Chemistry Research Journal, **2018, 3(1):122-126**

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

Synthesis and Comparative Study of Biodiesel from Refined Shea Butter and Black Seed Oil in Admixture

Bello Y. Makama[1], Idris Habibu[2]

[1]Department of Science and Maths, American University of Afghanistan
[2]Department of Chemistry, Kano University of Science & Technology. P.M.B. 3244 Wudil, Kano State, Nigeria

Abstract The environmental concern and decreasing reserves of fossil fuels has brought to bearan increasing study in the alternative low carbon sources of energy. Herein we reported optimize biodiesel production from Shea butter and black seed oils in admixture via base catalysed transesterification protocol. The optimum yield in the base catalysed transesterification was found to be 91%, 60oC, 6:1 methanol to oil ratio and 1% KOH catalyst. Under the same conditions, the optimum yield from the acid-base catalysed reaction was found to be 94%.

Keywords Shea butter oil, Black seed oil, transesterification, admixture, acid-base catalyse

Introduction

Shea tree (*Vitellaria paradoxa*) has remained a promising source of biodiesel. It is a deciduous tree which grows naturally in the wild, especially in the savannah belt of Africa [1]. Shea butter tree (*Vitellaria paradoxa*), also referred to Karité (French), which means “the tree of life” is an indigenous fruit tree of Sudano-Sahelian, Africa. It is believed to possess numerous healing characteristics [2]. In Nigeria, it is commonly found in the guinea savanna belt or zone of the country but seemingly absent in the arid zones [3].The specie is found scattered round the farmlands in Niger State, Nigeria. Shea butter is known variously in some local languages as: Emieemi (Yoruba), kadanya (Hausa), Ichamegh (Tiv), Okumeh (Ebira) and in the southern part commonly known as Ori [4]. Shea butter tree grows up to 9-12m high exceptionally 25m with large much branched crown covering about 5-10m. Africa produces about 1,760,000 metric tonnes (t) of raw Shea nuts annually from its wild trees mainly in the Savannah and Sahel regions. Producers, however, harvest only a fraction, about 35% (about 600,000t), which is then transformed into butter or exported as nuts. The Shea tree grows naturally in the wild of the dry Savannah belt of West Africa. Its range stretches from Senegal in the west to Sudan in the east, and into the foothills of the Ethiopian highlands. Shea trees thrives in 19 countries across the African continent. Seven West African countries (Ghana, Burkina Faso, Benin, Cote d’Ivoire, Nigeria, Mali and Togo) produce a total of about 500,000 tonnes of theShea nuts. These countries export an estimated 270,000 t as raw nuts and convert the remaining 230,000 tonnes into roughly 60,000 tonnes of crude Shea butter, half of which is later exported [5].

The black seed or rather black cumin plant (*Nigella sativa*) was originated from or otherwise cultivated in Turkey/Egypt. Cumin besides being used medicinally, was in the Middle Ages one of the commonest spice of European plant, indigenous to Upper Egypt, but from early times was cultivated in Arabia, India, China and in the countries boarding on the Mediterranean. *Nigella sativa* is an annual flowering plant, native to south and southwest

Asia. It grows to 20-30cm (7.9-12in) tall, with finely divided, linear (but not thread like) leaves. The flowers are delicate, and usually coloured pale blue and white, with five to ten petals. The fruit is a large and inflated capsule composed of three to seven united follicles, each containing numerous seeds. *Nigella sativa* belongs to the family *Ranunculaceae andis* called *Habbatus sauda* in Hausa. It is an annual herbaceous plant and is believed to be indigenous to the Mediterranean region but now it has been cultivated into other parts of the world including Africa [6,7]. The seeds are believed to have galactagogue, carminative, laxative and antiparasitic properties [8]. An antibacterial effect of the phenolics fraction of the seed oil was first reported [9]. Latter, the diethyl ether extract of *Nigella sativa* was also reported [10] to inhibit the growth of bacteria. Aqueous suspension of *Nigella sativa* seeds was reported to have an analgesic effect comparable to aspirin test on rat [11]. The antischisommicidal effect against *Schistosoma mansoni* and antimalarial activities have been studied [12, 13]. The chemical constituents of the fixed and volatile oils of *Nigella sativa* obtained from Iran have been reported [14]. *Nigella sativa* oil can be fully utilized for the manufacture of perfumery products, antimicrobial and antiseptic agents [15].

