

PREPARATION AND EVALUATION OF ALKYD RESIN FROM *Hura crepitans* (SAND BOX) SEED OIL.

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ABSTRACT

Alkyd resin from seed oil extract of *Hura crepitans* (sand box) have been prepared and evaluated for industrial application. The oil extracted was physicochemically characterized using Association of Official Analytical Chemists (AOAC) standard methods. The analytical data obtained are as follows: Iodine Value; 170.43g I₂/100g, Saponification Value; 235.15mgKOH/g, Acid Value; 3.10mgKOH/g, Free fatty acid Value; 10mg/g, Moisture Content; 0.06%, Specific Gravity; 0.92g/m, and Refractive Index; 1.47. Epoxidation of fatty acids in the seed oil extract was confirmed via Fourier Transform Infrared Spectrometry (FTIR). The alkyd resin was prepared via a one-pot process using alcoholysis-polyesterification reaction. Resin evaluation showed that: the drying time was 24 hours; it was soluble in acetone, methanol, ethanol and toluene; acid value was 6.50 after 180minutes; for chemical resistance it was observed that no effect on the prepared resin after 18hours and on immersion in 3M NaOH a total removal of the resin was observed after 24 hours. This infers that the prepared resin is a drying oil which makes it suitable for use in varnishes, paints, soap and other allied production.

Keywords: *Hura crepitans*, Alkyd resin, Alcoholysis-polyesterification.

INTRODUCTION

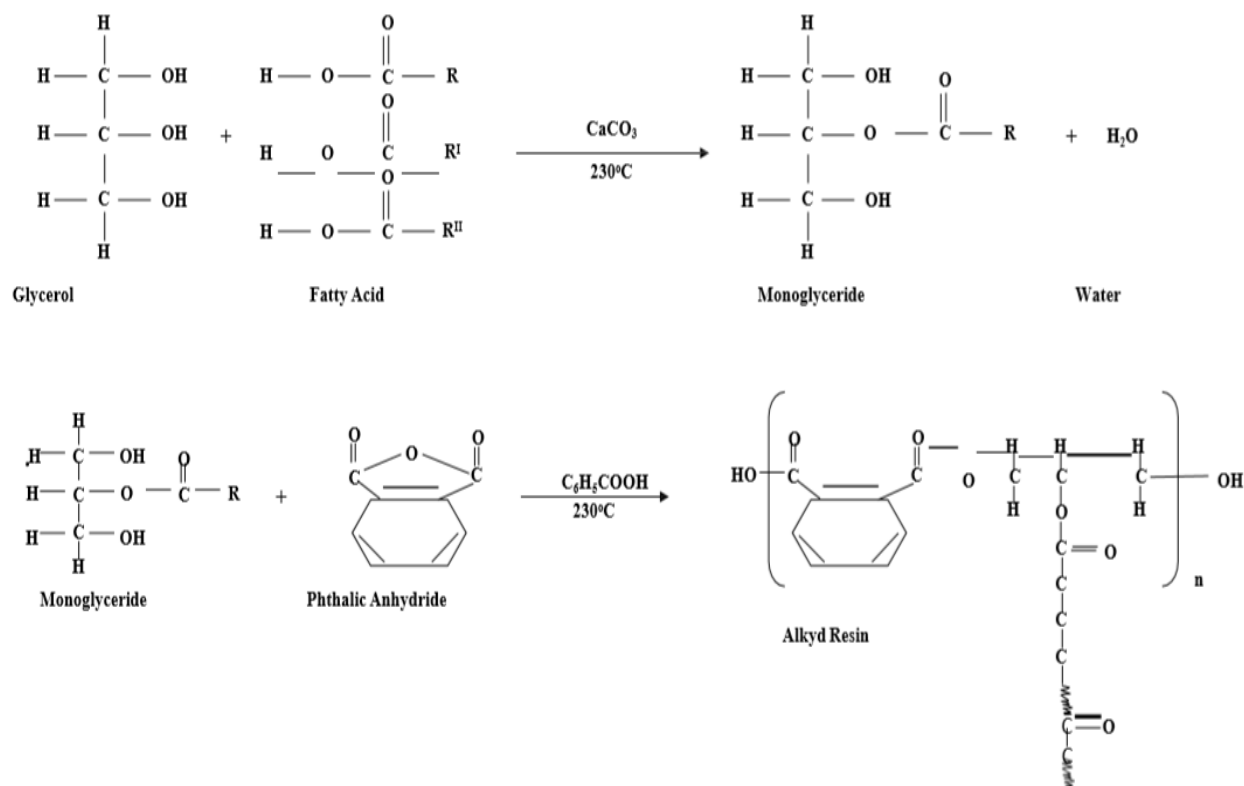
The implementation of sustainable and inedible oils to produce alkyd resin is anticipated to reduce the reliance on edible oils for industrial applications and thus helps to reduce the global food demand [23].

