

THERMAL STABILITY OF *VERNONIA GALAMENSIS* SEED OIL

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ABSTRACT. The physicochemical changes of refined vernonia oil-RVO (which naturally contains epoxidized triglycerides) upon heating was evaluated and is reported in this manuscript. A boiling point range of 183 °C to 190 °C (at 760 mm Hg) for the vernonia oil was obtained using the Siwoloboff's method. The oil changed its physical appearance and consistency in the course of the heating. A homogenous free-flowing beige-sand shade refined vernonia oil at room temperature (25 °C) was transformed irreversibly to an intense-brown shade, becoming increasingly more viscous with increase in temperature, and ceasing to flow momentarily at 188 °C. On cooling to room temperature, the oil solidified into a brown rubber-like elastic material. The oil also exhibited a reduction in its oxirane content from 1.39 ± 0.004 equivalent HBr kg^{-1} at 25 °C to 0.542 ± 0.002 equivalent HBr kg^{-1} at 70 °C. This signifies a 61% drop in oxirane content for the 45 °C temperature rise. These findings point towards a thermally driven polymerization and/or decomposition of the refined vernonia oil (RVO).

INTRODUCTION

In a number of industrial processes, operating mechanical equipment at moderate or very high temperatures is normal. For instance, in the fat/oil industry, the core process of hydrogenation is operable under temperature conditions of 218-232 °C per 20-40 lb per square inch [1]. Fat/oil deodorization is carried out at 218-246 °C in the Votator semicontinuous deodorizer [2] and ZSM-5 zeolite catalyzed upgrading of the seed oils to gasoline type fuel occurs at 370 °C with reasonable efficiency [3]. In numerous other oil processes such as distillation and bleaching, and uses as lubricants, industry feed stock and transport are undertaken at temperatures higher than 60 °C. But these high temperature operations must be done with the understanding that the stability of the raw materials and/or products need special attention to avoid unwanted side products.

Plant seed oils are particularly attractive as fuel for transport because their extraction procedure is simple and in principle, have demonstrated direct usability such as in diesel engines [4]. Sunflower, rape, safflower, peanut, castor bean, corn, and coconut oils when used as fuel in diesel engines, give performances similar to when the usual distillate fuel is used [5].

Special emphasis is being laid on developing plants like *Vernonia galamensis* that bring semi-arid land into agricultural productivity and produce oils with multiple chemical functionality since these offer little competition to existing food crops and a myriad possible uses [4, 6, 7, 8]. Though the potential commercial applications of the oil from this herbaceous annual, currently being developed as a commercial crop in Zimbabwe, Kenya, and Pakistan [7, 9] are well documented [7, 10-13], it is of paramount importance that its desirable physicochemical properties remain stable during upgrading and/or use. In automobile engines, for instance, viscosity stability of the fuel oil is essential so as to avoid carbon deposition around injection nozzles and in cylinder heads. High viscosities of engine oils result in poor atomization on injection into unmodified engines [5].

This paper describes the physical and chemical changes that result from heat treatment of *Vernonia galamensis* oil or vernonia oil. A comparative approach to qualitative and quantitative analyses of the oil's physical appearance, consistency, boiling temperature, and oxirane oxygen concentration before and after heat treatment, forms the basis of our evaluation of its thermal stability.

EXPERIMENTAL

Refined vernonia oil (RVO) was prepared from the crude oil by hexane extraction at room temperature. The oxirane oxygen concentration was determined using the argentimetric method [14, 15], which involved the use of hydrogen bromide in acetic acid and silver nitrate. A visual end point was employed. The boiling point of the RVO was determined using Siwoloboff's and vapour pressure methods [16-20].

Viscosity, refractive index (RI), and absorbance measurements on preheated RVO were made at 25 °C. The oil was initially heated to a required temperature then cooled back to 25 °C before the viscosity and absorbance determinations. A thermostated water bath was used to keep the oil at 25 °C before analysis. An Ostwald's viscometer was used for the viscosity determinations, whereas a Zeiss refractometer was used for RI measurements. The measurements were carried out in triplicate. A UV-visible spectrophotometer (Model PHARMACIA BIOTECH NOVA SPEC II) was used in the measurement of absorbance of the oil at 510 nm (wavelength of maximum absorbance, λ_{\max}).

Reagents. A 0.10 M sodium acetate solution was prepared by dissolving 53 g of anhydrous analytical grade sodium acetate in 1 litre of glacial acetic acid [15]. An Eosin Y indicator was prepared by dissolving 0.5 g in 10 mL of distilled water.

RESULTS AND DISCUSSION

Effect of heat on RVGSO stability. The most notable physical colour changes on vernonia oil upon heating are summarized in Table 1. Sample recovery and reuse in multiple determinations of boiling point *via* Siwoloboff's method was not possible with vernonia oil since the heating changed the oil irreversibly and the oil's consistency was visibly altered. Figure 1 shows the effect of temperature on absorbance (at $\lambda_{\max} = 510$ nm) of a preheated oil (to a desired temperature) measured at room temperature. It is clear from Table 1 and Figure 1 that vernonia oil changes colour shade and intensity upon heating. This suggests an irreversible transformation of the oil, possibly to yield a new form entirely different in composition.

