

Investigation of the chemical composition, characterization and determination of energy content for renewable energy source (biodiesel) produced from non-edible Ethiopian seeds' particularly castor seed (*Ricinus communis*) using homogeneous catalysis

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ABSTRACT

Biodiesel is a clean, renewable, biodegradable, environmentally benign, energy efficient and diesel substituent fuel used in diesel engine. It provides a feasible solution to the twin crises of fossil fuel depletion and environmental pollution. It is produced from renewable sources such as vegetable oils or animal fats by trans-esterification. Although this fuel has gained worldwide recognition for many years, it is not being widely commercialized like petroleum diesel in the world, not widely produced and used especially in our country Ethiopia. Analysis of fatty acid methyl ester composition of the biodiesel produced from castor oil was done with the help of GC-MS and 8 fatty acid methyl esters were identified. Acid and base catalyzed methods were used in the synthesis of biodiesel from castor seed oil. In addition to this the variables that affect the amount of methyl ester yield were determined and an optimum of 96.7 % fatty acid methyl ester (FAME) conversion was obtained at a methanol to oil molar ratio of 6:1, 1.0 % mass NaOH, 65 °C reaction temperature and 3 hour reaction time. The energy content of the oil and biodiesel were 39 MJ/Kg and 40.7 MJ/ Kg respectively which is determined by bomb calorimeter. Other physicochemical properties of the biodiesel were determined and all these lie within the ASTM and EN biodiesel standards except kinematic viscosity. Therefore, castor seed oil methyl ester could be used as an alternative energy resource in diesel engine by blending with petroleum diesel.

Keywords: castor oil; non -edible oil; biodiesel; trans-esterification; homogeneous catalyst; FAME; GC-MS

1. INTRODUCTION

Biodiesel is a clean, renewable, biodegradable, environmentally benign, energy efficient and diesel substituent fuel used in diesel engine. It is a carbon neutral fuel because there is no overall increase in CO₂ in the atmosphere due recycling by the growing plants used to feed the biodiesel industry [1].

Emissions of SO₂, SO₃, CO, un burnt hydrocarbons and particulate matter are lower than that of petroleum diesel [2,3].

It is produced by the trans-esterification of triglycerides. Trans-esterification is a three-step reversible reaction of vegetable oils or animal fats with a methanol to form fatty acid methyl esters (FAMES) and glycerol as a final product [4].

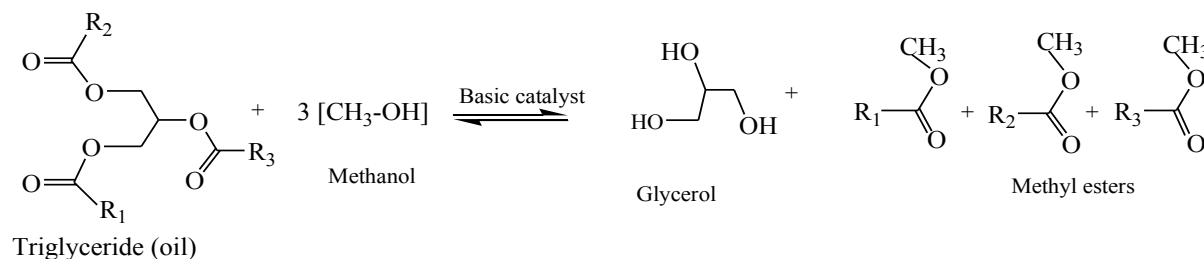
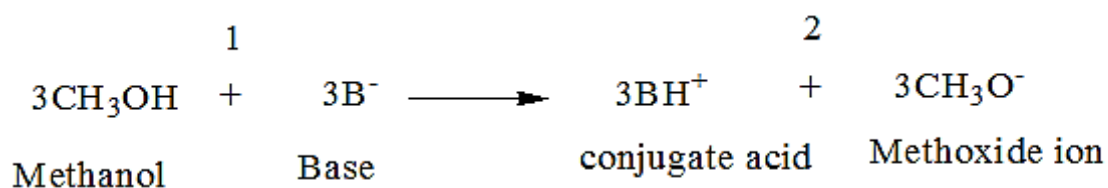


Figure 1. Base catalyzed trans-esterification processes.

The reaction mechanism for the formation of fatty acid methyl esters (FAME) is described as follows.