Alkyd resin is one of the most important binder chemicals in the coating industry, its distinctive properties which make it an essential raw material in surface coating industry includes: gloss retention, film flexibility, durability, good adhesion, solubility and chemical resistance [23]. Alkyd resin are products from the condensation polymerization of a polybasic acid (e.g phthalic anhydride, isophthalic acid e.t.c); a polyhydric alcohol (glycerol) and its triglycerides [15]. Over

the years some seed bearing plants in Nigeria have been characterized, giving useful information about their physico-chemical properties and chemical composition as well as their applications in various oil chemical fields, however the potentials of these seeds are still largely not fully utilised. [2] recommended the use of *Plukenetia conophora* and *Adenopus breviflorus* seed oils to produce alkyd resins. The analyses of the two seeds oils revealed that they possess high iodine values due to their high unsaturated acid contents. [10] reported that melon seed despite been used for daily meal in Nigeria has high potential for use in alkyd resin production due to its high linoleic acid content of

62%. Research works on alkyd resin preparation using *Thevetia peruviana* was also reported by [14] the result obtained gave 61- 64% oil yield. *Parinari polyandra* seed oil has desirable drying properties and gloss retention which makes it a good starting material to produce alkyd resin

[22]. An investigation on the synthesis of air-drying alkyd resin through the polymerization of non-drying palm oil using crude, neutralized and dehydrated palm oil with iodine value as 45 and 127 g/I₂100g respectively showed it was good for alkyd resin production [30].



Scheme 1: condensation – polymerization reaction between polybasic acid, polyhydric alcohol and triglycerides.

In the preparation and characterization of alkyd resins using Jordan Valley tomato seed oil, iodine value of 123g/I₂100g was obtained which classified the oil as a semi-drying, thus making it suitable for alkyd resin production [18].

Many plants that bear seeds especially in Nigeria and Africa are yet to be fully exploited to evaluate the potential benefits in harnessing them, and this

is due to insufficient research to determine their chemical and industrial importance [25]. One of such seed-bearing plants is *Hura crepitans*, commonly referred to as Sandbox tree mostly grown in cities and villages of the South-Western parts of Nigeria. The Kabba and Ijesha people of Kogi and Osun States refers to it as Odan Mecca and Aroyin respectively [3].

Therefore, this study seeks to prepare and evaluate alkyd resins from *Hura crepitans* seed oil extract and determine its suitability for use in industrial applications.

MATERIALS AND METHODS

Materials

Hura crepitans (Sand Box) was sourced from Akure metropolis in Ondo state, Nigeria. The plant was authenticated at the Centre for Ethenomedicine and Drugs Development, a subsidiary of Bioresources Development and Conservation Program (BCDP) Nsukka, Enugu State. The seeds were dehulled, sun dried, milled into fine meal using an electric blender (Excella

Model 7200) and stored in an airtight container for further use.

All reagents and solvents were of analytical grade and were used as received without further purification.

Methods

Seed oil Extraction

The *Hura crepitans* (sandbox seed oil) was extracted from the dried seeds (fig.1) by soxhlet extraction using n-hexane as solvent. A Weighed portion (80g) of the ground sample was extracted using a soxhlet extractor with n- hexane as solvent and the oil extract concentrated using a rotary evaporator.

