www.arpnjournals.com

A STUDY OF THE OXYGEN ABSORPTION CHARACTERISTICS OF UNSATURATED FATTY ACIDS OF LINSEED, RUBBER SEED, SOYBEAN AND MELONSEED OILS; EFFECT OF TEMPERATURE

Isiuku B. O.[1] and Ibemesi J. A.[2]
[1]Department of Chemistry, Imo State University, Owerri Imo State, Nigeria
[2]Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, Nigeria
E-Mail: obinnabisiuku@yahoo.com

ABSTRACT

The oxygen-induced polymerization of the fatty acids of soybean (S.B.A.), linseed (L.S.A.), rubber seed (R.S.A.), and melon seed (M.S.A.) oils were monitored manometrically at 10-minute intervals for five hours at 31.5, 45, 60, 75 and 90ºC. Moles of absorbed oxygen were calculated from pressures of un-reacted oxygen using the ideal gas equation. Plots of mmoles of absorbed oxygen against time at the various temperatures show parabolic rise in oxygen absorption, for all temperatures except for 90ºC when the optimum oxygen absorption was reached at about the fourth hour. Oxygen absorption rates were highest within the first 2.5hours for all temperatures except for 90ºC where the rates were highest within the first 1.5hours. Fifth-hour oxygen absorption values were plotted against temperature. The plots show that the optimum oxygen absorption temperature range for the acids was within the range of 60-75ºC. Oxygen absorption trends were generally not in conformity with degree of unsaturation.

Keywords: induced polymerization, oxygen absorption, temperature, linseed, melon seed, oil, fatty acids, soybean.

1. INTRODUCTION

The binder is the most important component of paints and varnishes. Alkyd resin binders which are of utmost importance in the manufacture of oil paints are manufactured using vegetable oils or fatty acids as one of the major materials (Paton, 1962: Martens, 1961: Kraft *et al.*, 1967). The vegetable oils mostly used for this purpose are the drying and semidrying ones. The alkyd resin paint binders when in thin films absorb atmospheric oxygen and form solids thereby coating the surfaces on which they are applied (Swern, 1979). The oxygen-absorption capability of the films rests on the unsaturated fatty acids present in the vegetable oils.

The oxidation of lipids is the subject of intense research (Frankel, 1998; Gerhard and Dunn, 2003). During exposure to air, unsaturated fatty compounds especially can form oxygenated species such as hydroperoxides and subsequent degradation products. The fatty acid composition of a fatty material is a major factor influencing oxidation (Gerhard and Dunn, 2003). Generally, the fatty acid composition of products derived from vegetable oils or animal fats corresponds to that of the parent oil or fat. Thus, the oxidation reaction of unsaturated fatty compounds with varying amounts of double bonds affects the quality and utility of fatty materials in diverse areas such as industrial applications.

The oxidation of fatty materials is affected by other factors, such as elevated temperature, light, the presence of metals, and other parameters that may accelerate oxidation (Mittelbach and Gangl, 2001;

Monyem *et al*., 2000; Canakei and Monyem, 1999; Simkovsky and Ecker, 1999; 1998: Thompson *et al*., 1998; Bondioli and Folegatti, 1996; Bondioli *et al*., 1995; Du Plessis *et al*., 1985; Du Plessis, 1982). Vegetable oils contain natural photo-sensitizers and are commercially sold under light. Not only are they susceptible to oxidation due to high concentration of linoleic or linolenic acid but they contain chlorophyll and their decomposition products which are potential photo-sensitizers thus, generating singlet oxygen in the presence of light and triplet oxygen. The singlet oxygen formed reacts with double bonds of unsaturated fatty acids to form the initial hydroperoxides which later break down and form radicals to initiate autoxidation (Maforimbo, 2002). Autoxidation of polyunsaturated lipids involves a free radical chain reaction that is most frequently initiated by exposure of lipids to light, ionization radiation, metal ions and metalloprotein catalysts. It starts when the first hydroperoxides decompose to alkoxy and hydroperoxy radicals. The radicals abstract hydrogen radical from vulnerable sites in monoenoic and polyenoic (e.g., linoleic and linolenic) fatty acids residues in the fat/oil (Coultate, 1996).

