Biodiesel Production from Roselle Oil Seeds and Determination the Optimum Reaction Conditions for the Transesterification Process

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Abstract
This study was performed to extract oil from Roselle seeds and to investigate the production of biodiesel fuel from crude Roselle oil by using alkali- catalyzed transesterification process. On the other hand, The process of alkali-catalyzed transesterification with methanol was carried out to examine the effects of reaction variables on the Roselle biodiesel yield percentage these variables included catalyst concentrations of 0.25–2.0% wt/wt of Roselle oil taken, oil to methanol molar ratios of 1:3–1:9, of oil, reaction temperatures of 30–75 o C, and reaction times of 20– 60 min. The Roselle oil extracted was analyzed by gas chromatography (GC), the optimum condition for produced Roselle biodiesel having been achieved at a catalyst concentration of 0.5% w/w of oil, a oil to methanol molar ratio of 1:3, a reaction temperature of 65 o C, and a reaction time of 40 min. At those conditions The Roselle biodiesel obtained analyzed and compared with international standards specifications ASTM found have a good specification.

Keywords
Roselle Seeds, Extraction, Triglycerides, Gas chromatography, Reaction conditions, Transesterification, Biodiesel

I. I. INTRODUCTION

The consumption and demand for the petroleum products are increasing yearly due to increase in population. The United States is the largest single consumer of fossil fuels in the world. Each year, the U.S. A. consumes 125 Billion gallons of gasoline and 60 Billion Gallons of diesel fuel. With the current energy consumption, the demand for finding an alternative feedstock for the energy needs is increasing. One such alternative feedstock is vegetable oil. Vegetable oil offers the benefits of a greener synthetic route for obtaining diesel fuel. This fuel source is commonly known as biodiesel, and can be synthesized on an individual level; then scaled up to industrial scale.[1]

Biodiesel is defined as the mono-alkyl esters of fatty acids derived from vegetable oils or animal fats. [2] In simple terms, biodiesel is produced by transesterification of large, branched triglycerides in to smaller, straight chain molecules of methyl esters, using an alkali or acid or enzyme as catalyst. There are three stepwise reactions with intermediate formation of diglycerides and monoglycerides resulting in the production of three moles of methyl esters and one mole of glycerol from triglycerides. The overall reaction is:

Alcohols such as methanol, ethanol, propanol, butanol and amyl alcohol are used in the transesterification process [3] [4]. Methanol and ethanol are used most frequently, especially methanol because of its low cost, and physical and chemical advantages. They can quickly react with triglycerides and sodium hydroxide is easily dissolved in these alcohols.[3]

Roselle (Hibiscus sabdariffa var sabdariffa L.) is an important crop in the tropics and subtropics. It seems to be of an African origin, and might have been domesticated as 6000 years ago in Sudan.[5] Hibiscus section Furcaria (Malvaceae), to which Roselle belongs, is a morphologically distinct natural group of more than 100 known species, many of which are handsome ornamentals with large, showy, delicate flowers. This group includes a number of fiber, food, and medicinal plants such as knave (H. cannabinus) and Roselle (H. sabdariffa). It also displays a remarkable amount of genome diversity in Sub-Saharan Africa, where the centre of genome diversity is found [6] and [5].

Roselle (Hibiscus sabdariffa L.), known in Sudan as "Karkade" is an important annual crop which grown extensively in Darfur and Kordofan States under rain fed conditions, where large quantities are produced for local consumption and export purposes. Central Bank of Sudan reported that the total exported quantities of dry calyxes of Roselle were 18531 and 15656 tons with total income 17.59 and 14.09 million US dollars in 2011 and 2012, respectively and Roselle seed expected likely to the dry calyxes of Roselle. [7]

The Roselle (Hibiscus sabdariffa L.) trees, harvested calyces with capsules, Roselle separating calyces by decoder and Roselle capsules containing seeds shown in Figure 1.1, Figure 1.2, Figure 1.3 and Figure 1.4.:

Figure 1.1 Roselle (Hibiscus sabdariffa L.) trees; Figure 1.2 Roselle (Hibiscus sabdariffa L.) harvested calyces with capsules; Figure 1.3 Roselle (Hibiscus sabdariffa L.) separating calyces by decoder; Figure 1.4 Roselle (Hibiscus sabdariffa L.) capsules containing seeds.[8]

