PARINARI OIL AS A POTENTIAL BIO-BASED FEEDSTOCK - A REVIEW

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ABSTRACT *Parinari polyandra* Benth is a tropical plant that is available in especially in the Northern parts of Nigeria and West Africa. Although, not many research works have been documented on *Parinari polyandra* oil, available researches on the plant and its oil have been in the domain of bio-processing, corrosion prevention applications, biomass characterisation, thermochemical processing, pharmaceuticals, product development and product testing. There is dearth of information on industrial utilization of *Parinari polyandra* oil which is a non-edible oil, that can serve as industrial raw material in Nigeria. This review presents the current and potential utilization of parinari oil as feedstock for bio-based products. The knowledge gap is discussed and prospects for future investigation are suggested.
Keywords: Parinari, seed, oil, bio-based feedstock, renewable, raw material

INTRODUCTION

The growing need for eco-friendly substitutes for petroleum-based industrial feedstock has been the driving force behind various researches on bio-based products development from numerous locally-available plant species. Some plants investigated as sources of non-edible seed oils for multiple applications include *Azadirachta indica* commonly known as neem (Aransiola *et al*., 2014), Mahua, *Madhuca indica* (Ghadge & Raheman, 2006), *Jatropha curcas* (Adeniyi, *et al*., 2018; Bouaid *et al*., 2012; Koh & Ghazi, 2011; Yusuf *et al*., 2012), Caper spurge , *Euphorbia lathyris L*. (Wei *et al*., 2007; Zapata *et al*., 2012), Honge oil, *Pongamia pinnata* (Aransiola *et al*., 2014), Avocado seeds (*Persea Americana*) (Adaramola *et al*.,2016; Paul & Adewale, 2018; Rachimoellah, *et al*., 2010), Yellow Oleander (*Thevetia peruviana M*.) (Aransiola *et al*., 2014), Tamanu (*Calophyllum inophyllum*) (Ong, *et al*., 2011), Crambe (*Crambe abyssinica* Hochst) (Aransiola *et al*., 2014) among others.

Parinari plant is yet to be fully studied and harnessed industrially (Odetoye et al, 2016). Ripe parinari fruits can be harvested around April and November of every year. The seed has a thick purple seed coat which contains an oily kernel, which on expression gives a high yield of oil (Afolabi *et al*.,2015) and a by-product meal. Researchers have reported the optimal extraction process parameters of parinari oil (Afolabi *et al*., 2015; Odetoye *et al*., 2016). In other non-industrial applications, extracts of the plant have been found to possess phytochemical, anti-inflammatory, and anti-microbial potentials (Abolaji *et al*., 2007; Bello & Lajide, 2011; Vongtau *et al*., 2004). Ighodaro *et al*, (2012) opined that the coconut water extract of parinari can be used to manage diabetes because it has antidiabetic, anti-cholesterolemia and anti-hyperlipidemia potentials.

Parinari oil is reported to be a non-edible drying oil due to its fairly high level of unsaturation (Afolabi *et al*., 2015; Odetoye *et al*., 2013). Therefore, the oil has high potentials for the production of bio-based products. Research efforts have been made towards understanding the composition, characteristics and utilization potentials of parinari for industrial product development and energy applications. This work gives a review of the utilization of parinari plant and suggests opportunities for product developments from parinari plant and oil.

The Parinari Plant

Parinari plant is a tropical plant that is available in the northern and central parts of Nigeria (Keay *et al*., 1989). It is also found in the savannah and West African grasslands from Ghana through to Cameroun (Vongtau *et al*., 2004). It belongs to the family of *Rosasceae* and is also known as *maranthes* parinari fruit. Some of its local names are: ***Aboidefin* or *Abere* (Yoruba)**, ***Abaddima* (Nupe)**, and ***Gwanjan kusa* (Hausa)** (Bello & Lajide, 2011; Vongtau *et al*., 2004). The tree is usually about 8 meters high, possesses glossy leaves that are elliptical and usually rounded at both ends as seen from Figure 1 (Afolabi *et al*., 2015).

The stem (tree trunk) of the plant is used in some rural settings in Nigeria for building and for the production of charcoal. The bark is rich in tannins and is used for tanning of leather works (Keay, *et al.*, 1989). The fruits are usually deep red or blackish purple colour (based on the variety), smooth fruits are about 2.5cm in length. The seed has a yellowish-white endosperm with a thick seed coat containing the oily mass (Figure 1). The seeds can give an optimal oil yield of about 64% (Afolabi *et al.*, 2015).

However, the process of obtaining the kernel is laborious. The physico-chemical characterisation of the oil and the thermochemical characterisation of the fruit shells have been reported (Odetoye, *et al.*, 2013.

Figure 1. The parinari fruit on the tree and de-hulled seeds (Odetoye, et al., 2013; Bello & Lajide, 2011)

Bio-Based Product Development from Parinari

A number of researchers have investigated the parinari oil and fruit shells as feedstock for the development of bio-based products. Motojesi et al. (2011) Investigated the variations in the composition of the seed oils of parinari seeds which were harvested from the same tree in April and November of the same year. The researchers reported an oil yield of 31.6 and 59.4% yields respectively. The analysis of the constituents of the oil on Gas Chromatography-Mass Spectrometry (GC-MS) indicated the presence of n-hexadecanoic acid (46.3%), phytol (26%), 9,12-octadecadienoic acid (18.10%) for seeds harvested in April while n-hexadecanoic acid (4.69%), arachidonic acid (43.38%), stigmasterol (13.41%), 9,12 Octadecadieonic acid (8.31%) were found in seeds harvested in November. The study suggested that the oil from April seeds may be more appropriate for producing biodiesel while that of November will be very suitable for producing alkyd resins based on the varying fatty acid compositions.

