The Impact of Blending Soybean Oil Fatty Acid (S.B.A.) With Melon Seed Oil Fatty Acid (M.S.A.) on the Oxygen Absorption of Soybean Oil Fatty Acid

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ABSTRACT

The oxygen absorption of the fatty acids of soybean (S.B.A) and melon seed (M.S.A) oils and their blends were monitored at 10-minute intervals for five hours at 31.5, 45, 60 and 90°C, using a manometer. 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, 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 fourth hour. Oxygen absorptions were highest within the first 2.5hours for all temperatures except for 90°C where the rates were highest within the first 1.5hours. Fifth-hour oxygen absorption values were plotted against temperature for various blend compositions. The plots show that the optimum oxygen absorption temperature range for the neat acids and the various blends lie within the range of 45-75°C. 50% M.S.A./50%S.B.A exhibited synergistic improvement in oxygen absorption while other blends show no positive effect on oxygen absorption of M.S.A but rather a decline.

Keywords: blending, melon seed, oil fatty acids, oxygen absorption, soybean, temperature

INTRODUCTION

Soybean oil is used extensively in the manufacture of drying oil products. It is also used in the manufacture of margarines and shortenings. The un-hydrogenated oil is used in blends with other oils, but its tendency to revert when exposed to air or high temperatures tends to limit its use (Mattil et al., 1964). In some texts, soybean oil is classified as semidrying and in some, as a drying oil because of its linolenic acid content (Goldsmith, 1949). Medium-oil alkyds, with alkyd ratios of about 39 to 45, constitute an intermediate all-purpose class which has good air-drying properties, but greater gloss and durability than the long-oil product. They are usually modified with either linseed or soybean oil (Mattil et al., 1964). The alkyd resin paint binders when in thin film absorb atmospheric oxygen and form solids thereby coating the surfaces on which they are applied (Swern, 1979). The oxygen absorption capability of the films rest on the unsaturated fatty acids present in the vegetable oils. Soybean oil is made up of 83 – 90% unsaturated fatty acids (Mattil et al., 1964). During exposure to air unsaturated fatty acid 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 the fatty materials in

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diverse areas of industrial application. 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 and Monyem, 1999; Simkovsky and Ecker, 1989, 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 (Ibemesi, 1990). Blending of fatty acids of melon seed with those of rubber seed and linseed oils improved the drying and other properties of melon seed alkyd products with synergistic drying performance as is evident from their percent fatty acid composition (Ochigbo and Ibemesi, 1994). The latter oil is already in high demand and in the coatings industry. The oil content of melon seed well surpasses that of soybean (Ejekeme and Ibemesi, 2007).

The aim of this work was to find out the impact of blending soybean oil fatty acids with the fatty acids of melon seed oil on the oxygen absorption of the acids with a view of encouraging the use of MSA industrially. Different ratios by weight of the fatty acids were employed in the study. The effect of temperature was also studied.

MATERIALS AND METHOD

Materials

The fatty acids of the oils of soybean (Glycine max(L) Merr.) and melon seed (colocynthis Vulgaris, Schrad) used in this work were prepared by Ochigbo (Ochigbo 1992). The metallic driers were Cobalt and Lead naphthenate. 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 dries as determined in our laboratory were found to be 24.98% Lead and 7.69% Cobalt. The oxygen as used was hospital oxygen gas (approx. 99.9% purity), a product of Niger Gas (Nig.) Ltd., Enugu, Nigeria.

Equipment

The equipment used in this work were Manometric Oxygen Absorption Unit (Figure 1), Haake E 52 Electrothermal Heater, Stuart Magnetic Stirrer/Hot plate, Edwards ED 50 High Vacuum pump, Thermometer (-10 – 110^{o}C), Watch and Sartorius Chemical balance.

Measurement of Rate of Oxygen Absorption of Fatty Acid Drier Mixture

Preparation of Fatty Acid-Drier Mixture

5.00g of each oil fatty acid or blend of fatty acids were accurately weighed into a 30 cm^3 -beaker. 0.03 and 0.10g of cobalt and lead naphthenates respectively were added to the sample. The acid-drier mixture was them mixed thoroughly using a glass rod. The amounts of driers added represent approximately 0.05 and 0.5wt % of cobalt and lead naphthenates respectively. The amount of each drier required was calculated using the equation.

