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OXYGEN ABSORPTION STUDIES OF FATTY ACIDS OF RUBBER SEED AND MELON SEED OILS AND THEIR BLENDS: EFFECTS OF TEMPERATURE AND BLENDING

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The oxygen absorption of rubber seed oil fatty acids (RSA) and melon seed oil fatty acids (MSA) and their blends were monitored at one hour interval for five hours at 31.5 °C, 45 °C, 60 °C, 75 °C and 90 °C. Moles of absorbed oxygen were calculated from pressures of un-reacted oxygen using the ideal gas equation. The oxygen absorption increased with time, the rate being high initially at all temperatures except for 90 °C when the optimum oxygen absorption was reached after about four hours. Pure RSA and blends containing higher proportion of RSA showed higher oxygen absorption than pure MSA at different test temperatures except for the initial period at 31.5 °C.

Keywords: Melon seed oil fatty acids, Oxygen absorption, Rubber seed oil fatty acids.

The paint industry plays a major role in the Nigerian economy. However, the contribution of this industry has significantly dwindled, mainly due to lack of raw materials. Most of the raw materials, especially the film forming, lipid base component are imported and not readily available. The source of this lipid base component is usually linseed oil, which is mostly made up of linolenic and linoleic acids. Rubber seed oil has a lipid composition that mimics that of linseed oil to some extent, containing considerable amounts of linolenic (16.3%) and linoleic (39.6%) acids. The total polyunsaturated fatty acids in rubber seed oil is about 79%, with iodine value of 135.3 making it a semi drying oil (Aigbodion and Pillai, 2000). Melon seed oil has acomposition of 69.21% unsaturated fatty acids and is also semi-drying oil with an iodine value of 119 (Mirjana and Ksenija, 2005). These two oils could probably replace linseed oil used as a lipid base in the paint industry either fully or partially.

The alkyd resin or fatty acid binders present in paints absorb atmospheric oxygen and form solids thereby coating the surfaces on which they are applied (Mattil *et al.*,1964). The oxygen absorption capability of such binders rest on the content of unsaturated fatty acids present in the vegetable oils.

During the drying of alkyd and oil paints, auto oxidation of unsaturated fatty acids take place to form oxygenated species such as hydro-peroxides with subsequent degradation products (Gerhard *et al*., 2003). 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 (Gerhard, 2005; Mittelbach, *et al*., 2001; Monyem, *et al*., 2000; Ejikeme and Ibemesi, 2007).

Blending of fatty acids of melon seed oil and linseed oil improved the drying and other properties of melon seed alkyd products with synergistic drying performance observed at certain blend composition (Ochigbo and Ibemesi, 1994). Melon seed oil compares well with soybean oil in drying performance as is evident from their fatty acid composition. The latter oil is already in high demand and in the coating industry.

The aim of this work is to find out the effect of temperature and time on oxygen absorption by pure and blends of fatty acids from rubber seed oil and melon seed oil. An attempt is also made determine the best blend composition and optimum temperature for maximum oil absorption using a manometric system.

The fatty acids of the oils of rubber seed (*Hevea brasiliensis*) and melon seed *(Colocynthis vulgaris, Schrad)* used in this work were prepared as reported earlier (Ochigbo and Ibemesi,1994). 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 estimated in our laboratory were found to be 24.98 per cent lead and 7.69 per cent cobalt. The oxygen gas (approx. 99.9 per cent purity) was a product of Niger Gas (Nig) Ltd., Enugu, Nigeria.

The equipments used in this work were Manometric oxygen absorption unit (Fig. 1), Haake E 52 Electrothermal heater, Stuart magnetic stirrer/hot plate, Eedwards 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

Five gram 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 represent approximately 0.05 and 0.5 wt. per cent of cobalt and lead naphthenates respectively. The amount of each drier required was calculated using the following equation.

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

Procedure of measuring the rate of oxygen absorption: Manometric oxygen absorption apparatus

The oxygen absorption apparatus (Fig. 1) used in this work was constructed by Mr. F. U. Ekezie, 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 thermally-lagged oil bath (E) containing a heater unit with thermometer (C) for temperature control. A thermometer (10-110 °C) was dipped in the oil bath for monitoring the temperature of the reaction mixture. F and G are mounting stands.