Methanol is the most frequently used alcohol for trans-esterification because of its low cost, highest polarity and the corresponding smallest size of the alkoxide group.

Basic and acidic substances can be used as catalysts for trans-esterification. The basic catalysts used for trans-esterification are hydroxides and alkoxides [5]. The most common acidic catalysts used are H₂SO₄, H₃PO₄ and HCl [5,6].

Currently, about 84 % of the world biodiesel production is met by rapeseed oil [7]. The remaining portion is from sun flower oil (13 %), palm oil (1 %), soybean and others (2 %) [8]. since more than 98 % of the biodiesel is made from edible oil, there are many claims due to the depletion of edible oil supply worldwide. Therefore in order to overcome these devastating phenomena, the feed stock for the biodiesel production must be replaced by non – edible oil. One such oil would be castor seed oil which is derived from castor plant. Castor oil, *Ricinus communis* is a member of the tropical spurge family, Euphorbiaceae, Genus: *Ricinus* and Species: *communis*. Castor is amongst the plants with the highest oil yield potential because of its high yield of seeds and the high oil content of its seeds. It may be possible to obtain a maximum of 2000 kg oil/ha [9] where as rape seed produces about 1000 kg oil /ha and soy bean only produces about 500 kg oil /ha [10]. Therefore, castor oil is a promising biodiesel source because of its highest oil yield potential, non-edible as a result it does not compete with food security.