II. Materials and Methods

A. *Materials*

In this research samples of Roselle (Hibiscus sabdariffa L) Seeds (ELrahad-1) were obtained from local market in El-Obeid – North Kordofan State in November 2015 (red calyces). The Roselle seeds were ground into powder using a Grinder (Model EM- 11, Sharp, Japan)., All chemicals used in the experiments such as hexane, methyl alcohol with density at 20o C (0.79) minimum assay (GC) 99.0%, methyl orange and alkaline base such as sodium hydroxide and potassium hydroxide with minimum assay (GC) 85.0% as catalyst for producing a biodiesel obtained from National Research Centre (NRC) - Aromatic medicinal plants Institute - Sudan.

B. *Equipments*

Sensitive weightier, Soxhlet, rotary evaporator, hot plate with magnetic stirrer, oven, micro computer ph meter, thermometer, separator fennel, flat bottom flask as a reactor conducted with condenser, Grinder, cylinder, bikers (500 volumes) and Gas chromatography mass spectrometer (GCM).

C. *Transesterification method*

Transesterification also called alcoholysis which is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis except that an alcohol is used instead of water this has been widely used to reduce the viscosity of the triglycerides. The transesterification is represented as

$$\underset{\text{Ester}}{RCOOR} + \underset{\text{Alcohol}}{R'OH} \rightleftharpoons \underset{\text{Ester}}{R'COOR'} + \underset{\text{Alcohol}}{ROH}$$

The methanol was used in this process, then it was called methanolysis.[9], [10] and [11]

D. *Experimental works*

1) *Extraction of Roselle oil*

1000 gram of (*Hibiscus sabdariffa* L.) seed powder were placed in a cellulose paper cone soxhlet and extracted with n-hexane for eight hours as show as in Figure 2 (a) bellow. The oil was recovered by evaporating off the solvent using rotary evaporator (Model N-1Eyela, Tokyo Rikakikal Co. Ltd. Japan) and then the oil poured into open biker and put it under fan for one night to evaporate any traces of n-hexane. The experiment taken for three times and the extracted oil average weight obtained was 191.1 gram. The sample of extracted Roselle oil shown in Figure 2 (b) bellow.

(a) **(b)**

Figure 2 (a) Roselle seeds in Soxhlet (b) sample of Roselle oil extracted.

The fatty acid composition in Roselle oil analyzed by gas chromatography and the density and average molecular weight were determined as (0.907 g/mL and 257.18 g/mol).

2) *Alkali-catalyzed transesterification*

The transesterification of crude Roselle oil with methanol by using potassium hydroxide (KOH) as catalysis was carried out in a laboratory-scale setup. The equipment used for this study consisted of a 250 mL flat-bottom reaction flask and hot plate with magnetic stirrer (Fisher Scientific, made in USA, model no. 11-501-7 SH). Reactions conducted in a three-neck round-bottom flask fitted with a condenser (to reduce the loss of methanol by evaporation) and a thermometer. The mixture in the reaction flask was heated and well-stirred at a constant stirring speed of 600 rpm this agree with [12] [13] for all test runs. The crude Roselle oil, methanol and potassium hydroxide were used in amounts established for each experiment, the oil preheated to the desired temperature (60o C) in the reaction flask. In order to maintain its catalytic activity the solution of potassium hydroxide in methanol was freshly prepared for each run since prolonged contact with air would diminish the effectiveness of the catalyst through interaction with moisture and carbon dioxide [12]. The potassium hydroxide-methanol solution was then added to the preheated oil in the reaction flask, at which point the time measurement began and stirring were continued. The optimum of reaction variables (reaction time, reaction temperature, catalyst concentration and oil to methanol molar ratio) were determined by considering one of it as times (20 to 60 min), reaction temperatures (30 to 75 oC), catalyst concentrations (0.25 to 2 wt. of KOH to wt. of oil), and Roselle oil to methanol molar ratios (1:3 to 1:9 oil to methanol) while the other variables remained constant at atmospheric pressure as shown as in table 1 below.