In this work, the fatty acids of linseed, soybean, rubber seed and melon seed oils were studied. The ready availability of soybeans, rubber seeds and melon seeds, and the possibility of using their oils in the development of alkyd resin paint binders attracted this research. The aim of the research was to compare the oxygen absorptions of the locally available oil fatty acids with that of linseed

which is imported with a view of reducing importation of linseed and boosting the nation's economy. The objective of the work was to see the effect of temperature on the oxygen absorption of the fatty acids using the manometric method.

2. EXPERIMENTAL

2.1 Materials

The fatty acids of linseed (*Linum usitatissimum* L.), soybean (*Glycine max* (L.) Merr.), rubber seed (*Hevea brasiliensis* (Kunth) Muell) and melon seed (*Colocynthis vulgaris*, Schrad) oils used in this work were prepared in the laboratory of the Chemistry Department, University of Nigeria, Nsukka (Ochigbo, 1992).

The metallic driers were cobalt and lead naphthenates. The cobalt naphthenate solution was obtained from Phina Paints (Nig.) Ltd., Awka, Nigeria. The metal concentrations of the two driers as determined were found to be 24.98% Pb and 7.69% Co. The oxygen gas used was hospital oxygen gas (approx. 99.9% purity), a product of Niger Gas (Nig.) Ltd., Enugu, Nigeria.

2.2 Preparation of Fatty acid-drier mixture

5.00g of each fatty acid were accurately weighed into a 30-cm^3 beaker. 0.03g of cobalt and 0.10g of Lead naphthenates solutions were added to the sample using teat-pipettes. The acid-drier mixture was then mixed thoroughly using a glass rod. The amounts of driers added represent approximately 0.05 and 0.50 wt % of cobalt and lead naphthenates respectively.
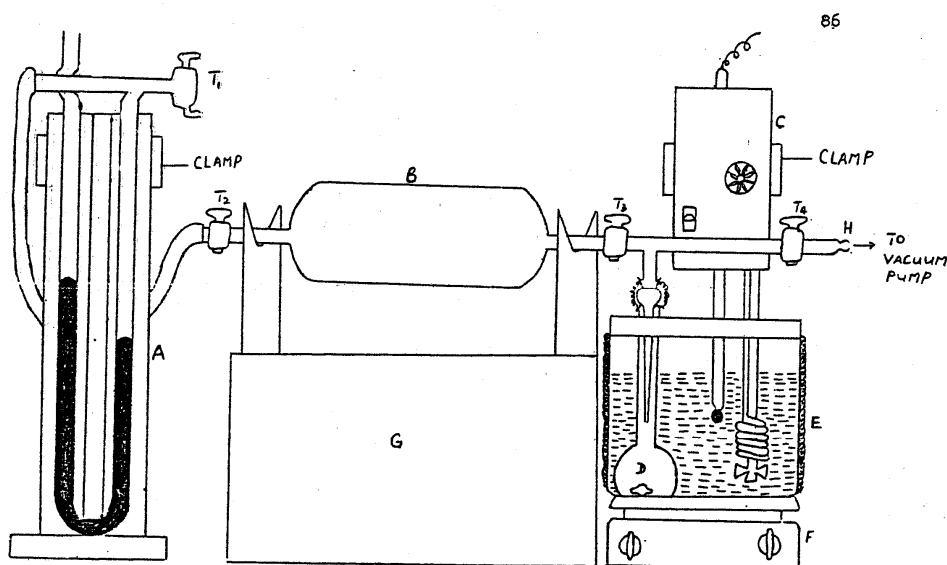
2.3. Measurement of the rate of oxygen absorption

Figure-1. Manometric Oxygen absorption apparatus.

The oxygen - absorption apparatus (Figure-1) used in this work was constructed by Ekezie F.U., a Chief Technologist in the Department of Chemistry, University of Nigeria, Nsukka. The system has a pressure manometer (A) linked to an oxygen gas reservoir (B) equipped with taps at both ends. The reservoir was connected to the reaction flask (D) immersed in a lagged oil bath (E) containing a thermometer unit (C) for temperature control. A thermometer (-10-110°C) was dipped in the oil bath for monitoring the temperature of the reaction mixture.