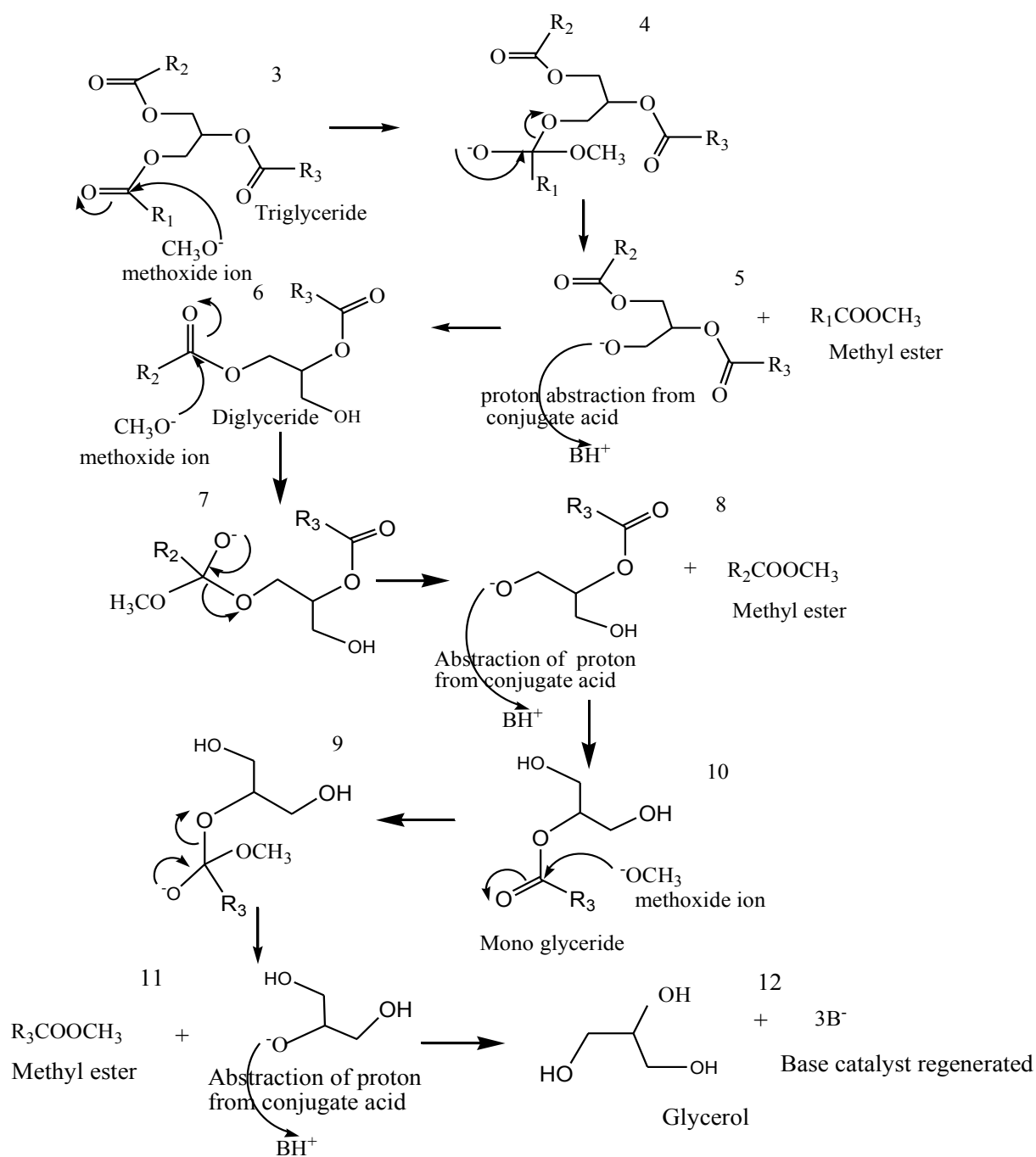


Figure 2. Reaction Mechanism for base catalyzed trans-esterification.

2. OBJECTIVES OF THE STUDY

2. 1. General objective

The general objective of this study was to investigate the chemical composition, characterization and to determine the energy content for the renewable energy source (biodiesel) produced from non-edible Ethiopian seeds' particularly castor seed (*Ricinus communis*) using homogeneous catalysis.

2. 2. Specific objectives

In order to address the aforementioned general objective, the following specific objectives were formulated:

- Extraction of the crude oil from the kernels of the castor seeds by soxhlet apparatus using n- hexane as an extracting solvent.
- Determine the optimum conditions/parameters (such as reaction temperature, alcohol-to-oil molar ratio, type and concentration of catalyst and reaction time) for the production of maximum amount of biodiesel.
- Determine the physicochemical properties of crude oil extract, oil blends, biodiesel and biodiesel blends such as acid value, density, kinematic viscosity, iodine value and higher heating values.
- Compare the physicochemical properties of castor oil, oil blends, biodiesel and biodiesel blends with the biodiesel standards (ASTM D6751 and EN14214 standards).
- Analyze the chemical composition of the biodiesel using chromatographic and spectroscopic techniques such as gas chromatography coupled with mass spectrometry (GC-MS).

3. MATERIALS AND METHODS

The experimental work was done in the organic laboratory of Department of Chemistry, Mekelle University.

3. 1. Plant materials

3. 1. 1. Castor seed collection

Fresh castor seeds were collected from Adigrat Eastern Tigray which is 898 km's far away from Addis Abeba toward north.

3. 2. Chemicals and reagents

Methanol (99 %), sodium hydroxide, sulphuric acid (98 %), n-hexane, sodium thiosulfate, phenolphthalein, ethanol (96 %), anhydrous sodium sulphate, and potassium hydroxide.

3. 3. Instrumentations

Soxhlet apparatus, Rotary evaporator, GC-MS, bomb calorimeter, viscometer, hot plate thermometer, round bottom flask, separatory funnel, mortar and pestle were used.

3. 4. Experimental design

3. 4. 1. Experimental Treatments

Two types of catalysts, acidic catalyst (H_2SO_4) and basic catalyst (NaOH) were used at different reaction temperatures to study which catalyst is better for optimum biodiesel production from castor oil. In addition to this blending of castor oil and biodiesel were conducted with petroleum diesel. Finally the physicochemical properties of the castor oil, biodiesel, blended biodiesel and blended castor oil were determined and compared with a set

of parameter according to European Standard, EN 14214 and American standard test and material, ASTM6751 [11,12].

Table 1. Experimental treatments.

