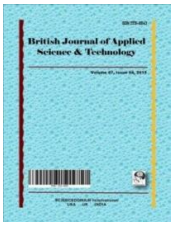

British Journal of Applied Science & Technology
8(3): 246-253, 2015, Article no.BJAST.2015.203
ISSN: 2231-0843

SCIENCEDOMAIN *international*
www.sciencedomain.org

Physico-chemical Characteristics and Fatty Acids Composition of Some Selected Nigerian Vegetable Oils for Quenching Medium

J. B. Agboola[1*], O. K. Abubakre[1], E. Mudiare[1], M. B. Adeyemi[1] and S. B. Hassan[2]

[1]Department of Mechanical Engineering, Federal University of Technology, Minna, Nigeria.
[2]Department of Metallurgical and Materials Engineering, University of Lagos, Akoka, Yaba, Lagos, Nigeria.

Authors' contributions

This work was carried out in collaboration between all authors. Author JBA designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript and managed literature searches. Authors OKA, EM, SBH managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/BJAST/2015/16177
Editor(s):
(1) Soichiro Nakamura, Department of Bioscience and Biotechnology, Shinshu University, Japan.
(2) Harshadrai M. Rawel, Institute of Nutritional Science, University of Potsdam, Germany.
Reviewers:
(1) Anonymous, Nigeria.
(2) Anonymous, Nigeria.
(3) Monsurat Jimoh, Chemical Engineering Department, Ladoke Akintola University of Technology, Nigeria.
Complete Peer review History: http://www.sciencedomain.org/review-history.php?iid=1071&id=5&aid=8715

Original Research Article

Received 13th January 2015
Accepted 16th March 2015
Published 8th April 2015

ABSTRACT

Four vegetable oils (cotton seed oil, palm kernel oil, neem seed oil and palm oil) were characterized with respect to their physicochemical properties and fatty acids profiles with the aim of investigating their suitability as quenching media for medium carbon steels. The physicochemical properties were determined by using appropriate ASTM methods. The fatty acid ester compositions were determined by a gas chromatographic analysis procedure. The results obtained showed that the different vegetable oils exhibited different viscosity and viscosity-temperature behaviour corresponding to their varying molecular structures and level of saturation. The following values were obtained for the various physicochemical parameters measured in cotton seed oil, palm kernel oil, neem seed oil and palm oil: viscosity value at 40ºC were (34.8, 41.69, 32.41 and 39.7) cSt; viscosity value at 100°C were (6.9, 8.94, 7.89 and 8.2) cSt; the Iodine values were (115.09,

**Corresponding author: E-mail: joe_agboola@yahoo.com;*

19.59, 120.16 and 35.90) g I_2/100 g while the acid values were (1.80, 0.22, 12.97 and 1.23) mgKOH/g respectively. The level of saturation of the fatty acids followed the decreasing order of palm kernel oil (0.25), palm oil (0.92), cotton seed oil (1.35) and neem seed oil (1.39). The results obtained showed that the vegetable oils under study are suitable as potential quenching media for carbon steels with palm kernel oil being the most suitable followed by cotton seed oil and neem seed oil. The least suitable among the oils is palm oil.

Keywords: Vegetable oil; physicochemical properties; fatty acids; quenching medium.

1. INTRODUCTION

Over the years, water and mineral based oils were the most commonly used media to quench steel because they were readily available. Although water quenching is faster and less costly than oil quenching, the degree of distortion that accompanies water quenching can be very high. Therefore oil quenching which is less severe than water quenching is generally preferred. However, because of environmental concerns and growing regulations over contamination and pollution, associated with the disposal of used petroleum based oils, it is of continuing interest to develop more environmentally friendly quenching media based on safer, renewable and biodegradable vegetable oils [1].

