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# Comparative Analysis of Physicochemical Properties of Fatty Polyamides from *Jathropha Curcas* and *Thevetia Nerrifolia* Seed Oils Dimer Acids

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## ABSTRACT

*Thevetia Nerrifolia* and *Jathropha Curcas* seed oils were extracted from their oil seeds by soxhlet extraction using petroleum ether (40-60°C) as solvent. The oils were characterized and the oil yield, refractive index acid value, saponification value, iodine value, colour and relative density were found to be 47.77%, 1.464, 4.365 (mg/KOH), 125.62 (mg/KOH), 98.48 (wij), 4<sup>+</sup> and 0.926 for *Thevetia Nerrifolia* seed oil and 46.56%, 1.496, 33.65 (mg/KOH), 175.12 (mg/KOH) 105.43 (Wij), 3 and 0.913 for *Jathropha Curcas* seed oil respectively. Dimer acids were prepared from these seed oils by heating 200g of each of the oils under nitrogen inert atmosphere in a four necked resin kettle at a temperature of 300°C for 12 hours. The Dimer acids werethen reacted with 1,2phenylene diamine at 210  $\pm$  10°C in an inert atmosphere for 2 hours to give a fatty polyamide of *Thevetia Nerrifolia* and *Jathropha Curcas* respectively. Analysis of the fatty polyamide in term of physicochemical properties shows that their properties compare favourably with those prepared from dimer acids from well known vegetable oils in the fatty polyamide synthesis.

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### Introduction

The first pioneer work in the synthesis of fatty polyamide from demeric fatty acids and their potentials in coating application was reported in 1944 [1]. Following this work, keen interest in, characterization and utilization of polyamide was shown.

In a typical preparation, 0.87 equivalent of polymeric fatty acid, 0.13 equivalent ethylene diamine and 0.15 equivalent [2,2-bis [4-(2-hydroxypropoxy) phenyl] Propane] were heated for 2 hours at 80°C, 2 hours at 240°C and 4 hours at 240°C. The product had softening point at 102°C, stable for more than 7 days in a 30% solution in primary alcohol, and had gel temperature of  $12^{\circ}$ C. Flexographic ink prepared from this product had high gloss and good adhesion. It was useful as an engraving ink diluting agent and for formation of thixotropic solutions [2].

In general, reaction times for preparation of fatty polyamides fall within the range of 4-6 hours. A catalytic procedure, in which the processing time was reduced to between 1-2.5 hours, was carried out [3]. The reaction conditions were the same as described except that a catalytic amount of  $H_3PO_4$  was added to the mixture.

Fatty polyamide are used as binders in printing ink [4], polyamide dispersion are used in hot melt adhesive applications as well as in coating such as inks [5]. Fatty polyamides are also used in improving the thixotropy of long oil alkyd resins [6], etc.

### Experimnetal

Thevetia Nerrifolia and Jathropha Curcas seeds were collected from Makurdi Local Government Area of Benue

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State. The seeds were sun dried and then oven dried at  $45^{\circ}$ C to constant weight and ground with porcelain mortar and piston to coarse particle size and stored in plastic containers for analysis. The oils were extracted using petroleum ether (40-60°C) on a soxhlet extractor for four hours [7]. The refractive index, acid value, saponification value, iodine value colour and relative density were determined using the method described by A.O.A.C. [8].

Dimer acids from the *Thevetia Nerrifolia* and *Jathropha Curcas* seed oils were prepared by heating 200g each of the oils in a four necked resin kettle under nitrogen inert atmosphere at a temperature of  $300^{\circ}$ C for 12 hours using 0.5% sulphur (based on the weight of oil) as catalyst [9].

The physico-chemical properties of the *Thevetia Nerrifolia* and *Jathropha Curcas* seed oils were determined using the methods described by ASTM D 1639-90 for acid value [10], ASTM D 1962-67 for saponification value [11], ASTM D 1541-60 for iodine value [12], ASTM D 4052 for relative density [13], ASTM D 1747 for refractive index [14] and ASTM D 1544 for colour [15].

The physicochemical properties of the dimer acids were determined by methods described above for the seed oils. The molecular weight of the dimer acids were determined by cryoscopy [16].

The physicochemical properties of the fatty polyamide were determined in terms of non-volatile contents; ASTM D 1259-61 [17],the number average molecular mass was determined by end group analysis [18], the amine number was determined by ASTM D 2074-07 [19], the viscosity in bubble

seconds by ASTM D 1545-13 [20], the acid values and colour were determined as discussed previously.

FTIR spectra of the dimer acids and the Fatty polyamideswere recorded to compare with other traditional dimer acids and fatty polyamide from well knownfeedstocks.