Methanol to oil molar ratio (T ₁)	Temperature in °C (T ₂)	% w/w of H ₂ SO ₄ to oil (T ₃)	% w/w of NaOH to oil (T ₄)	% V/V of oil to petroleum diesel ratio (T ₅)	% V/V biodiesel/ petroleum diesel ratio (T ₆)
3:1	45	3	1	20:80 = C20	10:90 = B10
6:1	55	4	2	25:75 = C25	20:80 = B20
9:1	65	5	3	30:70 = C30	30:70 = B30

Where: T = treatment, C = castor oil, B = Biodiesel

3. 5. Soxhlet extraction of castor oil and Percentage yield of the oil

The clean kernels were grounded in to powder by using pestle and mortar. After that 100 g of grounded kernel was loaded in to thimble in Soxhlet apparatus and extraction was carried out using 600 ml normal hexane at 68 °C (boiling temperature of hexane) for 24 h in an electrical heater. The mixture of the extracted oil and the hexane was separated by rotary evaporator and the percentage of the oil was calculated by the following formula:

$$\% \text{ Oil} = \text{Mass of Oil} \times 100 / \text{Mass kernel}$$

3. 6. Determination of the physicochemical properties

Density, specific gravity, kinematic viscosity, acid value, saponification value, iodine value, peroxide value and higher heating value of the castor oil, castor oil blend, biodiesel and biodiesel blends were determined.

4. RESULTS AND DISCUSSION

4. 1. Yield

From 4 kgs of castor seed 3 kgs of kernels and one gram shells were obtained. From this 75 % of the mass of the raw castor seed was kernel and the remaining 25 % was the mass of the shell.

From these kernels 2.1 liters of crude oil with a density of 953.2 kg/m³ was obtained. Then Mass of oil = density of oil x volume of oil = 953.2 kg/m³ x 2.1 L x 1 m³/1000 L = 2 kg of oil % oil extracted = Mass of oil x100/ Mass of seed = (2 kg x 100) / 3 kg = 66.67 %

4. 2. Physicochemical properties

The biodiesel, biodiesel blends and castor oil blends had lower specific gravity, density and kinematic viscosity compared to castor oil (Table 2). This is due to the fact that castor oil contains three esters combined together while the biodiesel contains a single ester.

Conversely biodiesel, biodiesel blends and castor oil blends had higher heating value than the castor oil. The main reason for the increased higher heating value of biodiesel,

biodiesel blends and castor oil blends is due their lower specific gravity and kinematic viscosity. Besides to this the higher heating values of the biodiesel blends were larger than the biodiesel but lower than the petroleum diesel. This is due further reduction in specific gravity and kinematic viscosity of the blends. The carbon residue of the oil was higher than the biodiesel, biodiesel blends, castor oil blends and petroleum diesel. This is due to the fact that there will be no complete combustion as a result of the higher kinematic viscosity of the oil. Even though the kinematic viscosity of petroleum diesel was lower than the biodiesel, biodiesel blends and castor oil blends its carbon residue was higher. This is because of the incomplete combustion of the non-oxygenated hydrocarbons and aromatic compounds in petroleum diesel. The higher heating value and carbon residue were increasing as the amount of the petroleum diesel increases in the blend. The main reason for the increasing of the higher heating value is the decrease of specific gravity and kinematic viscosity of the blends. The higher heating values of biodiesel blends and castor oil blends lie between the heating values of their constituents.

Generally the physicochemical properties of the biodiesel, biodiesel blends and castor oil blends (up to C₂₅) lie within the biodiesel standard limits except kinematic viscosity for B₁₀₀ (i.e 8.02 mm²/sec). This is out of the range of the ASTM D6751 and EN14214 biodiesel standards. Hence to decrease the kinematic viscosity of the biodiesel it is necessary to blend with petroleum diesel. The blended biodiesel and castor oil blends kinematic viscosities (B₃₀, B₂₀, B₁₀, C₂₀ and C₂₅) were within the biodiesel standard limits and similar physicochemical properties to petroleum diesel. Therefore these biodiesel blends and castor oil blends can be used in diesel engine to substitute petroleum diesel (Table 2).

Table 2. Physicochemical properties of castor oil, castor oil blends, biodiesel, biodiesel blend and Petroleum diesel.

