Production and characterization of biodiesel fuels from castor oil utilizing methanol

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The growing global demand for energy with expected fossil fuel shortages stresses the search for alternative energy resources. Moreover, the high fossil energy consumption with its adverse impact on environment and climate changes calls for cleaner fuels. One of the most alternative fuel sources is the extraction of biofuels from Castor oil by trans esterification process. In this paper experimental studies were carried out to produce a biofuel from castor oil using trans esterification process. The trans esterification process occurs between castor oil and methanol in the presence of potassium hydroxide as a catalyst. Nuclear magnetic resonance (NMR) test has been conducted to ensure that the reaction gives good results of glycerol and methyl ester (biofuel). The biodiesel fuel was produced by mixing biofuel with different amounts of diesel. Improvement of biodiesel using variable blending ratios: (B5, B10, B15, B20, and B30) was studied. The produced biodiesel fuel was evaluated in terms of its thermo physical and chemical characteristics such as flash point, firing point, and calorific value. Results showed that the produced biodiesel has similar properties with diesel fuel. Results are compared with other published experimental data.

Keywords: Fossil energy, Alternative energy resources, Castor oil, Trans esterification process.

INTRODUCTION

The increasing awareness of the depletion of fossil fuel resources and the environmental benefits of biodiesel fuel has made it more attractive in recent times. Its primary advantages deal with it being one of the most renewable fuels currently available and it is also non-toxic and biodegradable. It can also be used directly in most diesel engines without requiring extensive engine modifications. However, the cost of biodiesel is the major hurdle to its commercialization in comparison to petroleum-based diesel fuel. The production of biodiesel from desert plants offers an economic and environmental friendly fuel.

Castor oil is a vegetable oil obtained from the castor bean (technically castor seed) that has an unusual structure and multiple uses. It is obtained by pressing the seeds of the castor plant, (Ricinus Communis, Euphorbiaceae) (Mohammed et al., 2008). It is a colorless to very pale yellow liquid with mild or no odor or taste. It is a triglyceride in which approximately 90% of fatty acid chains are ricinoleate. Oleate and linoleates are the other significant components (National Renewable Energy Laboratory "Biodiesel Handling and Use Guide", U.S. Department of Energy and its contractors, Fourth Edition, Retrieved 2011). The major advantages are its non-edibility, high productivity (3 tons annually/acre), Low cultivation costs, low water needs, high oil concentration and easy oil extraction (Bureau of statistics Government of the Punjab Lahore "Punjab Development Statistics" Bureau of Statistics Government of the Punjab, 2-Begum Road, Lahore, 2011). Moreover it is suitable for farming with the possibility of using waste water for irrigation.

Methods of oil extraction from castor bean include cold pressing and organic solvents .Trans esterification process is a way to convert Castor oil to biodiesel. Trans esterification is the process of exchanging the organic group of an ester with the organic group of an alcohol. These reactions are often catalyzed by the addition of an acid or a base catalyst (Schuchardt et al., 1998) as:

$$\text{Castor oil} + \text{Methanol} \xRightarrow{Transesterification} \text{Glycerin} + \text{Biodiesel}$$

Biodiesel is an oily liquid synthesized from fatty material. It has a light yellow color and mild odor and a bitter taste, it has many advantages such as: Renewable, it can be extracted from vegetable oil, Potential for Carbon Neutral lifecycle, simple to make, Non-toxic, Biodiesel is free from sulphur (< 0,001 %), the only alternative fuel that does not require engine modification or retuning, safer for storage and handling than petroleum diesel, Can be used neat or blended in any ratio with petroleum diesel and dramatically reduced emissions.

(Encinar et al ., 2010) carried out a Transesterification reaction in a 1000 mL spherical reactor, provided with thermostat, mechanical stirring, sampling outlet, and condensation systems. The reactor was preheated to 65 ºC to eliminate moisture, and then 500 g of castor oil was added. When the reactor reached its established temperature, the methanol and the catalyst were added, amounts calculated for each experiment, and the stirring system was connected, taking this moment as time zero of the reaction. At evenly spaced intervals, 1.5 cm^3 of sample withdraw for later chromatographic analysis. Biodiesel properties of reaction conditions: CH_3OK as catalyst, 1 wt. %; methanol/oil, 9:1, 65 ºC, 3 h, 700 rpm. Each experiment was prolonged for 3 hours, and thus the conversion to esters was practically complete.