## **Results and Discussion**

The physicochemical properties of *thevetia nerrifolia* and *Jathropha Curcas* are shown in Table 1.0. From Table 1.0, the oil yield of *Thevetia Nerrifolia* seed oil was found to be 47.47, which was slightly higher than that of *Jathropha Curcas* seed oil of 46.56 The yields are appreciable and shows that the oils has potential in surface coating industry and in the manufacture of oleochemicals.

The saponification value of *Thevetia Nerrifolia* seed oil was found to be 125.62. This value is lower than that for *Jathropha Curcas* of 175.12. Saponification value indicates the average molecular weight of the oil. A high saponification value indicates that the oil contained higher proportions of low molecular weight fatty acids [21]. This result shows that *Jathropha Curcas* seed oil has lower molecular weight fatty acids more than *Thevetia nerrifolia* seed oil.

Acid value of *Thevetia Nerrifolia* seed oil was found to be 4.365; this value is lower than that of *Jathropha Curcas* seed oil of 33.65. Acid value of oil measures the extent to which the glycerides had been decomposed by lipase action. The decomposition is usually accelerated by heat and light. The acids that are usually formed include free fatty acids, acid phosphate and amino acids. Free fatty acids are formed at a faster rate than the other acids [22]. The result indicated that *Jathropha Curcas* seed oil is more prone to this decomposition action.

The iodine value of *Thevetia Nerrifolia* seed oil was found to be 98.48 which is lower that of *Jathropha Curcas* seed oil of 105.43. This is an indication that *Thevetia Nerrifolia* seed oil is non-drying, whereas *Jathropha Curcas* seed oil is semidrying. The closeness of the *Thevetia Nerrifolia* seed oil value to that of semi drying oils shows that there are high levels of poly unsaturated fatty acids [23].

The refractive index of 1.464, the relative density of 0.926 and the colour (Gardner) of  $4^+$  for *Thevetia Nerrifolia* seed oil and 1.496, 0.913, and 3 for *Jathropha Curcas* seed oil all conforms to the values given by literature for other vegetable oils. This is an indication that the oils extracted were of high degree of purity.

Table 1.0. Physicochemical Properties of Thevetic	ı
Nerrifolia and Jathropha Curcas seed oils	

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Property Thevetia N	lerrifolia Jathropl	ha Curcas Value
Oil yield (%)	$47.47\pm0.026$	$46.56\pm0.26$
Refractive index	$1.464\pm0.001$	$1.496\pm0.02$
Acid value (mg/KOH)	$4.365\pm0.017$	$33.65\pm0.02$
Saponification value (mg/KOH)	$125.62 \pm 0.31$	$175.12\pm0.43$
Iodine value (Wij's)	$98.48 \pm 0.02$	$105.43 \pm 0.27$
Colour (Gardner)	$4^{+}$	3
Relative density	$0.926\pm0.003$	0.913 ± 0.03`

The results of the physicochemical characterization of dimer acids prepared from *Thevetia Nerrifolia* and *Jathropha Curcas* seed oils are shown from Table 2.0.

The molecular mass of the dimer acids were 540.62 for *Thevetia Nerrifolia* seed oil and 492.54 for *Jathropha Curcas* respectively. These values are lower than what is expected when dimer methyl ester were to be used [24]. This is due to fact that crude dimers contain 30% monomeric acids which lowers the average molar mass.

Also the acid values of 119.26 for *Thevetia Nerrifolia* seed oil and 122.85 for *Jathropha Curcas* were lower than the expected values of 125.62 for *Thevetia Nerrifolia* seed oil and 175.12 for *Jathropha Curcas*, the saponification values of the respective oils. This is an indication that the oils were not completely hydrolyzed into acids.

The saponification value, viscosity, refractive index, iodine value and colour of the dimer acids whose values are 192.68 (mgKOH/g), 5032.33 (mpa.s/25°C), 1.4690, 98.56 (Wij's) and 12<sup>+</sup> for *Thevetia Nerrifolia*dimer acid and 189.55 (mgKOH/g), 5081.47 (mpa.s/25°C), 1.466, 97. 78 and 12<sup>+</sup> for *Jathropha Curcas* dimer acid all compare favourably with each other and the dimer acids from well known traditional oils.

Table 2.0. Physicochemical Properties of Dimer Acids from *Theevetia Nerrifolia* and *Jathropha Curcas* Seed Oils

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Analytical parameter	Value for TNSO	value for JCSO		
Acid value (mg/KOH)	$119.26\pm0.03$	$122.85 \pm 0.73$		
Molecular mass (g)	$540.62 \pm 0.02$	$492.54 \pm 0.005$		
Colour (Gardner)	$12^{+}$	$12^{+}$		
Refractive index	$1.4690 \pm 0.26$	$1.466\pm0.053$		
Viscosity (mpa.s/25°C)	$5032.33 \pm 0.31$	$5081.47 \pm 0.23$		
Saponifcationvalue(mgK	OH/g) 192.68 ± 0.02	$189.55 \pm 0.031$		
Iodine value (Wij's)	98. 56 $\pm$ 0.02	$97.78 \pm 0.001$		

The results of the physicochemical characterization of the dimer acids are corroborated by the FTIR spectra of the dimer acid from *Thevetia Nerrifolia*seed oil and *Jathropha Curcas* seed oil, Figure 1 and 2 respectively.



