KINETIC AND THERMODYNAMIC EVALUATION OF THE EPOXIDATION OF ALLANBLACKIA FLORIBUNDA SEED OIL FOR INDUSTRIAL APPLICABILITY

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ABSTRACT

Epoxidation of seeds oils has attracted research concerns due to its industrial significance. Allanblackia floribunda seed oil (ASO) was subjected to epoxidation at different temperatures with a view to establishing its kinetics and thermodynamic properties for possible industrial applications. The seed oil was extracted and characterized for its physicochemical properties using conventional methods. The percentage oil content, peroxide value, iodine value, acid value and saponification value were found as 63%, 4.55 meq/kg, 34.9 gI2/100g, 0.64 mg KOH/g and 201.8 mg KOH/g respectively. Oil was found as non-drying with fatty acid content of high molecular weight. Oils with such characteristics are known to be stable against rancidity and possible oxidation. Oxirane analysis gave data which shows the rate of epoxidation dependence on temperature and time. This satisfies the possibility of epoxidizing ASO oil and confirms the formation of epoxidized oil from its seed. Pseudo-zero order kinetics with respect to oxirane formation was found from the epoxidation kinetics. Their rate constants were seen as 0.025 hr⁻¹, 0.028 hr⁻¹ and 0.04 hr⁻¹ at 50 °C, 60 °C and 70 °C respectively. Ea, ∆H ≠, ∆S ≠ and ∆G ≠ were found as 33.73 kJmol⁻¹, 17.04 kJmol⁻¹, -0.224kJmol⁻¹ K⁻¹ and 91.632 kJmol⁻¹ respectively. Thermodynamic evaluation shows that the epoxidation process was kinetically favorable, but thermodynamically unfavorable for enthalpy, entropy and Gibb’s energy; as such the process is not spontaneous at the temperatures studied. The result herein presents substantial reference data on the modification of ASO for diverse applicability and constitutes valuable literature database on the epoxidation of ASO for industrial applications.

Keywords: Allanblackia floribunda seed oil (ASO), Kinetics, Thermodynamics, Pseudo zero order

INTRODUCTION

One significant source of pharmaceutical raw materials, industrial materials and nutritional oils is seed oil (Oderinde et al., 2009). Seed oils can be used as precursors for a wide variety of useful products and industrial materials. One of such materials of industrial significance is epoxidized oil. Seed oils can be epoxidized at the points of their unsaturated double bonds in the fatty acid molecules to viable oxygen active agents. Epoxidation is a simple chemical reaction by which olefinic double bond is converted by an active oxygen agent, peroxy acid or peracid, to a cyclic three-membered ring structure containing oxygen, commonly called oxirane or epoxide. Different products of commercial and industrial value can be derived from seed
oils via optimized process modification, one of which is epoxidized oil. Seed oils can be epoxidized by active oxygen agents to produce oxirane modified products. The diverse applications of epoxidized vegetable oils are well known (Dominguez-Candela et al., 2022). They have been found to have both current and potential applications in various fields including surface coatings where they are used to reduce the volatile organic component (VOC), to formulate anti-corrosive coatings, alkyd resin chemical intermediates for organic synthesis and plastic/natural rubber processing, insecticides, lubricants, detergents emulsifiers and wax’s (Chiang et al., 2014; Tee et al., 2015; Sahoo et al., 2018). They have been reported to have major applications as stabilizers/plasticizers in vinyl polymers (Tee et al., 2015; Folarin and Ayinde 2016). The major field of application of epoxidised vegetable oil is in processing of vinyl polymers where they are used as plasticizer/stabilizers due to their excellent physical and chemical quality such as heat and light stability and other characteristic they impact on the polymer (Tee et al., 2015). Epoxidized lin seed oil and soya bean oil are commonly employed in this regard. Seed oils can also be modified with metals to give metal carboxylates which could stabilize PVC as a result of being thermally stable within the temperature range employed for processing it (Folarin and Ayinde 2017). Poly vinyl chloride (PVC) is a versatile industrial thermoplastic with varying applications in all its forms, both flexible and rigid forms. Due to its morphology and thermal instability, it is not suitable to be used alone hence its application with metal carboxylated seed oils by compounding and moulding as additives which helps to serves as plasticizers and stabilizers. Earlier report has shown the preparation of copper and nickel carboxylates and their calcinated derivatives from castor seed oil that exhibited antimicrobial activity (Folarin et al., 2013). Their applications have led to high demand for these vegetable oils and consequently increase the cost of these seed oils. The seed oil of A. floribunda has been well characterized and information available in the literature revealed that it is non-drying oil. However, there is no record of its utilization in the preparation of epoxides. An investigation into the possible usage of A. floribunda seed oil in preparing epoxides and determining its oxirane content brings out the significance of this study. The epoxidation of low cost Allanblackia floribunda seed oil for technical and industrial applications therefore becomes necessary. Thus compelling the need to epoxidize an inexpensive vegetable oil such as Allanblackia floribunda seed oil for non-edible and technical applications, since there are no reported literatures on the epoxidation of Allanblackia floribunda seed oil. The feasibility of the epoxidation, kinetic evaluation and thermodynamic characterization of the process for possible industrial, economic and technical applications constitutes the focus of this study.

