Nigerian Research Journal of Chemical Sciences (ISSN: 2682-6054)
Volume 13, Issue 1, 2025

Extraction and Characterization of Plants Source Oil for Application in Paint Production

*Wase, Joseph Terlumun, Peter Ajakaiye Egwaikhide, Samuel Peter Malu

Department of Chemical Sciences, Faculty of Pure and Applied sciences Federal University Wukari, Taraba State, Nigeria.

Corresponding Author: joseph.wase@yahoo.com

Accepted: January 26, 2025. Published Online: February 6, 2025

ABSTRACT

In this research, oil was extracted from rice bran (*Oryza sativa*) and lemon grass (C*ymbopogon citratus*) by using n-hexane as an extracting solvent. The characterization was conducted to determine the physical and chemical properties of the extracted oils. It was observed that the oils ranged in colour from pale yellow (rice bran oil) to deep yellow (lemon grass). The percentage compositions of individual fatty acids were found to be 4.7% Ricinoleic acid, 4.42% Oleic acid, 4.0% Palmitic acid and 3.1% Lauric acid. For lemon grass oil it was revealed that the oil contains a high iodine value of 115.6 and saponification value of 145.7 respectively. The percentage composition of individual fatty acids was 3.5% Ricinoleic acid, 3.3% Oleic acid, 4.4% Palmitic acid, and 2.3% Lauric acid. These percentages indicate that these oils are semi drying oils suitable for industrial purposes. The results revealed that rice bran oil can be used in the paint, varnishes and soap manufacturing industries due to its high iodine value (93) and saponification value (188). The high iodine and saponification values indicate its potential for use in akyd resin preparation.

Keywords: Alkyd resin, drying, oil, paint, physicochemical properties.

INTRODUCTION

Plant seeds have been used since ancient times as sources of vegetable oil. Examples of some plant seeds that have been conventionally exploited commercially for paint production include soya-beans, cotton seed, groundnut, corn, palm seeds and sunflower [1].

A wide variety of vegetable oils of varying quantity are available on the Nigerian markets. Oils/fats are obtained basically from two sources namely, animal and vegetable sources [2]. Oils recovered from vegetable seeds or nuts by solvent extraction or mechanical pressing are termed 'crude vegetable oils' and they contain various classes of lipids. They consist primarily of neutral lipids which include tri-, di- and monoacylglycerols, free fatty acids

and polar lipids such as phospholipids. They also contain a minor amount of unsaponifiable matter that includes phytosterols, tocopherols and hydrocarbons such as squalene [2]. Soybean is the dominant oilseed produced in the world, due to its favourable agronomic characteristics, its high quality protein and its valuable edible oil.

The term oil is used in generic sense to describe all substances that are greasy or oily fluid at room temperature [4]. Generally, fats are considered as extracted triglycerides/lipids that are liquid under the same condition. Fats and oils belong to a larger group of naturally occurring substances called lipids. Because lipids serve as a convenient means of rapid heat transfer, they have found increasing use in commercial frying operations [5]. Fats and oils are non-volatile substance insoluble in water but soluble in organic solvent. They constitute along with protein and carbohydrates, the major food stuffs and are widely distributed in nature. From chemical point of view, oils and fats are products of the reaction between a triol (glycerol) and three molecules of fatty acids. In Nigeria, the demand for vegetable oil has ever been widening as industrialist rely mostly on the popular vegetable oil such as palm kernel oil, soya bean oil, cotton seed oil and coconut seed oil for preparation of various products [6,7].

Apart from food processing industries, fats and oils (several lipid) components can also be used in other industries such as cosmetics, pharmaceuticals, biodiesel, and paints. The remaining 20% utilization is between animal and chemical industries [7]. The appreciably high levels of unsaturated fatty acids in both soyabean and groundnut oils depict that these oils can be classified as non-drying. This non-drying attributes qualifies the oils for use in the paint industry [8].

