EXTRACTION, CHARACTERIZATION AND EPOXIDATION OF CASTOR SEED OIL

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ABSTRACT

Chemical epoxide modification appears to be one way toward the objective of substituting raw materials for industrial products, and epoxidized vegetable oils offer intriguing options as a raw material substitute for industrial chemicals.. The oil from castor seeds was extracted using a soxhlet extractor and the percentage yield for castor oil was 49 %. The characterization of castor oil yielded the following results: iodine value 88.52g I_2/100g, acid value 1.148 mgKOH/g, saponification value 185.8 mgKOH/g, specific gravity 0. 9223 g, peroxide value 156.2 mEq/kg, and pH value 5.7. The oil was epoxidized in the presence of sulphuric acid using 30 % aqueous hydrogen peroxide as an oxygen donor and glacial acetic acid as an oxygen carrier. The fresh oil and the product of the epoxidation reaction were characterized using FTIR analysis, which revealed the disappearance of the carbon-carbon double bond peak at 1746.71 cm^{-1} and the formation of the epoxide peak at 1743.93 cm^{-1}. Curing time analysis revealed the strength of the synthesized epoxide, with castor epoxide hardening at 25 min and commercial epoxide hardening at 8 min. Castor oil can be utilized as a raw ingredient in a variety of industrial applications, including water treatment, soap production, paint formulation, and laminate production.

Keywords: Curing time, Functional group, Industry, Acid value, Peroxide value, Iodine value

INTRODUCTION

Castor bean (*Ricinus communis L*) is a plant that belongs to the Euphorbiaceae family and is widely distributed in tropical, subtropical, and temperate regions worldwide. It is native to Africa. The plant may be cultivated almost anyplace and is resistant to insects and drought. 'Variety minor' seeds are classified as the most prevalent variety in Northern Nigeria (Yusuf *et al.,* 2013). Although most botanists today think that all castor beans belong to the same species, early taxonomists tried to divide the bean family into subspecies based on physical characteristics. The majority of these strains interbreed readily, and many of these phenotypic features are only inherited (Azadmard *et al.,* 2011). It is the only species in the monotypic genus Castorrum and the subphylum Castorrum. The Latin name for tick is *Ricinus* (Ewing, 1971). Although castor beans grow quickly overall, they are cold-hardy and need a long frost-free season to thrive. Similar to the rest of the plant, the seeds are often found in low concentrations. It also includes the water-soluble toxin ricin. Usually, solvent extraction or mechanical pressing are used to obtain castor oil from dried castor seeds (Akinnusotu *et al.,* 2018). Castor bean is an important oilseed crop that produces ricinoleic acid-rich oil (Azadmard *et al.,* 2011). Castor oil has the potential to replace petroleum-based products in the development of small businesses, according to Haruna (2019), it is a biodegradable, renewable, and sustainable, accounting for approximately 90% of the oil's content (Markovic and Bastic, 1976). Ricinoleic acid (12-hydroxyoctadeca-9-enoic acid), a trifunctional fatty acid, is responsible for castor oil's versatility in the chemical industry (Haruna, 2019). China, India, and Brazil produced the majority of the world's castor oil in 2005 and 2006 (Azadmard *et al.,* 2011). Ethiopia, Thailand, and Paraguay also make a little contribution to castor oil production. The entire global production of castor beans in 2005 was more than one million tons per year (Anonymous, 2005). Changes in castor oil prices and insecurity in supply have made the international castor oil market exceedingly volatile, increasing demand for biodiesel and other vegetable oils. Castor oil processing and production have been driven globally by medical and industrial purposes. The FDA recently approved castor oil as a direct food additive for taste and/or adjuvant usage (Azadmard *et al.,* 2011). Alharbawy et al., *(*2014) conducted research on the hot and cold extraction processes used to create oil from seeds of wild castor beans (*Ricinus communis L.).* The hot extracted oil yielded values that were near to the conventional characteristic values for castor oil, but the cold oil yielded values that were within range for some but not for others. Methanolysis has also contributed in the synthesis of biodiesel from oil extracted using cold or hot processes. Duel (1951) conducted a study on castor oil, revealing high oil extraction yields and recommending that seed commercialization in Nigeria be considered. The oil was discovered to be of high quality and capable of being employed not just as a food additive in the food industry, but also in industrial applications such as cosmetics, soaps, paints, and energy production. Enkuahone (2018) researched the extraction of castor oil and its use in the creation of detergents; he found the detergents to be outstanding, particularly in terms of sudsing and colour following their examination. Abitogun et al*.,* (2008) conducted a characterization study and advised that the oil can be commercialized and used in the food industry, both as a food additive and for industrial purposes. Yusuf et al., (2015) conducted research in Katsina, Nigeria, he extracted castor oil by mechanically cold-pressing the seeds of the wild castor plant (*Ricinus communis L.*). It was discovered to have industrial potential. (Olalekan and Akinyinka, 2018) conducted a comparison of the direct, elemental, and physicochemical properties of Nigerian castor oil, proximal examination revealed the presence of fat, ash, and protein. According to Babu and Gouda (2014), castor oil fatty acid, methyl ester epoxide was produced using an in-situ epoxidation technique for use as a biological lubricant base stock. Epoxides have superior thermos oxidative stability.