Properties	C ₁₀₀	C ₃₀	C ₂₅	C ₂₀	B ₁₀₀	B ₃₀	B ₂₀	B ₁₀	P ₁₀₀
Specific gravity	0.95	0.92	0.886	0.88	0.882	0.873	0.860	0.856	0.845
Density at 15 °C	950	920	886	88	882	873	860	856	845
Kinematic viscosity at 40 °C	180	14.64	5.89	5.64	8.02	4.8	4.5	3.78	2.86
Acid value	0.24	0.22	0.08	0.062	0.08	0.002	1.8x10 ⁻³	3.4x10 ⁻⁴	-----
Free fatty acid	0.32	0.11	0.04	0.031	0.04	0.001	9x10 ⁻⁴	1.7x10 ⁻⁴	-----
Saponification value	140	30.24	23.62	18.84	11.54	3.79	1.068	0.276	-----
Flash point	-----	92	88.56	86.3	175	92	90.56	87.3	67.5
Higher heating value	39	39.98	41	41.86	40.7	43.3	44.90	44.93	45.5
Peroxide value	20	14.4	11.3	9.86	28	24.4	22.2	20.28	-----
Iodine value	76	64	54.32	49.86	76	56	51	43	-----
Carbon residue	0.09	0.053	0.0498	0.0492	0.028	4.3x10 ⁻³	5.2x10 ⁻³	7.2x10 ⁻³	0.049
Ester content	-----	-----	-----	-----	96.7	-----	-----	-----	-----

4. 3. Effect of different variables on trans-esterification process

Table 3. Methyl ester content, as function of catalyst type and mass weight of catalyst at methanol/oil molar ratio, 9:1; reaction temperature, 55 °C; reaction time of 3 hours.

Type of catalysts	Mass weight of catalyst, wt. %	Temperature	Methyl ester content, w/w %
H ₂ SO ₄	3	55	45
	4	55	46
	5	55	46.4
NaOH	1	55	90
	2	55	94
	3	55	88

Table 4. Methanol /oil molar ratio influence on the amount of methyl ester content, at fixed reaction temperature (65 °C), reaction time 3 hours and mass Weight of catalysts.

Methanol to oil molar ratio	catalyst	% W of catalyst	w/w % of methyl ester content
3:1	H ₂ SO ₄	3 wt. %	47
6:1			49.8
9:1			52
3:1	NaOH	1 wt. %	75
6:1			96.7
9:1			94

Table 5. Influence of the reaction temperature on the methyl ester content, catalyst type, NaOH; catalyst amount, 1 wt. %; methanol/oil molar ratio, 9:1.

Temperature in °C	Type of catalyst	Mass weight % catalyst	Methyl ester content, w/w %
45	NaOH	1 wt.%	89
55			92
65			94