(Efeovbokhan et al., 2012) produced a biodiesel using the following procedure:

46.5g of methanol (absolute) and 50.0g of the castor oil were first measured in two separate beakers that have been previously washed and dried. 0.5g (1% by weight) of the catalyst (pure potassium hydroxide) was weighed and dissolved in the methanol and the resultant solution was then charged into the reactor and pre-warmed. The stirrer speed was set to 4 rev/s and the oil which was also pre-warmed in a separate beaker was carefully added to the sodium ethoxide in the reactor and was then subjected to heating at varied times of trans esterification reactions. At the end of the reaction, the reaction mixture was poured into a separating funnel and left to stand for approximately 24 hours, this was to allow for distinct phase separation. The phases were then separated to recover the biodiesel for further purification and drying. (Bello et al., 2011) added 3 g/liter of sodium hydroxide to methanol in a mixer and stirred at 350 rpm until it is completely dissolved. It was then mixed with the castor oil in a 250 mL reactor equipped with a heater, magnetic stirred at a relatively high molar ratio of 6 to 1 to bias the reaction toward higher yield. Because of the very high viscosity of the oil, it was next stirred at 1000 rpm for 3 hours at 60°C for the reaction to take place. The mixture was allowed to settle for 8 hours to drive the reaction to completion and for the mixture to separate into two layers of biodiesel and glycerol, which is denser at the bottom. The mixture was then separated using a separating funnel. Tannic acid was added to the biodiesel to neutralize any remaining base catalyst and washed with distilled water to remove impurities such as diglycerine and monoglycerine, catalyst, soap and excess methanol which can affect combustion and exhaust emission. The washing was done by mixing with 20 vol. % distilled water and stirred gently for ten minutes. It was allowed to settle and it separated into two layers of pure biodiesel and hydrated methanol with the lighter biodiesel at the top, which was separated using a separation funnel. The procedure was repeated three times before being heated to 120 °C to remove any water vapor still present.

Blends of biodiesel and conventional hydrocarbon-based diesel are products most commonly distributed for use in the retail diesel fuel marketplace. A system known as the "B" factor is used to state the amount of biodiesel in any fuel mix where 100% biodiesel is referred to as **B100.** 20% biodiesel, 80% diesel is labeled **B20.** Blends of 20% biodiesel and lower can be used in diesel equipment with no, or only modifications. Biodiesel can also be used in its pure form (B100), but may require certain engine modifications to avoid maintenance and performance problems.

Experimental work

Potassium hydroxide was added to methanol in a mixer and stirred for 10 to 15 minutes until it is completely dissolved. It was then mixed with the castor oil in a reactor equipped with a heater, magnetic stirred at 70ºC. Stirring was continued and the product was placed in a separating funnel and left over night for glycerin to settle to the bottom of the funnel and then removed in a measuring cylinder. The impure methyl ester (biofuel) was washed with Sulfuric acid (98% concentration) and distilled water, prior to drying in the furnace at 150 °C for two hours. To ensure pure biofuel is obtained, Nuclear Magnetic Resonance test (NMR) was carried out. Figure1 shows the experimental set up including Magnetic stirring hot plate, Magnetic stirring bar, Crucible (1000 ml), Funnel separator (1000 ml), Beaker (2000 ml), Graduated cylinder (250ml), Chemical scales, Thermometer (0:100ºC), Chemical equipment holder, Stopwatch, Furnace, and Condensing system.

The results obtained by converting castor oil into methyl ester using different amounts of castor oil, with methanol as a reagent, and potassium hydroxide as catalyst at different times of reaction is given in table 1.

The thermo physical properties obtained from trans esterification processes at the different reaction conditions are shown in table 2.