Various techniques such as mechanical extraction, solvent extraction, traditional extraction and super critical fluid extraction are used to obtain oil from the seeds. The solvent extraction has become the most popular method of extraction of oil because of its high percentage of oil recovery from seeds. Solvent extraction bridges the gap between mechanical extraction which produces oil with high turbidity metal and water content and supercritical fluid extraction which is very expensive to build and maintain its facilities. The vegetable oils used in oil-modified alkyd resins are usually extracted either by mechanical press or solvent extraction [9, 10].

Hexane is the most common solvent used in rice bran oil extraction. This solvent is cheap and efficient, but it is a petroleum-based solvent, volatile, flammable, and dangerous for humans and for the environment. [11].

Fats and oils, and their several lipid components can extensively be used in the food and also in cosmetics, pharmaceuticals, biodiesel, paints and other industrial utilization. [12]. Oils from most edible oil seeds are used in the food industry, though there is growing emphasis on industrial utilization as feedstock for several industries with about 80% of the world production of vegetable oils for human consumption. The remaining 20% utilization is between animal and chemical industries, [12]. The ability of a particular oilseed to fit into the growing industries depends on its utilization potential, rate of production, availability and ease of the processing technology.

The aim of this research is sourcing of plants source oils for the formulation of oil paints. Emphasis was on improving the quality of alkyd resin using rice bran oil and lemon grass oils as alternative for high cost oils like linseed oil. It was achieved by extraction of oils from rice bran and lemon grass by solvent extraction method. Physicochemical parameters of the oils including refractive index, acid value, iodine value, saponification value, peroxide value, and free fatty acid were determined following the methods of AOAC [11]. The extracted oils were then used in the formulation of paint and a quality control check was conducted on the formulated paint.

The characteristics of oils from different sources depend mainly on their compositions, and no oil from a single source can be suitable for all purposes thus the study of their constituents is important.

This study focuses on oils extracted from rice bran and lemon grass, the physicochemical parameters of these oils will be determined.

MATERIALS AND METHODS

Rice bran, and lemon grass were sourced from Zaki-biam, Ukum local government area in Benue State, Nigeria. The samples were sun dried and stored in polythene bags prior to analysis.

Oil extraction

The rice bran and lemon grass were prepared by washing and drying the samples. Solvent extraction method was used to extract the oils from rice bran and lemon grass

A solvent (hexane) was used to dissolve the oil in rice bran pellets, forming a mixture called miscella.

Desolventization: The mixture was heated to evaporate the solvent.

Distillation: The solvent was separated from the oil to ensure the oil is pure.

Solvent recovery: The solvent was captured and recycled for future extractions.

Extraction of lemon grass oil.

Mixing: Lemon grass was added to a solvent in the flask

Steeping: The mixture was stood to extract the oil

Decanting: The extract was poured into another container

Separating: Ethanol was added to the extract and separated from the mixture in a separating funnel.

Removing ethanol: The mixture was placed in a water bath to remove (excess) ethanol.

Weighing: The oil yield was determined by weighing the extract.

Determination of the physicochemical properties of the crude oils

The determination of physicochemical parameters of the oils for refractive index, acid value, iodine value, saponification value, peroxide value, free fatty acid and specific gravity were conducted following the methods of AOAC [11].

Colour: Colour measurement was done by visual comparison [12].

Acid value: Approximately 25 ml of ethanol was added to 1 g of each oil extract in a conical flask. This was titrated against 0.1 M KOH solution using phenolphthalein as indicator.

Saponification value: Approximately 2 g of each oil sample was hydrolyzed by adding 25 ml of ethanolic solution of KOH and refluxing on a steam bath for 1 hour with occasional shaking. While the solution was still hot, 3 drops of phenolphthalein indicator was added and the excess KOH solution was titrated against 0.5 M HCl acid.

Percentage free fatty acid: The percentage of free fatty acids as oleic acid, the number of milligrams of potassium hydroxide required to neutralize the fatty acids resulting from complete hydrolysis of one gram of oil, was determined by the method of [13].

Refractive index: The refractive indices, 0/D (RI), of the crude oils samples were measured using a refractometer connected to a thermostatically controlled water bath that maintained the temperature of the refractometer at 30±0.1 °C.