4. 4. GC-MS analysis of biodiesel prepared from castor oil

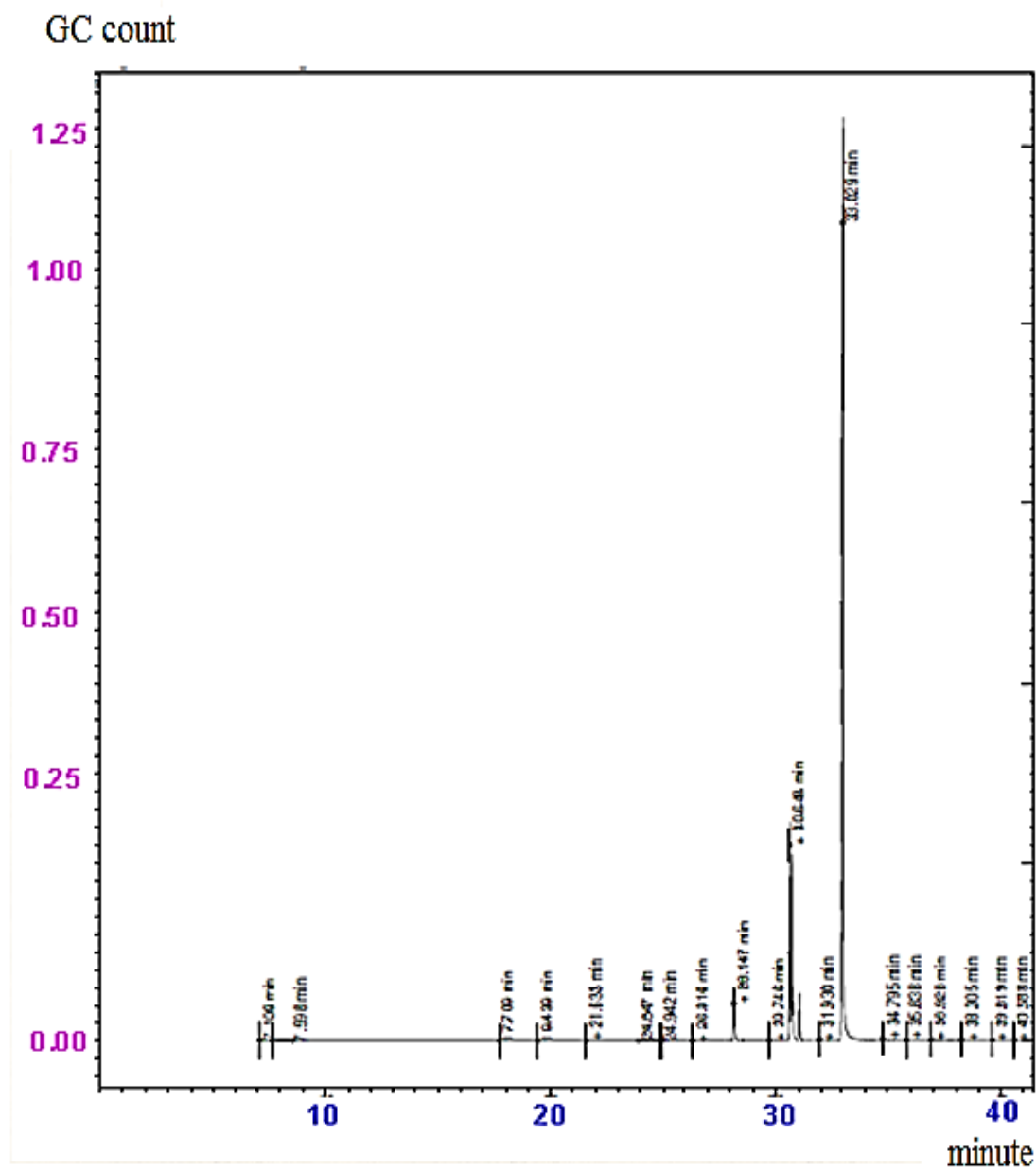


Figure 3. GC Chromatogram of FAMES of castor oil.

Table 6. Chemical composition of FAMES of castor oil by GC-MS analysis.

No	Name of compound	Molecular formula	Molecular weight	Retention time (min)	Amount %
1	9-Octadecenoic acid, 12-(acetyloxy)-methyl ester	C ₂₁ H ₃₈ O ₄	354	29.746	0.2
2	Heptadecanoic acid, 14-methyl-methyl ester	C ₁₉ H ₃₈ O ₂	298	28.147	11.0
3	Octadecanoic acid, 14-methyl-methyl ester	C ₂₀ H ₄₀ O ₂	312	30.648	39.4
4	Pentadecanoic acid, 14-methyl-methyl ester	C ₁₇ H ₃₄ O ₂	270	33.029	40.5
5	8-Octadecenoic acid, methyl ester (E)-	C ₁₉ H ₃₆ O ₂	296	30.738	8.9
6	Cyclo propane octanoic acid, 2-octyl-,methyl ester	C ₂₀ H ₃₈ O ₂	310	31.932	Trace
7	9,12,15-Octadecatrienoic acid, 2,3-dihydroxy methyl ester	C ₁₉ H ₃₂ O ₄	324	29.383	Trace
8	Hexadecanoic acid, 15-methyl- methyl esters	C ₁₈ H ₃₆ O ₂	284	32.183	Trace

4. 5. Analysis of mass fragmentation of FAMES

The mass fragmentation for the major fatty acid methyl ester pentadecanoic acid, 14-methyl-methyl ester (40.5 %) from the eight methyl esters identified by GC-MS were worked out and from the 10 prominent peaks of it, one is the molecular ion peak (M^+) at $m/z = 270$ which is abundant and formed by removing of one electrons from the molecule. The most abundant peak is at $m/z = 74$ which is also called the base peak. This fragment results from a McLafferty rearrangement, which is formed by transferring of γ -hydrogen atom from the acid moiety to the carbonyl oxygen through a six membered cyclic transition state and the C₂-C₃ bond cleavage (figure 4). The peak at $m/z = 227$ was due to loss of an isopropyl radical from the molecular ion to form a fragment of the type $[(CH_2)_{12}CO_2CH_3]^+$ (Figure 4). Besides to the above mentioned mass fragmentation peaks of Pentadecanoic acid, 14-methyl- methyl ester several additional mass fragment peaks were observed.