Table 1. External appearance and consistency of *Vernonia galamensis* oil at different temperatures.

Temperature (°C)	External appearance and consistency
22	Free flowing-beige homogeneous liquid
50	Free flowing-beige homogeneous liquid
70	Viscous-brown homogeneous liquid
100	Viscous-intense brown liquid
154	Intense brown rubber-like solid material
200	Dirty-brown viscous liquid

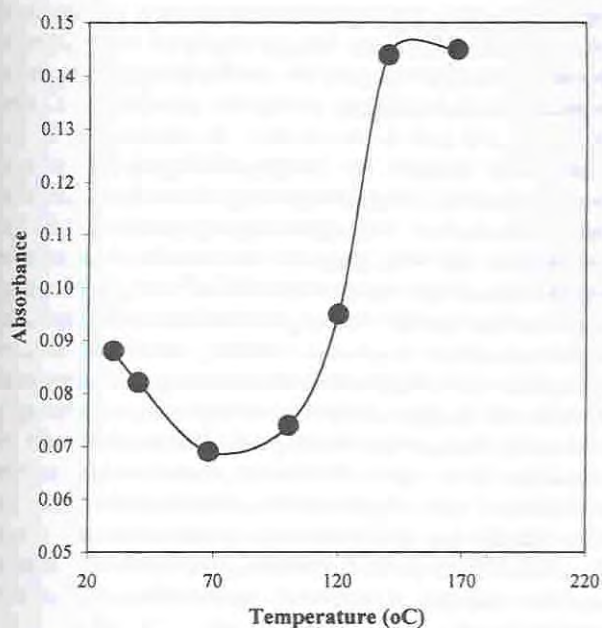


Figure 1. Effect of temperature on light absorbance by vernonia oil at 510 nm.

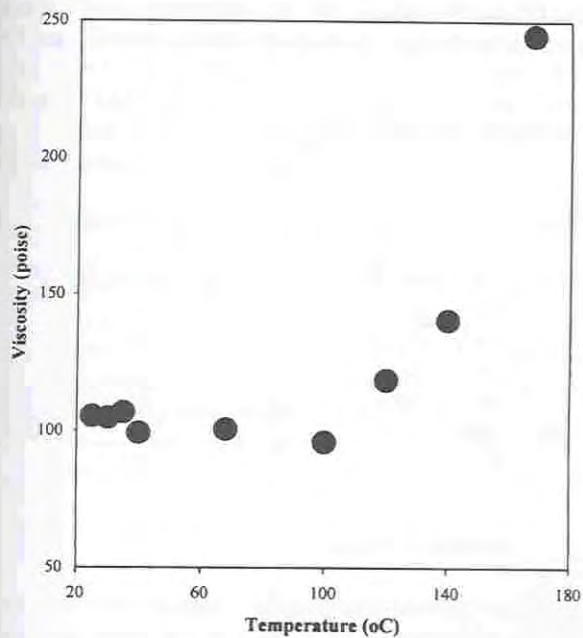


Figure 2. Effect of temperature on the viscosity (measured at 25 °C) of a pre-heated vernonia oil.

Also evident was the increasing viscosity (measured at 25 °C) of the preheated oil with temperature. Figure 2 shows the variation of viscosity of a pre-heated oil with temperature. It is evident from this figure that the preheated vernonia oil exhibits insignificant changes in viscosity in the 25-100 °C temperature range, a gradual increase in the 100-135 °C range and a rapid increase beyond 135 °C.

From separate heating experiments (without the heating-cooling cycle), vernonia oil showed remarkable changes in its flow ability. From free-flowing oil at room temperature, the oil sample became increasingly more viscous with increasing temperature. The viscosity peaked at about 188 °C, where within a short time span, the oil ceased to flow momentarily. Further heating restored its original flow ability, but destroyed the oil's original homogeneity. The "new" oil showed the presence of black curds interspersed in the entire sample. Cooling of the heated oily material to room temperature resulted in a rubbery-like elastic solid residue. It is possible that vernonia oil undergoes polymerization and/or decomposition upon heating. Literature survey reveals that some oils (such as avocado) decompose upon heating, giving off a repugnant smell and exhibit colour change upon heating [19]. The results of the effect of heating vernonia oil further elucidates Kent *et al.*'s observation that butanolysis of vernonia oil for 144 hours at 118 °C resulted in a dark mixture which contained little of the hydroxy butoxy esters [18]. Our findings indicate that conditions employed by Kent and co-workers were thermally severe. It is documented that epoxy functional groups have the potential for extensive cross-linking, especially amongst neighboring hydrocarbon chains to form interpenetrating polymer networks [14].