Iodine Value (IV): A mathematical relationship between refractive index and iodine value (IV) has been described by Perkins [14] as 0/D (RI) = 1.45765+0.0001164 IV 30. The reverse relationship was used to calculate the iodine value of rice bran oil since the RI is known [15, 16]

Paint preparation

The basic operation in manufacturing of paints (oil based and water based) is the dispersion of pigment in the paint media. There variation in composition and handling methods.

Production of paint drier

This was done by calculating the mass of sodium hydroxide (NaOH) that will react with certain volume of oil (20 cm^3) using saponification value of the oil and the mass of the NaOH to produce soap used for the drier production.

The saponification value of the rice bran oil was 188.80 mg. Since the saponification value of the rice bran oil was determined to be 188.8 mg NaOH/g oil, it means that 1 mg of the oil require 188.80 mg of NaOH which implies

$$\frac{188.80}{1000} = 0.1888\text{g of NaOH}$$

Therefore 20 g of the oil will require 0.1888g ×20 =3.776 of NaOH which implies that 20 g of rice bran oil require 3.776 mg of NaOH

From the relation; 1mole of NaOH =40 g _____1000 cm^3

Xmole of NaOH=x g_____10 ml

40 g_____1000 cm^3

Total gram=3.776+0.4=4.176g of NaOH

Chemistry of the Reaction

$$RCOOH + NaOH \longrightarrow RCOONa + H_2O$$

Where R=alkyl group soap.

Formulation of paint

Using the formulation of Ezeagba et al [17], 11.82 g of the pigment (titanium dioxide) was crushed with piston for proper mixing and then incorporated 45.45 g of binder (alkyd resin)

with proper mixing, then 42.57 g of solvent (xylene) was added, with continuous mixing for proper blending to form paint. Table 1 shows the list of raw materials and quantity used

Table 1. Raw materials and quantity used

Raw materials	Quantity used (g)
Pigment (titanium)	11.82
Xylene (solvent)	42.57
Alkyde resin (binder)	Pigment (TiO2)
Mixer drier (cobalt,lead and manganese)	10.0
Antiskin	5.0
Zinc naphthanate	5.0

Quality Control Test on the Formulated Paint

Paint application on a surface

A rough abestos plate was cleaned properly and allowed to dry. A coat of the paint was applied and allowed to dry for hours. Adhesive tape method was used. A piece of pressure sensitive adhesive tape was applied to the panel and the area covered by the tape cut round through to the asbestos with razor blade. The end of the tape was then pulled sharply at right angle to the panel.

Water Resistance

In this test, initial panel was used. After application of paint sample on the panel the brush out were allowed several hours (about 24 h) to dry. The test panel were immersed in a beaker of water and allowed to remain for 48 hours.

Drying Time

The paint samples were applied and the time was noted. They were then allowed to remain for some time being monitored at some interval.

Brushability and Weathering Test

A hard brush was used to brush out the paint samples. After the brush out, the paints were exposed to the atmosphere to determine the effect of weather change on it. The two most important agents of weathering are sunlight and rain.

RESULTS AND DISCUSION

Physicochemical properties

The studied physicochemical properties of rice bran oil and lemon grass oil are presented in Table 2. The colour of the oils ranged from light yellow to golden yellow. All are odourless liquids at room temperature. Table 2 shows physicochemical properties of rice bran oil and lemon grass oil.

Table 2: Physicochemical properties of rice bran oil and lemon grass oils

Samples	Rice bran oil	Lemon grass oil
Acid value mg/g	5.2307 - 5.2116	6.9465 - 6.5811
refractive index	1.4600 - 14600	1.4800 - 1.4800
Iodine value g/100g	93.7000 - 93.5000	115.6000 - 116.7000
Saponification value mg/g	188.7000 - 188.8000	145.7000 - 145.5000
% FF acid Oleic	4.4235 - 4.4177	3.3081 - 3.4918
Laurie acid %	3.1372 - 3.1279	2.3462 - 2.4764
Ricinoleic %	4.6745 - 4.5507	3.4958 - 3.6899

Acid value

Acid value is taken as an important indicator of oxidation of oil. It is the number of mg of potassium hydroxide required to neutralize the free acid in 1 g of the substance. Acid-base titration technique in non-aqueous solvents mostly used for determination of acid value in oil.