TABLE 1 Reactions with different reaction parameters

Run No.	Reaction temperature(^{o}C)	reaction time (min)	Catalyst concentration (w/w of oil) %	Oil to methanol molar ratio
1	30	40	0.5	01:06
2	50	40	0.5	01:06
3	65	40	0.5	01:06
4	75	40	0.5	01:06
5	50	40	0.5	01:03
6	50	40	0.5	01:09
7	50	20	0.5	01:06
8	50	60	0.5	01:06
9	50	40	1	01:06
10	50	40	2	01:06
11	50	40	0.25	01:06

After the reaction, the mixture was allowed to settle by gravity for 24 h in the separator funnel. Two layers were formed: the upper layer consisted of methyl ester, methanol traces, residual catalyst and other impurities. Whereas the lower layer consisted of glycerin, excess methanol, catalyst and other impurities. The glycerin layer was then drawn off and the methyl ester layer (Biodiesel layer) was purified by washing with hot distilled water at 60 ^{o}C until the washing water had a PH value similar to that of distilled water. The hot distilled water-to-crude methyl ester ratio was 1:1. The washing step was done gently to prevent the possibility of loss of methyl ester due to emulsion formation as shown as in Figure 3.

Figure 3 Biodiesel washing with hot distal water

Next, the methyl ester layer was dried under reduced pressure at 70 ^{o}C by rotary evaporator. Finally, the volume of pure products from the reactions measured and was analyzed by using the standard test according to ASTM method to determine its properties.

III. RESULTS AND DISCUSSIONS

A. Characterization of the crude Roselle oil extracted

The extracted Roselle oil obtained was analyzed in University of Khartoum , faculty of science had clear, viscous, yellow in color, without having undergone any further refining for use as a biodiesel feedstock and has a density, average molecular weight, oil percentage 0.907 g/mL and 257.18 g/mol 19.11 % respectively and the fatty acid composition in Roselle oil analyzed by gas chromatography as shown an in Figure 4 and table 2 below this results is considered closely with results obtained by *Eltayeib et al [14]*. Slightly differ in acid compositions depends on the quality of seeds, which may affected by the number of irrigations, fertilizer ...etc

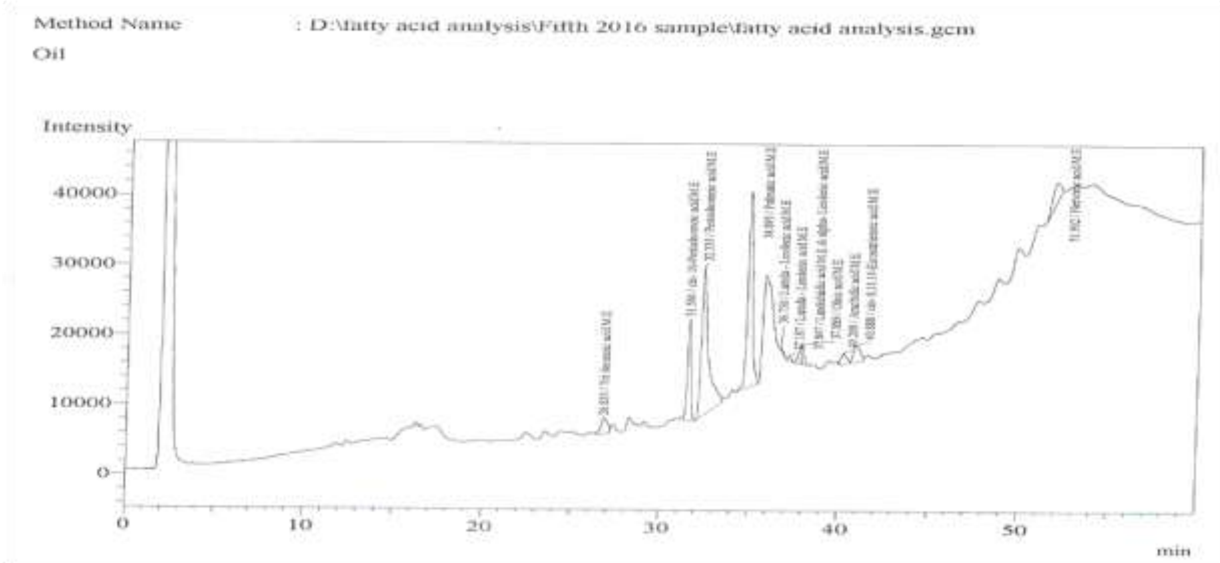

Figure 4 Fatty acids in Roselle seed oil (red calyces) by GC

TABLE 2 Roselle seed oil composition, oil percentage and molecular weight in (red calyces) by GC