These were m/z ratios of 87, 55, 43, 41, 143, 69, and so on. The peak at $m/z = 87$ is due to bond cleavage between C₃ and C₄ and the formation of $[(CH_2)_2CO_2CH_3]^+$. The peak at $m/z = 143$ is due to bond cleavage between C₇ and C₈ and the formation of $[(CH_2)_6CO_2CH_3]^+$. The peak at $m/z = 43$ is due to bond cleavage between C₁₃ and C₁₄ and the formation of $CH_3^+CHCH_3$. The peak at $m/z = 41$ is due to bond cleavage between C₁₃ and C₁₄ as a result there is a formation of $CH_3\cdot CHCH_3$ radical. This radical further undergo fragmentation and two hydrogen atoms were removed from it and the peak $m/z = 41$ was appeared due to the formation of $CH_2=C^+CH_3$. The peak at $m/z = 55$ is due to bond cleavage between C₁₂ and C₁₃ leading to the formation of $CH_2CH_2CH_2CH_3$ radical. This radical further undergo fragmentation and two hydrogen atoms were removed from it, the peak $m/z = 55$ appeared due to the formation of $^+CH_2CH=CHCH_3$. The mass fragmentations of Pentadecanoic acid, 14-methyl-methyl ester were diagrammatically described as follows (Figure 5).

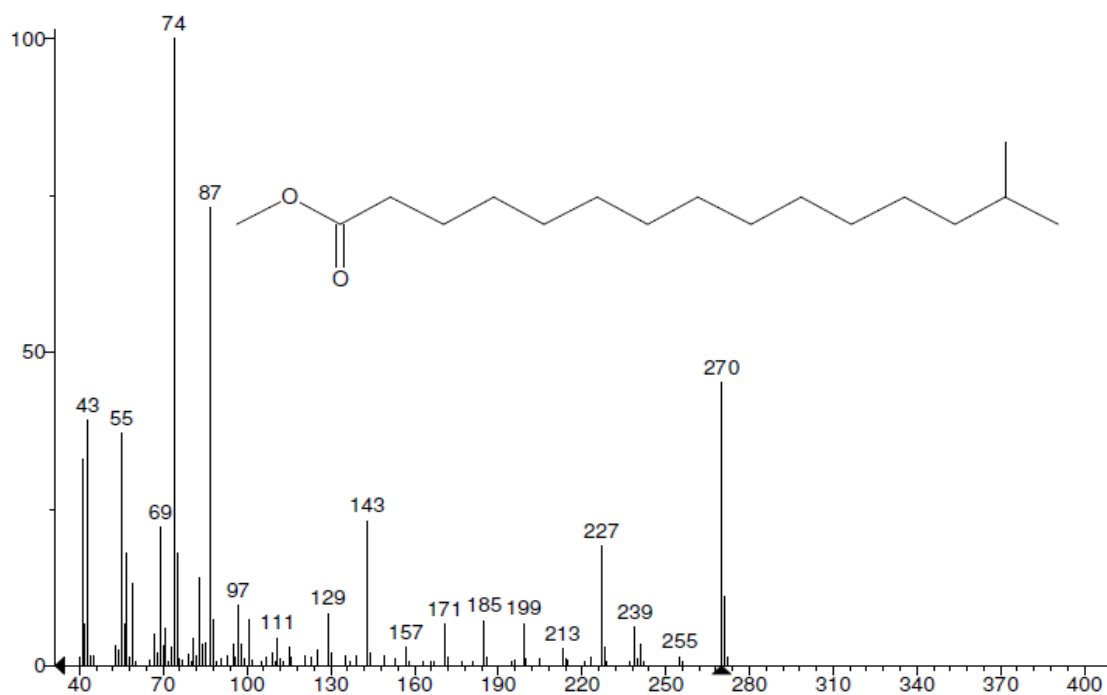


Figure 4. Mass spectra of Pentadecanoic acid, 14-methyl- methyl ester.