The acid value and free fatty acid content are important parameters used for the characterization and quality assessment of edible fats and oils [18] .The higher the acid value and free fatty acid content, the lower the quality of the oil. The acid value additionally increases with the age of an oil as tryglcerides decompose into fatty acids and glycerols as an effect of time [18].

The acid values ranged from 5.212 to 6.945 in rice bran and lemon oils, respectively. These values however accounted for the presence of free fatty acids in the oils as an indication for the presence and extent of hydrolysis by lipolytic enzymes and oxidation [18]. Low acid value in oil indicates that the oil will be stable over a long period of time and protect against rancidity and peroxidation. The acid value of type-1linseed oil for paint is 6.0, according to Gordon [19].

Acid value is used as an indicator for edibility of an oil and suitability for use in the paint and soap industries [20].

Refractive index of an oil is the ratio of speed of light at a defined wavelength to its speed in the oil/fat itself. This value varies with wavelength and temperature, the degree and type of unsaturation, the type of substitutions of component fatty acids and with accompanying substances. Refractive index is widely used in quality control to check for the purity of materials and to follow hydrogenation and isomerization [21]. The refractive index of a thin film of oil is typically between 1.3 and 1.5. depending on the type of oil. Most transparent media have a refractive index between 1 and 2 for visible light [22]. Both the rice bran oil and the lemon oils have their refractive index values within the acceptable range of 1.4600 to 1.4800 respectively according to Codex Standards for fats and oils from vegetable/plant sources [23].

The iodine value is a measure of the degree of unsaturation and it is an identity characteristic of seed oils, making it an excellent raw materials for soaps cosmetics industries [24]. For the rice bran and lemon oils, iodine value ranges from 93.700 in rice bran oil to 116.700 in lemon grass oil [25]. The iodine value could be used to quantify the amount of double bond present in the oil which reflects the susceptibility of the oil to oxidation. Oils with iodine value less than 100g I_2/100g of oil are non-drying oils; correspondingly, Aremu et al [20] reported that the lower the iodine value the lesser the number of unsaturated bonds; thus the lower the susceptibility of such oil to oxidative rancidity. Therefore, non-drying oils are not suitable for ink and paint production due to their non-drying characteristics but may be useful in the manufacture of soaps and can be regarded as liquid oil. A good drying oil should have iodine value of 130 and above semi-drying oils have an iodine value of 100-130 and dry to a certain degree when exposed to the oxygen [20]. High iodine value is seen as a pointer to the presence of high percentage of unsaturated fatty acids in the oil; as such amount of iodine that will be absorbed by the unsaturated acids would be higher [26].

The saponification value is in the range of 145.500 to 188.800 for lemon grass oil and rice bran oil respectively. Saponification value is a measure of oxidation during storage, and also indicates deterioration of the oils. An increase in saponification value in oil increases the volatility of the oils. It enhances the quality of the oil because it shows the presence of lower molecular weight components in 1g of the oil which will yield more energy

on combustion [27]. It has been reported by Pearson [28] that oils with high saponification values contain high proportion of lower fatty acids. Therefore, low saponification value of oils indicate that they contain high proportion of higher fatty acid and can be regarded as non-edible oils. . The saponification value (SV) of oils suitable for paint is typically between 172-199.32mgKOH/g. it is the range for oils like olive (184-196), soybean (189-195), and sunflower (188-194).

Free fatty acid is the percentage by weight of a specified fatty acid (e.g. percentage of oleic acid) [29]. High concentrations of free fatty acids are undesirable in crude vegetable oils because they result in large losses of the neutral oil during refining. In crude fat, free fatty acids estimate the amount of oil that will be lost during refining steps designed to remove fatty acids [20]. High levels of free fatty acids especially linoleic acids are undesirable in finished oils because they can cause off-favours and shorten the shelf life of oils. The quantity of free fatty acid in oil is an indication for its overall quality. They may be formed through hydrolysis or in the advanced stages of oxidation. An excessive amount of free fatty acids lowers the smoke point of oil and will cause 'popping' of the oil during cooking [20]. High quality oils are low in free fatty acids. In refined vegetable oils, the lower the free fatty acid the more acceptable the oil is to man in terms of palatability. From the results of the oils, the percentage of free fatty acid ranges from 2.346 to 4.675 in lemon oil and rice bran oil respectively.

