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Oxygen Absorption Studies of Unsaturated Fatty Acids of Linseed and Melon Seed Oils; Effects of Temperature and Blending

[1]B.O. Isiuku and [2]J.A. Ibemesi
[1]Department of Chemistry, Imo State University, Owerri, Imo State, Nigeria
[2]Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, Nigeria

Abstract: Manometric oxygen induced polymerization of the fatty acids of Linseed (L.S.A) and Melon Seed (M.S.A) oils and blends of the fatty acids were monitored at 10 min intervals for 5 h at 31.5, 45, 60, 75 and 90°C. Moles of absorbed oxygen were calculated from pressures of un-reacted oxygen using the ideal gas equation. The moles of absorbed oxygen were plotted against time for the acids and their blends at the various temperatures. The plots in general show parabolic rise in oxygen absorption with time for each acid and blend for all temperatures except for 90°C when the optimum oxygen absorption was reached at about the 4th h. Oxygen absorptions were highest within the first 2.5 h for all temperatures except for 90°C where the rates were highest within the first 1.5 h. The 5th h oxygen absorption values were plotted against temperature for various blends. The plots show that the optimum oxygen absorption temperature range for the neat acids and the various blends was in the range of 60-75°C. Results also show marked improvement in the oxygen absorption characteristics of M.S.A. with synergistic effects in some cases especially when L.S.A. is 60-80% in the blend.

Key words: Oxygen absorption, unsaturated, fatty acids linseed, melon seed, oils, temperature, blending

INTRODUCTION

Air-drying architectural coatings are made with drying oils such as linseed, tung or dehydrated castor oil or blends of any of these with semi-drying oils. The latter oils are used mainly for medium or short oil alkyds. Blending of seed oils of tung, rubber, karrinota, karanja and neem, respectively with linseed has been used to improve some performance characteristics of the alkyd products such as colour, drying rate, hardness etc. (Anamtharaman *et al.*, 1992; Ejikeme and Ibemesi, 2007; Pokorny and Pokorna, 1965).

The alkyd resin paint binders when in thin film absorb atmospheric oxygen and form solids thereby coating the surfaces on which they are applied (Sivern, 1979). The oxygen absorption capability of the films rested on the unsaturated fatty acids present in the vegetable oils.

During exposure to air, unsaturated fatty compounds 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 of industrial applications. The oxidation of fatty materials is affected by other factors such as elevated temperatures, light, the presence of metals and other parameters that may accelerate oxidation (Mittelbach and Gangl, 2001; Monyem *et al.*, 2000; Canakei *et al.*, 1999; Simkovsky and Ecker, 1999; Thomson *et al.*, 1998; Bondioli and Folegatti, 1996; Bondioli *et al.*, 1995; Du Plessis *et al.*, 1985; Du Plessis, 1982).

The potential of melon seed oil in the development of alkyd resin paint binders has been shown. Blending of fatty acids of melon seed oil with those of rubber seed and linseed oils improved the drying and other properties of melon seed alkyd products with synergistic drying performance observed at certain blend compositions (Ochigbo and Ibemesi, 1994).

Continued interest in the use of melon seed oil despite the present high domestic demand for its seed as an important soup ingredient, its nutritive value having been established (Oyenuga and Fetuga, 1975), arises from the following reasons: the leguminous melon crop grows readily in almost all parts of Nigeria and requires very little attention from planting to harvesting. Also, the development of industrial use for melon seed oil can act as an additional incentive to boost the cultivation of melon seed. Melon seed oil is semi-drying and compares well with soybean oil in drying performance as is evident

Corresponding Author: B.O. Isiuku, Department of Chemistry, Imo State University, Owerri, Imo State, Nigeria

from their percent fatty acid composition. The latter oil is already in high demand and in the coatings industry. The oil content of melon seed (>40%) well surpasses that of soybean (ca 20%) (Ejikeme and Ibemesi, 2007). Studied the oxygen absorption characteristics of linseed and melon seed oils at room temperature.