MATERIALS AND METHODS

Sample area and materials
Allanblackia floribunda seeds were collected from the University Farm, Olusegun Agagu University of Science and Technology, Nigeria. The University is situated at Igodan which is a small community along Okitipupa-Igbokoda express way, located in the Southern Senatorial District of Ondo State, South Western Nigeria. It lies within the coordinates of longitude 4.77°N to 4.86°N and latitude 6.44°E to 6.62°E of the equator. Identification of the seeds was done at the University Botanical Herbarium under the supervision of Prof Aworinde D.O, who is the taxonomist. The voucher number of the identified seed is OAUSTECH/BH003/VN321. Analytical grade hydrogen peroxide, formic acid and other chemicals were standardized and used without further purification.

Seeds pretreatment
The seeds were removed from its pod, sun-dried for two weeks and ground.
Extraction of the oil
Soxhlet extraction technique was employed for the oil extraction with n-hexane as the extracting solvent.

Physico-chemical characterization of the oil
Acid, peroxide, iodine and saponification values were determined using standard procedures (Standard method for the analysis of oils, 1994; AOAC, 1995; Kardash and Turyan, 2005). The colour of the oil was observed by visual inspection at room temperature.

Epoxidation process
Epoxidation reactions were carried out with peracid generated in situ by reacting various amounts of acetic acid and hydrogen peroxide with the oil at different temperatures, using the methods described by Rangarajan et al., (1995) with some modification, and Okieiman et al., (2005). Oxirane content was determined titrimetrically following standard method (Jeffery et. al., 1994; Aigbodion et al., 1999).

Kinetics and thermodynamic studies
Epoxidation kinetics of ASO (0.13moles) using peracid generated in situ from the addition of formic acid (0.09 9moles) and 30% hydrogen peroxide (0.44moles) to the oil were carried out at 50, 60 and 70°C respectively. The reaction progress was followed by withdrawing aliquots of the reaction mixture at time intervals of 30 minutes, placed in a separating funnel where the aqueous layer is drawn off and oil layer washed with successive portions of hexane until acid-free. The aliquot was analyzed for percentage oxirane content using standard methods (Jeffery et. al., 1994; Aigbodion et al., 1999). Kinetics of epoxidation was followed as oxirane formation rate dependence on temperature (50 °C -70 °C).

RESULT AND DISCUSSION
Table 1: Physicochemical properties of Allanblackia floribunda seed oil

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>Yellow</td>
</tr>
<tr>
<td>Saponification value (mgKOH/g)</td>
<td>201.8</td>
</tr>
<tr>
<td>Acid value (mgKOH/g)</td>
<td>0.64</td>
</tr>
<tr>
<td>Peroxide value (meq/kg)</td>
<td>4.55</td>
</tr>
<tr>
<td>Iodine value (gI₂/100g)</td>
<td>34.9</td>
</tr>
<tr>
<td>% oil content</td>
<td>63</td>
</tr>
</tbody>
</table>

