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RESEARCH PAPER

Extraction, Characterization and Epoxidation of Cotton Seed Oil

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ABSTRACT

Epoxidized vegetable oils are promising candidates as raw material substitutes for industrial applications. The Chemical modification of epoxies appears to be a pathway towards achieving this goal of replacing raw materials with industrial products. In this study, oil was extracted from cottonseed using a Soxhlet extractor, yielding 35% cottonseed oil. The results obtained in the cottonseed oil characterization were determined as follows: an iodine value of 114.7gI_2/100g, acid value of 0.66mgKOH/g, saponification value of 191.2mgKOH/g, specific gravity of 0.923g, peroxide value of 10.42mEq/kg, pH 4.1. The oil was epoxidized using 30% aqueous hydrogen peroxide as the oxygen donor and glacial acetic acid as the oxygen carrier in the presence of sulphuric acid as catalyst. The fresh oil and the products of the epoxidation reaction were characterized using FT-IR analysis, the results of which indicated the disappearance of the carbon-carbon double bond peak at 1655 cm^{-1} and the appearance of the epoxide peak at 785 cm^{-1}. The analysis also showed the strength of the synthetic epoxy, cotton epoxy cured in 21 minutes versus commercial epoxy cured in 8 minutes. Vegetable oils that have undergone epoxidation are interesting alternatives to replace raw materials in industrial applications. Epoxies can potentially be chemically altered in order to replace raw materials with industrial goods. The following conclusions were drawn from the cottonseed oil characterisation results: the specific gravity is 0.923g, peroxide content is 10.42mEq/kg, pH is 4.1, iodine value is 114.7gI_2/100g, acid value is 0.66mgKOH/g, and saponification value is 191.2mgKOH/g. FT-IR analysis was employed to characterize the fresh oil and the epoxidation reaction's products.

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INTRODUCTION

Cotton is a profitable crop known for its fibers, it was first discovered in the wild in Africa and has been used for centuries to weave clothing. This has helped launch a number of textile industries in northern Nigeria. There are a number of medical benefits of the cotton plant [21]. Cobra snake drops in the eyes are treated topically using the liquid extracted from the leaves [3]. When cotton seeds and fibers are ready, then the capsules open, revealing the white fibers inside. In addition to fibers and linters, seeds also contain 20–25% high-quality protein, carbs, lecithin, and sterols, as well as an oily core that is encased in a tough, black shell [5]. Cotton is a lucrative crop. Clothing has been woven for generations using this fiber, which was first found in the wild in Africa. This assisted in the establishment of several textile companies in northern Nigeria. The cotton plant has a variety

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of health advantages [19]. Cotton is a temperate climate shrub or tree that belongs to the Malvaceae family, Gossypies family, genus Gossypium. While it grows naturally as a perennial plant, it is grown as an annual crop for commercial purposes. Botanically speaking, cotton balls are classified as fruits. The main cultivated cotton species of commercial importance include Hirsutum, Barbadense, Arboreum and Herbaceum. Many different cultivars of these species have been developed by conventional breeding to produce cotton with improved agronomic traits and improved cotton fiber and cottonseed traits [6]. Accordinf to [7], cottonseed oil underwent some physicochemical investigations such as: moisture content, specific gravity, refractive index, ignition point, flash point, smoke point, viscosity, and pH are examples of physical parameters. Free fatty acid (oleic acid), acid value, saponification value, and iodine value are the chemical parameters. According to different analyseses, the oil is of good quality and can be used not only as a food additive in the food sector but also for industrial purposes. It finds application in the manufacture of energy and cosmetics, soap, paint, and other household and personal care products [5]. This indicated that the oil had very low free fatty acid levels, so transesterification was performed using methanol and caustic soda as catalysts. The fatty acid profiles were measured with a gas chromatograph analyzer and determined to be highly unsaturated. Based on these findings, we concluded that it can be used as an alternative fuel for diesel engines. A higher cetane number allows the engine to burn fuel more efficiently and reduce harmful emissions [6]. A study conducted by [1] to investigate the extraction and characterization of cottonseed oil by solvent extraction, in the study, the analytical method was used to determine the chemical, physical and approximate composition of the oil. The researchers concluded that cottonseed oil has great potential for use as a domestic and industrial oil and as a promising alternative to lubricants and stabilizers. Chemical modification of the fatty acid chains present in triglycerides appears to be one way towards this goal of replacing petroleum products, concluding that the synthesized epoxide can be used as an excellent substitute for petroleum products. [10] reported that the fatty acid composition of cottonseed oil showed that the oil contained two unsaturated fatty acids (octadeca-9-enoic acid and octadeca-9,12-dienoic acid). The most abundant unsaturated fatty acids were present and the most abundant saturated fatty acid was hexadecanoic acid [23].

