

Extraction, Characterization and Modification of Castor Seed Oil

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Abstract

This paper carried out experimental study, through extraction and characterization of both crude and refined castor oil. Normal hexane was used as solvent for the extraction process. The oil produced was refined through degumming, neutralization and bleaching process using local adsorbent (activated clay). The characterization analysis revealed that tested parameters, which include specific gravity, refractive index, acid value, saponification value and iodine value for both crude and refined castor oil produced, were within the ASTM standard specifications. In fact the iodine value obtained (84.8) for the refined oil indicates that the oil could certainly be used as lubricant, hydraulic break fluid and protecting coatings. The oil was modified via sulphation method to produce Turkey – red oil that was tested on wooden material, paper and cloth. The test revealed that the Turkey – red oil produced is suitable to be used as a good dyeing agent and polish.

Keywords

Castor seed, Castor crude oil, Castor refined oil, Neutralization, Degumming, Bleaching, Adsorbent

Introduction

Castor oil is pale amber viscous liquid derived from the seeds of the plant *Ricinus Communis*, sometimes known as *ricinus oil* [1]. Castor oil is one of the few naturally occurring glycerides that approach being a pure compound, since the fatty acid portion is

nearly nine-tenths *ricinoleic*.

A crude Castor oil is a pale straw colour [1-2] but turns colourless or slightly yellowish after refining and bleaching. The crude oil has distinct odour, but it can easily be deodorized in the refining process. Like any other vegetable oils and animal fats, it is a triglyceride, which chemically is a glycerol molecule with each of its three hydroxyl group esterified with a long chain fatty acid. Its major fatty acid is the unsaturated, hydroxylated 12-hydroxy, 9-octadecenoic acid, known familiarly as *Ricinoleic acid*. The fatty acid composition of a typical castor oil contains about 87% of ricinoleic acid.

Castor plant (*Recinus Communis*) from which castor beans and oil are subsequently derived grows naturally over a wide range of geographical regions and may be activating under a variety of physical and climatic regimes. The plant is however essentially a tropical species, although it may grow in temperate regions [2]. Literature revealed that Castor beans contains about 30-35 percent oil [1-2] which can be extracted by variety of processes or combination of processes, such as hydrate presses, continuous screw presses and solvent extraction. However the most satisfactory approach is hot pressing using a hydraulic press, followed by solvent extraction [1, 3].

However, castor oil and its derivatives are used in the production of paints, varnishes, lacquers, and other protective coatings, lubricants and grease, hydraulic fluids, soaps, printing inks, linoleum, oil cloth and as a raw material in the manufacturing of various chemicals *sebacic acid* and *undecylenic acid*, used in the production of plasticizer and Nylon [4].

This paper is however aimed at extraction, characterization and modification of castor seed oil. This will be achieved through the realization of the following objectives:

- Extraction of Castor Oil from Castor beans through solvent extraction process;
- Characterization of crude and refined castor oil for easy identification, and also to assess it quality;
- Modification of the refined castor oil.

Methodology

Castor Beans Processing

The castor beans undergo various processing in the course of its preparation for extraction. The unit operations involved are:

- *Clearing*: The castor beans had some foreign materials and dirt which was separated by hand picking.
- *Drying*: The cleaned beans were sun dried in the open, until the casing splits and sheds the seeds. The beans were further dried in the oven at 60°C for 7hrs to a constant weight in order to reduce its moisture content, which was initially at about 5 to 7%.
- *Winnowing*: The separation of the shell from the nibs (cotyledon) was carried out using tray to blow away the cover in order to achieve very high yield.
- *Grinding (size reduction)*: Mortar and pestle were used to crush the beans into a paste (cake) in order to weaken or rupture the cell walls to release castor fat for extraction.