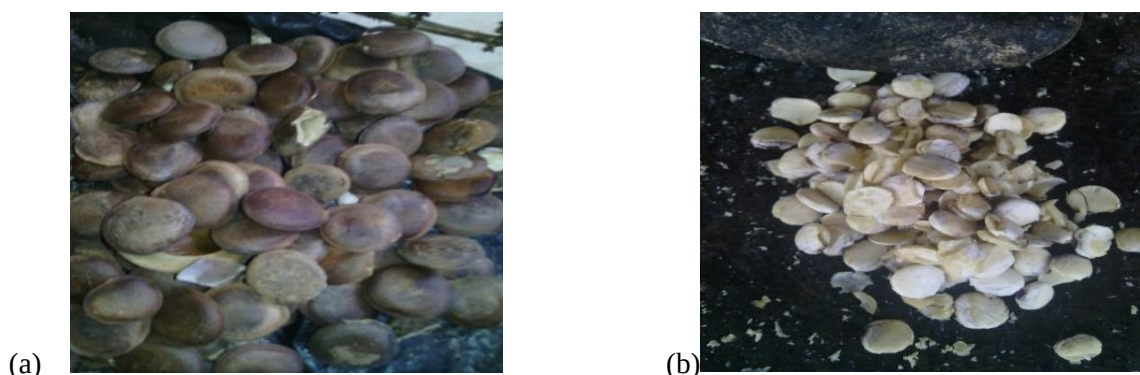


Figure 1 : shows (a) matured and dry pods of *Hura crepitans* (b) dehulled seed of *Hura crepitans*

Characterization of the Oil Extract

The physicochemical properties of the *Hura crepitans* seed oil extract: refractive index, iodine value, saponification value, acid value, free fatty acid and specific gravity analysis was determined using the Association of Official Analytical

Chemists (AOAC) 1990 standard analytical methods.

The Fourier Transform Infrared Spectrometry (FTIR) spectral analysis of the sand box seed oil extract and the epoxidized seed oil extract was scanned in the 4000 – 650 cm^{-1} range using

CAREY630 machine. The spectra is as shown in figure 2(a) and 2(b) respectively.

Synthesis of the *Hura crepitans* Seed Oil Extract Alkyd Resin

The resin was prepared via 2 stage epoxidations followed by alcoholysis-polyesterification in a 500ml 3 neck reactor fitted with a reflux condenser, nitrogen gas inlet and thermometer over a magnetic stirrer.

Epoxidation stage:

The epoxidation of *Hura crepitans* (sand box) seed oil extract was carried out as described by [13], with slight modification, the flask was immersed in a water bath and 91.6g of *hura crepitans* seed oil extract was introduced followed by calculated amount of 26.7g glacial acetic acid and 2.47g of concentrated sulphuric acid the mixture was allowed to attain a reaction temperature of 50°C with continuous stirring for 30minutes the calculated amount of 181.1g of 30% aqueous hydrogen peroxide was added dropwisely for 30 minutes to avoid peroxide coagulation. addition of calculated amount of for about 30 minutes while the agitation continues, while aliquot amount of the reaction mixture was taken at every 1 hour and the first taken 1 hour after the addition of hydrogen peroxide. The reaction mixture was allowed to stir for 6 hours [24].

The sample mixture was poured into a separatory funnel and 5% sodium chloride and 5% sodium biocarbonate were added to neutralize the acetic acid in the oil, the aqueous layer was drawn off

while the oil layer was washed consecutively with warm distilled water until test with litmus paper indicates it was acid free [6].

Alcoholysis – polyesterification stage:

The measured amount of phthalic anhydride, glycerol and fatty acid was in the ratio (1:1:1) and CaCO_3 as catalyst. 35g of *Hura crepitans* seed oil extract and 0.28g of CaCO_3 was injected into the reaction vessel and heated to 120°C with agitation (500rpm), 16.45g of glycerol was added and the temperature was raised to 180-190°C for 30minutes. Aliquot of the reaction mixture was taken and dissolved into anhydrous methanol to check its solubility. Alcoholysis stage was determined when the reaction mixture became soluble and clear in anhydrous methanol, the reaction temperature was cooled to 140°C [16].

The 35g of phthalic anhydride and 6.72g of benzoic acid were added into the mixture and temperature raised to 230-250°C in the presence of Nitrogen gas injected into the reaction vessel, aliquot was taken every 30 minutes to determine the decrease in acid value to below 10 and was kept at this temperature for 4 hours [27]. The control resin was also prepared via the same procedure.

Performance Evaluation of Formulated Resin:

The resin was evaluated using drying time, solubility, and chemical resistance. The drying time was evaluated according to the method described by [7] with slight modification. It was determined using Aluminum plate which was

washed and cleansed with ethanol to ensure the surface is free of impurities and the resin was evenly applied on the surface with the drying time was monitored. The drying schedule for the alkyd films was observed with; set to touch after 30 minutes, surface dry after 1 hr, dry after 2 hrs and completely dried after 24 hours, while the control resin was set to touch after 20 minutes, surface dry after 30 minutes and completely dried after 1 hr this is due to the absent of oil.

In order to test for solubility, 0.5 g of the resin was dissolved in 10ml of benzene, acetone, toluene and ethanol in accordance with the method described by [18] and [21].