Peak no.	**Name**	**Percentage (%)**	**Molecular weight g/mol**
1	decanoic acid	3.6926	178.26
2	pentadecenoic acid	12.0982	242.3975
3	pentadecenoic acid	35.2829	242.3975
4	Palmatic acid	33.2440	256.4241
5	linolenic acid	0.1965	278.44
6	linolenic acid	0.5261	278.44
7	Linolelaidic acid	1.9506	280.45
8	Oleic acid	1.4421	282.4614
9	Arachidic acid	2.2646	304.4669
10	Eicosatrienoic acid	3.9613	306.48276
11	Nervonic acid	5.4310	366.62
Total	11	100.0	Sum Mwt =257.18

B. Properties of Biodiesel

Biodiesel produced is very clear, yellow in color, and was analyzed and compared with the fuel properties of biodiesel as per ASTM Standards. The Roselle oil, however, was found to have much higher values of fuel properties, especially kinematic viscosity and density restricting the direct use as a fuel in diesel engine. After transesterification, the kinematic viscosity and density values reduced to permissible limit. The flash and pour points were in a limit of safe storage and handling conditions. Also the cetane number, sulfur content and total acid number it's had good results as comparing with stander biodiesel. The table 3 and Figure 5 bellow shown Properties of Roselle biodiesel in comparison with ASTM specifications and samples of clear biodiesel respectively.

TABLE 3 Properties of Roselle biodiesel in comparison with ASTM specifications

Property	Test method	Unit	Roselle biodiesel	Biodiesel specification(ASTM)
Density at 15 ^{0}C	ASTM D4052	g/mL	0.8829	--
Pour point	ASTM D97	^{0}C	+3.0	-15-10
Flash point	ASTM D93	^{0}C	172.0	Min. 130
Kinematics viscosity at 40 ^{0}C	ASTM D445	cSt	5.320	1.9-6
Sulfur content	ASTM D4294	mass%	0.0255	Max. 0.02
Total acid number (TAN)	ASTM D664	mg KOH/g	0.04	Max. 0.5
Cetane number	Chart	--	53	48-65

Figure 5 samples of clear biodiesel

C. *Optimize the reaction variables*

The optimum of reaction variables (reaction time, reaction temperature, catalyst concentration and oil to methanol molar ratio) were determined by considering one of it while the other variables remained constant. After an optimum was attained, this value was maintained constant, and then the optimum of the next variable was determined. These parameters determined by record its effecting on the biodiesel yield % as in table 4.

TABLE 4 biodiesel Yield percentages

Run no.	Biodiesel Yield %
1	86.52701
2	90.85336
3	99.50606
4	80.03749
5	93.01654
6	34.6108
7	86.52701
8	90.85336
9	82.20066
10	67.05843
11	58.40573

1) Catalyst concentration

Effect of variation of amount of catalyst on yield percentage was studied. Catalyst amount was varied in the range of 0.25% to 2.0% (wt/wt of the Roselle oil taken) while the other parameter studied remaining constant as shown in experiments run (2, 9, 10 and 11) above. As in Figure 6 show yield vs. catalyst concentration, the yield increased firstly with the increase of catalyst amount from 0.25% to 0.5%. But, with further increase in the catalyst amount from 1.0% to 2.0%, the yield decreased due to soap formation.[15] Obtained their best result at 0.5 wt % catalyst amount which is 90.9 % yield.