According to Haruna (2019), the discovery and development of castor oil provides an industrial feedstock, particularly for small and medium-sized businesses in Nigeria. Danjuma et al., (2017) investigated the moisture content, specific gravity, refractive index, ignition point, flash point, smoke point, viscosity, and pH of castor oil. The chemical criteria that suggested that it may be utilized to generate biodiesel were free fatty acid (oleic acid), acid value, saponification value, and iodine value (Nangbes *et al.,* 2013).

MATERIALS AND METHOD
Sample Collection
In Gombe State, Nigeria, the Federal College of Education (Tech) was the location of the castor seed harvest.

Sample Preparation
The seed beans underwent various processes in the course of its preparation for extraction.
The unit operation involved are: (Akpan *et al.,* 2006)
i. Clearing: By hand, some dirt and unnecessary particles from the castor beans were removed. **ii**. Drying: The cleaned beans were sun-dried until the seeds fell out of the casing. The beans original 5 to 7% moisture content was then reduced by drying them for 7 hrs at 60 °C in an oven to a consistent weight.
iii. Winnowing: Using a tray, the shell was separated from the nibs (cotyledon) in order to increase yield, and the cover was blown off.
iv. Grinding (size reduction): The beans were ground into a paste (cake) with a mortar and pestle in order to break down the cell walls and release the castor oil for extraction.

Oil Extraction
According to Danjuma et al. (2017), In a flask with a round bottom, 300 ml of hexane were added. 10 g of the sample were placed in the thimble and put into the middle of the extractor. 40 to 60 ^{0}C was the temperature range at which the Soxhlet was heated. As the solvent boiled, the vapor rose through the vertical tube and into the top condenser. The filter paper thimble in the middle, which contained the solid sample that was to be removed, was filled with the liquid condensate. The extract slowly seeped through the thimble's pores, into the siphon tube, and back into the flask with a round bottom. This was let to go on for 30 min. After that, the tube was removed, dried in the oven, cooled in a desiccator, and weighed again to determine the amount of oil extracted. Further extraction was carried out at 30 min intervals until the sample weight at further extraction and the previous weight matched. The experiment was repeated by adding 5 g of sample to the thimble. The weight of oil extracted was determined every 30 min, the resulting oil-containing mixture was boiled to recover the solvent from the oil.

Determination of the Percentage of Oil Content.
In a soxhlet system, 250 g sample was defatted exhaustively with normal hexane at 60 ^{0}C, to prevent solvent leaks, the extract was kept in storage for about a day. The weight of oil recovered from the extract was then expressed as a percentage of the sample's dry mass weight (Kabo *et al.,* 2020).

$$\% \text{ Oil yield} = \left(\frac{weight\ of\ oil - weight\ of\ cake}{weight\ of\ sample} \times 100 \right)$$

Determination of acid value
In a 250 ml beaker, 25 ml of diethyl ether and 25 ml of ethanol were combined using the procedure given by (Danbature *et al.,* 2017) The resulting mixture was added to 10 g of oil in a 250 ml conical flask, along with a few drops of phenolphthalein indicator. With constant shaking, the mixture

was titrated with 0.1 M NaOH until a dark pink colour was detected and the volume (V_0) was recorded. The following is how the free fatty acid and acid values were calculated:

$$\% \text{FFA} = \frac{M \times Vo}{1000} \times \frac{Molecular\ masss \times 100}{weight\ of\ the\ sample}$$

Where:
Vo = volume of titration (titre value)
M = molar concentration of NaOH
W = weight of the sample
Acid value = 1.99×FFA

Determination of pH value
A method described by Arinola and Eunice (2013) was adapted in which 2 g of oil was placed into a clean dry 250 ml beaker and 13 ml of hot distilled water was slowly mixed into the sample in the beaker. It was chilled in a water bath to 25 ^{0}C. Before the pH electrode was placed into the sample and measured, it was calibrated using a buffer solution with a known pH.