With tap T_2 closed, the system was evacuated for five minutes leaving taps T_4 and T_3 open. Tap T_4 then closed, and by gradually opening tap T_2, the manometer section was also evacuated of air using the vacuum created in the reservoir. A pressure drop usually resulted from the above, and was indicated by a rise in mercury height in the right arm of the manometer. The trapped air in the manometer was also removed into the oxygen gas reservoir. The movement of the mercury meniscus in the arms of the manometer was carefully monitored to avoid any possible spill over of the mercury. A second evacuation of the reservoir was done to remove any air which might have entered it from the manometer.

After this evacuation, tap T_4 was closed to cut off the system from the atmosphere. Oxygen gas of about 99.9% purity from the oxygen source was then gradually introduced into the reservoir through a connecting tube fitted at the end (H), by opening taps T_3 and T_4, while tap

www.arpnjournals.com

T_2 remained temporarily closed to allow oxygen to collect for about one minute, and build up a little pressure in the reservoir. After one minute, tap T_2 was carefully opened. There followed a gradual increase in mercury height in the left arm of the manometer which was carefully monitored and stopped when the height reached 43.00cm. The tap T_4 was immediately closed and T_3 closed later.

With tap T_3 still closed, the reaction flask was removed from the system for weighing and introducing the acid-drier mixture. After weighing the reaction flask containing a magnetic stirrer and the acid-drier mixture, it was reconnected to the system and immersed in the oil bath. It was evacuated of air and equilibrated for 30 minutes at the reaction temperature. The acid-drier mixture was stirred by means of the magnetic stirrer set at a constant speed.

After equilibration of the reaction mixture, tap T_3 was opened to allow oxygen into the reaction flask for the auto-oxidation. As soon as oxygen gas entered the reaction flask, there was an instantaneous drop in mercury height in the left arm of the manometer. The oxygen pressure at this height gave the initial oxygen pressure. The changes in mercury heights in both arms of the manometer were recorded at 10-minute intervals. At the end of each reaction (after five hours), the system was quickly vented to air, the reaction flask removed from the oil bath, allowed to cool, and the inside of the mouth and outside walls of the flask cleaned with tissue wetted with acetone. The reaction flask was then reweighed to get the mass of the non-volatile component of the reaction product after evacuation. The reactions were carried out at 31.5, 45, 60, 75 and 90°C.

3. RESULTS AND DISCUSSIONS

3.1 Effects of temperature

The oxygen absorptions during the oxygen-induced polymerization of L.S.A, R.S.A., and M.S.A. were monitored manometrically at 10-minute intervals for 5 hours. The moles of unreacted oxygen (n) at any time t were calculated from the oxygen pressures using the ideal gas equation.

$$p = (76 + \Delta h) \text{ cm} \qquad (1)$$

where p is pressure in atmospheres, Δh, difference in mercury height in cm.

$$pV = nRT \qquad (2)$$

where p is the pressure of unreacted oxygen in atmospheres, V, the volume of the reaction system (the oxygen absorption apparatus i.e., 3.022dm^3), R, the universal gas constant (i.e., 0.08205dm^3 atm. mol^{-1}K^{-1}) and T, 302K, the average room temperature. The number of

moles of oxygen absorbed (n_a) at each instant was obtained from the difference in the moles of gas at time zero (n_o) and time, t (n_t).

$$n_a = n_o - n_t \qquad (3)$$

The pressure values and moles of unreacted oxygen at the various temperatures, though monitored at 10 - minute intervals, are reported here at 60 - minute intervals for brevity. Moles of absorbed oxygen for L.S.A, R.S.A. and M.S.A were plotted against time as shown in Figures 1 - 5 for 31.5, 45, 60, 75 and 90°C respectively. The figures show parabolic rise in oxygen absorption with time for each fatty acid. However, at 90°C the optimum oxygen absorption was reached at about the fourth hour. Oxygen absorption rates were generally highest within the first 2.5hours for all the temperatures except for 90°C where the absorptions were highest within the first 1.5hours.

The fifth-hour oxygen-absorption values were plotted against temperature, Figure-6, for L.S.A., S.B.A, R.S.A. and M.S.A. The figure shows the optimum temperatures in brackets: L.S.A. (75°C), R.S.A. and S.B.A. (60°C) and M.S.A (45°C). It can then be said that oxygen absorption for the acids was generally optimum in the vicinity of 60°C with a fall thereafter.