The seed oil content is found to be 63% as presented in Table 1, which is in agreement with the value reported in literature (Crocket, 2015). The oil content shows the richness of Allanblackia floribunda in seed oil. The yellow colour observed is peculiar to most seed oils. The saponification value as seen in Table 1 is comparable with those earlier reported (Wilfred et.al., 2010; Crocket, 2015), which indicates that the oil is significantly rich in high molecular weight fatty acids. Coconut oil is rich in low-molecular weight fatty acids and has a saponification value consistent with what exist in literature (Wahyudi et.al., 2018). The value is lower than that reported for Cocosnucifera oil (Obasi et al., 2012), but comparable with that for palm oil (Bereket and Alemayehu, 2016). Oil of very high saponification value indicates the presence of low molecular weight fatty acids content which has more glyceride molecule per gram of fat than high molecular weight acids (Solomon et al., 2016; Wahyudi et al., 2018). The value is consistent with those reported for palm oil and groundnut oil (Musa et. al., 2012, Wali et. al., 2015; Babatunde and Bello, 2016). The peroxide value of 4.55meq/kg is consistent with that reported for palm oil (Babatunde and Bello, 2016), and in line with the recommended standard of less than 10 meq/kg (CODEX, 2005). Low peroxide value of oil indicates its...
ability to resist oxidative deterioration. A high peroxide value will cause the oil to be unstable and become easily rancid (Babatunde and Bello, 2016, Folarin et al., 2017). Low peroxide and acid value of 4.5meg/kg and 0.61 mgKOH/g respectively (Table 1), gives characteristics of great stability and resistance against rancidity and possible oxidation (Folarin et al., 2017). The iodine value of the oil is seen to be 34.9 I$_2$/100g (Table 1). The iodine value obtained is in the range 34 – 39 g I$_2$/100g$^{-1}$, which had also been reported for the oil (Wilfred et al., 2010; Crocket, 2015); further confirming the oil as non-drying since it is less than 100 I$_2$/100g. Fixed oils have been classified into three categories on the basis of iodine value. Non-drying oils which have values less than 100, semi drying oils which have values between 100 –130 and drying oils whose values are between 130 – 200 I$_2$/100g. The value is lower than recommended iodine value for palm oil which is 50–55/gram and nuog oil variety which is 112–129/gram (Bereket and Alemayehu, 2016).

![Graph](image)

Fig. 1: Profile of % oxirane formed against time for the different temperatures studied

The percentage of oxirane contents at different temperatures (50 °C-70 °C) of epoxidized *allanblankia floribunda* seed oil are represented as Fig. 1 above. The percentage of oxirane contents increase at increasing time and temperature. The epoxidation of the oil which was monitored by its oxirane content proceeds faster with increasing temperature as seen in Fig. 1. Although previous studies on epoxidation of seed oils have reported an increase in oxirane content with increasing temperature which was followed by subsequent reduction at the optimum temperature and time (Aigbodion et al., 1999, Okiemen and Okiemen 2001; Shuangfei and Wang, 2011); such trend is not observed for the epoxidation process of *allanblankia floribunda* seed oil in the temperature ranges studied. This shows that the epoxidation process is not complete within the temperature range studied. Complete epoxidation is expected to occur at much higher temperatures, as it has always been observed from previous studies that complete epoxidation is always accompanied by an opening of the epoxyl ring occasioned by hydroxylation. (Aigbodion et al., 1999, Okiemen and Okiemen 2001; Shuangfei and Wang, 2011). An increase in reaction temperature is expected to increase the rate of epoxide
formation. The observed trend here agrees with previous studies on epoxidation of other seed oils (Aigbodion et al., 1999, Okiemen and Okieimen 2001). The result however satisfies the possibility of epoxidizing *allanblackia floribunda* seed oil and confirms the formation of epoxidized oil from *allanblackia floribunda* seed through the established oxirane formation.

Table 2: Kinetic data for Oxirane rate dependence on temperature.

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>ln(C\textsubscript{hpo} - C\textsubscript{ep}) at 50°C</th>
<th>ln(C\textsubscript{hpo} - C\textsubscript{ep}) at 60°C</th>
<th>ln(C\textsubscript{hpo} - C\textsubscript{ep}) at 70°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>3.360</td>
<td>3.360</td>
<td>3.339</td>
</tr>
<tr>
<td>1</td>
<td>3.350</td>
<td>3.357</td>
<td>3.335</td>
</tr>
<tr>
<td>1.5</td>
<td>3.340</td>
<td>3.341</td>
<td>3.315</td>
</tr>
<tr>
<td>2</td>
<td>3.335</td>
<td>3.330</td>
<td>3.301</td>
</tr>
<tr>
<td>2.5</td>
<td>3.320</td>
<td>3.323</td>
<td>3.275</td>
</tr>
<tr>
<td>3</td>
<td>3.294</td>
<td>3.282</td>
<td>3.237</td>
</tr>
</tbody>
</table>