Operation of Soxhlet Extractor

300ml of normal Hexane was poured into round bottom flask. 10g of the sample was placed in the thimble and was inserted in the centre of the extractor. The Soxhlet was heated at 60°C. When the solvent was boiling, the vapour rises through the vertical tube into the condenser at the top. The liquid condensate drips into the filter paper thimble in the centre, which contains the solid sample to be extracted. The extract seeps through the pores of the thimble and fills the siphon tube, where it flows back down into the round bottom flask. This was allowed to continue for 30 minutes. It was then removed from the tube, dried in the oven, cooled in the desiccators and weighed again to determine the amount of oil extracted. Further extraction was carried out at 30 minutes interval until the sample weight at further extraction and previous weight becomes equal. The experiment was repeated by placing 5g of the sample into the thimble again. The weight of oil extracted was determined for each 30 minutes interval. At the end of the extraction, the resulting mixture (*miscella*) containing the oil was heated to recover solvent from the oil.

Determination of Moisture Content of the Seeds

40g of the cleaned sample was weighed and dried in an oven at 80°C for 7hrs and the weight was taken after every 2hrs. The procedure was repeated until a constant weight was obtained. After each 2 hours, the sample was removed from the oven and placed in the desiccator for 30 minutes to cool. It was then removed and re-weighed. The percentage moisture in the seed was calculated from the formula: $\text{Moisture} = 100(W_1 - W_2)/W_2 \%$, where W_1 = Original weight of the sample before drying; W_2 = Weight of the sample after drying.

Determination of the Percentage of Castor Oil Extracted

30g of the sample was placed in the thimble and about 150ml of normal hexane was poured into the round bottom flask. The apparatus was heated at 60°C and allowed for 3hrs continuous extraction using Soxhlet apparatus. The experiment was repeated for different weights of the sample, 35g, 40g and 50g. At the end, the solvent was distilled and the percentage of oil extracted was determined.

Characterization of the Extracted Castor Oil

Determination of Acid Value

25ml of diethyl ether and 25ml of ethanol was mixed in a 250ml beaker. The resulting mixture was added to 10g of oil in a 250ml conical flask and few drops of phenolphthalein were added to the mixture. The mixture was titrated with 0.1M NaOH to the end point with consistent shaking for which a dark pink colour was observed and the volume of 0.1M NaOH (V_0) was noted. Free Fatty Acid (FFA) was calculated as: $V_0/W_0 \cdot 2.82 \cdot 100$, where 100ml of 0.1M NaOH = 2.83g of Oleic acid, W_0 = sample weight; then Acid Value = FFA \cdot 2.

Determination of Saponification Value

Indicator method was use as specified by ISO 3657 (1988). 2g of the sample was weighed into a conical flask; 25ml of 0.1N ethanolic potassium hydroxide of was then added. The content which was constantly stirred was allowed to boil gently for 60min. A reflux condenser was placed on the flask containing the mixture. Few drops of phenolphthalein indicator was added to the warm solution and then titrated with 0.5M HCl to the end point until the pink colour of the indicator just disappeared. The same procedure was used for other samples and blank. The expression for saponification value (S.V.) is given by: $S.V = 56.1N(V_0-V_1)/M$, where V_0 = the volume of the solution used for blank test; V_1 = the volume of the solution used for determination; N = Actual normality of the HCl used; M = Mass of the sample.

Determination of Iodine Value

The method specified by ISO 3961 (1989) was used. 0.4g of the sample was weighed into a conical flask and 20ml of carbon tetra chloride was added to dissolve the oil. Then 25ml of Dam's reagent was added to the flask using a safety pipette in fume chamber. Stopper was then inserted and the content of the flask was vigorously swirled. The flask was then placed in the dark for 2 hours 30 minutes. At the end of this period, 20ml of 10% aqueous potassium iodide and 125ml of water were added using a measuring cylinder. The content was

titrated with 0.1M sodium-thiosulphate solutions until the yellow colour almost disappeared. Few drops of 1% starch indicator was added and the titration continued by adding thiosulphate drop wise until blue coloration disappeared after vigorous shaking. The same procedure was used for blank test and other samples. The iodine value (I.V) is given by the expression: $I.V = 12.69C(V_1-V_2)/M$, where C = Concentration of sodium thiosulphate used; V_1 = Volume of sodium thiosulphate used for blank; V_2 = Volume of sodium thiosulphate used for determination, M = Mass of the sample.