It is clear from Table 1 that increasing time of reaction, amount of castor oil and/or amount of methanol leads to yield improvement (increase in the glycerin amount). And from table 1 and 2 it can be concluded that increasing time of reaction, amount of castor oil and amount of methanol leads to improvement in the value of flash point

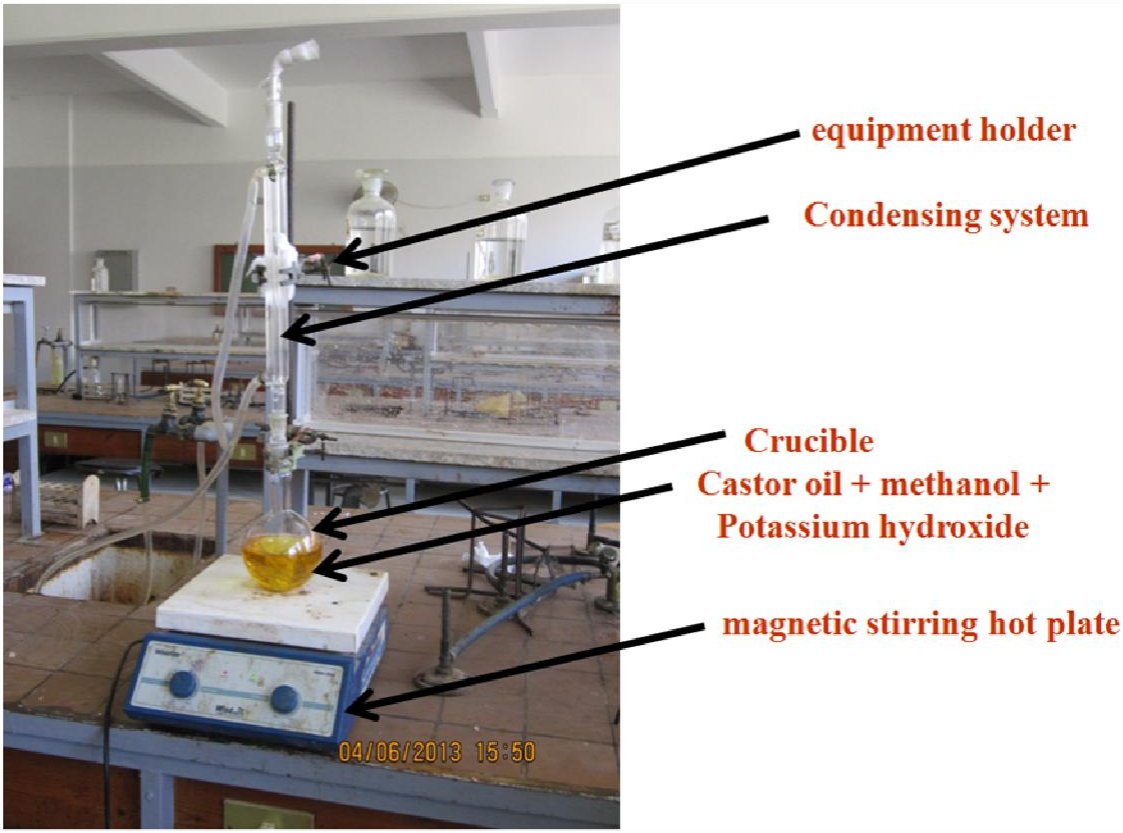

Figure 1. The experimental instruments and equipments

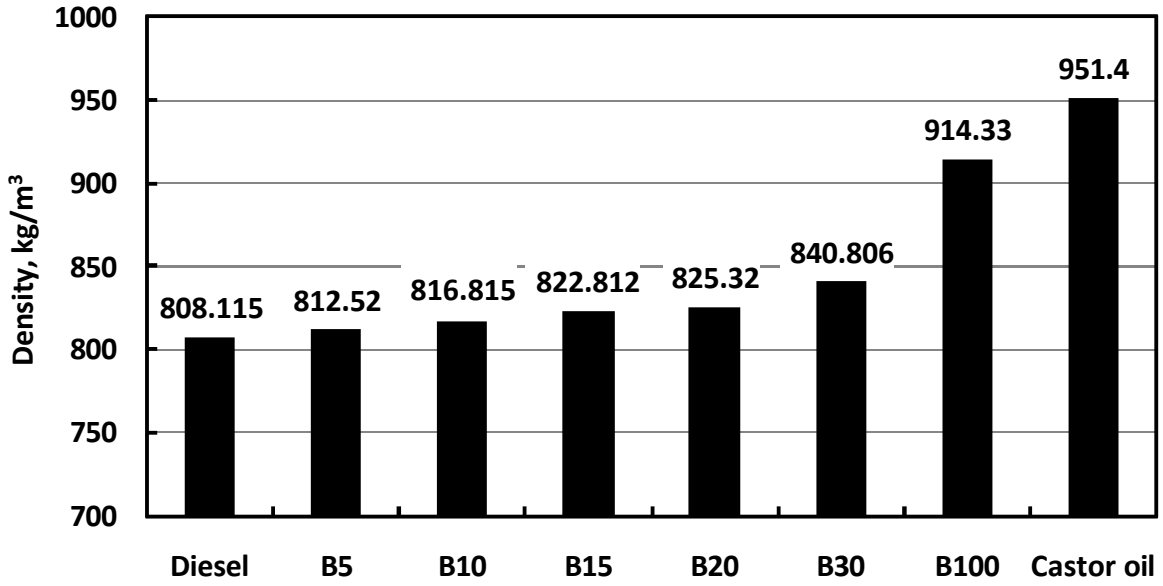

Figure 2. Density of different blends of castor biodiesel and diesel fuel