Quenching medium serves two primary functions namely, to facilitate hardening by controlling heat transfer and to enhance the wetting of steel thereby minimizing distortion and cracking [2]. In order to be a viable alternative, the quenchant must have high oxidation resistance, low sludge formation, acceptable heat-transfer characteristics, and a high flash point, besides being environmentally friendly. Currently vegetable oils are one of the most commonly identified renewable, biodegradable and non-toxic alternatives [3].

Vegetable oils are esters of glycerol and fatty acids of various lengths (about 14 to 20 carbon atoms) and degrees of unsaturation [4]. The usefulness of vegetable oils is determined by their compositions and physicochemical properties. However the differences in their physicochemical properties are due primarily to their chain length, degree and position of unsaturation which in turn determines their application. All oil has fixed combination of the different fatty acids present in it, but the proportions of these vary with locality, soil, season, and other factors. This accounts for differences between the same species of oil from different places, or harvested at different times. It is also the reason why different vegetable oils exhibit different inherent properties or why one vegetable oil may be favoured for an application, such as quenching relative to another [5]. Hence, the study of their constituents is important.

Quenching oil characterization is necessary to ensure optimal quench process control by monitoring quality variations throughout the oil's life time. This is accomplished by measuring a series of physicochemical properties which includes viscosity, acid number, iodine number and flash point. In addition to physicochemical properties characterization, fatty acid profile should also be determined [6].

Quenching oil's performance is dependent on its viscosity [7]. Due to degradation, oil viscosity changes with time. Viscous oil will produce a more stable vapour blanket, consequently slowing down the cooling rate. In practice, low viscosity oil, typically 20 mm^2s^{-1} at 40ºC is usually preferred because a faster cooling rate is achieved and less drag out occurs. Viscosity is measured by the standard ASTM D 445 (ISO 3104). The viscosity is reported in centistokes (cSt), equivalent to mm^2/s in SI unit. Typically, the viscosity is reported at one of two temperatures, either 40ºC or 100ºC [8].

Another parameter of importance is the viscosity index (VI). Viscosity index is a unitless number, used to indicate the temperature dependence of an oils kinematic viscosity [9]. It is based on comparing the kinematic viscosity of the test oil at 40ºC, with the kinematic viscosity of two reference oils - one of which has a VI of 40ºC, the other with a VI of 100ºC - each having the same viscosity at 100ºC as the test oil. Tables for calculating VI from the measured kinematic viscosity of oil at 40 and 100ºC are referenced in ASTM D2270.

Acid number (AN) is defined as the number of milligram (mg) of potassium hydroxide required to neutralize the free fatty acids present in one gram (1 g) of the oil sample. It is an indication of

the level of oxidation in quenching oil [10]. Oxidation of the quench oil takes place due to repeated heating and cooling and forms organic acids, thus giving an increase in acid number. The oxidation reactions lead to polymerized and cross-linked molecules, which are insoluble in the oil and results in sludge formation. The formation of oxidation constituents in base oil, decrease the stability of the vapour phase and increase the maximum cooling rate thereby increasing the rise of distortion and cracking. The higher the acidity levels of any oil, the higher its aggression on the quenching bath [11]. Oils with low acid value are good candidates to be used as quenchants. AN is determined by a titration procedure using potassium hydroxide (KOH) and is reported as milligram of KOH per gram of sample (mgKOH/g).

Iodine number of oil is the amount of iodine (g) absorbed by 100 g of oil. Iodine number measures the level of unsaturated fatty acids present in the oil [12]. Iodine number is determined according to ASTM D5554-95.

Flash point of oil is the lowest temperature at which the application of a flame causes the vapour above the oil to ignite. The flash point is the maximum safe operating temperature of the oil and changes in flash point indicates contamination of the quench bath [13]. There are two types of flash point test procedures – closed –cup or open –cup. In the close –cup measurement, (ASTM D93), the liquid and vapour are heated in a closed vapour – confined area. The flash point of quenching oil should be high for two reasons. The first reason is that the flash point indicates that the oil does not contain volatile constituents, which would prolong the vapour blanket stage and slow the quenching rate. The second one is that the risk of fire is reduced.