Determination of Specific Gravity

Density bottle was used to determining the density of the oil. A clean and dry bottle of 25ml capacity was weighed (W_0) and then filled with the oil, stopper inserted and reweighed to give (W_1). The oil was substituted with water after washing and drying the bottle and weighed to give (W_2). The expression for specific gravity (Sp.gr) is: $Sp.gr = (W_1-W_0)/(W_2-W_0)$ = Mass of the substance / Mass of an equal volume of water.

Determination of Viscosity

A clean, dried viscometer with a flow time above 200 seconds for the fluid to be tested was elected. The sample was filtered through a sintered glass (fine mesh screen) to eliminate dust and other solid material in the liquid sample. The viscosity meter was charged with the sample by inverting the tube's thinner arm into the liquid sample and suction force was drawn up to the upper timing mark of the viscometer, after which the instrument was turned to its normal vertical position. The viscometer was placed into a holder and inserted to a constant temperature bath set at 29°C and allowed approximately 10 minutes for the sample to come to the bath temperature at 29°C. The suction force was then applied to the thinner arm to draw the sample slightly above the upper timing mark. The afflux time by timing the flow of the sample as it flow freely from the upper timing mark to the lower timing mark was recorded.

Determination of Refractive Index

Refractometer was used in this determination. Few drops of the sample were transferred into the glass slide of the refractometer. Water at 30°C was circulated round the glass slide to keep its temperature uniform. Through the eyepiece of the refractometer, the dark portion viewed was adjusted to be in line with the intersection of the cross. At no parallax error, the pointer on the scale pointed to the refractive index. This was repeated and the mean value noted and recorded as the refractive index.

Determination of pH Value

2g of the sample was poured into a clean dry 25ml beaker and 13ml of hot distilled water was added to the sample in the beaker and stirred slowly. It was then cooled in a cold-water bath to 25°C. The pH electrode was standardized with buffer solution and the electrode immersed into the sample and the pH value was read and recorded.

Refining of Extracted Castor Oil

Preparation of Clay ([5])

The clay sample was obtained from the Jikpan – Bosso – River bank, Bosso town, Minna, Niger State, Nigeria. The clay was ground and then mixed with water. Impurities such as sand and stone were removed. To activate the clay, 2M HCl was added to the clay slurry and the mixture was boiled for 2hrs at about 100°C. The mixture was then washed with water to remove acid, dried and ground.

Degumming and Neutralization ([5, 6])

The extracted oil was degummed by the addition of boiling water. The mixture was stirred for 2 minutes and allowed to stand in the separating funnel. Thereafter, the aqueous layer was removed. The procedure was repeated to ensure removal of most gums. For the neutralization, about 60g of the degummed oil was poured into a beaker and heated to 80°C, after which 40ml of 0.1M NaOH was added and stirred to a uniform solution. Sodium chloride (about 10% of the weight of the oil) was added to help settle out the soap formed. This was transferred into a separating funnel and allowed to stand for 1h; the soap formed was separated from the oil. Hot water was added again and again to the oil solution until the soap remaining in solution was removed. The neutralized oil was then drawn off into beaker.

Bleaching ([6])

50g of neutralized oil was poured into a beaker and heated to 90°C. Activated clay (15% by weight of oil) was added. The mixture was stirred continuously for 30 minutes. The temperature was allowed to rise to 110°C for another 30 minutes. The content was filtered hot in an over at 70°C.

Modification of the Refined Castor Oil: Sulphation

20g of oil was warmed at 35°C. 15ml of concentrated sulphuric acid (98%) was then added and the reaction was allowed to completion with constant stirring. After, the product was washed with hot distilled water and left to stand for 2 hrs, after which water was then

removed. And the sulphuric acid ester formed was finally neutralized with 10ml of 0.1M Sodium Hydroxide.

Results and Discussion

Obtained results for various tests carried out on the sample are tabulated below.