MATERIALS AND METHODS

Materials: The fatty acids of the oils of linseed (*Linum usitatissimum* L.) and melon seed (*Colocynthis vulgaris*, Schrad) used in this study were prepared by in the Department of Chemistry, University of Nigeria, Nsukka, Nigeria. The metallic driers were cobalt and lead naphthenates. The cobalt naphthenate solution was obtained from Phina Paints (Nig.) Ltd., Awka, Anambra State, Nigeria and the Lead naphthenate solution from Morgan Paints (Nig.) Ltd. Enugu, Nigeria. The metal concentrations of the two driers as determined in the laboratory were found to be 24.98% lead and 7.69% cobalt. The oxygen gas used was hospital oxygen gas (approx. 99.9% purity), a product of Niger Gas (Nig.) Ltd., Enugu, Nigeria.

Equipment: The equipment used in this research were Manometric Oxygen Absorption Unit (Fig. 1), Haake E 52 electrothermal heater, Stuart magnetic stirrer/hot plate, Edwards ED 50 high vacuum pump, thermometer (-10-110°C), watch and Sartorius chemical balance.

Measurement of rate of oxygen absorption of fatty acid drier mixture

Preparation of fatty acid-drier mixture: About 5 g of each oil fatty acid or blend of fatty acids were accurately weighed into a 30 cm^3 beaker. About 0.03 and 0.10 g of cobalt and lead naphthenates, respectively were added to the sample.

The acid-drier mixture was then mixed thoroughly using a glass rod. The amounts of driers added represented approximately 0.05 and 0.5 wt/wt% of cobalt and lead naphthenates, respectively. The amount of each drier required was calculated using the equation:

$$\text{Mass of drier} = \frac{\text{Mass of oil (or acid)} \times \text{Metal (\%)}}{\text{Metal in drier (\%)}}$$

Procedure for measuring the rate of oxygen absorption: The oxygen absorption apparatus (Fig. 1) used in this study 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 of air for 5 min leaving taps T_4 and T_3 open. Tap T_4 was 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

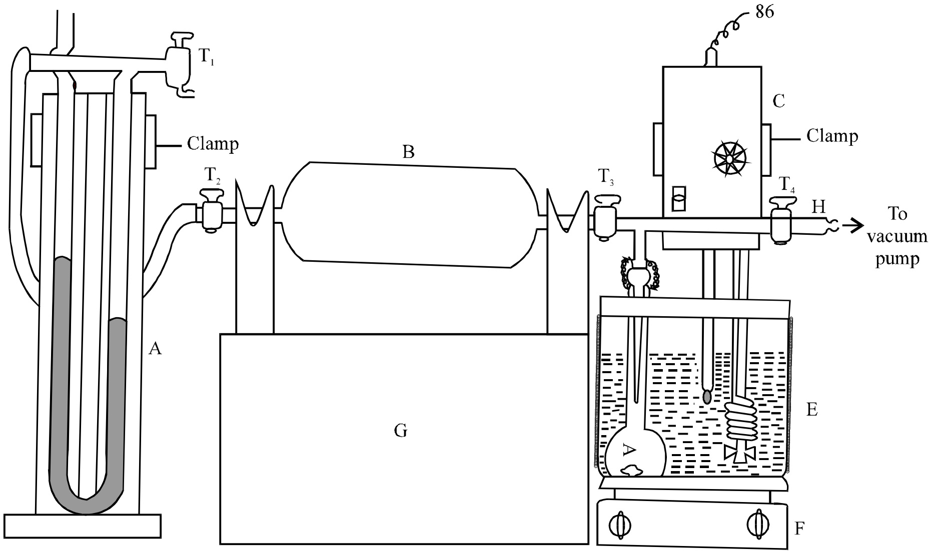

Fig. 1: Manometric oxygen absorption apparatus

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 T_2 remained temporarily closed to allow oxygen to collect for about 1 min and build up a little pressure in the reservoir. After 1 min, 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 cm. 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 introduction of the acid-drier mixture. After weighing, the reaction flask containing a magnetic stirrer and the acid-drier mixture was reconnected to the system and immersed in the oil bath. It was evacuated of air and equilibrated for 30 min 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 min intervals. At the end of each reaction (after 5 h), 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 paper 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.