but a slight decrease in heating value. The 4th trail gives the largest amount of glycerin because of increasing the time of reaction and the amount of castor oil and methanol. Theoretically, optimal values of flash point and fire point are found in 4th trial. The difference between the 3rd and 4th trials in flash point is 4 °C this difference value is not large it may be a result of change in room temperature or inaccuracy of measuring instruments.

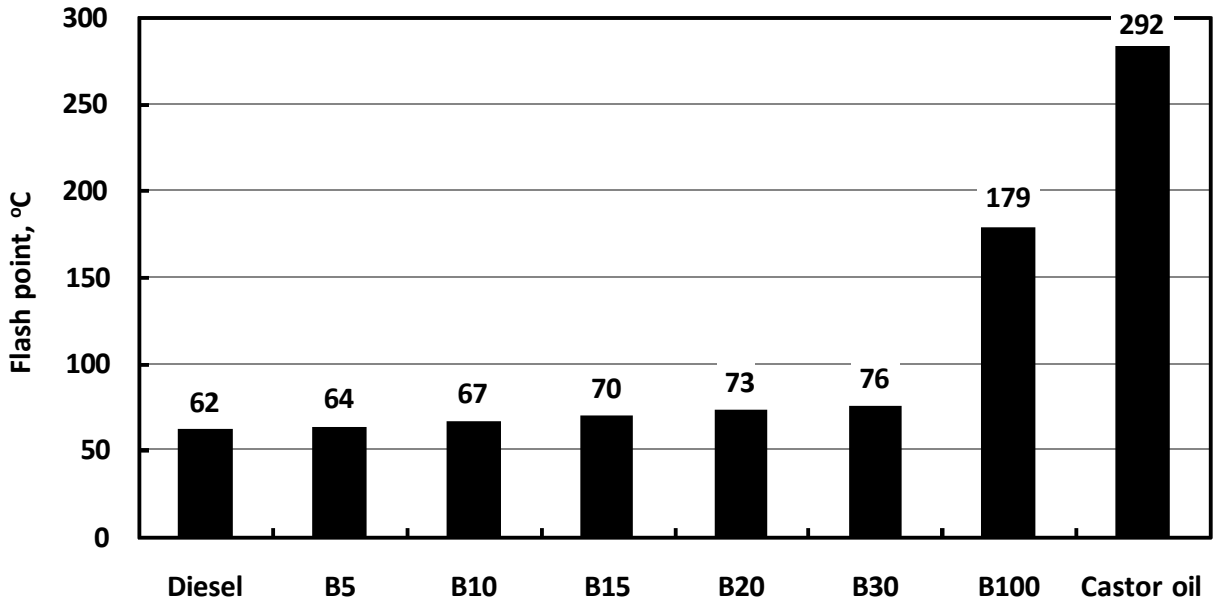

Figure 3. Flash point of different blends of castor biodiesel and diesel fuel

Table 1. Results from transesterification of castor oil under various reaction conditions.