The chemical resistance of the prepared alkyd resin was determined in two media, distilled water and NaOH solution [21].

RESULTS AND DISSCUSSION

The yield of the *Hura crepitans* seed oil extract was gotten as 34.50%.

Table 1: Physicochemical Parameters of *Hura Crepitans* Seed Oil

S/N	Parameters	CHC
1	Acid value (mgKOH/g)	3.10
2	Free fatty acid	2.10
3	Iodine value (mg/I ₂ /g)	170.43
4	Saponification value (mg/KOH/g)	235.15
5	Specific gravity	0.92
6	Refractive index	1.47
7	Viscosity	44.71
8	pH	4.60
9	% yield (%)	34.50
10	Moisture content (%)	0.06
11	State at room temperature	Liquid
12	Odour	Sweet
13	Colour	Light Yellow

CHC =Crude *Hura crepitans

The physicochemical properties of sand box seed oil are as shown in Table 1. Refractive index is the measure of the probable chances of rancidity development in seed oil as refractive index increases the number of double bonds increases [8]. The refractive index value of *Hura crepitans*

seed oil extract at 27 °C was found to be 1.47 which agrees with values reported for conventional oils; for soyabean (1.471), orange (1.473) and pumpkin (1.473) by [18]. The refractive index of this oil confirms the presence

of high number of carbon atoms in its fatty acid [11].

The iodine value is a measure of the degree of unsaturation in the oil and could be used to quantify the amount of double bonds present in the oil, this reflects the susceptibility of oil to oxidation, the iodine value reported here is 170.07 g I₂/100 g which is greater than 130 suggests the presence of high percentage of unsaturated fatty acids in the oil and could be classified as drying oil.

Specific gravity measures the relative density of a seed oil, *Hura crepitans* has specific gravity of 0.92 which is close to the value reported for tomatoes seed oil (0.918) by [18] and 0.917 reported for both pumpkin and soyabean seed oil by [19].

Saponification value is the number of KOH required to neutralize 1g of oil. The saponification value is 235.15 mgKOH/g which is closer to the 238.50 mgKOH/g reported for *Lagenaria siceraria* by [10], this value (SV) obtained agrees with values for most vegetable oils ranging from 188 - 253 mgKOH/g [26] and [5]. The saponification value of these oil shows that the oils have low unsaponifiable matter [18]. This indicates that the oil has potential application in the production of soap, shampoos, paint driers, resins for surface coating and in the manufacture of shaving cream [28].

The acid value measures the rancidity of an oil due to free fatty acid formed during decomposition of triglyceride. The acid value of

Hura crepitans is 3.10 mgKOH/g which is within the acceptable range 0-3mgKOH/g of oils [8] for it to have application in cooking and for industrial purposes, and also the free fatty acid is 2.10 which is also in a close range with the 2.20 of *Lagenaria breviflora* which was reported by [10] in the physicochemical properties, fatty acids composition and antioxidant activity of some cucurbits seed oils.

Viscosity of oil is its resistance to flow and shear due to gravity, *Hura crepitans* viscosity is 44.71 which is higher than 38.60 of jojoba seed oil according to [31]. *Hura crepitans* has a high viscosity which is applicable to most seed oils, thus has high resistance to flow which is a good quality in oils for alkyd preparation. The pH of *Hura* is 4.60 which was observed at 27 °C.

The percentage moisture content indicates that the seed oil could be stored for a long period without deterioration [1]. Seed oils with high contents of moisture undergo enzymatic reactions which can affect other properties of the oil such as acid value and free fatty acid; *Hura crepitans* has a low moisture content of 0.06 %.

Some physical observation was made; the state of the oils at room temperature was liquid. However, the colour of the oil does not determine what it should be used for excepting in some cases where bright colour is a very important consideration such as in pigmented coatings, the colour of *Hura* oil is pale yellow the boiling point of the oil ranges between 220 – 330 °C.