The observed rise in oxygen absorption with temperature can be attributed to increasing number of activated acid molecules; this number appears optimized at about 60°C (i.e., temperature of optimum absorption). The fall in oxygen absorption observed beyond this optimum temperature may be due to significant occurrence of oxygen de-absorption which the reacting acid system (in which the forward reaction is exothermic) may undergo as a means of getting rid of the excess heat input at its state of equilibrium (Ibemesi and Igwebuike, 1990).

3.2 Effect of nature of fatty acids

The effect of the nature of the fatty acids on oxygen absorption is also evident from Figures 1-5. The level of oxygen absorption is seen to be dependent not only on the type of fatty acid but also on the temperature of absorption as summarized below. Also, the findings of Igwebuike in 1989 on similar studies on the parent oils designated L.S.O., R.S.O., S.B.O., and M.S.O, are quoted for comparison (Igwebuike, 1989).

i)   At 31.5°C: The order in oxygen absorption is:
L.S.A. > S.B.A. > R.S.A. > M.S.A. except within the first 2.5hours when M.S.A absorbed more than R.S.A. and also within the last hour when L.S.A. and S.B.A. absorbed equally. The order reported for the oils is:
L.S.O = R.S.O. > S.B.O. >> M.S.O. Both trends do not strictly show the dependence of oxygen absorption on the degree of unsaturation.

www.arpnjournals.com

ii   At 45ºC
        L.S.A. >> R.S.A. > S.B.A. > M.S.A.
        For the oils
        L.S.O. ≈ R.S.O. ≈ S.B.O. > M.S.O.

        The trends at 45ºC somehow follow the order of degree of unsaturation.

iii   At 60ºC: The trends in oxygen absorption are:
        R.S.A > L.S.A. > S.B.A. >> M.S.A.
        and for the oils,
        L.S.O. > M.S.O. > R.S.O. > S.B.O.
iv   At 75 and 90ºC
        L.S.A. > R.S.A. = S.B.A. >> M.S.A.
        For the oils,
        M.S.O. > L.S.O. ≈ R.S.O. ≈ S.B.O.

        The trends at 60ºC and above show that the fatty acid of melon seed oil (M.S.A.) failed to show the marked increase in oxygen absorption reported for the parent oil (M.S.O.). The reason for this is not clear.
        The degree of unsaturation of an oil or a mixture of fatty acids is dependent on the amount of oleic, linoleic and linolenic acids present (Chatfield, 1952). Iodine value is a generally accepted index of measuring degree of unsaturation. Alternative and quick ways of measuring degree of unsaturation involve the use of the following unsaturation indices (U.I) (Igwebuike, 1989)

U.I. 1 = (%linoleic + %linolenic) X (%linolenic)/100
U.I. 2 = 0.6(%oleic) + 1.6(%linoleic) + 2.0(%linolenic)

        The iodine value (IV) and thiocyanogen value (TV) can also be employed to determine the percentages of saturated, oleic, linoleic and linolenic fatty acids in an oil or mixture of fatty acids. For a semidrying or nondrying oil containing no linolenic acid,

%Saturated fatty acid = 100 - {%oleic + %linoleic}
%Oleic acid = 2.339TV - 1.214IV}
%Linoleic = 1.155IV - 1.160TV}

        For semidrying and drying oils containing saturated, oleic, linoleic and linolenic acids, when the percentage saturated fatty acids is known,

0 = 1.5829TV - (1.1751IV + 0.64165S) + 64.16
Li = 1.2531IV - (3.1466TV + 1.6855S) - 168.55
Le = 1.5637TV - (0.0780 + 1.3271S) - 132.71

where O, S, Li and Le represent percentages of oleic, saturated, linoleic and linolenic acids respectively.
        To further relate oxygen absorption to the degree of unsaturation, the oxygen absorptions for M.S.A., R.S.A., S.B.A. and L.S.A. at the fifth hour with respect to their iodine values are shown in Table-1.

Table-1. Iodine values and fifth - hour oxygen absorptions of L.S.A., R.S.A., S.B.A. and M.S.A. at 31.5, 45, 60, 75 and 90ºC.

