to reduce viscosity. In order to get better yield from castor oil biodiesel it should be refined to have a better quality biodiesel yield.

The maximum Biodiesel obtained from Sesame oil under current research was 98.78% with 1 % NaOH. This finding was related to the study conducted by Ferdous *et al*., who also got 98.0% Biodiesel from Sesame oil with 1 % NaOH as lye (Ferdous *et al.*, 2013)

By comparing the Biodiesel production, the highest yield of 98.78% was reported both in case of Waste Cooking oil and Sesame oil followed by 82.19% from Castor oil. Arjun *et al.* (2008) reported 40% yield from chemical transesterification of WCO by using 1.0 % NaOH which is not in accordance with current research and the difference might be due to different molar ratio of methanol to oil, reaction time and temperature used (Chhetri *et al.*, 2008)

The Biodiesel densities obtained from all sources were ranges between 0.82 – 0.9 gm/cm3 (Table: 4), which is near to the American Society of Testing and Materials reported density of 0.82 max for Diesel. The residual methanol reduces the density of biodiesel and therefore the biodiesel requires a few washings. Acid Values were also calculated for the different biodiesel level that has been shown in Table 4, which is due to the presence of the free fatty acids in the biodiesel. The HPLC of biodiesel produced confirmed the trans-esterification process by showing a high peak in between 3 – 5 minutes in chromatogram, whereas FFA obtained were within 0 to 1 minute, these peaks are less visible. The peaks obtained in 1 to 3 minutes,5 to 7 minutes and 7 to 8 minutes were of MAG, DAG and TAG respectively, this finding is in harmony with the studies conducted by of Nicola *et al*., 2008 (Figure 1) (Standard A.S.T.M. 2003).

Conclusion: Waste cooking oil, castor and sesame oil can be utilized as renewable sources for producing eco-friendly biodiesel.

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