Trial No.	Amount of Castor oil (ml)	Amount of methanol (ml)	Amount of catalyst (potassium hydroxide) (g)	Reaction time (Hours)	Amount of glycerin	
					ml	%
1	250	65	2.4	6	10	4
2	250	65	2.4	7	15	6
3	500	130	4.8	9	28	5.6
4	500	130	4.8	10	57	11.4

Table 2. The thermophysical results from transesterification of castor oil under various reaction conditions

Trail No. / Properties	1	2	3	4
Heating value (MJ/kg)	39.160	39.0	39.032	38.576
Flash Point (°C)	188	182	183	179
Firing point (°C)	200	204	202	207
Density (kg/m^3)	937.98	914.78	921.09	914.33
Glycerin amount (ml)	10	15	28	57

Different mixing ratios of biofuel and diesel were used from the fourth trial. The produced biodiesel was evaluated as a fuel according to its thermo physical and chemical parameters such as flash point, firing point**,** Nuclear magnetic resonance test (NMR) and calorific value. The NMR test shows that the reaction gives good results of glycerol and methyl ester, mixing ratios such as B5, B10, B15, B20, and B30.

RESULTS AND DISCUSSION

Comparison among pure oil, pure biodiesel, different mixing ratios and Diesel in terms of thermophysical properties are shown in table 3. The density and flash points of different mixing ratios are also shown in Figs 2, 3 respectively. It is clear from Table 3 that pure Castor oil has the highest density, flash point, and fire point. Pure

Table 3. Comparison between pure oil, pure biodiesel, different mixing ratios and diesel in terms of thermophysical properties (at room temp. approximately 34 °C)

Properties	Castor oil	B100	B5	B10	B15	B20	B30	Diesel
Density (Kg/m^3)	951.4	914.33	812.52	816.815	822.812	825.32	840.068	808.115
Flash point (°C)	292	179	64	67	70	73	76	62
Fire point (°C)	320	207	70	74	76	79	80	68
Heating value (MJ/kg)	--	38.576	41.759	41.626	41.408	41.2352	40.810	41.900

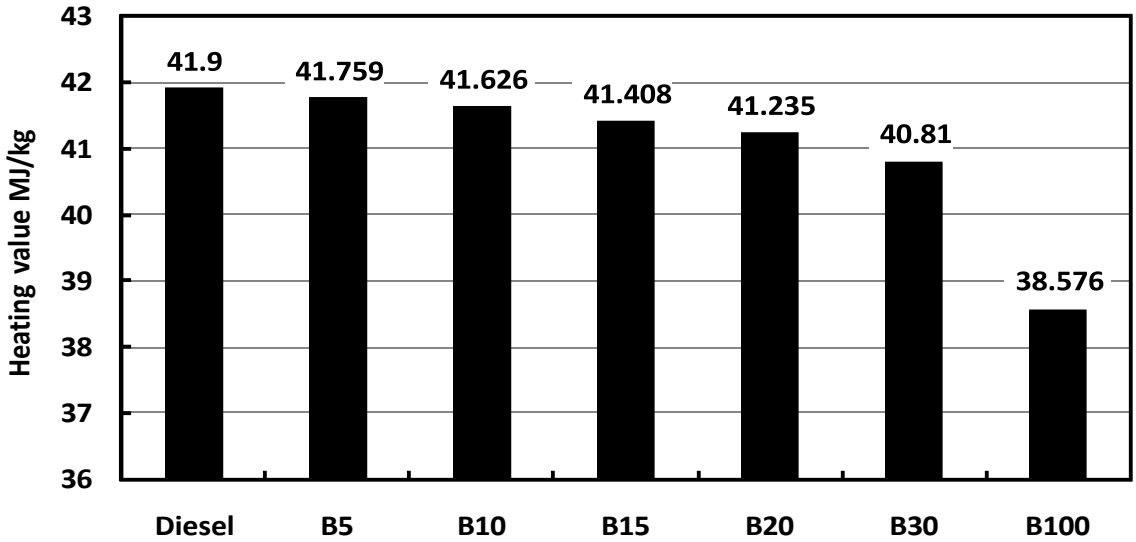

Figure 4. Heating value of different blends of castor biodiesel and diesel fuel.