OIL FATTY ACID	IODINE VALUE	5TH HOUR OXYGEN ABSORPTION mmol/g				
		31.5ºC	45ºC	60ºC	75ºC	90ºC
Linseed	175	2.24	250	2.64	2.76	2.38
Rubberseed	140	2.06	2.32	2.84	2.24	1.92
Soybean	128	2.24	2.12	2.64	2.32	1.92
Melonseed	120	0.18	2.12	2.06	1.74	0.18

The table shows the following trends in oxygen absorption

a) **At 31.5ºC**

    L.S.A. = S.B.A. > R.S.A. > M.S.A

b) **At 45ºC**

    L.S.A. > R.S.A. > S.B.A. = M.S.A.

c) **At 60ºC**

    R.S.A. > L.S.A. = S.B.A. > M.S.A.

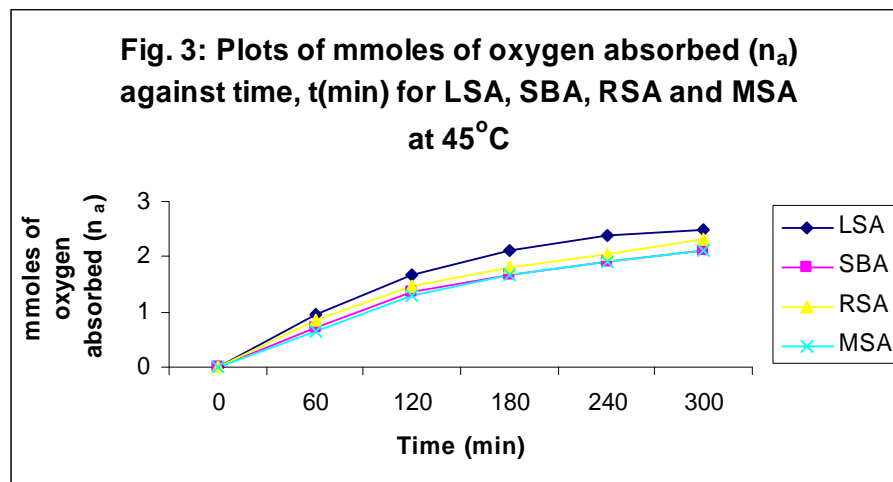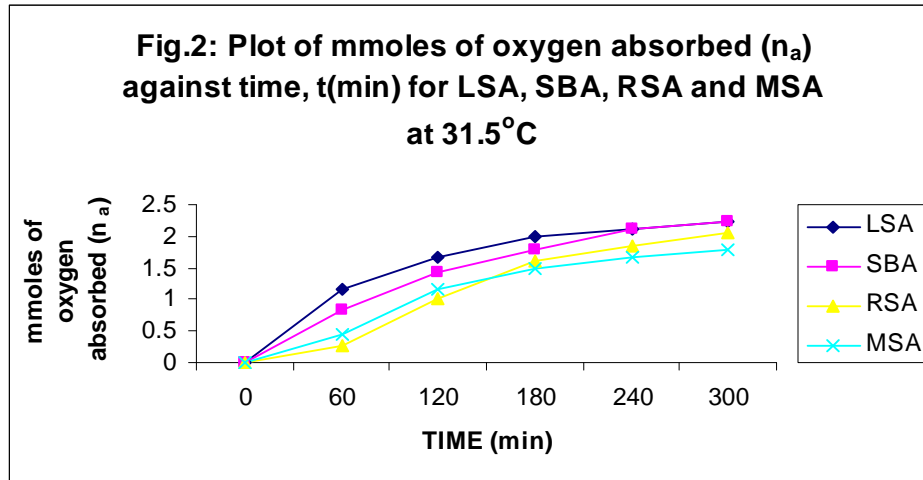d) **At 75ºC**

    L.S.A. >> S.B.A. > R.S.A. >> M.S.A.

e)   At 90°C

L.S.A. >> R.S.A. = S.B.A. > M.S.A.