EXPERIMENTAL

Materials and Methods

Sample collection and preparation

The cotton seeds were bought from Gombe main market Gombe state Nigeria. The seed beans underwent various processing in the course of its preparation for extraction [2].

The unit operation involved are:

i. Clearing: The cotton seeds had some foreign materials and dirt which were separated by hand picking.

ii. Drying: The cleaned beans were sun-dried in the open, until the casing splits and sheds the seeds. The beans were further dried in an oven at 60°C for 7hrs to a constant weight in order to reduce its moisture content, which was initially around 5 to 7%.

iii. Winnowing: The separation of the shell from the nibs (cotyledon) was carried out using a tray to blow away the cover in order to achieve a very high yield.

iv. Grinding (size reduction): Mortar and pestle was used to crush the beans into a paste (cake) in order to weaken or rupture the cell walls to release cotton fat for extraction.

Oil Extraction

300 mL of hexane was poured into the round bottom flask. A 10g sample was placed in a thimble and inserted into the center of the extractor. The Soxhlet was heated to 40-60°C. As the solvent boiled, the vapor rose through a vertical tube into the upper condenser. The liquid condensate dripped onto the central filter paper thimble containing the solid sample to be extracted. The extract seeped through the pores of the thimble and filled the siphon tube where it flowed back into the round bottom flask. This lasted for 30 minutes. It was then removed from the tube, dried in an oven, cooled in a desiccator, and weighed again to determine the amount of oil extracted. Additional extractions were performed at 30-minute intervals until the sample weight in the additional extractions was equal to the previous weight. The experiment was repeated by re-adding 5g of the sample to the thimble. The weight of extracted oil was measured in-house every 30 minutes. At the end of the extraction, the resulting mixture containing oil was

heated to recover the solvent from the oil [7].

Determination of the Percentage of Oil Content.

A 250 g sample was thoroughly degreased with normal hexane at 60° C. in a Soxhlet apparatus. Extracts were stored for approximately one day to remove solvent spills, and the recovered extract (oil weight) was expressed in terms of the percentage of the dry matter weight sample [13].

$$\%\ \text{Oil yield} = \frac{\textit{weight of oil} - \textit{weight of cake}}{\textit{weight of sample}} \times 100$$

Determination of acid value

Using the procedure described by [8], 25 mL of diethyl ether and 25 mL of ethanol were mixed in a 250 mL beaker. The resulting mixture was added to 10 g of oil in a 250 ml Erlenmeyer flask and a few drops of phenolphthalein indicator were added to the mixture. The mixture was titrated with 0.1 M NaOH with constant shaking until a deep pink color was observed and the volume (V) was recorded. Free fatty acids and acid numbers were calculated as follows:

$$\%\text{FFA} = \frac{M \times Vo}{1000} \times \frac{\textit{Molar mass} \times 100}{\textit{weight of sample}}$$

Where:
Vo = volume of titration (titre value)
M = molar concerntration of NaOH
Acid value = 1.99×FFA

Determination of pH value

The procedure of [4] was adopted; 2 g of oil was poured into a clean and dry 250 mL beaker, and 13 mL of hot distilled water was added to the sample in the beaker and gently stirred. It was then cooled to 250° C with a water bath. A pH electrode was standardized with a buffer solution of known pH; the electrode was inserted into the sample, and the pH reading was recorded.