Some vegetable oils have been characterized based on their fatty acid profile, but most have not been adequately evaluated. The objective of this work therefore is to characterize physicochemical properties and the fatty acids profiles of cotton seed oil, palm kernel oil, neem seed oil and palm oil with a view to investigating their suitability as quenching media for medium carbon steels.

2. MATERIALS AND METHODS

2.1 Determination of Physicochemical Properties of Oil

The oils under investigation (cotton seed oil, palm kernel oil, neem seed oil and palm oil) are typical vegetable oils produced in Nigeria. Cotton seed and neem seed oil were obtained from Zaria, Northern Nigeria. Palm kernel oil and palm oil were purchased at a local market in Akure, Ondo State, Nigeria. Investigation of physicochemical properties of the oils in this study considered those properties that directly affect their use as quenchant. Such properties include: Viscosity, acid value, Iodine value and Flash point.

2.2 Determination of Viscosity

The viscosity of each sample of the oils was measured according to ASTM D445-06 (2011). The oil sample was placed into a glass U-tube. The sample was drawn through the tube using suction until it reached the starting position indicated on the tube side. The suction was then released, allowing the sample to flow back through the tube under gravity. The resistance of the oil flowing under gravity through the capillary tube measured the oils kinematic viscosity. The Kinematic viscosity is the product of the measured flow time and the calibration constant of the viscometer. The viscosity is reported in centistokes (cSt), equivalent to mm^2/s in SI unit, and is calculated from the time it takes oil to flow from the starting point to the stopping point using a calibration constant supplied for each tube. An average of independent five measurement of viscosity test at temperatures of 40ºC and 100ºC for each sample was reported.

2.2.1 Calculation of viscosity index from kinematic viscosity

Viscosity index is an arbitrary number indicating the effect of change of temperature on the kinematic viscosity of oil. A high viscosity index signifies relatively small change of kinematic viscosity with temperature. The viscosity index oil was calculated from its viscosities at 40 and 100ºC. The procedure for the calculation is given in ASTM Method D 2270-74 for Calculating Viscosity Index from Kinematic Viscosity at 40 and 100ºC.

$$\text{Viscosity index (VI)} = \frac{L-U}{L-H} \times 100 \quad (1)$$

Where:

- L= Kinematic viscosity at 40ºC of an oil of 0 viscosity index having the same kinematic viscosity at 100ºC as the oil whose viscosity index is to be calculated;
- U= Kinematic viscosity at 40ºC of the oil whose viscosity index is to be determined;
- H= Kinematic viscosity at 40ºC of an oil of 100 viscosity index, and having the same kinematic viscosity at 100ºC as the oil whose viscosity index is to be calculated.

Basic values for L and H for kinematic viscosity at 40 – 100ºC can be found in standard viscosity index tables.

2.3 Determination of Acid Number

As oil degrades, it forms acidic by-products. Chemical analysis can identify and measure these by-products. The acid number (AN) is the most common method employed. The AN was determined by a titration procedure using potassium hydroxide (KOH) and was reported as milligrams of KOH per gram of sample (mgKOH/g). AN is given by the expression [10]:

$$AN = \frac{56.1 \text{ x NV}}{\text{W}} \quad \text{[mg KOH / g]} \quad (2)$$

Where

56.1 = molar mass of the KOH
V = Volume of KOH solution in ml
N = Normality of KOH solution
W = Weight of sample in g

2.4 Determination of Iodine Value

The iodine value is a measure of the degree of unsaturation in oil and could be used to quantify the amount of double bonds present in the oil which reflects the susceptibility of oil to oxidation. Iodine number was determined according to ASTM D5554-95.