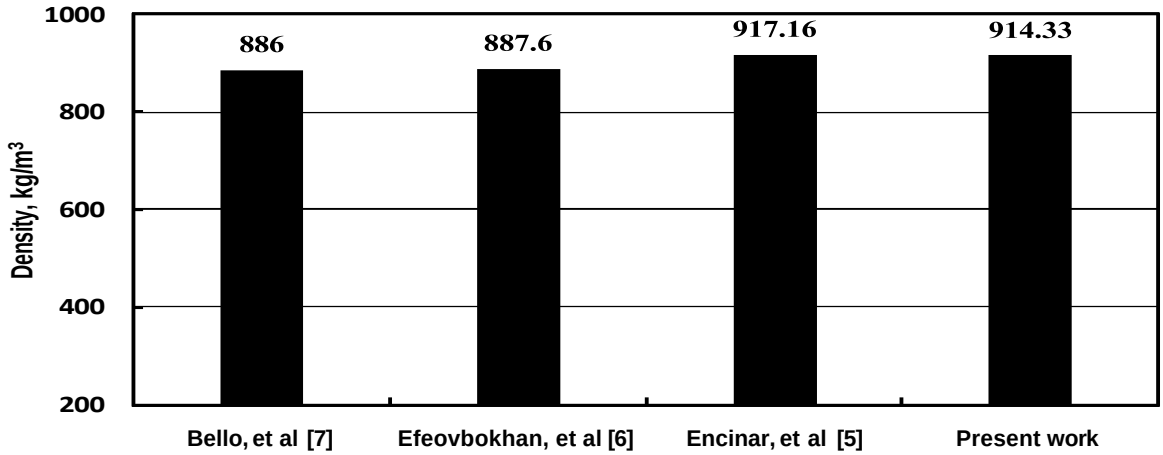

Figure 5. comparison between different trans esterification methodologies and the proposed experimental work results

biodiesel from castor oil (B100) is expensive and has a high flash point and fire point making it one of the safest of all alternative fuels from the combustibility point of view. Thermo physical properties of B5 are the closest to diesel making B5 to be the best blend over B10, B15, B20 and B30 in terms of thermo physical properties only. However this blend was not experimented with in engine performance. Figure 4 shows that the heating value is slightly decreased with the increase of the mixing ratio.

Different trans esterification methodologies to produce biofuel from castor oil are compared with the proposed methodology in Figs 5 and 6 in terms of density, heating value and flash point. Figures 7 and 8 show comparison between the different methodologies and proposed