RESULTS AND DISCUSSION

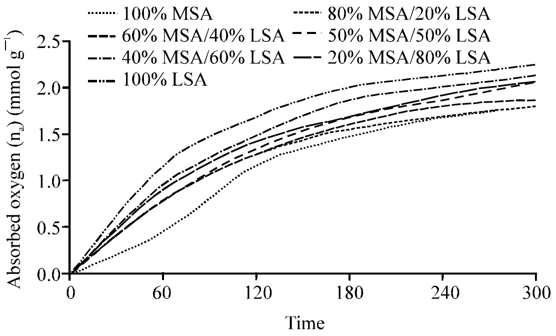

Fig. 2: Plots of mmoles of oxygen absorbed (n_a) vs. time (min) for MSA/LSA blends at 31.50°C

Effect of temperature: The oxygen absorptions during the oxygen-induced polymerization of 100% L.S.A; 80% L.S.A/20% M.S.A; 60% L.S.A/40% M.S.A; 50% L.S.A/50%M.S.A; 40%L.S.A/60%M.S.A; 20% L.S.A/80% M.S.A and 100% M.S.A designated as 1, 2, 3, 4, 5, 6 and 7, respectively were monitored manometrically at 10 min intervals for 5 h at 31.5 45, 60, 75 and 90°C. The moles of un-reacted oxygen (n) at any time (t) were calculated from the oxygen pressures using the ideal gas equation. The pressure of the oxygen gas at any instant during the auto-oxidation of the fatty acids is related to the difference in mercury height (Δh) of both arms of the manometer by the equation:

$$P = 76+\Delta h \qquad (1)$$

Where:

P = The pressure of the gas in atmospheres
h = The difference in mercury heights in cm

The number of moles of un-reacted oxygen (n) at each time interval can be obtained using the ideal gas equation:

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

Where:

p = The pressure of un-reacted oxygen in atmospheres
V = Volume of the reaction system (oxygen absorption apparatus) = 3.022 dm^3
R = The gas constant = 0.08205 dm^3 atm mol^{-1} k^{-1}
T = The average room temperature = 29°C

The number of moles of oxygen absorbed at each instant is obtained from the difference in the moles of gas at the beginning of the reaction (n_o) and at time t, (n_t) i.e.,

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

The pressure values and moles of un-reacted oxygen at various temperatures were used to calculate the respective moles of absorbed oxygen (n_a) which are plotted against time in Fig. 2-6 for the L.S.A and M.S.A and blends at 31.5, 45, 60, 75 and 90°C. Each figure shows a parabolic rise in oxygen absorption with time. The 5th h

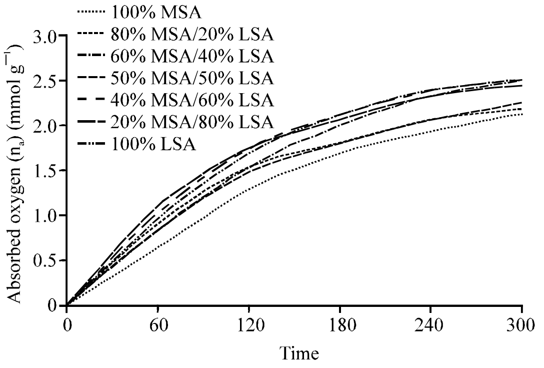

Fig. 3: Plots of mmoles of oxygen absorbed (n_a) vs. time (min) for MSA/LSA blends at 45°C