Experimental Methods

Plant Material

A refined black seed and Shea butter oils were obtained from a local marked (Rimi Market), Kano State, Nigeria

Experimental Procedure

A base catalysed transesterification

To a stirred solution of methanol 120mL, was added KOH, 0.179 (1% w/w) and the stirring continues until all the KOH had dissolved. The resulting methoxide solution was added to preheated oil admixture 20mL. The reaction was heated to 45^{o}C for a period of 60min with constant stirring. The reaction was stopped and the product was added into a 250mL separating funnel and allowed to stand overnight, two distinct layers were observed. The bottom layer which contains Glycerol was drained off and the upper layer (biodiesel) was collected. The reaction was repeated for temperatures; 50^{o}C, 55^{o}C, 60^{o}C and 65^{o}C.

Acid-based catalysed transterification reaction

To a preheated oil admixture 20mL was added methanol 48mL (40% v/v). The resulting mixture was stirred gently for 5 minutes until it became murky. Two drops H_2SO_4 acid (95%) were added and the temperature was kept at 60^{o}C for another 1h. The reaction was stopped and allowed to cool for 2h. The methanol-water fraction at the top layer was removed and the oil was collected. 120mL of the freshly prepared methoxide was mixed with pre-treated oil above; this mixture was then transferred into a beaker connected with stirring device under reflux condition. The mixture was stirred for an hour with a temperature kept at 60^{o}C. The reaction was stopped and poured into separating funnel and allowed to stand overnight. Two layers were observed. The bottom layer (glycerol) was drained off and the top layer (biodiesel) was collected.

Crude Biodiesel Purification

Neutralization of the bio-diesel

1 mL of 0.1 M H_2SO_4 acid was mixed with crude biodiesel and allowed to settle for some hours and the dark suspensions formed were drained off gently into a clean beaker.

Washing of the biodiesel

The clean biodiesel treated above was washed with warm deionised water (30% v/v of the biodiesel) two times to remove all soluble salts and suspensions.

Drying of the bio-diesel

Finally, the washed fatty acid methyl ester (FAME) was dried in an oven at a temperature of 110^{o}C to let the expected water and residual methanol molecules escape.

The percentage yield of a clear pure biodiesel recovered after it has been washed and dried was calculated using the following relation.

% yield of biodiesel = $\frac{\text{volume of biodiesel recovered}}{\text{Volume of the reactants used}} \times 100$

(Oil admixture & methoxide)

pH Determination

The biodiesel sample was agitated thoroughly. Then, the pH value was determined by using Exstik pH meter, model pH100. 20 mL of the biodiesel sample was poured into the flat surface pH electrode, and then the pH meter was inserted into it. The bar graph was observed carefully until a steady value was observed. The pH value was noted and recorded.

Determination of Specific Gravity

A clean density bottle marked 50mL was taken and the following measurements were recorded to ascertain the exact value of the specific gravity of the pure biodiesel at 33^{o}C.

Measurements:

Weight of a clean, dried empty density bottle, M_o=14.197g

Weight of a density bottle filled with distilled H_2O, M_1=67.073g

Weight of a density bottle filled with biodiesel, M_2= 59.725g

Now, the specific gravity of the pure biodiesel produced was calculated using the following equation.

$$S.G = (M_2-M_o/ M_1-M_o)$$

Where S.G. = is the specific gravity of the biodiesel

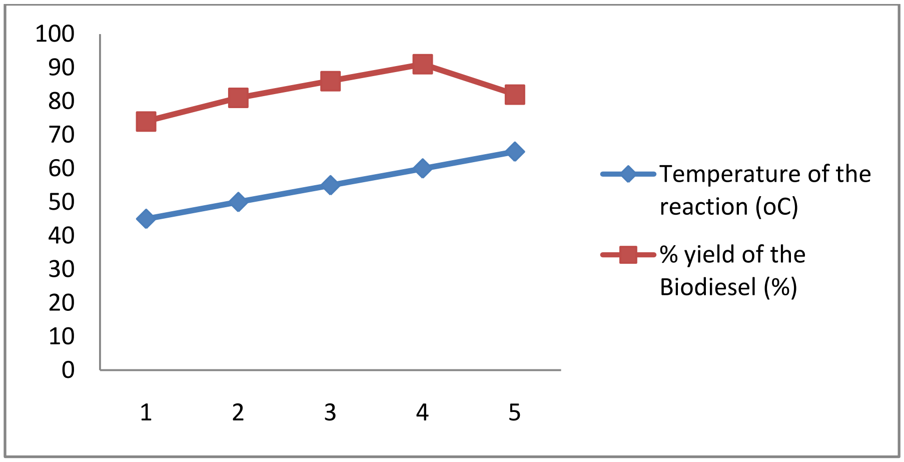
M_o, M_1 and M_2 are the weight measured above.