Table 1. Determination of Moisture Content

Time (h)	0	2	4	6	7
Weight (g)	420	412.52	406.25	402.58	402.57

Chemical analysis (Refined oil)

Using the various formulae as indicated in the experimental procedure, chemical properties of the virgin (unrefined) and the refined oil were evaluated and results are presented in Table 3.

Table 2. Physical Properties of the Crude and Refined Castor Oil

Property	Crude Castor Oil	Refined Castor Oil
Specific gravity	0.9587	0.9587
Viscosity at 28°C [St]	9.42477	6.4842
Refractive Index at 28°C	1.4686	1.4674
pH	6.11	6.34
Colour	Amber	Amber

Table 3. Chemical Properties of the Crude and Refined Castor Oil

Property	Crude Castor Oil	Refined Castor Oil
Acid Value [mg NaOH/g of Oil]	1.148	0.869
Saponification Value [mg KOH/g of Oil]	185.83	181.55
Iodine Value [g I ₂ /100g of Oil]	87.72	84.8

Table 4. Determination of Percentage Oil Extracted

Determination	Value(g)
Weight of empty flask (M ₁)	108.6
Weight of thimble (W ₁)	3.13
Weight of sample + thimble (W ₂)	33.13
Weight of Sample (W ₂ -W ₁)	30
Weight of empty flask +Oil (M ₂)	160.15
Weight of Oil (M ₂ -M ₁)	51.55
2nd Weight of Sample	35.1
3-rd Weight of Sample	40.2
4-th Weight of Sample	50

The percentage of oil extracted = 33.2%; percentage moisture content = 4.15 %.

Table 5. ASTM specification for Quality Castor Oil

Property	Ranges	Selected
Specific gravity 20/25°C	0.957-0.968	0.962
Refractive Index, n_D	1.476-1.479	-
Saponification Value	175-187	181
Un-saponification Value	0.3-0.7	0.7 (Max %)
Iodine Value	82-88	85
Hydroxyl Value	160-168	160(Minimum)
Viscosity at 25°C	6.3-8.8 St	-
Acid Value	0.4-4.0	3
Colour (Gadner)	Not darker than 2-3	3.0 (Maximum)

Discussion

The results obtained for the percentage moisture content, 4.15% shows a variation from the report [3] who reported a moisture content of the range of 5 to 7 percent. The result obtained from the percentage oil content 33.2% fall within the range of the percentage oil content (30 – 55%) of castor beans found in literature ([1, 2]), depending on the variety. Though, something close to 100% yield (basing on 55% oil content of the castor bean) would have been expected, the mode of extraction is a very important parameter affecting the yield as reported [7]. It is reported that the best available method for extraction of castor oil at present is by the use of hydraulic pressing ([1, 3, 7]). Table 2 presents a comparison between the physical properties of the crude and refined castor oil obtained in this work. The specific gravity values for both crude and refined oil are obtained to be the same, (0.9587). This is in agreement with the standard reported in literature [8]. Differences were observed between the value obtained for the viscosity of the crude and refined oil. The value of the viscosity of the crude castor oil (9.42477st) was found to be outside the recommended standard range of 6.3 – 8.8st [8], while the refined oil's viscosity of 6.4842st is quite within range. This may be attributed to the fact that some impurities and other components were removed during refining. The refractive index analysis shows that there is no significant difference between the value obtained for crude oil, 1.4686 and that of the refined oil, 1.467. Comparing this result with the ASTM values that ranges from 1.476 – 1.479 (ASTM, D960-52, 1952, Table 5), a little difference is noticed. However, this little difference can be considered being within an acceptable experimental error range that can be attributed to the presence of some

impurities and other component of the crude oil mixture. Thus, the refractive index of both crude and refined castor oil was in agreement with ASTM specification.