The assertion that vernonia oil undergoes irreversible change upon heating is further justified by the refractive index-temperature study. Figure 3 shows the influence of heating on the refractive index of a preheated vernonia oil measured at 25 °C. The sudden change in refractive index-temperature curve (Figure 3) at about 100 °C confirms the irreversible nature of the changes taking place on vernonia oil upon heating. Moreover, both Figures 2 and 3 show similar trends.

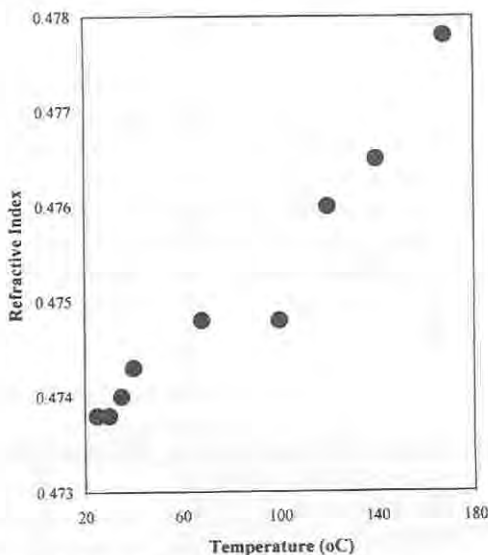


Figure 3. Effect of temperature on the refractive index of a pre-heated vernonia oil measured at 25 °C.

The vapour pressure-temperature data on vernonia oil together with the Clausius-Clapeyron equation (i.e., $\ln P = \Delta H_{\text{vap}}/RT + C$, where P is the vapour pressure, ΔH_{vap} is the enthalpy of vaporization, T is the absolute temperature, R is the gas constant in J/mol K^{-1} , and C is a constant) were used to determine the enthalpy of vaporization (ΔH_{vap}) and boiling point of vernonia oil. From the linear plot, ΔH_{vap} was determined as $-24.32 \text{ kJ mol}^{-1} \text{ K}^{-1}$ with a corresponding boiling point of $154 \text{ }^\circ\text{C}$. There was no observable sign of oil polymerization and/or decomposition similar to that observed during the direct heating procedure for determining the boiling point using the Siwoloboff's method. It is presumed that the temperature determined indirectly from data obtained by the vapour pressure method is the true boiling point of RVO. This method has been confirmed to allow for the prediction of both vapour pressure and boiling points within a small percent error [20].

Effect of temperature on oxirane content of RVGSO. Using the titrimetric method to follow the changes in oxirane oxygen concentration [O_{ox}] it is evident that there exists a correlation between the oxirane content and the temperature of the vernonia oil (Table 2). The results indicate that the oxirane-oxygen concentration of the oil decreases on average at a rate of about 1.36% per degree rise in temperature. This finding is in agreement with reports by several authors that vernonia oil obtained by solvent extraction at room temperature has a higher oxirane content and less free fatty acids than that obtained via the much higher temperature Soxhlet extraction procedure [8]. The rationalization of this correlation is based on the fact that the epoxy ring is a highly strained heterocyclic moiety of vernoloyl-glycerides with an angle of 60° between the cyclic ether bonds [21]. Though the epoxy group is sterically hindered due to the triglyceride molecule conformation [22-24], the epoxy moiety remains sensitive to thermal perturbations due to its high energy resulting from angle distortions. The implications are that, bulky attacking groups cannot affect the epoxy ring-cleavage. However, the small ring angle-strain in combination with enhanced bond vibrations due to heat energy, is sufficient to rupture the ring, forming transiently and intramolecular carbocation-anion pair that have a high energetic potential and charge to engage in intermolecular reaction with identical neighbouring molecules. This results in simple dimers and/or polymer formations.

Table 2. Variation of the oxirane oxygen concentration [O_{ox}] as a function of temperature (K).

Temperature (K)	[O_{ox}] equivalent HBr $\text{kg}^{-1} \pm \text{SD}$
298	1.390 ± 0.004
303	1.386 ± 0.004
313	1.240 ± 0.002
323	0.887 ± 0.004
333	0.701 ± 0.003
343	0.542 ± 0.002

CONCLUSION

Although oils with multiple chemical functionality such as RVO are considered renewable resources, and could act as alternatives to petroleum as feed stock, they pose exceptional challenges to workers in search for their potential applications. The temperature induced physical changes in the chemical functionality of the original biosynthetic forms complicates their synthetic utilities and potential direct usage.

This work reports on the boiling point and the $-\Delta H_{vap}$ of RVO and the thermal instability nature of the oil for the first time. The authors recommend that the oil be stored hermetically at temperatures at or below those of the solvent during extraction so as to preserve the oxirane content of the oil at the extraction time. The formation of a rubbery residual on heating the oil suggests a possible thermal-induced polymerization reaction as opposed to decomposition. As to whether decomposition or polymerization (or both) processes occur on heating RVO, remains the subject of mechanistic and kinetic investigations.

It is clear at this stage that RVO is generally not suitable as a feed stock in high temperature conventional oil upgrading industrial operations, automobile engine applications and deep frying processes. RVO should, however, find suitable applications in the polymer industry.

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