Figure 1. FTIR Spectrum of Dimer Acid from *Thevetia* Nerrifoliaseed oil



Figure 2. FTIR Spectrum of Dimer Acid from Jathropha Curcas Seed Oil

The FTIR shows a peak at  $1710.92 \text{ cm}^{-1}$  due to C=O stretch of carboxylic acid group for *Thevetia Nerrifolia* seed

oil dimer acid. This peak is however absent from *Jathropha Curcas* dimer but there appear a peak at 1742.74 cm<sup>-1</sup> due to C=O of an ester indicating incomplete hydrolysis of the oil to acid. A peak at 1280 cm<sup>-1</sup> for *Thevetia Nerrifolia* imer was due to axial deformation of dimer C-O bond, this correspond to the peak at 1266.31 cm<sup>-1</sup> for *Jathropha Curcas* dimer.

The results of the physicochemical characterization of fatty polyamide formed by the reaction of the dimer acids from *Thevetia Nerrifolia* and *Jacthropha Curcas* with 1, 2-Phenylene diamine are shown in Table 3.0

 Table 3.0. Physicochemical Properties of Fatty Polyamide

 from Thevetia Nerrifolia and Jathropha Curcas Dimer

 Acids

<u>د</u>	Acius	
Analytical Parameter	Value TNSO	Value for JCSO
% non-volatile (% wt)	$65.63 \pm 0.17$	$71.75\pm0.28$
Acid value (mg/KOH)	$30.61\pm0.05$	$34.33 \pm 0.44$
No. average molar mass (g/mol)	$1.782\pm0.20$	$1.653\pm0.43$
Viscosity (bubble second)	$97.6\pm0.26$	$91.2\pm0.20$
Colour (Gardner)	9	9+
Amine number (mg/KOH/g)	$36.84 \pm 0.10$	$39.77\pm0.06$

From Table 3.0, the low molar masses are attributable to the presence of substantive amount of monofunctional monomeric fatty acids in dimer acid intermediate. However it does not impair its usefulness as a thixotropizing agent for alkyd resin [25]

In spite of the low molar masses, 65.63% and 71.75% solutions in xylene gave viscosities of 97.6 and 91.2 seconds respectively. The values are high and are attributed to H-bonded inter-chain interaction that would increase the viscosity. The high acid and amine values suggest a low extent of reaction.

The FTIR spectra of the Fatty polyamide are given in Fig. 3 and 4 for *Thevetia Nerrifolia* and *Jathropha Curcas* respectively.



Figure 3. FTIR Spectrum of Fatty Polyamide from *Thevetia Nerrifolia* Dimer Acid

The FTIR spectra shows the presence of characteristic amide peaks at 1544.07 cm<sup>-1</sup> corresponding to (amide II) for *Thevetia Nerrifolia* fatty polyamide and 1543.71 cm<sup>-1</sup> for *Jathropha Curcas* fatty polyamide. This is also another peak at 1644.37 cm<sup>-1</sup> corresponding to (amide I) for *Thevetia Nerrifolia* fatty polyamide and 1643.41 cm<sup>-1</sup> for *Jathropha Curcas* fatty polyamide. These peaks establish the amide nature of the products.

The absorption peaks at 763.84  $\text{cm}^{-1}$  for *Thevetia Nerrifolia* fatty polyamide and 765.77  $\text{cm}^{-1}$  for *Thevetia* 

*Nerrifolia* fatty polyamide are due to 1,2-substitution of benzene ring of the diamine moiety.



*Jathropha Curcas* Dimer Acid

The peaks at  $1735.99 \text{ cm}^{-1}$  and  $1254.74 \text{ cm}^{-1}$  for *Thevetia Nerrifolia* fatty polyamide and  $1735.99 \text{ cm}^{-1}$  and  $1256.67 \text{ cm}^{-1}$  for *Jathropha Curcas* fatty polyamide are due to the carboxylic acids and amine groups of the polyamides. **Conclusion** 

Fatty Polyamide prepared from *Thevetia Nerrifolia* and *Jathropha Curcas* Dimer acids shows comparable physicochemical properties as those prepared from Dimer acids frm other well known oils in the synthesis and hence these non-edible vegetable oils can be used as a replacement for those oils that are mostly edible for commercial production of dimer acids and Fatty Polyamides.

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