Table 2: Result of physiochemical analysis of Epoxidized *Hura crepitans* seed oil

Parameters	<i>Hura crepitans</i>
1. Acid value (mgKOH/g)	3.80
2. Iodine value (mgI ₂ /g)	15.42
3. Saponification value (mgKOH/g)	150.00
4. Oxirane value (%)	2.71

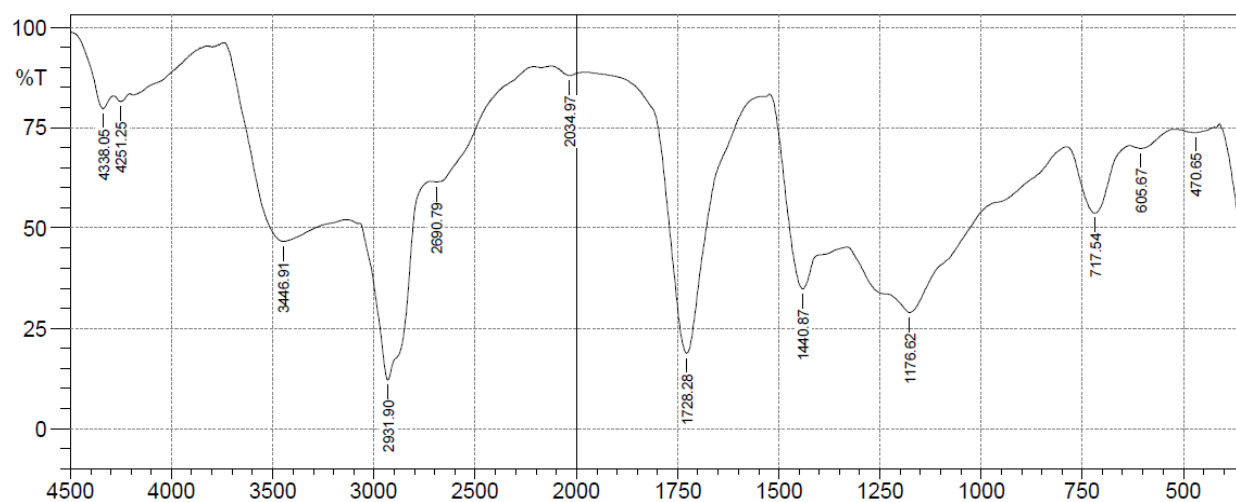


Figure 2(a): FT-IR of Crude *Hura crepitans* Seed

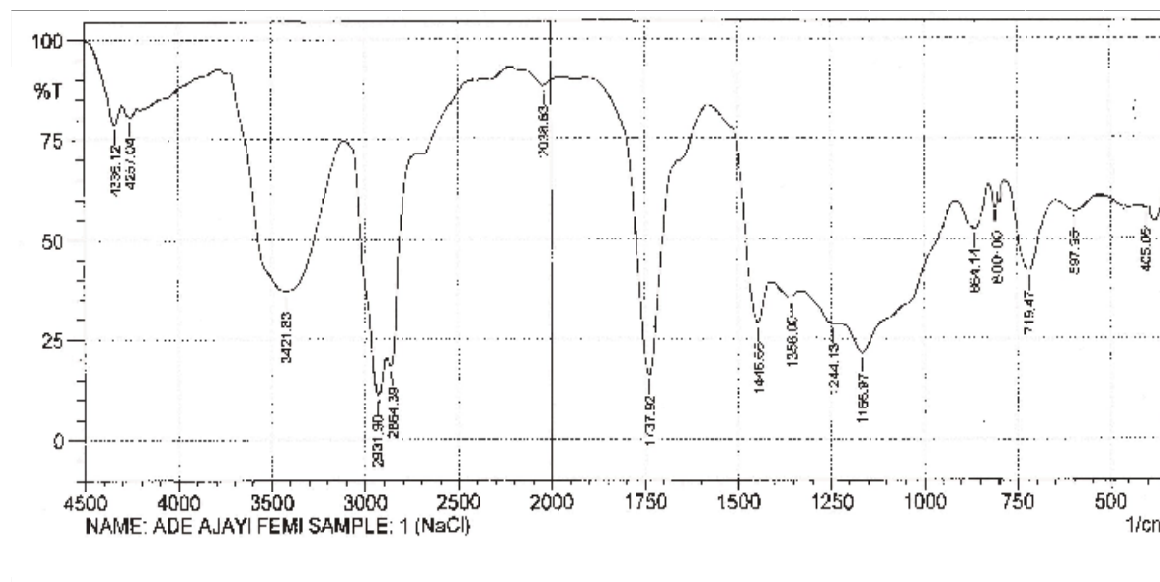


FIG 2(b): FT-IR of Epoxidized *Hura crepitans* Seed Oil

The FT - IR spectra for both crude and epoxidized *Hura crepitans* seed oil extract are as shown in figure 2a and 2b. The observed peaks at 1438-1440 and 2928-2931 corresponds to -C-H rock from alkanes, 1728-1734 corresponds to -C=O stretch from saturated aliphatic of fatty acid and 3000-3050 corresponds to C – H stretch from aromatic, while for the epoxidized 825-800 from oxirane, 1446-1448 corresponds to C-C stretch (in – ring) from aromatic and 2928-2931