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

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Procedure of Measuring the Rate of Oxygen Absorption

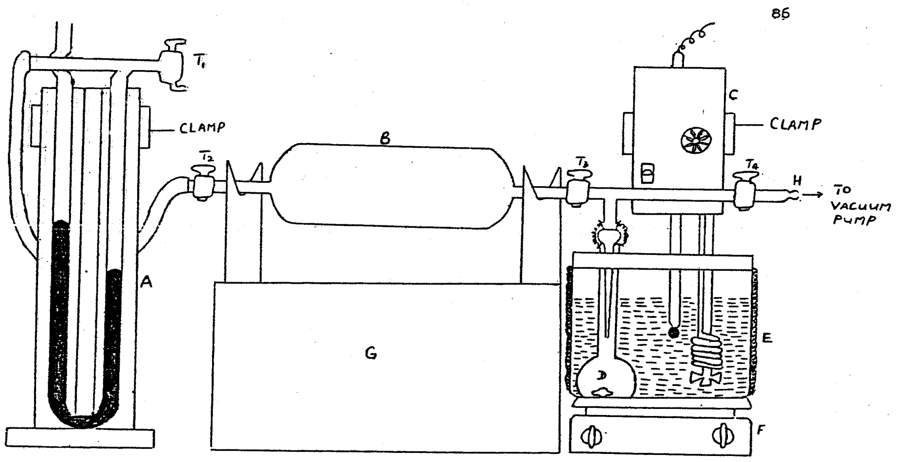

Figure 1. Manometric Oxygen Absorption Apparatus

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^{o}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 spillover 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 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

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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.

RESULTS AND DISCUSSION

Effects of Temperature and Blend Composition

The effects of composition of blends of fatty acids on oxygen absorption are evident from figures 2 – 6. The figures show a temperature-dependent composition effects on oxygen absorption as summarized 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>4>5>>1>6>3>2

Except for the first two hours when 7 and 4 absorbed equally and also 2 and 3 while 6 absorbed more than 1 during the first 1.5hrs. The trend in maximum oxygen absorption is

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

This trend shows that blends 2 and 3 absorbed less amount of oxygen than M.S.A.

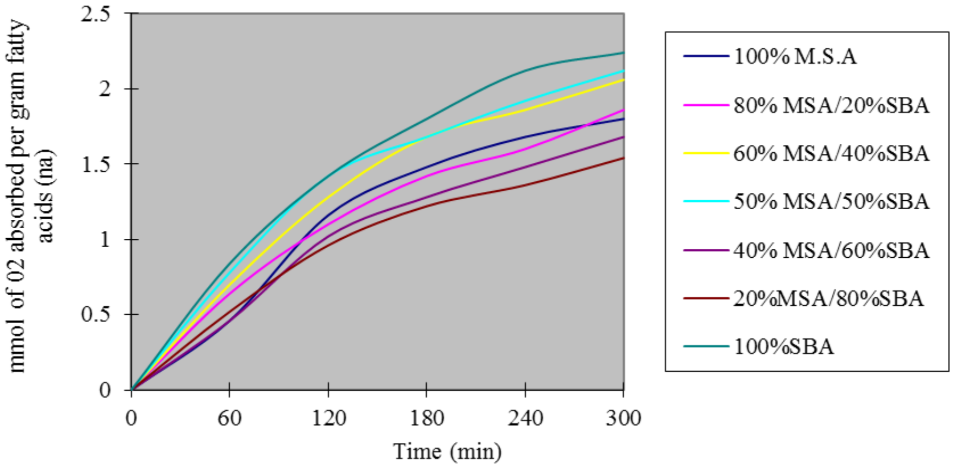

Figure 2. Plots of mmoles/g of Oxygen absorbed (n_a) vs time for MSA/SBA blends at 31.5°C

At 45°C

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

Except for the fifth hour when 1 and 7 absorbed equal amount of oxygen. The trend shows much improvement in oxygen absorption of blend 3 which topped the others. All the blends absorbed more oxygen than the parent neat acids hence blending M.S.A. with S.B.A. leads to synergistic improvement at 45°C.

At 60°C

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

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Except for about the first 2.5hrs when the oxygen absorptions of 2, 3 and 6 were almost equal and greater than that of 4. 7 absorbed more than 5 during the last hour. The trend in maximum oxygen absorption is

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

This order shows more of a linear improvement on the oxygen absorption of M.S.A.