With the tap T2 closed, the system was evacuated for five minutes leaving taps T4 and T3 open. Tap T4 was then closed, and by gradually opening tap T2, the manometer section was also evacuated of air using the vacuum created in the reservoir. A pressure drop usually created from the above 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 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 T4 was closed to cut off the system from the atmosphere. Oxygen gas of about 99.9 per cent purity from the oxygen source was then gradually introduced into the reservoir through a connecting tube fitted at the edge (H) with control value by opening taps T3 and T4 while tap T2 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 T2 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

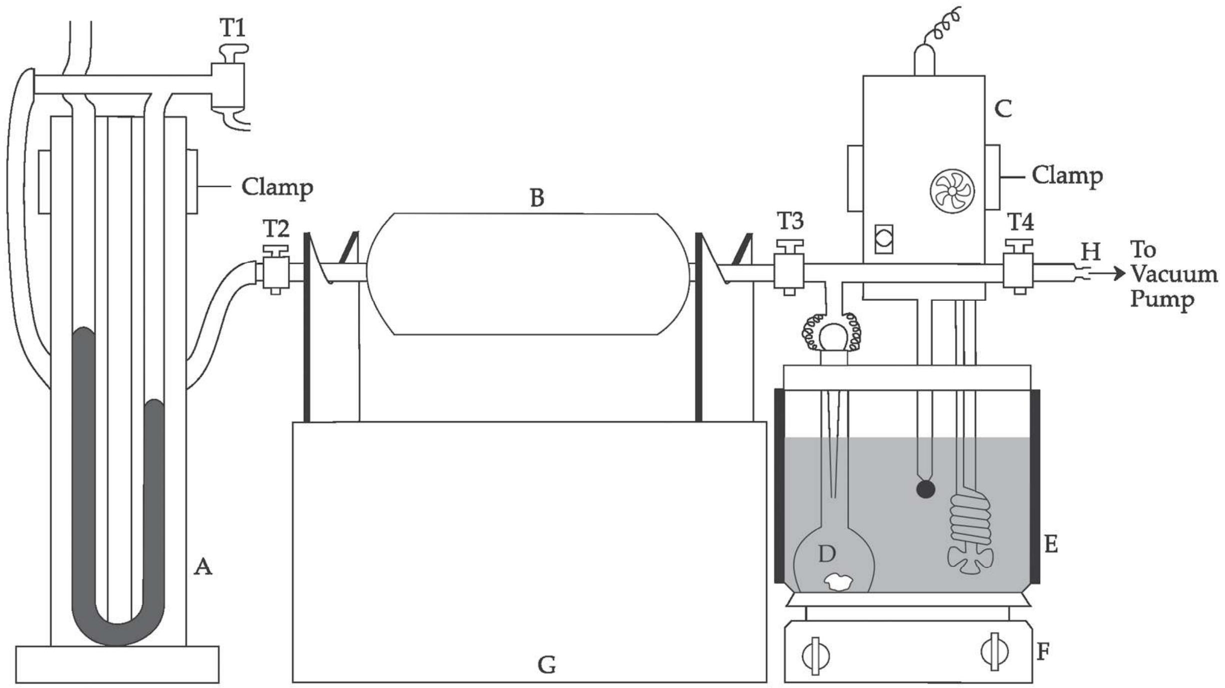

Fig. 1. Oxygen absorption apparatus

Table 1. **Oxygen absorbed in millimoles by pure fatty acids and blends at a temperature of 31.5 °C during intervals of one hour**

Time (min)	Millimoles of oxygen absorbed/gram of fatty acid						
	RSA/MSA						
	0/100	20/80	40/60	50/50	60/40	80/20	100/0
0	0	0	0	0	0	0	0
60	0.46	0.64	0.64	0.58	0.96	0.64	0.26
120	1.16	1.1	1.1	1.16	1.6	1.28	1.02
180	1.48	1.48	1.28	1.42	1.92	1.68	1.6
240	1.68	1.74	1.48	1.6	2.12	2.0	1.86
300	1.8	1.8	1.68	1.74	2.24	2.18	2.06

Table 2. **Oxygen absorbed in millimoles by pure fatty acids and blends at a temperature of 45 °C during intervals of one hour**

Time (min)	Millimoles of oxygen absorbed/gram of fatty acid						
	RSA/MSA						
	0/100	20/80	40/60	50/50	60/40	80/20	100/0
0	0	0	0	0	0	0	0
60	0.64	0.7	0.9	0.9	0.96	0.96	0.84
120	1.28	1.28	1.54	1.48	1.60	1.74	1.48
180	1.68	1.68	1.86	1.86	1.92	2.06	1.80
240	1.92	1.92	2.12	2.12	2.18	2.38	2.06
300	2.12	2.12	2.38	2.38	2.38	2.56	2.32

Table 3. **Oxygen absorbed in millimoles by pure fatty acids and blends at a temperature 60 °C during intervals of one hour**

Time (min)	Millimoles of oxygen absorbed/gram of fatty acid						
	RSA/MSA						
	0/100	20/80	40/60	50/50	60/40	80/20	100/0
0	0	0	0	0	0	0	0
60	0.84	0.84	0.84	0.78	1.22	0.96	1.48
120	1.28	1.42	1.48	1.36	1.80	1.54	2.12
180	1.68	1.74	1.80	1.74	2.12	1.86	2.44
240	1.86	1.92	2.06	2.0	2.32	2.12	2.7
300	2.06	2.12	2.32	2.18	2.44	2.32	2.82