0.4 g of the sample was weighed into a conical flask and 20 cm^3 of carbon tetrachloride was added to dissolve the oil. Then 25 cm^3 of Dam's reagent was added to the flask using a safety pipette in fume chamber. Stopper was then inserted and the content of the flask was vigorously swirled. The flask was then placed in the dark for 2 hours 30 minutes. At the end of this period, 20 cm^3 of 10% aqueous potassium iodide and 125 cm^3 of water were added using a measuring cylinder. The content was titrated with 0.1M sodium thiosulphate solutions until the yellow colour almost disappeared.

Few drops of 1% starch indicator was added and the titration continued by adding thiosulphate drop wise until blue coloration disappeared after vigorous shaking. The same procedure was used for blank test and other samples

The iodine value (I.V) is given by the expression [12]:

$$I.V. = \frac{12.69C(V1-V2)}{M} \quad (3)$$

where

- C= Concentration of sodium
- V_1= Volume of sodium thiosulphate ($Na_2S_2O_3$) solution used to titrate the blank,
- V_2 = Volume of sodium thiosulphate solution used to titrate the sample.
- M = Mass of the sample

2.5 Determination of Flash Point

Flash point of oil is the lowest temperature at which the application of a flame causes the vapour above the oil to ignite. The flash point was determined using Pensky – Martens closed – cup method (EN 180 2719) standard. The cup was filled with the oil sample to be tested. The sample was heated at a slow, constant rate with continual stirring. A small flame was directed into the cup at regular intervals to the liquid surface. If a flash occurs in the cup, it indicates that the temperature of the tested liquid has reached (or exceeded) the flash point. The flash point was then measured respectively in the closed cup.

2.6 Determination of Oxidation Potential

The relative reactivity to oxidative degradation of the stearic, oleic, linoleic and linolenic esters in the triglyceride structure are 10, 10,100 and 200, respectively [1]. It is also known that the overall reaction rate of a process is the sum of the various individual reaction rates of the process. Since vegetable oils possess different fatty acid components, each with a particular and different oxidation rate, the overall oxidation rate is approximately equivalent to the sum of the oxidation rates of the fractional composition of the components.

The relative propensity for oxidation of the different vegetable oils with respect to their composition was determined from fatty acid composition data obtained by gas chromatography and the relative reactivity for oxidation reported by Kodali [10]. The first step in this assessment was to determine the molar quantities of each component in a given quantity of the vegetable oil. The molar quantities of each component are then multiplied by the relative reactivity for oxidation. These component oxidation propensities are summed up and normalized to provide a total potential for oxidation of each oil.

The fatty acid ester composition of the vegetable oils was determined by a gas chromatographic analysis procedure [7].

3. RESULTS AND DISCUSSION

Table 1 shows the physicochemical characteristics of the vegetable oils. Table 2 shows the fatty acid constituents of the vegetable oils while Table 3 shows Oxidation Potential of the Vegetable Oils.

4. DISCUSSION OF RESULTS

Viscosity Index (VI) is the rate at which the viscosity of oil will change as the temperature changes. The viscosity indices of the oils were determined according to ASTM D2270. The viscosity index (VI) values of the oils under study were consistent with the report of Fasina et al. [8]. In all cases, the VI values of the vegetable oils were significantly high, which means that the viscosity of the oils would not change much with variations in temperature. Among the vegetable oils, palm kernel oil is more stable to temperature changes. Based on heat flow, neem seed oil and cotton seed oil would extract heat faster. However, the higher stability to oxidation exhibited by Palm kernel oil compensates for its lower viscosity index value.

The acid values of the vegetable oils under study are generally low. Acid value of 0.00 to 3.00 mgKOH/g oil is recommended for oils used in quenching [10]. All the oils, except neem seed oil with the highest value of 12.97 mgKOH/g fall within the maximum limit.

Iodine value is a measure of the degree of unsaturation and is used to quantify the amount of double bonds present in the oil which reflects the susceptibility of oil to oxidation. Among the different oils analyzed, neem seed oil and cotton seed oil exhibited the highest iodine values which reflected the presence of high percentage of unsaturated fatty acids in the oil. The iodine values compared favourably to iodine value of standard oil.