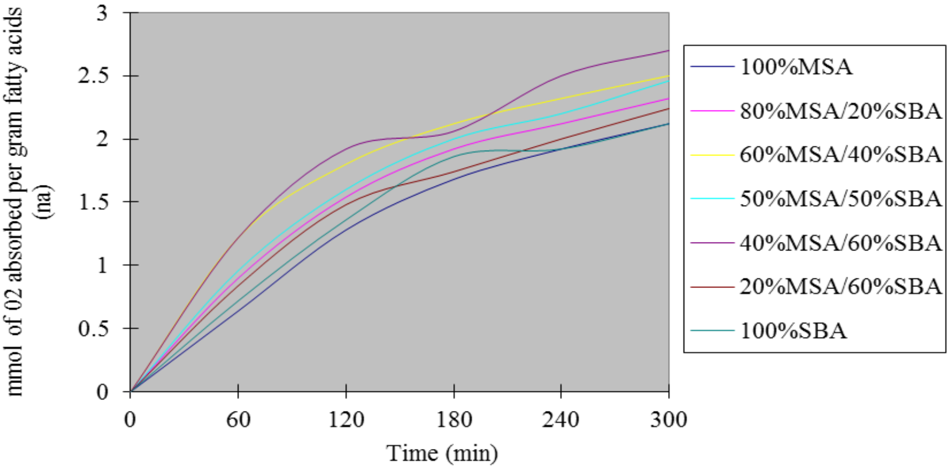

Figure 3. Plots of mmoles/g of Oxygen absorbed (na) vs time for MSA/SBA blends at 45^{o}C

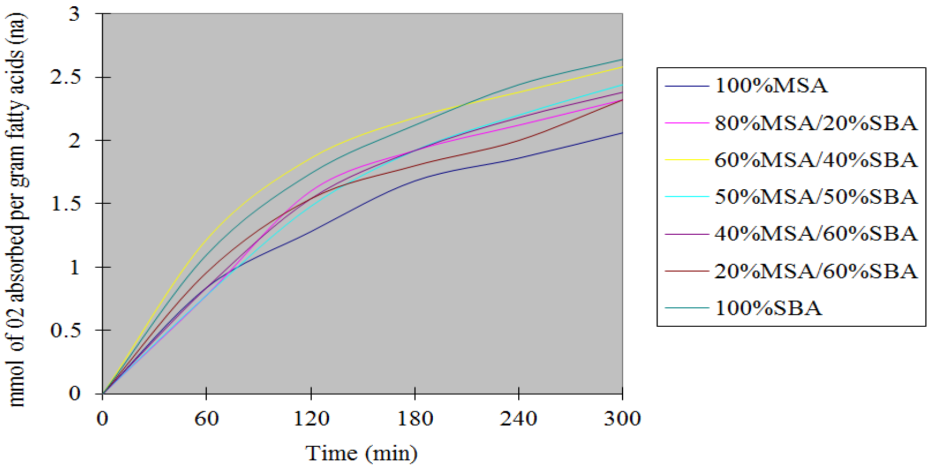

Figure 4. Plots of mmoles/g of Oxygen absorbed (na) vs time for MSA/SBA blends at 60^{o}C

At 75^{o}C

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

Except for about the first 1.5hrs when 1 absorbed more than 2 and the last hour when 4 absorbed more than 2 and 1. The trend in maximum oxygen absorption is

6>7>>3>5>4 ≈2>1

This trend shows improvement in oxygen absorption when M.S.A is blended with S.B.A. However, synergistic improvement was observed with only blend 6 which contained 20% M.S.A.

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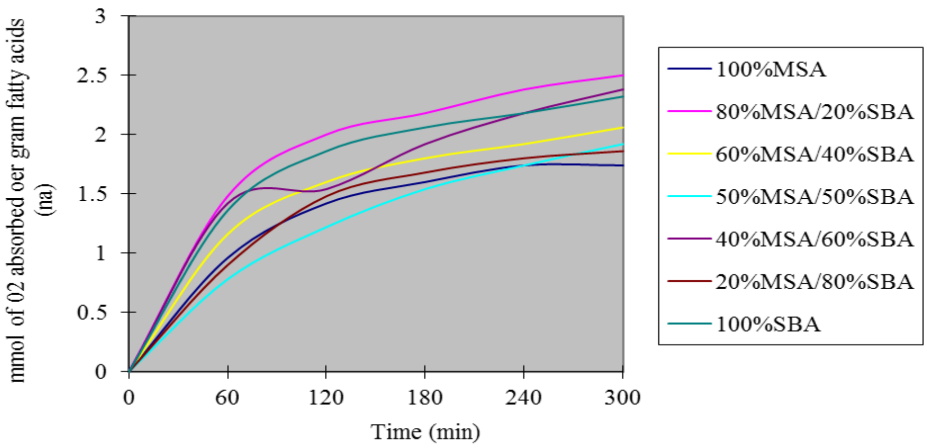