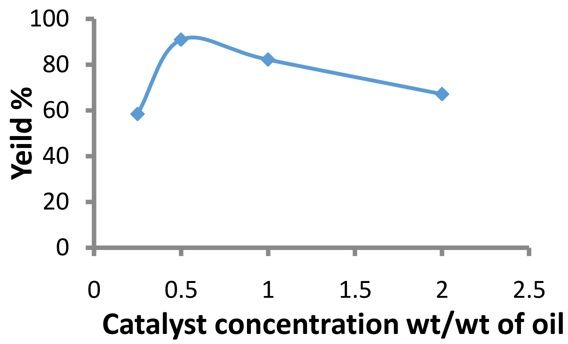

Figure 6 Yield % vs. catalyst concentration

2) Reaction time

Effect of variation of reaction time on yield percentage was studied. Reaction time was varied in the range of 20 to 60 min. while the other parameter studied remaining constant as shown in experiments run (2, 7 and 8) above. Figure 3.3.2 show yield vs. reaction time, the yield increased versus time from 20 minutes to 40 minutes and remaining constant with the increase of time. The best result at 40 minutes which is 90.9 % yield. As in Figure 7 below

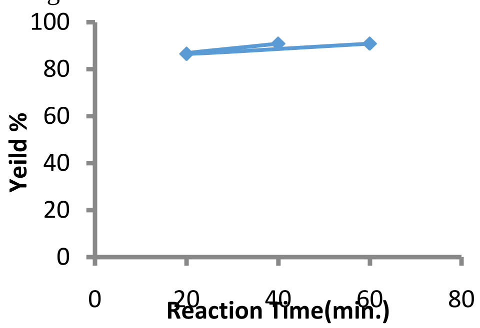

Figure 7 Yield % vs. reaction time (min.)

3) Reaction temperature

Effect of variation of reaction temperature on yield percentage was studied. Reaction temperature was varied in the range of 30 to 75 ^{o} C. while the other parameter remaining constant as shown in experiments run (1-4) above. Figure 3.3.3 show yield vs. reaction temperature. The yield increased from temperature 30 to 65 ^{o} C due to increasing in reaction constant and after that decrease due to evaporation of methanol. The best result at 65 ^{o} C which is 99.5 % yield. As in Figure 8 below

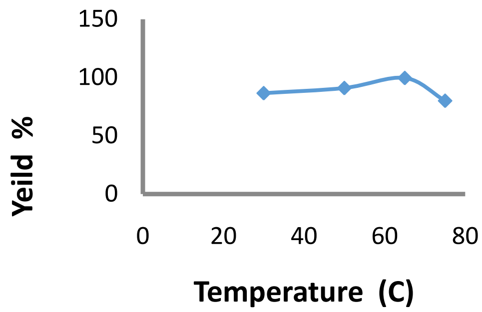

Figure 8 Yield % vs. reaction temperature (C)

4) Oil to Methanol Molar Ratio

Stoichiometrically, the methanolysis of Roselle oil requires three moles of methanol for each mole of oil. Experimentally investigated the effecting of oil to methanol molar ratio on the yield percentage by taken varied molar ratio as 1:3, 1:6 and 1:9 While the other parameter remaining constant as shown in experiments run (2, 5 and 6) above. The best result obtained 93% yield at 1:3 as in Figure 9 below

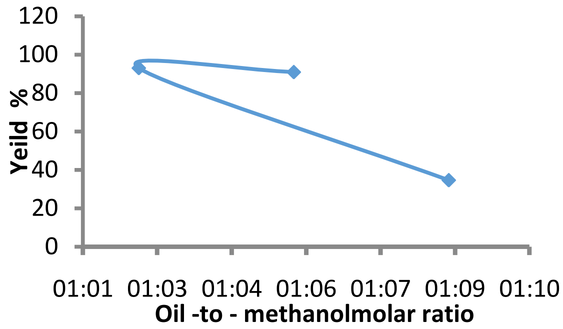

Figure 9 Yield % vs. oil to methanol molar ratio

I. CONCLUSIONS

This study demonstrates that biodiesel can successfully be produced from crude Roselle oil by alkali-catalyzed transesterification reaction with methanol in the presence of a catalyst potassium hydroxide (KOH)and considered alternative fuels, which will reduce pollution and protect the environment.

Transesterification reaction for the production of biodiesel was found to be very promising from the results obtained. The optimum conditions for the production of biodiesel from Roselle oil were reaction temperature 65 ^{o} C, molar ratio of oil to methanol of 1:3, catalyst concentration of 0.5 wt% and reaction time of 40 min.

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