Determination of saponification

Two grams of oil was weighed into a flask. An alcoholic potassium hydroxide solution of 25^{0}C was then added, and the mixture was brought to a gentle boil and subsequently refluxed for 1 hour. The contents of the flask were stirred frequently. Then 1% of phenolphthalein indicator was added and titrated with 0.5 M HCl to a permanent pink color. Titration was performed while the solution was still hot [7]. Blank value is also measured under the same conditions.

Determination of Iodine Value

Wij's method was adopted to determine the iodine value, as described by [8], and 0.2 g of oil was weighed into a 250 ml Erlenmeyer flask. 10 ml of carbon tetrachloride was added to it, and another 250 ml Erlenmeyer flask was used as a blank container. 25 ml of Wij's reagent was added to each of the two flasks. The mixture was mixed well and left in the dark for 1 hour. After adding 15ml of 10% potassium iodide solution and 100 ml of distilled water, the contents of both flasks were titrated with a 0.1 M sodium thiosulfate standard solution. A starch indicator was used towards the endpoint with continuous shaking during the titration to ensure that the iodine in the carbon tetrachloride layer was transferred to the aqueous layer. The weight of iodine absorbed by 100 g of fat was estimated as:

Iodine value =

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

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

Determination of specific gravity

A density bottle was used to measure the density of the oil. A clean dry 25 ml density bottle was weighed and marked W1. The dry density bottle was filled to the mark with water and the new weight was recorded as W2. Water was replaced with oil and recorded as W3 [22].

The expression of specific gravity is as follows:

Specific gravity =

$$\frac{\textit{mass of the substance}}{\textit{mass of an equal volume of water}}$$

$$\text{i.e SG} = \frac{W3 - W1}{W2 - W1}$$

Determination of moisture content

Three evaporating dishes were washed, dried in an oven at 105° C for 1 hour, cooled in a desiccator, and weighed. A 20 g oil sample was weighed into each of three dry evaporation dishes, removed while drying in an oven at 105 °C, and weighed every 2 h until constant weight was reached [22].

The following formula was used to calculate the moisture content:

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

Epoxidation of Oil

The method described by [12] was employed; about 20 ml of the oil was placed in a 500ml three-necked flask, equipped with a thermometer, a separating funnel, and a magnetic stirrer. Acetic acid at a molar ratio of 0.5:1 to the oil and sulphuric acid catalyst. 3% weight of hydrogen peroxide and acetic acid was added to the oil. A hydrogen peroxide molar ratio of 1.5:1 to the oil was also added drop-wise to the mixture for 5 minutes, thereby preventing heat surge due to exothermic nature of epoxidation reactions. The mixture was then stirred at room temperature (20-27^{0}C) for 5 hours.

Determination of peroxide value of cotton seed oil

The procedure described by [15] was adopted in which 30 ml of glacial acetic acid/chloroform (3:2 v/v) and saturated potassium iodide solution (0.5 ml) were added to liberate iodine by reaction with peroxide. The resulting solution was titrated against sodium thiosulfate solution (0.01M) using a starch indicator until the yellow colour disappeared. Peroxide value was calculated as:

$$\text{PV}\left(\frac{meq}{kg}\right) = \frac{M(S-B)\times 1000}{\text{weight of sample in gram}}$$

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

Characterization of Epoxide Oil

Fourier Transformed Infrared (FT-IR) Spectroscopic analysis was used to analyse and characterize the epoxide synthesized.