Figure 5. Plots of mmoles/g of Oxygen absorbed (na) vs time for MSA/SBA blends at 75°C

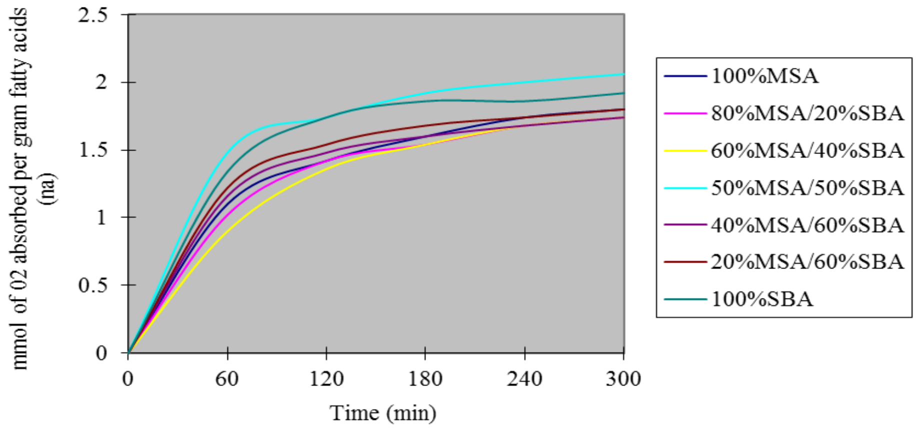

Figure 6. Plots of mmoles/g of Oxygen absorbed (na) vs time for MSA/SBA blends at 90°C

At 90°C

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

Except for the last 1.5hrs when 2 and 1 absorbed equally as well as 3, 5 and 6. The trend in maximum oxygen absorption is

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

This trend shows that blend 4 exhibited synergistic improvement in oxygen absorption while other blends show no positive effect on oxygen absorption of M.S.A. but rather a decline.

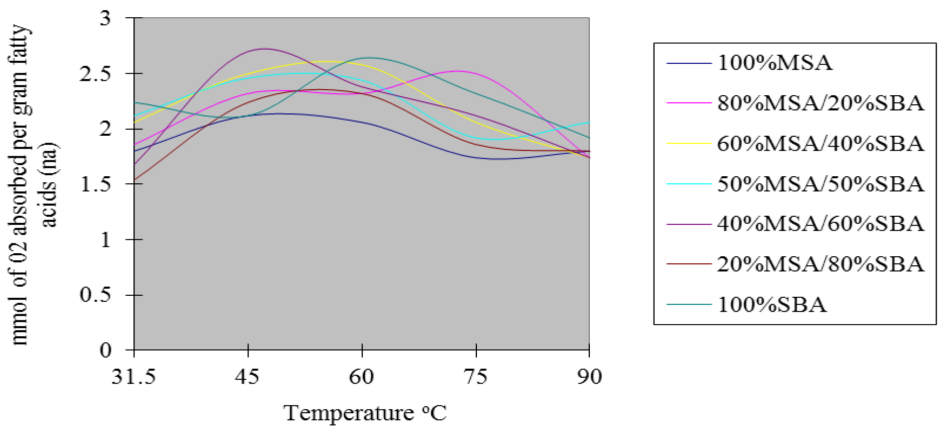

Figure 7. Comparison of 5th-Hour Oxygen absorption of the various blends at 31.5, 45, 60, 75 and 90°C

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 (Isiuku, 2012) and Ochigbo and Ibemesi, 1994). Who carried out similar studies at temperatures of 31.5 – 90^{o}C and room temperature. 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

This work shows that the optimum temperature of oxidative polymerization of the fatty acids of oils of melon seed, soybean and their blends lie within 45 – 75^{o}C. The oxygen absorption characteristics of melon seed oil fatty acid can be improved by blending with soybean oil fatty acid up to the level of 60 – 80%. However, a decline in the oxygen absorption of melon seed oil fatty acid was observed to occur when blended with fatty acid of soybean oil at 31.5 and 90^{o}C.

The synergistic oxygen absorption performance of the blends can be of importance in the formulation of alkyd resin paint binders using soybean oil. This is due to the fact that the oxidative polymerization depends on the fatty acid content of the oil.

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