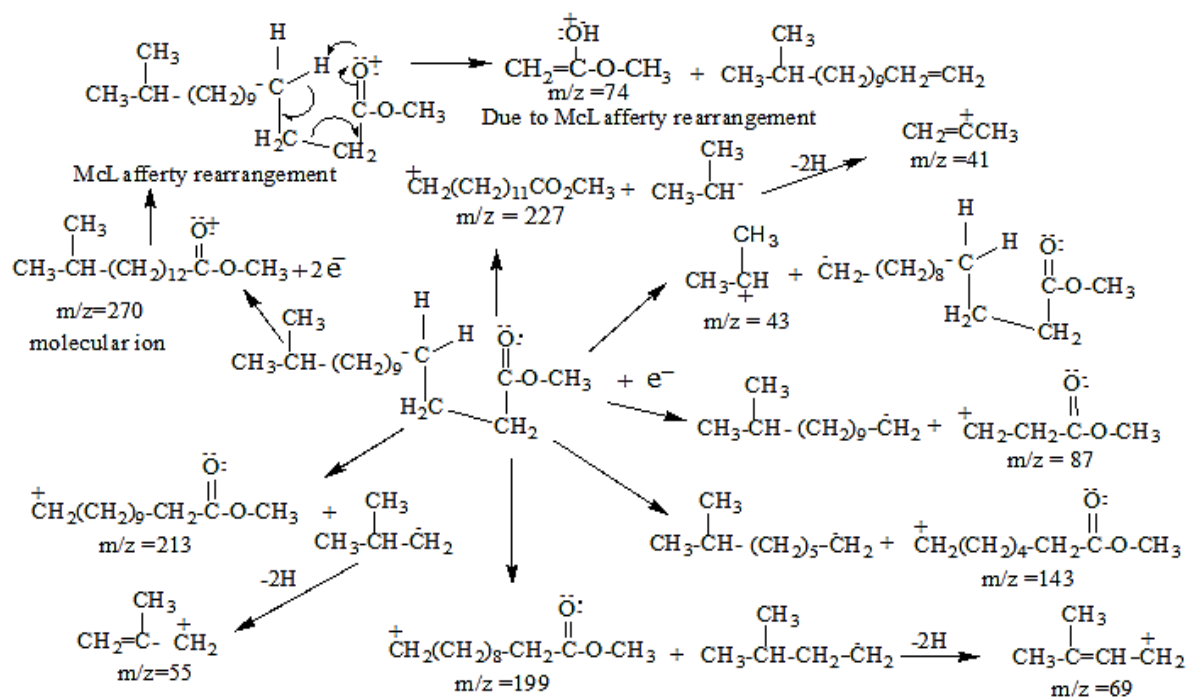


Figure 5. Mass fragmentation of Pentadecanoic acid, 14-methyl- methyl ester.

4. CONCLUSIONS

In this study, the four trans-esterification parameters affecting the yield of biodiesel such as reaction temperature, molar ratio of methanol to oil, type and mass weight of catalyst have been studied. In addition to this the oil, oil blends, biodiesel and biodiesel blends have been analyzed by employing analysis of physicochemical parameters and chromatographic technique coupled with spectroscopic technique (GC-MS) for identification of their chemical compositions. Our result indicates that all the process variables have significant effect on the yield of the biodiesel and a maximum of biodiesel yield (96.7 %) was obtained from raw castor oil by using the optimum process parameters such as methanol to oil molar ratio of 6:1, 1 % of NaOH, reaction temperature of 65 °C and reaction time of 3hours. Therefore, it can be concluded that NaOH is an effective catalyst for the production of biodiesel from castor oil via homogeneous trans-esterification. The main advantage of trans-esterification reaction conducted for biodiesel production in this study was to lower the high kinematic viscosity of the oil. The kinematic viscosity of the oil was reduced from 180 mm²/sec to 8.02 mm²/sec. All the physicochemical properties of the biodiesel produced from castor were determined and meet the ASTM specification except viscosity for B100 which is 8.02 mm²/sec. Therefore it was needed to blend with diesel fuel to bring it to the limits for biodiesel.

Recommendation

In this research, the biodiesel production process was done by using only homogeneous catalysts and methanol. Therefore, further research is warranted to check which catalyst (homogeneous or heterogeneous) is more effective and gives optimum amount of biodiesel.

Since enough ethanol will be available in Ethiopia in the future due to plantation of many sugar factories, future research on investigation of biodiesel production using heterogeneous catalyst and ethanol is recommended.

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