Also, the pH value of the crude oil which was found to be 6.11 indicate that the oil is more acidic compared to 6.34 pH obtained for the refined oil. This may be as result of degumming and Neutralization carried out during the refining process. The chemical properties analysis shown in Table 3 indicates that the acid value of crude and refined oil is 1.148mg NaOH/g of oil and 0869mg NaOH/g of oil respectively. The value is higher in crude oil due to free fatty acid present; while it less for the refined oil as a result of the chosen strength 0.1M of NaOH used in the treatment of the crude oil, which must have neutralized some of the free fatty acid present in it. In addition, both values fall within the range specified in literature [8]. Table 3 shows the results for the saponification value of the crude and refined oil that were found to be 185.83mg KOH/g of oil and 181.55mg KOH/g of oil respectively. This shows that, for the crude oil, more alkaline would be required to enable it neutralize the available freely fatty acid librated by the oil, when compared with the refined oil. The saponification value of both crude and refined castor oil, are highly comparable with the result specified for quality castor oil [8] as shown in Table 5. Also, the result obtained for the Iodine value of crude oil 87.72 using Dam's reagent shows increase in the average degree of unsaturation of the oil, as such the amount of iodine which can be absorbed by unsaturated acids would be higher, compared to 84.80 after it was refined . As a result of their agreement with standard, both the crude and refined oil could be classified as a non-drying oils [8], since their iodine values are lower than 100. Certainly, the oil could be use extensively as lubricants and hydraulic brake fluids.

The refined oil was modified for a specific use by means of sulphation process to produce Turkey – red oil which may be use in polishes, as a dyeing and wetting agent. The sulphated castor oil produced was observed to be of high viscosity. This was due to the fact that sulphuric acid used added itself across and unsaturated bond of the oil, yielding a saturated product. However, a little kind of pungent smell was perceived from the sulphated castor oil. This may be as result of the excess un-reacted acid in the oil which has no effect on the intended end use. The modified sulphated castor oil has been tested on wood, a piece of white cloth and a piece of paper. It stuck to the materials and a shining surface was obtained when the wood dried, while the colour is not easily removed from the cloth.

Conclusion

The percentage oil content of castor seed was found to be 33.2% of the total weight of 155.30g. As such a satisfactory result cannot be achieved by solvent extraction process using laboratory Soxhlet apparatus. The castor oil produced in this research work was analyzed for specific gravity, Viscosity at 28°C, refractive index at 28°C, acid value, saponification value and iodine value. Their respective values are 0.9587, 9.42477 St, 1.4686, 1.148, 185.83 (mg KOH/g oil) and 87.72 (mg Na₂SO₃/g oil) for crude oil and 0.9587, 6.4842 St, 1.4678, 0.8669, 181.55 (mg KOH/g oil) and 84.80 (mg Na₂SO₃/g oil) for the refined oil. Most of the values comply with the standard specified by ASTM (D960-52, 1952). The oil is of good quality and could be recommended suitable for industrial usage. The refined castor oil was modified by means of sulphation and Turkey-red oil was obtained which can be use as a wetting and dyeing agent and in the finishing of cotton and linen.

References

- [1] Marter A. D., *Castor: Markets, Utilization and Prospects*, Tropical Product Institute, G152, p. 55-78, 1981.
- [2] Weise E. A., *Oil seed crops*, Tropical Agriculture Series, p. 31-53, Longman, 1983.
- [3] Salunke D. K., Desai B. B., *Post-harvest Biotechnology of Oil Seeds*, CRC Press, p. 161-170, 1941.
- [4] Dole K. K., Keskar V. R., *Dehydration of castor oil*, *Curr Sci.*, 19(8), p. 242-243, 1950.
- [5] Nkpa, N. N., Arowolo T. A., Akpan H. J., *Quality of Nigerian palm oil after bleaching with local treated clays*, *JAOCS*, Journal of the American Oil Chemists' Society, 66(2), p. 218-222, 1989.
- [6] Carr R. A., *Refining and degumming system for edible fats and oils*, *JAOCS*, 55, 766-770, 1976.
- [7] Janson H., *Castor oil production and processing*, United Nations, p. 4-13.
- [8] Lew Kowitzeh J. I., *Chemical Technology and Analysis of oils, Vol. 2: Fats and waxes*, Macmillan, 1909.