Table 4. **Oxygen absorbed in millimoles by pure fatty acids and blends at a temperature of 75 °C during intervals of one hour**

Time	Millimoles of oxygen absorbed/gram of fatty acid						
(min)	RSA/MSA						
0/100	20/80	40/60	50/50	60/40	80/20	100/0	
0	0	0	0	0	0	0	0
60	0.96	0.90	0.78	0.78	1.28	1.28	1.28
120	1.42	1.42	1.28	1.28	1.80	1.74	1.80
180	1.6	1.68	1.48	1.68	2	2	2.08
240	1.74	1.8	1.68	1.80	2.12	2.12	2.18
300	1.74	1.86	1.74	1.86	2.18	2.12	2.24

Table 5. **Oxygen absorbed in millimoles by pure fatty acids and blends at a temperature of 90 °C during intervals of one hour**

Time	Millimoles of oxygen absorbed/gram of fatty acid						
(min)	RSA/MSA						
	0/100	20/80	40/60	50/50	60/40	80/20	100/0
0	0	0	0	0	0	0	0
60	1.1	0.96	1.36	0.9	1.16	1.36	1.48
120	1.42	1.42	1.6	1.36	1.54	1.68	1.74
180	1.6	1.48	1.74	1.6	1.6	1.8	1.86
240	1.74	1.54	1.86	1.74	1.68	1.8	1.92
300	1.80	1.68	1.92	1.80	1.68	1.8	1.92

Table 6. **Oxygen absorbed in millimoles by pure fatty acids and blends after 5h at temperatures of 31.5, 45, 60, 75 and 90 °C**

Temperature	Millimoles of oxygen absorbed/gram of fatty acid						
(°C)	RSA/MSA						
	0/100	20/80	40/60	50/50	60/40	80/20	100/0
31.5	1.8	1.8	1.68	174	2.24	2.18	2.06
45	2.12	2.12	2.38	2.38	2.38	2.56	2.32
60	2.06	2.12	2.32	2.18	2.44	2.32	2.82
75	1.74	1.86	1.74	1.86	2.18	2.12	2.24
90	1.8	1.68	1.92	1.8	1.68	1.8	1.92

reached 43 cm. The tap T4 was immediately closed and T3 closed later.

With tap T3 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 was 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, the tap T3 was opened to allow oxygen into the reaction flask for 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 height 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 ^{o}C.

The oxygen absorption during oxidation of fatty acids and blend of fatty acids from rubber seed and melon seeds were monitored manometrically at one hour intervals for 5 hours, at 31.5, 45, 60, 75 and 90 ^{o}C (Tables 1 - 6). The moles of un-reacted oxygen at any time (t) were calculated from the oxygen pressures using the ideal gas equation. The pressure of oxygen gas at any time during the auto-oxidation of fatty acids is related to the difference in mercury height of both arms of the manometer. The number of moles of oxygen absorbed at each instant is obtained from the difference of moles of gas at the beginning of the reaction and at time t. The pressure value and moles of un-reacted oxygen at various temperatures were used to calculate the moles of absorbed oxygen (n_a).

The oxygen absorption capability, for the pure and blends of fatty acids increases with time up to 300 minutes and with temperature from 31.5 ^{o}C to 45 ^{o}C. At 60 ^{o}C pure RSA and RSA/MSA 60/40 shows slightly higher oxygen absorption than that at 45 ^{o}C. With further increase in temperature (75-90 ^{o}C) the oxygen absorption ability decreases for pure fatty acids and the blends.

Pure RSA and blends containing higher proportion of RSA show higher oxygen absorption than pure MSA at all different test temperatures except for the initial period at 31.5 ^{o}C. Blends of RSA and MSA containing higher proportion of RSA show higher oxygen absorption than pure RSA at lower temperatures of 45 and 31.5 ^{o}C.

Rubber seed oil contains higher proportion of unsaturated fatty acids than melon seed oil. Rubber seed oil is made up of about 80.5% unsaturated fatty acids (Ramadhas, 2004) while melon seed oil has by composition 69.21% unsaturated fatty acids. There is high susceptibility of non conjugated fatty acids like linoleic acid for auto-oxidation. This comes from the presence of bis allylic hydrogen atoms which have relatively low bond dissociation energy of 75 kcal/mol (Gorkum, 2005) and can easily be abstracted resulting in radical chain initiation and thus auto-oxidation. Thus it is expected that pure RSA and RSA/ MSA blends with higher proportion of RSA have higher oxygen absorption ability.

The auto-oxidation as measured by oxygen absorption by fatty acids of pure melon seed oil, pure rubber seed oil and their blends is high at 45°C than higher temperatures in the range 75-90 °C. Oxygen absorption is high for blends of fatty acids when the fatty acid content from rubber seed is high.

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