![Graph](image)

**Fig. 2:** Pseudo zero order profile for the epoxidation of *Allanblackia floribunda* seed oil at 50°C
There are two step processes for in situ epoxidation reaction; peracetic acid formation as first step and the reaction of peracetic acid with the unsaturation or double bond in the oil as second step (Shuangfei and Wang, 2011). If the rate determining step is presumed to be the first step with the concentration of peracid constant throughout the reaction, the following rate equation applies:

\[ \frac{dC_{ep}}{dt} = k (C_{hp0} - C_{ep}) \cdot C_{aa0} \]  

where \( k \) is the rate constant, \( C \) is the concentration of components, subscripts \( hp0 \), \( aa0 \) and \( ep \) denote initial concentrations of hydrogen peroxide, acetic acid, and epoxides, respectively. Integration of Eq. (1) yields the rate equation for the epoxidation process as,

\[ \ln(C_{hp0} - C_{ep}) = -K \cdot C_{aa0} \cdot t + \ln(C_{hp0}) \]  

The plot of \( \ln(C_{hp0} - C_{ep}) \) vs. time should yield straight lines for those reactions with negligible degradation of oxirane, with a slope of \(-K\) (Shuangfei and Wang, 2011).
The main reaction is

\[
R_2-\text{CH}=\text{CH}-R_2 + \text{RCOOH} \rightarrow R_2-\text{CH}-\text{CH}-R_2 + \cdot \text{RCOOH}
\]

The kinetics of the epoxidation of *Allanblackia floribunda* seed oil is expressed in terms of oxirane rate dependence on temperature as presented in Table 2. The kinetics for the epoxidation process of *Allanblackia floribunda* seed oil is found to be pseudo zero order with respect to oxirane formation in the presence of very high concentration of hydrogen peroxide (30%), as compared to the percentage oxirane content formed. Linear profiles were obtained for the plots of \(\ln(C_{\text{hpo}} - C_{\text{ep}})\) vs. time for all the temperatures studied (50°C-70°C) as presented in Fig. 2-4. Regression coefficients \(R^2\) values ranged from between 0.887-0.938, which shows good linearity; thus accounting for their pseudo zero order kinetics. Linearity in the pseudo zero order plots satisfies the conditions and features of pseudo zero order kinetics when compared to other kinetics models tested. This is consistent with the kinetics of in situ epoxidation of jatropha seed oil using peroxyacetic acid (Okiemen and Okiemen, 2001), and the epoxidation kinetics of unsaturated fatty acid methyl esters in the presence of \(\text{SO}_3\text{H}\)-functional Bronsted-Acidic ionic liquid as catalyst (Shuangfei and Wang, 2011). Their rate constants were found as 0.025\(\text{hr}^{-1}\), 0.028\(\text{hr}^{-1}\) and 0.04\(\text{hr}^{-1}\) for the epoxidation process at 50°C, 60°C and 70°C respectively. The epoxidation rate is seen to increase with increasing temperature. A similar trend in the rate of epoxidation has been reported by Okiemen and Okiemen, (2001); Shuangfei and Wang, (2011); except for the fact that at the optimum temperature, there were deviation from linearity which was due to complete epoxidation followed by hydroxylation.

**Table 3:** Thermodynamics and kinetics parameters for the epoxidation of *Allanblackia floribunda* seed oil

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Rate constant (k) (\text{(hr}^{-1}))</th>
<th>(1/T)</th>
<th>(k h/k_B T) (\times 10^{15})</th>
<th>(\ln [k h/k_B T])</th>
</tr>
</thead>
<tbody>
<tr>
<td>50°C (323K)</td>
<td>0.025</td>
<td>0.0031</td>
<td>3.72</td>
<td>-33.23</td>
</tr>
<tr>
<td>60°C (333K)</td>
<td>0.028</td>
<td>0.0030</td>
<td>4.04</td>
<td>-33.14</td>
</tr>
<tr>
<td>70°C (343K)</td>
<td>0.040</td>
<td>0.0029</td>
<td>5.59</td>
<td>-32.82</td>
</tr>
</tbody>
</table>