Determination of curing time

Commercially available hardeners and epoxy resins were purchased from the market. The hardener and epoxy were mixed and the cure time was recorded. The synthesized epoxy and hardener were also mixed and the time required for mixing was recorded. The cure time was the time at which each mixture was no longer tacky and was recorded as cure time [16].

RESULTS AND DISCUSSION

Table 1. presents the physico-chemical properties of the extracted cottonseed oil. The acid number was found to be 0.66 mg KOH/g. This is a low number, indicating that this oil is edible and has a long shelf life without going rancid [18]. Oils with low acid numbers are generally reported to have high saponification values, consistent with the results obtained for the saponification value of 191.2 mg KOH/g. Therefore, cottonseed oil is suitable for soap making. The iodine value, which indicates the degree of unsaturation of vegetable oil, was found to be 114.7 g/100g for cottonseed oil. This value classifies the oil as semi-drying. [9] suggested that an iodine value above 100 classifies an oil as semi-drying or drying, while below 100 is a non-drying oil. The values obtained are close to those of pumpkin seed oil with an iodine value of 100 g/100 g [14]. A peroxide level of 10.4 meq/kg was found to be used as an indicator of the degree of oxidation of the oil. This indicates that the oil is fresh, as the peroxide level in fresh oil is usually less than 10 meq/kg [11]. The pH of cottonseed oil was found to be 4.1. This may be due to different chemicals used to control cotton pests. A specific gravity of 0.923 was obtained which is close to its value of 0.918 for pumpkin seed oil [17]. The extracted cottonseed oil exhibited a reddish-brown colour with a pale taste and odour as a result of the

Table 1. Physico-chemical Analysis of cottonseed oil

Parameters	Result
Moisture content	0.980
Specific gravity (g)	0.923
Acid value (mgKOH/g)	0.660
Saponification value (mgKOH/g)	191.2
Iodine value (gI2/100g)	114.7
pH value	4.100
Peroxide value (mEq/kg)	10.40
Percentage of oil (%)	35.20
Volume of oil (ml)	112.0

Table 2. Curing test

Epoxide	Curing time (min)
Commercial epoxy resin	8
Cotton oil epoxide	21

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

Castor Oil	S/N	peak	Functional group
	1	3473.47cm^{-1}	-OH group present
	2	3007.92 cm^{-1}	Sp2 -CH
	3	2854.42 cm^{-1}	Sp^3 -CH
	4	2925.24 cm^{-1}	Sp^3 -CH
	5	1744.84 cm^{-1}	-C=C
Epoxidized Castor Oil	6	3472.26cm^{-1}	-OH group present
	7	3009.20 cm^{-1}	Sp2 -CH
	8	2853.94 cm^{-1}	Sp^3 -CH
	9	723cm^{-1}	-C-O peak (Epoxy peak)

oil's unrefined nature.

Table 2 showed that the synthesised cotton seed epoxide can be used as hardeners; it is therefore necessary to carry out some industrial treatments because of the wider range between commercial epoxide and the synthetic cotton epoxides before application.

From the FT-IR Data of Cotton seed oil and epoxidezed oil in Table 3. It is clear that the peak related to carbon-carbon double bonds from cottonseed oil at 1744.84cm^{-1} disappeared on epoxidation, and the epoxy groups were found in epoxidized cottonseed oil at 723cm^{-1}, indicating that all of the carbon-carbon double bonds were turned into epoxy groups. [20] reported the presence of epoxy groups at 722–833 cm^{-1}, which is in agreement to the study.

CONCLUSION

In this study, the FT-IR analysis of synthesized epoxide showed the disappearance of the carbon-to-carbon double bond peak in the oil and the presence of epoxide peak. The study also confirmed that cotton seed oil can be an alternative source in the production of many useful industrial chemicals that are derived mostly from non-renewable sources such as petroleum that requires expensive technology. Therefore, transforming vegetable oil into epoxide, which is also a raw material for many industries, should be a good initiative in the direction of new sources of raw materials.

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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