Quality Control Test on the Formulated Paint

During the early stage of Paint product development, criteria on physical and performance properties are set based on the purpose and application of the paint product. Those agreed properties then became the test specification for the product development.

Relevant test properties were then selected for the manufacturing control test. Manufacturing control tests, also known as quality control tests are conducted during and immediately after the manufacturing process either physical, performance and stability. These are usually conducted to determine:

Whether the paint contains the proper ingredients and in the correct amount

Whether the standard manufacturing procedures are followed during the process

Whether the paint meets established manufacturing control specifications.

Testing of coating during product development are categorized into two: physical test and performance test.

Table 3 shows the result for some quality control test carried out using rice bran oil for alkyd resin preparation and paint formulation.

Table 3. Quality control test on rice bran oil

	STTT	DFT	SDT	DHT
Blank	285	331	363	397
0.1	120	138	153	180
0.2	98	110	120	136
0.3	70	81	94	120

STTT=set to touch time, DFT= dust free time, SDT= surface dry time, DHT=dry hard time,

The application of resins as binder is due to their drying ability, a thin layer of alkyd resin film dries fast on exposure to air [29].

Drying time of paint depends on the environment, mainly on temperature and humidity. The result revealed that oil paint had the drying surface time of 24 hours which is in conformity with the standard

Testing the rate of drying which measures the time required for the paint to reach a certain stage of drying. The measure after application indicates the period of “set-to-touch time”, “dry-to-handle’, “dust-free time”, “dry hard time”, and “surface dry time”. It guides the painter when to recoat.

It is very important in a paint, from the result in table 4.2 the set to touch time is 70-285 min. equivalent to 4.75 hours which is within the range of good paints. However the set to touch time keep reducing with increase in concentration of the alkyde resin (rice bran oil),in 10ml of the paint manufactured which indicate that little quantity of the alkyde resins will serve better in paint manufacture.

The dust free time, surface dry time and dry hard time has the following values 331 min., 363 min., and 397 min. respectively the time increases corresponding to when each time was determined. Both dust free time, surface dry time and dry hard time decreases with increase in concentration of the alkyd resin (rice bran oil).

The paint film applied on a brushed tinplate pane became hard dry in not more than 24 hours from the time of the application.

Weather resistance

The paint having the fine particles size distribution ranges showed considerably better water resistance properties, while coarser or larger particle size would tend to provide a weak effect or path through which moisture could travel to the substrate resulting in blistering, softening and eventual distribution of delamination and adhesion failure of the coating and corrosion of the metal substrate.

Brushability

The paint brush easily possess good leveling property when applied at a spreading rate of approximately 10ml per liter to a cream faced, gypsum plaster board. These complies with the Standard Organization of Nigeria.

An assessment of a coating‘s application properties such as roller and brush loading, ease application (e.g.brushability, roller skidding, sprayability).

Table 4. Summary of the results

Colour	Good
Drying time	24 hours
Adhesion	Excellent
Water Resistance	Good
Brushability	Very good

CONCLUSION

The suitability of rice bran (*Oryza sativa* cover) oil and lemon grass (C*ymbopogon citratus*) oil in the preparation of alkyd resin and gloss paint formulation was investigated. The physicochemical characterization of the oils indicated that they are semi-drying in nature. Based on the iodine value and addition of modern paint additives make the oils suitable for alkyd resin preparation. Oils that are non-drying in nature can be changed to drying oils by epoxidation.

Both rice bran oil and lemon grass oil can be considered as potential industrial raw material. Many derivatives such as paint, varnishes, soap etc. may be prepared from the oils because of their higher iodine and saponification value. The drying performance of the alkyd resins appears quite good, hence exploitable for the formulation of an oil paint.

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