Determination of saponification
A flask was filled with two grams of oil. The mixture was then gently boiled for 1 hr under a reflux condenser with 25 cm^3 of the alcoholic potassium hydroxide solution added. At regular intervals, the flask's contents were swirled. Then 1 cm^3 of phenolphthalein indicator was added and titrated to permanent pink colour using conventional 0.5 M HCl. Titrations were performed while the solution was still hot (Danjuma *et al.,* 2017). Under the same conditions, the blank was also identified.

Determination of Iodine Value
Wijs method was used to calculate the iodine value, as reported by Danbature et al., (2017), in which 0.2 g of oil was weighed and placed in a 250 ml conical flask. 10 cm^3 of carbon tetrachloride was poured in to it, as well as a blank 250 ml conical flask. Each flask was filled with 25 ml of Wijs reagent. The mixture was thoroughly mixed and left in the dark for one hour. After adding 15 cm^3 of 10 % potassium iodide solution and 100 cm^3 of distilled water, the contents of both flasks were titrated with standard 0.1 M sodium thiosulphate solution. To ensure that the iodine in the carbon tetrachloride layer was transported to the aqueous layer, a starch indicator was utilized near the endpoint with continuous shaking during the titration. The amount of iodine absorbed per 100 g of fat was calculated as follows.

$$\text{Iodine value} = \frac{100 \times difference\ in\ titre\ value \times thiosulphate\ factor}{weight\ of\ fat\ used}$$

1 cm^3 of 0.1 M sodium thiosulphate = 0.0127 g of iodine

Determination of specific gravity
The oil's density was measured using a density bottle. On a 25 ml dry and clean density bottle, W_1 was written. After adding water to the dried density container to the designated level, the new weight was noted as W_2. W_3 was produced when oil was used in place of water, as explained by (Sani *et al.,* 2023). The expression of specific gravity is as follows:

$$\text{Specific gravity} = \frac{mass\ of\ the\ substance}{mass\ of\ an\ equal\ volume\ of\ water}$$

i.e $SG = \frac{W_3 - W_1}{W_2 - W_1}$

Determination of moisture content
Three evaporating dishes were cleaned, dried in an oven at 105 ^{0}C for one hour, chilled in a desiccator, and weighed. 20 g of the oil sample was weighed into each of the three dry evaporating plates and dried in an oven at 105 ^{0}C for two hours at a time until a constant weight was attained (Yirankinyuki *et al.,* 2018).

Tto calculate moisture content, the following formula was used:

Moisture content $= \frac{average\ loss\ in\ weight\ of\ oil}{weight\ of\ the\ oil\ in\ gram} \times 100$

Epoxidation of Oil

Goud et al., (2007) outlined a modified method for conducting an epoxidation process in which a 500 ml flask with three necks and a thermometer, separating funnel, and magnetic stirrer was filled with 20 ml of oil. The oil was treated by adding 3 % weight of hydrogen peroxide and acetic acid to the oil and sulfuric acid catalyst at a molar ratio of 0.5:1. Drop by drop, for five minutes at 10 %, a 1.5:1 molar ratio of hydrogen peroxide to oil was also added to the mixture (to prevent heat surge owing to the exothermic nature of the epoxidation reaction). The mixture was then agitated for 5 hrs at ambient temperature (20-27 ^{0}C).

Determination of peroxide value of castor oil

Nkafamiya et al., (2007) presented a procedure in which 5 g of oil was placed in 30 ml glacial acetic acid/chloroform (3:2 v/v) and a saturated solution of potassium iodide (0.5 ml) was added to liberate iodine by reacting with the peroxide. The resultant solution was titrated against a solution of sodium thiosulphate (0.01 M) using a starch indicator until the yellow colour vanished. The following formula was used to compute the peroxide value:

$$PV(\frac{Meq}{kg}) = \frac{M(S-B)\times 1000}{weight\ of\ the\ sample\ in\ g}$$

Where:
B = Blank titre value
PV = peroxide value
S = sample titre value
M = molarity of sodium thiosulphate solution (0.01 M)

Characterization of Epoxidized Oil

Fourier Transformed Infrared (FTIR) Spectroscopic analysis was used to analyze the epoxide synthesized.

Determination of curing time

The epoxy resin and commercial hardener were purchased from Gombe's main market. After mixing the hardener and epoxy resin, the hardening period was noted. It was also recorded how long it took to combine the hardener and synthetic epoxide. The point at which every combination lost its tactility was known as the curing time, and it was noted at that point.