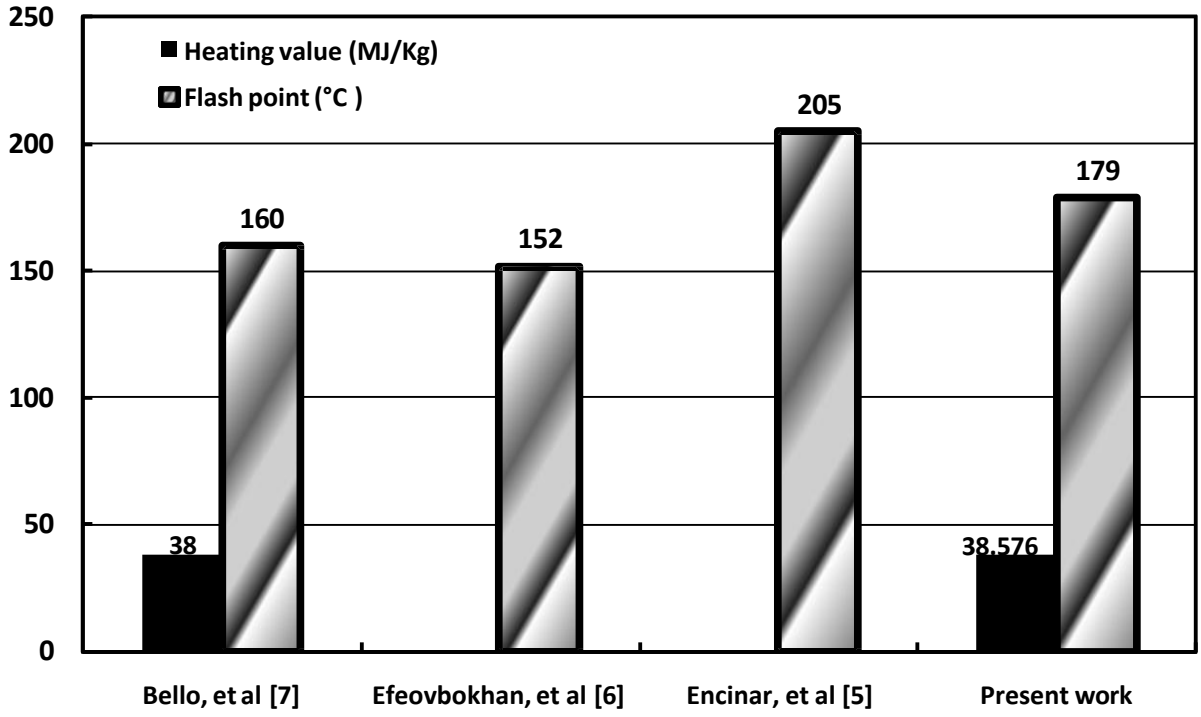

Figure 6. Comparison between thermo physical properties of castor biofuel produced by published methods and the present work

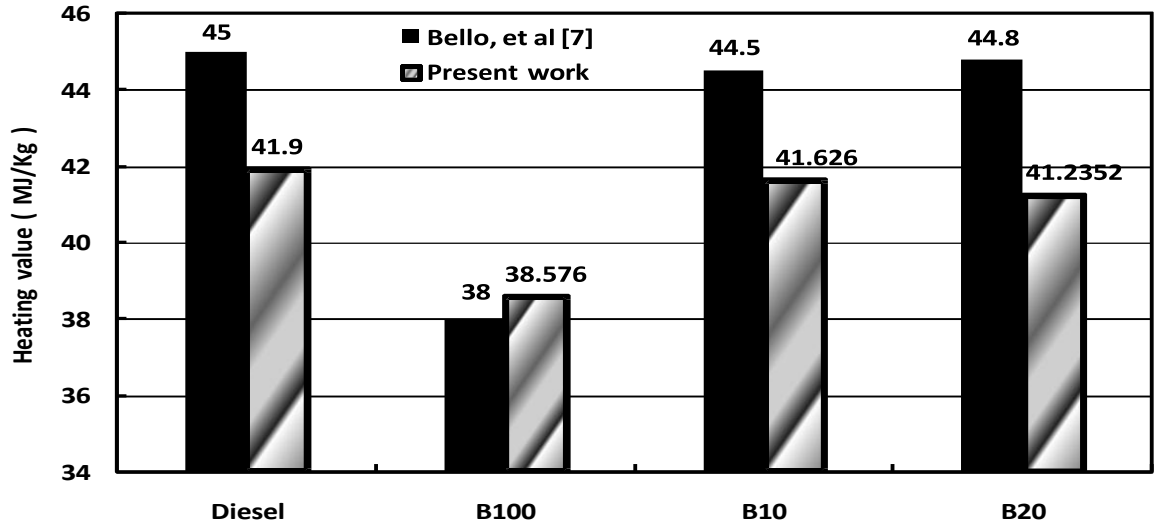

Figure 7. Comparison between blends of published methods and the present work in terms of heating value

methodology for different biodiesel blends (B10 and B20) is presented in terms of heating value and flash point.

It is clear from Fig. 5 that biofuel produced by the (Encinar et al.) method has the largest value of density while (Bello et al., 2011) method gives the lowest density with the proposed methodology in between. Figure 6 shows that proposed methodology gives higher heating value than method, but heating values of (Efeovbokhan., et al.) and (Bello et al., 2011) methods were not recorded. The lowest flash point is given by (Efeovbokhan et al) method but the flash point given by the proposed methodology is slightly higher.