These trends agree with those reported earlier. Table-1. also shows that the optimum temperatures of oxygen absorption in brackets are M.S.A. (45°C), S.B.A. and R.S.A. (60°C) and L.S.A. (75°C). These values agree with those reported in section 3.1.
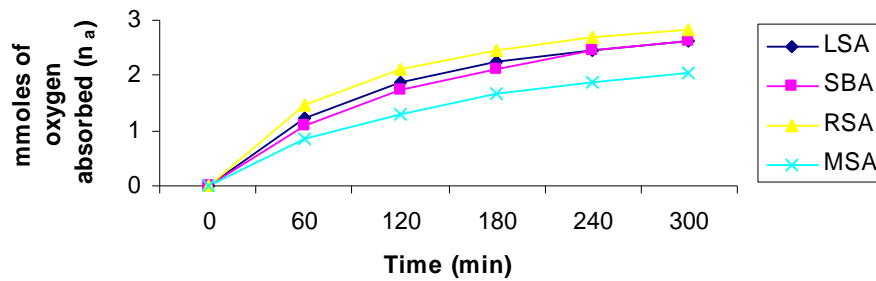
4. CONCLUSIONS

This work shows that the optimum temperature of oxidative polymerization of the fatty acids of oils of melon seed, rubber seed, soybean and linseed at temperatures below 100°C lie within the range of 60-75°C. Oxygen absorption trends were generally not in conformity with degree of unsaturation.
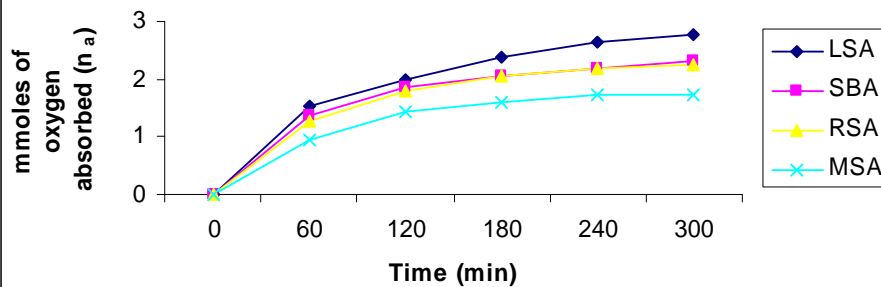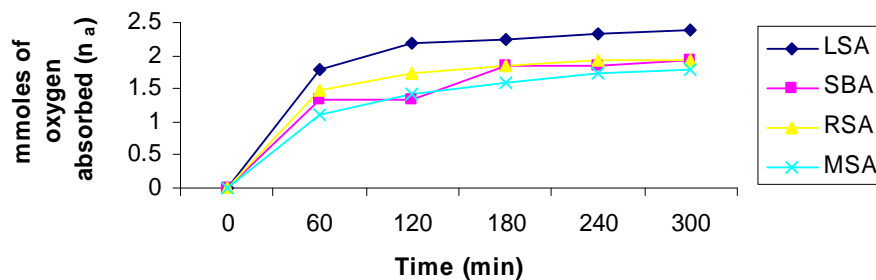
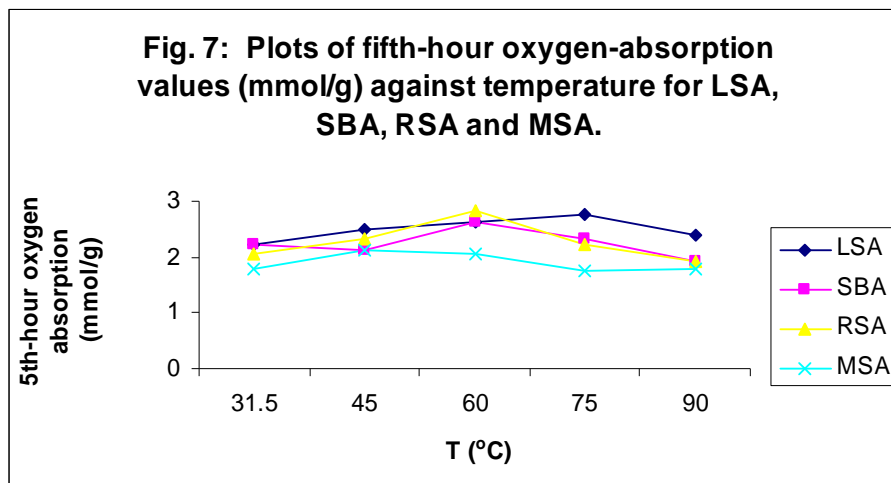**Fig.2: Plot of mmoles of oxygen absorbed (n_a) against time, t(min) for LSA, SBA, RSA and MSA at 31.5°C**

Fig. 3: Plots of mmoles of oxygen absorbed (n_a) against time, t(min) for LSA, SBA, RSA and MSA at 45°C

ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

Fig. 4: Plots of mmoles of oxygen absorbed (n_a) against time, t(min) for LSA, SBA, RSA and MSA at 60^oC

Fig. 5: Plots of mmoles of oxygen absorbed (n_a) against time, t(min), for LSA, SBA, RSA and MSA at 75^oC

Fig. 6: Plots of mmoles of oxygen absorbed (n_a) against time, t(min) for LSA, SBA, RSA, and MSA at 90^oC

www.arpnjournals.com

Fig. 7: Plots of fifth-hour oxygen-absorption values (mmol/g) against temperature for LSA, SBA, RSA and MSA.