The flash points of the oils were in agreement with standard values (190-210ºC) reported for standard oils. High flash points reported for the oils indicate that the oil does not contain volatile constituents which could prolong the vapour blanket stage and slow the quenching rate. Secondly, the risk of fire is reduced.

The results of fatty acid ester composition of the oils show that the two most common saturated fatty esters in the vegetable oils used for this study are palmitic and stearic, while the unsaturated ester are oleic and linoleic. The unsaturated/saturated ratio of Cotton seed oil, neem seed oil, palm kernel oil and palm oil are in the order of:

Palm kernel oil < palm oil < Cotton seed oil < Neem seed oil.

In general, the higher the degree of unsaturation of vegetable oils fatty acids, the more susceptible they are to oxidative deterioration. Among the vegetable oils evaluated, palm kernel oil is the most saturated and most stable with respect to quenching while Neem seed oil is the least saturated and more susceptible to oxidative deterioration. While high levels of saturated fatty acids are desirable to increase oil stability, with respect to quenching, high levels of saturated fatty acids reduces heat flow.

Table 1. Summary of physicochemical properties of the quenching media

	Viscosity at 40ºC (cSt)	Viscosity at 100ºC (cSt)	Viscosity index	Acid number (mg KOH /g sample)	Iodine number (g I_2/100 g sample)	Flash point (ºC)
Cotton seed oil	34.8	6.9	166.31	1.80	115.09	226
Neem seed oil	32.41	7.89	149.55	12.97	120.16	244
Palm kernel oil	41.69	8.94	145.13	0.22	19.59	246
Palm oil	39.7	8.2	188	1.23	35.90	172

Table 2. Percentage composition of fatty acids present in samples of vegetable oils (W %)

Oil	Saturated				Monounsaturated	Polyunsaturated	Others	Total unsaturated	Total saturated	Unsat / Sat ratio
	Lauric acid*(a)*	Myristic acid*(b)*	Palmitic acid*(c)*	Stearic acid*(d)*	Oleic acid*(e)*	Linoleic acid*(f)*		*(e+f)*	*(a+b+c+d)*	
	$CH_3(CH_2)_{10}COOH$	$CH_3(CH_2)_{12}COOH$	$CH_3(CH_2)_{14}COOH$	$CH_3(CH_2)_{16}COOH$	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	$CH_3(CH_2)_4CH=CH(CH_2)CH=CH(CH_2)_7COOH$				
	12:0*	**14:0***	**16:0***	**18:0***	**18:1****	**18:2****				
Cotton seed oil	-	-	32.47	9.08	19.05	37.32	2.08	56.37	41.55	1.35
Neem seed oil	-	0.97	16.23	23.87	48.12	9.37	1.44	57.49	41.07	1.39
Palm kernel oil	43.37	16.30	16.52	2.76	12.05	7.52	1.48	19.57	78.95	0.25
Palm oil	-	1.0	45.88	2.7	38.22	9.8	1.1	45.32	49.32	0.92

Table 3. Oxidation potential of the vegetable oils

Vegetable oil	Contribution to total oxidation potential (%)						Relative total potential for oxidation ratio
	Lauric acid	Myristic acid	Palmitic acid	Stearic acid	Oleic acid	Linoleic acid	
Cotton seed oil	-	-	0.13	0.03	0.67	15.04	15.87
Neem seed oil	-	0.004	0.06	0.08	1.70	3.77	5.61
Palm kernel oil	0.21	0.07	0.06	0.009	0.42	3.03	3.73
Palm oil	-	0.004	0.17	0.009	1.35	3.95	5.48

Since vegetable oils possess different fatty acid components, each with a particular and different oxidation rate, the overall oxidation rate is approximately equivalent to the sum of the oxidation rates of the fractional composition of the components. This is the reason why different vegetable oils exhibit different inherent properties or why one vegetable oil may be favoured for an application, such as quenching relative to another.