Figure 7 shows that the heating value of pure biodiesel (B100) produced in the present work is higher than that of the pure biodiesel produced by (Bello et al., 2011). The heating values of blends (B10, B20) of the present work are slightly lower than blends (B10, B20) of (Bello et al., 2011) because the heating value of the diesel

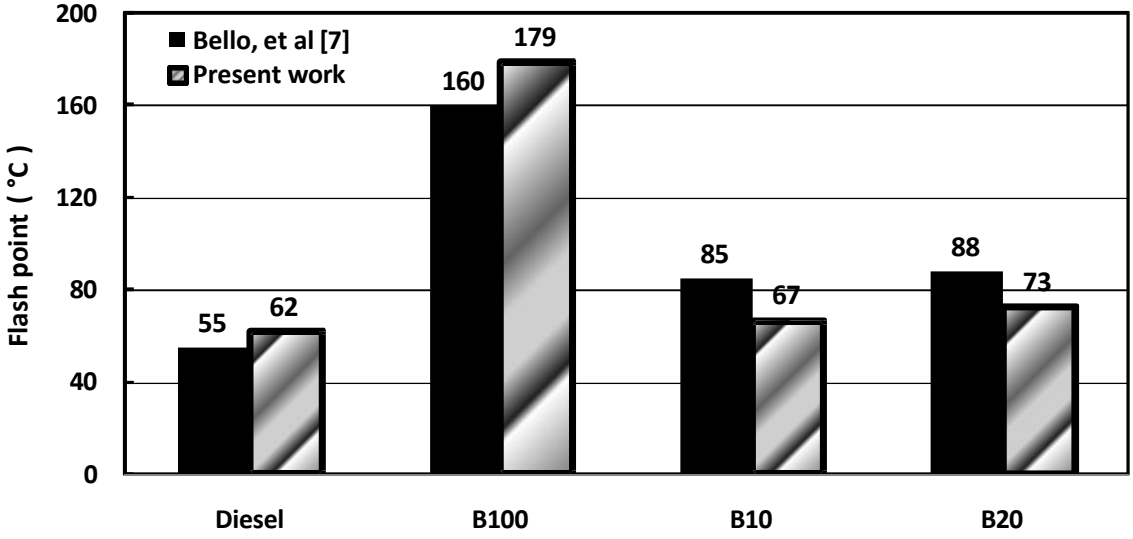

Figure 8. Comparison between blends of published methods and the present work in terms of flash point

used in (Bello et al.,2011) is higher than the heating value of the diesel used in the present work. Figure 8 shows that the flash point of pure biodiesel (B100) of the present work is higher than that of B100 of (Bello et al.,2011). On the other hand the flash point of (B10, B20) of (Bello et al.,2011) is higher than that of the same blends in the present work. Flash point of diesel used in (Bello et al.,2011) is lower than that of diesel used in the present work.

Differences in results between different methodologies including the present work are due to changes in experimental conditions and materials. (Bello., et al) were using higher stirring speed and used tannic acid for washing allowing 3 hours for reaction. (Efeovbokhan., et al) added sodium ethoxide to the castor oil in the trans esterification process, while (Encinar., et al) used CH_3OK as a catalyst and allowed 3 hours for reaction. In the present work potassium hydroxide was used as a catalyst, with sulphuric acid for washing and 10 hours to make the reaction.

Finally, any change in catalyst, time of reaction ,temperature of reaction, amount of castor oil, alcohol type (methanol, ethanol), and/or amount of alcohol makes a signification effect in the yield improvement and thermophysical properties of the resulting biofuel.

CONCLUSION

According to the present study biofuels became indispensable now as an alternative to fossil fuels. Castor oil is an ideal candidate as a raw material for trans esterification. Biofuels from castor oil are an excellent and practical alternative to fossil fuels. The high solubility of castor oil in methanol results in a high biodiesel yield even with minimum use of a catalyst which, under industrial conditions leads to high reduction in the cost of production. The most appropriate catalyst for this process was found to be potassium hydroxide. The best ratio of methanol to castor oil is 1:3 by volume, for basic catalysis. The best temperature for the reaction was found to be 70 °C. Increasing the time of reaction leads to increasing the amount of glycerin causing yield improvement. Make the trans esterification process in large scale gives good results with slight different than small scale. B5 blend was found to be the best mixing ratio in terms of thermo physical properties. However, other mixing ratios (B10, B15, B20, and B30) are slightly different than B5.

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