Result and Discussions

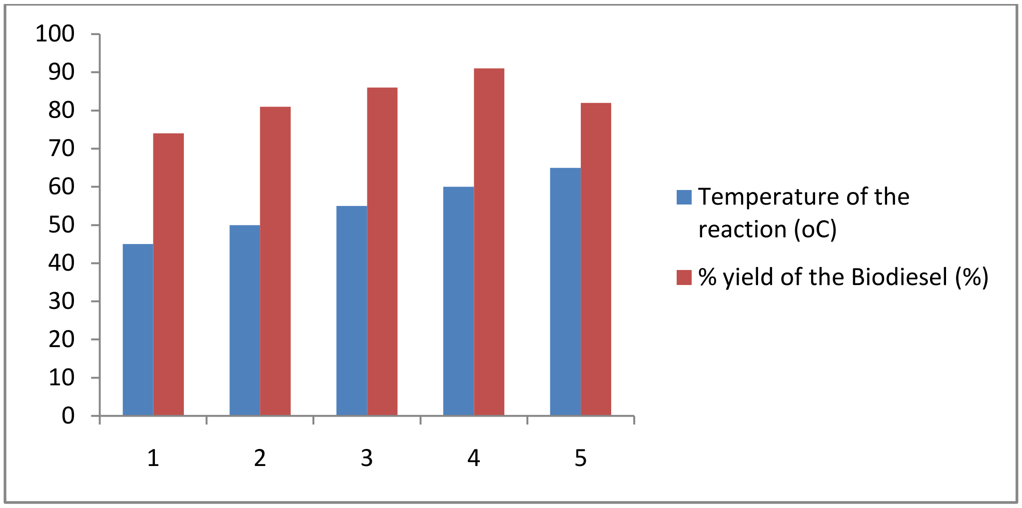
Table 1: Result of the experiments conducted

S/n	Reaction temperature	Methanol / oil ratio	Catalyst amount (%)	Volume before purification (ml)	Volume after purification (ml)	% yield of the biodiesel recovered
1	45^{o}C	6:1	1% w/w	107.8	103.2	74%
2	50^{o}C	6:1	1% w/w	113.8	112.8	81%
3	55^{o}C	6:1	1% w/w	127.0	121.8	86%
4	60^{o}C	6:1	1% w/w	132.0	127.2	91%
5	*60^{o}C	6:1	1% w/w	134.6	132.1	94%
6	65^{o}C	6:1	1% w/w	117.0	115.0	82%

*Result of acid-base transesterification reaction of the oil admixture at optimized condition



Scheme 1: A graphical result of the transesterification protocol



Scheme 2: The graph and bar chat for the effect of temperature on the percentage yield of transesterification reaction

Table 2: Biodiesel Physicochemical Characteristics Compared With ASTM and EN Standard

S/n	Parameters	Value obtained	Standard value (ASTM & EN)
1	pH	7.20	7.0---7.99
2	Specific Gravity	0.86	0.86---0.90
3	Colour	Golden yellow	Golden yellow

The results obtained based on the effect of temperature on the percentage yield of bio-diesel generated from this oil admixture as the feedstock are presented in table 1, above. The best yields were obtained for the methyl esters produced via a one step base catalysed transesterification and a two-step acid-base catalysed transesterification methods at temperature of 60^{o}C, with the methyl ester yield being 91% and 94% respectively. It was envisaged that at 60^{o}C, the molecules of the triglycerides of the oil admixture had high kinetic energy and this increased the collision rate and therefore, improved the overall process by favouring the formation of methyl esters, while at lower reaction temperature there was lesser collision of reacting molecules and thus, reduced the percentage yield as seen in the same table 1. The reason for this behaviour is due to the endothermic nature of the reaction. The higher reaction temperature would favour endothermic reaction, thus increasing the rate of reaction as well as bio-diesel yield. However, at 65^{o}C, it was noted that there was a drop in the yield; this could be attributed to the increased vaporization of the methanol used in the reaction due to the proximity of the reaction temperature to the boiling point of methanol (i.e. 64.7^{o}C). The pH and specific gravity values were found to conform to ASTM and EN norms. It is worth mentioning that the present study has enabled us to confirm that Shea butter and black seed oil in admixture may be used as a feedstock to obtain biodiesel.