From the compositional analysis of the vegetable oils and calculation of the relative molar oxidation rate, it is possible to estimate the relative instability of the overall composition of the vegetable oils used for this work. The results obtained and reported in Table 3 shows the following order of oxidative stability:

Palm kernel oil > palm oil > Neem seed oil > cottonseed oil.

This analysis shows that Palm kernel oil would be expected to be the most stable to oxidative degradation while cotton seed oil is the least stable among the vegetable oils evaluated. Oxidative stability decreases with increase in number of double bonds.

Saturated oil will resist evaporation more. High evaporation stability reduces smoke formation and has a considerable effect on consumption and thus on oil bath economics. Oils having good oxidation stability forms less sludge, very little change in the basic property and thus have long service life.

5. CONCLUSION

From the results obtained, it can be concluded that high viscosity Index (VI) of all the oils connotes that their viscosity would not change much with temperature variation. High percentage of saturated fatty acids (palmitic and stearic) in the composition of the vegetable oils used for this study guarantees their stability to oxidative degradation. High flash points reported for the oils indicated that the oils does not contain volatile constituents and will not catch fire easily. The results of the physicochemical properties reported show that the vegetable oils are suitable as potential quenching media for carbon steels with palm kernel oil being the most promising.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Agboola JB. Performance assessment of selected nigerian vegetable oils as quenching media during heat treatment of medium carbon steel, PhD Thesis, Department of Mechanical Engineering, Federal University of Technology, Minna, Nigeria; 2014.
2. Prabhu KN, Fernandez P. Determination of wetting behaviour spread activation energy and quenches severity of bioquenchants. Metallurgical and Materials Transaction. 2007;38(4):631-640.
3. Shuhui MA. Characterization of the performance of mineral oil based quenchants using CHTE Quench Probe System, M.Sc. thesis, Faculty of Materials Science and Engineering, Worcester Polytechnic Institute; 2002.
4. Gunstone FD. The chemistry of oils and fats, sources, composition, properties, and uses. Oxford, Blackwell Publishing Ltd, 400; 2004.
5. Fernandez P, Prabhu KN. Comparative study of heat transfer and wetting behavior of conventional and bioquenchants for industrial heat treatment. International Journal of Heat and Mass Transfer. 2008; 51(3-4):526-538.
6. Kodali DR. High performance ester lubricants from natural oils. Industrial Lubrication and Tribology. 2002;54(4): 165-170.
7. American Society of Testing and Materials, D2270, Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 and 100ºC; 1986.
8. Fasina OO, Hallman H, Craig-Schmidt M, Clements C. Predicting temperature-dependence viscosity of vegetable oils from fatty acid composition. Journal of American Oil Chemical Society. 2006; 83(10):899-903.
9. American Society of Testing and Materials, D445-06, Standard Test for Kinematic Viscosity. UW Madison Formula SAE Department of Chemistry University of California - Davis, CA 95616, Chemistry 2B Laboratory Manual, Summer; 2011.
10. Canale LCF, Fernandes MR, Augustinho SCM, Totten GE, Farah AF. Oxidation of

vegetable oils and its impact on quenching performance. International Journal of Materials and Product Technology. 2005; 24(1-4):101-125.

11. Dauqan MA, Sani HA, Kasim ZM. Fatty acids composition of four different vegetable oils by gas chromatography. 2nd International Conference on Chemistry and Chemical Engineering, Singapore; 2011.
12. American Society of Testing and Materials, D5554-95 Reapproved 2009. Standard Test Method for Iodine number. New York. American Society of Testing and Materials. 2006;16:45-50.
13. European Committee for Standardization (ECS), EN ISO 2719, Determination of flash point – Pensky-Martens closed-cup method, ECS, Brussels, Belgium; 2003.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history.php?iid=1071&id=5&aid=8715