REFERENCES

Patton T. C. 1962. Alkyd Resin Technology, Formulating Techniques and Allied Calculation, John Wiley, New York, USA.

Martens C. R. 1961. Alkyd Resins, Reinhold, New York, USA.

Kraft W.M., Januse E. G. and Sughrue O.J. 1967. In Treatise on Coatings, R.R. Myers and J.S. Long Eds. Vol.1, Part 1, Chapter 3, Marcel Dekker, New York, USA.

Swern D. 1979. Bailey's Industrial Oil and Fat Products. Vol. 1, 4th Ed., Wiley and Sons. pp. 701-709.

Frankel E.N. 1998. Lipid Oxidation, The Oil Press, Dundee, Scotland. p. 19.

Gerhard K., Dunn R.O. 2003. Dependence of oil stability index of fatty compounds on their structure and concentration, and presence of metals. J. Amer. Oil Chem. Soc. 80(10): 1021-1025.

Mittelbach, M., Gangl S. (2001) Long storage stability of biodiesel made from rapeseed and used frying oil. J. Amer. Oil Chem. Soc. 78: 573- 577.

Monyem A., Canakei M., Van Gerpen J.H. 2000. Investigation of biodiesel thermal stability under simulated in-use conditions. Appl. Eng. Agric. 16: 373-378.

Canakei M., Monyem A. 1999. Trans. ASAE. 42: 1565-1572.

Simkovsky N.M., Ecker A. 1999. Effects of antioxidants on the oxidative stability of rapeseed oil methyl esters. Erdoel, Erdgas, Kohle. 115: 317-318.

Simkovsky N.M., Ecker A. 1998. Einfluβ von Licht und. Tocopherolgehalt auf die Oxidationsstabilitat von Fettsauremethylestern, Fette/Lipid. 100: 534-538.

Thompson J.C., Peterson C.L., Reece D.L., Beck S.M. 1998. Two-year storage study with methyl and ethyl esters of rapeseed. Trans. ASAE. 41: 931-939.

Bondioli P., Folegatti L. 1996. Evaluating the oxidation stability of biodiesel: An experimental contribution. Riv. Ital. Sostanze Grasse. 73: 349-353.

Bondioli P., Gasparoli A., Lanzani A., Fedeli E., Veronese S., Sala M. 1995. Storage stability of biodiesel. J. Am. Oil Chem. Soc. 72: 699-702.

Du Plessis L.M., De Villiers J.B.M., Van de Walt W.H. 1985. Stability studies on methyl and ethyl fatty acid esters of sunflower seed oil. J. Amer. Chem. Soc. 62: 748-752.

Du Plessis L.M. 1982. Plant oils as diesel fuel extenders: Stability tests and specifications on different grades of sunflower seed and soyabean oils. CHEMSA. 8: 150-154.

Maforimbo E. 2002. Evaluation of capsicum as a source of natural antioxidant in preventing rancidity in sunflower oil. J. Food Technol. Africa. 7(2): 68-72.

www.arpnjournals.com

Coultate T.F. 1996. Food, The Chemistry of Its Components. 3rd Ed., pub. The Royal Society of Chemistry.

Ochigbo S.S. 1992. Master's Degree Thesis, Department of Chemistry, University of Nigeria, Nsukka, Nigeria.

Ibemesi J.A. and Igwebuike C.D. 1990. Proceedings of the Nigerian Academy of Science. 2: 69-78.

Igwebuike C.D. 1989. Master's Degree Thesis, Department of Chemistry, University of Nigeria, Nsukka, Nigeria.

Chatfield H.W. 1952. Examination of varnish-making vegetable oils. Paint Manuf. 22: 90-94, 247-249, 255.