Conclusion

An intensified effort to provide an alternative source of fuel has been a major subject of discussion in recent years, due to fuel crisis between the oil rich regions and others without oil within the same country and even around the globe, price instability and above all a focus on environmental stability. This study reports the optimized condition (6:1 methanol to oil ratio, 60mins reaction period, 1% KOH catalyst and 60^{o}C reaction temperature) of the production of biodiesel from oil admixture (Shea butter and black seed oil) as alternative to petro-diesel. The same optimal reaction condition of a two-step acid base catalysed method and one-step base-catalysed method were compared in the synthesis of biodiesel from the oil admixture. It can be concluded that a two-step acid-base catalysed method had a higher bio-diesel yield (94%) than a one step base-catalysed method (91%) at the same optimal reaction condition, and the bio-diesel recovered via a two step acid-base catalysed method gives a faster phase separation of the products with a longer reaction period.

References

1. Zargari, D. (1990). Medical Plants. Tehran Univeristy press, Tehran, 43-44.
2. Azza, M. M., Nadia, M., & Sohair, S. (2005). Nigella sativa seed oil against Schistosoma mansoni in different stages. Men. Inst. Oswaldo. Cruz. Rio de Janeiro, (100), 205-211.
3. A, A. H., & Zainal-Abidin, B. (2007). *In Vivo* Antimalarial tests of Nigella Sativa (Black seed) in different extracts. American Journal Pharmacol. Toxicol, 2(2), 46-50.
4. A., R. M., & Al-Ghandi, M. (2002). A Review of the Pharmacotherapeutic Effects of Nigella sativa. Pakistan Journal of Medical Research, (41), 77-83.
5. Adamu, H. M., Ekanem, E. O., & Baluma, S. (2010). Identification of Essential Oil Components from Nigella sativa seed by Gas Chromatography-mass Spectroscopy. Pakistan Journal of Nutrition, 9(10), 966-967.
6. Adegbehin, J. O., & Omigeh, J. (1993). Agroforestry Diagnostic Survey of some parts of Niger state of Nigeria. Agroforestry Systems, (22), 1-55.
7. Addaquay, J. (2004). The Shea butter value chain Refining in West Africa. West Africa Trade Hub Techniclal Report, (3), 1-29.
8. Amin, G. (1991). Popular Medicinal Plants of Iran. Irannian Research Institute of Medicinal Plants, Tehran, Iran, 80.
9. B, N., Mojab, F., Javidnia, K., & Amoli, M. (2003). Chemical Composition of the fixed and Volatile Oils of Nigella Sativa L. From Iran. Zeitschrift Naturforschung, (58), 629-631.
10. Boffa, J. M. (1999). Agroforestry parkland System in Sub-Saharan Africa. Forest Conservation Guide, (34).
11. Enweremadu, & Alamu. (2009). Development and Characterization of biodiesel from shea nut butter. International Agrophysics, (24), 29-34.
12. H., T. H., Masloun, H., & Dakhakhany, M. The antibacterial properties of Nigella sativa seed, Active principle with some clinical application. J. Egypt Med. Assoc, 48(Suppl), 187-202.
13. Keay, R. W. (1989). An Outline of Nigeria Vegetation. Government Printer Lagos Nigeria, 37.
14. Makama, B. Y., Temitope, B., Clifford, N., & Okoro, L. N. (2011). Synthesis and calorific value for biodiesel by methanolysis os castor and olive oils in admixture. American Journal of Basic and Applied Science, 5(11), 874-878.
15. Mozoffarine, V. (1998). A Dictionary of plants Names. Farhang Moaster Publishers, Tehran, 365.
16. S., H. M., & Hatem, M. (1991). Studies on the Antimicrobial Properties of Nigella sativa seed. J. Ethnophamacol, (34), 275-278.