![Eyring plot of \(\ln(k h/k_B T)\) versus \(1/T\) for kinetics analysis of the epoxidation of *Allanblackia floribunda* seed oil](image)

**Fig. 5:** Eyring plot of \(\ln(k h/k_B T)\) versus \(1/T\) for kinetics analysis of the epoxidation of *Allanblackia floribunda* seed oil
All thermodynamic parameters were determined from data presented in Table 3 above. Arhenius equation was used in determining the activation energy ($E_a$), using the temperature dependence of the reaction rate constants according to the equation:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left( \frac{T_2 - T_1}{T_2T_1} \right)$$

The activation energy obtained is observed to be lower than the values reported for the epoxidation of unsaturated fatty acid methyl esters (Shuangfei and Wang, 2011) and epoxidation of jatropha seed oil (Okiemen and Okiemen, 2001), respectively. The lower activation energy found in this study when compared to others reported in literature (Okiemen and Okiemen, 2001; Shuangfei and Wang, 2011) indicates slightly lower temperature dependence of the epoxidation rate as against others. The higher the activation energy, the more energy that is required for the epoxidation to occur. The Eyring equation below with an Eyring plot of $\ln (kh/kB T)$ versus $1/T$ (Fig. 5) gives a line with a slope of $-\Delta H^*/R$ from which the enthalpy of activation ($\Delta H^*$) is calculated and intercept of $\Delta S^*/R$ from which the entropy of activation ($\Delta S^*$) was obtained.

$$\ln \frac{k h}{kB T} = \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}$$

The enthalpy of activation ($\Delta H^*$), entropy of activation ($\Delta S^*$) and Gibb’s free energy ($\Delta G^*$) obtained from the Gibb’s thermodynamics equation $\Delta G^* = \Delta H^* - T\Delta S^*$; were all determined to be 17.04 kJmol$^{-1}$, -0.224 kJmol$^{-1}$ K$^{-1}$ and 91.632 kJmol$^{-1}$ respectively. The enthalpy of activation ($\Delta H^*$) and Gibb’s free energy ($\Delta G^*$) values were lower when compared to the values of 62.8 kJmol$^{-1}$ for enthalpy and 127.6 kJmol$^{-1}$ for Gibbs free energy reported by Shuangfei and Wang (2011) for the epoxidation of unsaturated fatty acid methyl esters. They were also lower compared to values of 64.73 kJmol$^{-1}$ for enthalpy and 102.63 kJmol$^{-1}$ for Gibbs free energy reported for the epoxidation of jatropha seed oil (Okiemen and Okiemen, 2001). However entropy of activation ($\Delta S^* = -0.19$ kJmol$^{-1}$ K$^{-1}$) is seen to be in the same range with the entropy value of -0.128 kJmol$^{-1}$K$^{-1}$ reported for Shuangfei and Wang, (2011) for the epoxidation of unsaturated fatty acid methyl esters; and slightly lower than -0.128 kJmol$^{-1}$K$^{-1}$ reported for the epoxidation of jatropha seed oil (Okiemen and Okiemen, 2001).

Activation enthalpy ($\Delta H^*$) value of 17.04 kJmol$^{-1}$ indicates that the epoxidation process is endothermic. The thermodynamic data shows that the epoxidation process is not spontaneous and hence unfavourable for enthalpy (Since $\Delta H^* > 0$), entropy (Since $\Delta S^* < 0$) and Gibb’s energy (Since $\Delta G^* > 0$) at the temperatures studied.

**Conclusion**

The feasibility of using *Allanblackia floribunda* seed oil in the preparation of epoxidised *Allanblackia floribunda* seed oil has been established from this study. The epoxidation process is temperature dependent, therefore higher oxirane yield can still be obtained at higher temperatures above 70 °C. The kinetic and thermodynamic investigation shows that the epoxidation process is kinetically favorable but thermodynamically unfavorable; as such the process is not spontaneous at the temperatures studied. The result herein presents substantial reference data on the modification of ASO for diverse applicability and constitutes valuable literature database on the epoxidation of ASO for industrial applications. The findings indicates that *Allanblackia floribunda* seed oil is a potential raw material for production of epoxidized *Allanblackia floribunda* seed oil of high epoxide content, having commercial value especially as plasticizer/stabilizers for poly vinyl chloride as well as other significant industrial applications.
References