corresponds to -C-H form alkanes, 3421-3466 corresponds to O-H stretch from polyols. The resin was evaluated using drying time, solubility and chemical resistance. The result formulated for the crude and epoxidized resin is as shown in table 3, 4 and 5 respectively. In Table 4, all alkyds were completely soluble in the solvents, this agrees with solubility from other seed oils used for resin production.

Table 3: Drying Time of the Resin

Drying Time	HCSOR	CR
20 minutes	set to touch	set to touch
30 minutes	set to touch	surface dry
1 hour	surface dry	dry through
2 hours	dry	dry through
24 hours	dry through	dry through

Where: HCSOR is the *Hura crepitans* seed oil resin, and CR is the control resin

Table 4: Solubility of the Resin

Solubility	HCSOR	CR
1. Acetone	soluble	soluble
2. Methanol	soluble	soluble
3. Ethanol	soluble	soluble
4. Toluene	Soluble	soluble

Where: HCSOR is the *Hura crepitans* seed oil resin, and CR is the control resin

Table 5: Chemical Resistance of the Resin

Chemical Resistance	Time(hrs)	HCSOR	CR
1. Distilled H ₂ O	6	NE	NE
	8	NE	NE
	18	NE	NE
2. 3M NaOH	8	whitening	whitening
	16	Blistering	Blistering
	24	Removal	Removal

NE: No effect

*It was examined after the films were air dried for 1 hour.

Table 6: Acid Value of the Resin

Acid value	Time(min)	HCSOR	CR
	0 minute	-	-
	30 minutes	50.00	80.00
	60minutes	20.50	30.00
	90minutes	18.50	25.00
	120minutes	16.00	20.00
	150minutes	14.00	16.00
	180minutes	6.50	5.0

Table 3 shows the drying schedule of the alkyd film, drying is an oxidative process in which oxygen is been absorbed at the double bond of the unsaturated fatty acid, it is also based on the percentage of oil present in the alkyd resin formulation, here the drying time was observed in- door under room temperature, and at 24 hours the resin was thoroughly dried, and this shows comparable coating properties to other reported oil modified resin.

Table 4 shows the solubility of the *Hura crepitans* alkyd resin examined in different solvent, it was observed that the alkyd resin was soluble in all solvent this was same as reported by [18] in the preparation and characterization of alkyd resins of Jordan valley tomato oil.

The chemical resistance of the formulated alkyd resin described in table 5 was immersed in two solvent media, there was no effect on alkyd film after immersion in distilled water for 18 hours. The immersion of alkyd film in water for 18 hours

is enough time to examine the water resistance. When the alkyd film was immersed in strong alkali solution, 3M NaOH there was whitening of the film after immersion time of 8 hours, blistering after immersion time of 16 hours and removal after immersion time of 24 hours, its strong resistance to 3M NaOH with total removal, shows the alkyd resin has high chemical resistance and can be used as formulation in coating industry. This was also same in the synthesis and characterization of palm oil based air drying alkyd resin for surface coating reported by [30].

Table 6, shows the acid value of the resin, there is no common standard to compare alkyds resins, each alkyd resin has its own properties. The low acid value 6.50mgKOH/g of the synthesized resin in this study shows its stability and good starting material for alkyd production and in paint industry which is same as reported by [29]. The alkyd resin that has acid number of less than 15 is suitable for application in chemical industry and for surface coating.

CONCLUSION

Hura crepitans is a non-edible seed which is not grown but has a good percentage of oil yield and high saponification and iodine value could be classified as an important industrial oil that could be used for surface coating. The formulation of alkyd resin using this processed seed oil extract has also been described. This study shows that *Hura crepitans* seed oil extract is a good starting

material for the production of alkyd resin for various surfaces. The drying time, acid value, chemical resistance of the produced resin shows that this seed oil is promising in the oil chemical industry. This study also shows that some quality parameters of the manufactured alkyd resins are comparable with resins from other seed oils.

RECOMMENDATIONS

It is recommended that further studies be carried out on the alcoholysis-polyesterification of other locally available non-edible seed oils majorly in the wild to increase the data bank of seed oils which can be used in oil chemical industry.

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