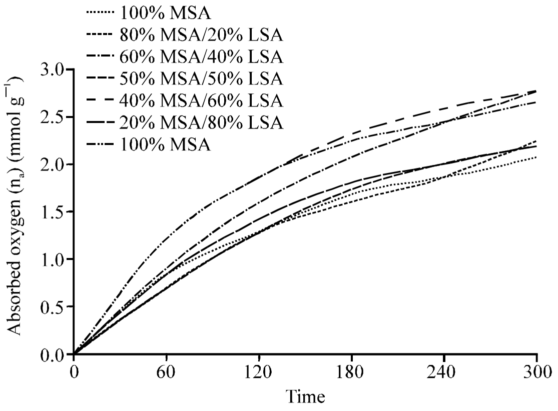

Fig. 4: Plots of mmoles of oxygen absorbed (n_a) vs. time (min) for MSA/LSA blends at 60°C

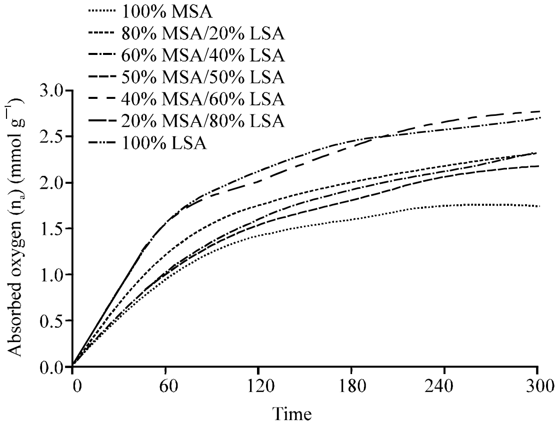

Fig. 5: Plots of mmoles of oxygen absorbed (n_a) vs. time (min) for MSA/LSA blends at 75°C

oxygen absorption values were taken as maximum and are plotted against composition of blend (Fig. 7). The Fig. 7 shows the following optimum temperatures for various blends in brackets: 45°C (3), 60°C (5 and 6) and 75°C (2 and 4). These optimum temperature values are in the same range observed for M.S.A (1) and L.S.A (7).

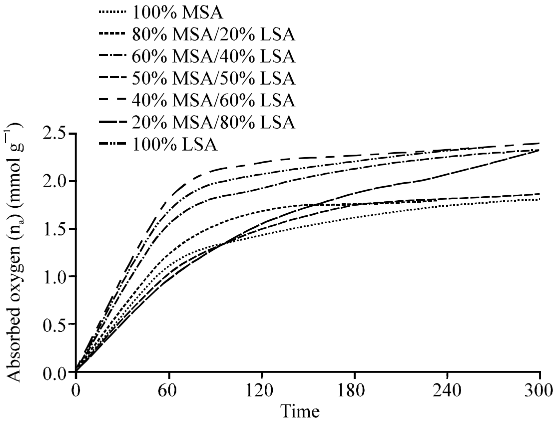

Fig. 6: Plots of mmoles of oxygen absorbed (n_a) vs. time (min) for MSA/LSA blends at 90°C

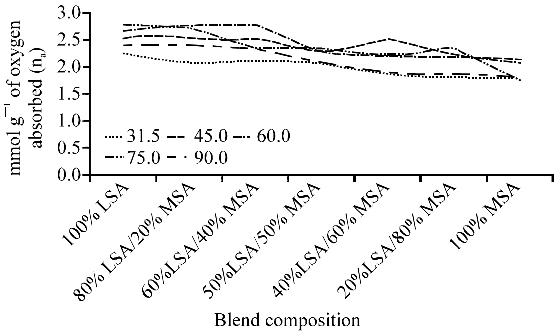

Fig. 7: The 5th h oxygen absorption (n_a) mmol g^{-1} vs. Blend composition

Effect of blend composition: The effects of composition of blends of fatty acids on oxygen absorption are evident from Fig. 2-7. The figures show temperature-dependent composition effects on oxygen absorption as shown below for the pure fatty acids (1 and 7) and the blends (2-6). At 31.5°C, the trend in oxygen absorption is:

7>5>6>4>3>2>1

except for the first 2.5 h when blends 3 and 2 absorbed equally and the last 2.5 h when 2 and 1 also absorbed equally. The 5th h oxygen absorption values (Fig. 7) show the following trend:

7>5>6 = 4>>3>2 = 1

At 45°C:

7 = 5>6>3>4≈2>1

except for the last 1.5 h when 3 absorbed >6 and the first 2 h when 3 and 2 absorbed equally. The 5th h oxygen absorption values show the trend:

7 = 5 = 3>6>>4>2>1

The above trends show improvement in oxygen absorption of blend 3. At 60°C:

5>7>6>>3>2>4≈1

except for the last hour when 6 absorbed >7, 4>1 and 2 and 3 absorbed equal amounts of oxygen. The 5th h oxygen absorption values showthe trend:

5 = 6>7>>4>3 = 2>1

This trend shows synergistic improvement in oxygen absorption by blends 5 and 6. At 75°C:

7≈6>>2>4>5≈3>>1

except for the last hour when blends 5, 4 and 2 absorbed almost equally and >3. The 5th h oxygen absorption values show the trend:

7>6>>5 = 4 = 2>3>>1

The performance of 2 is unusually high at this temperature. At 90°C:

7>6>5>>4>3 = 2>1

except for the first 2.5 h when 2 absorbed >4 and also the first 1.5 h when 1 absorbed >3. The 5th h oxygen absorption value show the trend:

7 = 6>5>>4>>3 = 2>1

The trends are in conformity with degree of unsaturation. From the above summaries, blends 5 and 6 with compositions 40% M.S.A/60% L.S.A and 20% M.S.A/80% L.S.A, respectively exhibit outstanding oxygen absorption characteristics, particularly at 60-75°C. In general, the trends in oxygen absorption do not seem to depend on the cumulative degree of unsaturation of the blends; rather they reflect a synergistic effect. This observation agrees with the findings of Ochigbo who carried out similar studies at room temperature only. The reason for the non-conformity in trend of oxygen absorption with degree of unsaturation and the cause of the synergistic effect are unknown.

CONCLUSION

In this study, the oxygen absorption characteristics of the fatty acids of linseed and melon seed oils and their blends was investigated.

The objective of the study was to determine manometrically the effects of temperature and blending on the oxygen absorption of the fatty acids of linseed and melon seed oils at higher temperatures (31.5, 45, 60, 75 and 90°C).

REFERENCES

Anamtharaman, N., S. Govindaraju and S. Krishnamoorthy, 1992. Synthesis and characterization of alkyd resins of Aranja and neem oils. Res. Ind., 37: 100 -105.

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

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

Canakei, M., A. Monyem and J. Van Gerpen 1999. Accelerated oxidation processes in biodiesel. Trans. ASAE., 42: 1565-1572.

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

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

Ejikeme, P.M. and J.A. Ibemesi, 2007. New alkyd resin systems from blends of melon seed and soybean oils: The case of prntaerythritol as polyhydric alcohol. J. Chem. Soc. Nigeria, 30: 184 -190.

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

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

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

Ochigbo, S.S. and J.A. Ibemesi, 1994. Oxygen absorption characteristics of blends of fatty acids from seed oils of rubber, watermelon, soybean and linseed. Ind. J. Nat. Rubber Res., 7: 107 -113.

Oyenuga, V.A. and B.L. Fetuga, 1975. Some aspects of the biochemistry and nutritive value of the watermelon seed (*Citrullus vulgaris* schrad). J. Sci. Food Agric., 26: 843-846.

Pokorny, J. and V. Pokorna, 1965. Drying properties of seed oil from Siberian pine. Potravinarska Technol., 6: 285-290.

Simkovsky, N.M. and A. Ecker, 1999. Effects of antioxidants on the oxidative stability of rapeseed oil methyl esters. Erdvel. Ergas. Kohle., 115: 0179-3187.

Sivern, D., 1979. Bailey's Industrial Oil and Paint Products. 4th Edn., Vol. 1, Wiley and Sons, New York, pp: 701-709.

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