RESULTS AND DISCUSSION

Table 1: Physico-chemical Analysis of castor oil

Parameters	Result
Moisture content	0.2000
Specific gravity (g)	0.9223
Acid value (mg KOH/g)	1.1480
Saponification value (mg KOH/g)	185.80
Iodine value (gI$_2$/100g)	88.520
pH value	5.7000
Peroxide value (m Eq/kg)	156.20
Percentage of oil (%)	49.550
Volume of oil (ml)	152.50

Table 1 shows castor oil has a low acid value of 1.148, a low iodine value of 88.52, and a low peroxide value of 156.2, but a reasonably high specific gravity of 0.922 and saponification value of 185.8. These results were favourable when compared to ASTM standards and general specifications for industrial-grade castor oil (WHC, 2012). The oil's low acid value and pH of 5.7 indicate a low free fatty acid (FFA) concentration. The acid value of an oil is a measure of its FFA content. The iodine value, on the other hand, is a measure of the oil's unsaturation level, and the peroxide value is related to the oxidation level due to hydroperoxide generation at double bond locations. As a result, double bond unsaturation in oils is one of the most critical characteristics influencing lipid oxidation. The hydroxyl group on C-12 is thought to prevent the double bond on C-9 of ricinoleic acid against hydroperoxide production in castor oil (ICOA, 2013). The low iodine value of the seed oil indicates a low unsaturation level, which is typical with non-drying oils. This indicates that the oil may not be acceptable for use as an alkyd resin in paint formulation or as a varnish (Kyari, 2008), but it may be suitable as a lubricant or hydraulic braking fluid. Again, the comparatively high saponification value of 185.8 indicates that the oil could be used in the soap and cosmetics industries.

Table 2: Curing Test Result

Epoxide	Curing time (min)
Commercial epoxy resin	8
Castor oil epoxide	25

Table 2 demonstrates that the synthesized castor oil epoxide can be utilized as hardeners, however, some industrial treatment is required due to the greater range between commercial epoxide and the produced castor epoxide.

Table 3. Result of FT-IR spectrum of castor seed oil and epoxidized castor seed oil.

	S/N	Peak	Functional group
Castor oil	1	3443.98cm^{-1}	-OH group present
	2	3008.97 cm^{-1}	Sp^2 -CH
	3	2925.14 cm^{-1}	Sp^3 -CH
	4	1746.71 cm^{-1} weak	-C=C

Epoxidized castor oil	5	3422.38 cm^{-1}	-OH group present
	6	3008.57 cm^{-1}	Sp^2 -CH
	7	2856.08 cm^{-1}	Sp^3 -CH
	8	1743.93 cm^{-1} strong	-C=O (Epoxy peak)

As seen in Table 3 above, the FTIR spectrum has multiple absorption peaks. The FTIR peaks of castor oil showed an unsaturation content of 1746.71 cm^{-1} (C=C). However, after the epoxidation of castor oil, unsaturation peaks in the same range vanished, and new peaks formed at 1743.93 cm^{-1} (Pearson's, 1981). The emergence of epoxy peaks at 1743.93 cm^{-1} and C-O peak at 1419.61 cm^{-1} indicated that an epoxidation process occurred with sulphuric acid as a catalyst. The change in functionality in this range shows that all of the unsaturation content was converted into an epoxide product. Salimon et al., (2012) discovered that the quaternary carbons are represented by the distinctive signals in the FTIR spectra of ricinoleic acid around 823-843 cm^{-1} The oxirane ring's formal name. The absence of C=C linkages in the epoxide spectra further corroborated the nearly complete conversion of double bonds to oxirane (98.5%). In this investigation, FTIR spectra revealed a trace of - OH absorption peak at around 3000-3564 cm^{-1}, indicating the presence of hydroxyl groups in castor oil and its epoxide. These hydroxyl groups are from ricinoleic acid, which is the most abundant fatty acid in C-O composition (Vleck and Petrovic, 2006).

CONCLUSION

The FTIR spectrum demonstrated the effective synthesis of castor oil epoxide, with the epoxide peak forming at 1743.93 cm^{-1} and the fresh oil's carbon-carbon double bond peak disappearing at 1746.71 cm^{-1} after a 25 min curing period. The study also shown that castor seed oil can serve as a substitute source for a number of vital industrial compounds that are normally produced using expensive technologies and non-renewable resources like petroleum. Therefore, turning vegetable oil into epoxide (a raw material used in several industries), might be a step in the right direction in the search for novel raw materials.

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