Odetoye et al. (2013) reported the work on the search for locally-available biodegradable renewable source of alkyd resins for paint production due to the high cost of imported alkyd resins. The study investigated the preparation of four sets of alkyd resin using 35%, 50%, 60%, and 75% oil formulations of parinari seed oil using a two-stage alcoholysis-polyesterification method. The authors found that the rate of poly-esterification depended on the amount of oil used during synthesis. Also, they evaluated the properties of the alkyds (film characteristics, drying times, solubility and water or acid resistances). It was observed that the drying properties improved when cobalt naphthenate drier was added to the alkyds and exposed to outdoor temperature. The alkyds were used to formulate white gloss paints, considering a pigment-volume concentration of 20.67% in the gloss paint. The workers reported that the formulation compares well with paints formulated with a commercial standard resin. In addition, Odetoye *et al*. (2013) used FTIR and NMR analysis to confirm the glycerol-phthalate structure alkyd resin thus produced from parinari oil.

Further work (Odetoye et al, 2013) was done to valorise the shells which constitute waste whenever the interior kernels are de-hulled from them. In an earlier work, (Odetoye *et al*, 2014) the volatile matter (78.2%), ash (4.7%) and fixed carbon(17.1%) contents, elemental composition and cellulose

(45.4%), hemicellulose (6.4%), extractives (18.1) and lignin contents (30.1%) of the shells, were determined by using proximate, ultimate and structural composition analyses respectively. A calorific value of 20.5 MJ/kg was obtained for the shell while the DTG (derivative thermo-gravimetric) and TGA profiles indicated that the pyrolysis of parinari fruit shells is feasible. Moreover, the cellulose and hemicelluloses contents indicated a relatively higher rate of pyrolysis. It was reported that the thermochemical characteristics of parinari shell compared well with established biomass used for bio-oil production (Odetoye *et al.*, 2013).

Further work on pyrolysis of parinari fruit shell via an intermediate pyrolysis process for the production of bio oil was also reported (Odetoye *et al*., 2013). The bio-oils were obtained by using a fixed bed reactor at a temperature range of 375–550°C and characterized to determine their physicochemical properties. The study showed that the most abundant organic compounds present were acetic acid, toluene, 2-cyclopenten-1-one, 2-furanmethanol, phenol, guaiacol and 2,6-dimethoxyphenol. Odetoye, *et al*. (2014) found that the bio-oil produced at 550 °C had a higher quantity of desirable compounds than those produced at lower temperatures, however the presence of acetic acids in the bio-oil suggests the need to upgrade the bio-oil before it can be utilized as a fuel source.

An earlier work on the optimization of the extraction process of parinari seed oil was carried out by Afolabi *et al.* (2015). In the study, oil was extracted from the seeds of parinari by using solvent (n-hexane and petroleum ether) extraction method and the process was optimized by using response surface methodology (Central Composite Design) to determine the effect of solvent residence time, temperature, solid/solvent ratio and solvent types on the yield of parinari seed oil. Afolabi *et al*. (2015) obtained an optimal yield of 64% at a temperature of 60°C, residence time of 4 hours and solid/solvent ratio of 0.05g/ml using n-hexane as solvent. The results indicated that the physicochemical characteristics of the parinari oil as in Table 1 and that extraction temperature had the greatest effect on the oil yield followed by residence time, solid/solvent ratio and solvent type.

In another study, the effect of process parameters on the quality characteristics of extracted parinari oil was investigated (Odetoye *et al.*, 2016). The study parameters were temperature (60-70 °C), time (2-6 h), solid-solvent ratio (0.03-0.08 g/cm^3) and solvent types (n-hexane and petroleum ether) while the quality characteristics were saponification, acid and iodine values. The study showed that temperature and time had significant influence on the physicochemical properties of parinari oil. Response Surface Methodology (RSM) based analysis of variance indicated that the models obtained were all significant ($p < 0.0001$). The results indicated that the optimum quality (Table 1) was attained at a temperature of 60 °C, time of 2 h, and a solid to solvent ratio of 0.07 g/cm^3 by using n-hexane solvent with 87% desirability. The workers suggested that the findings of the work may be helpful for potential scaling up of the parinari oil extraction process.

The search for bio-based catalysts for parinari oil transesterification motivated Amos et al. (2016) to investigate rice husk ash (RHA) and cocoa pod ash (CPA) as viable catalysts and compare the results with that of potassium hydroxide catalyst. The researchers obtained a parinari oil

Table 1. Optimum values for Parinari oil extraction process (Odetoye et al., 2016)

Process parameters	Optimum values
Time (hr) A	2
Temperature (°C) B	60
Solid/solvent ratio(g/ml) C	0.07
Solvent type D	n-Hexane
Oil yield (%)	54.04
Acid value (mg KOH/g oil)	2.45
Iodine value (mg I_2/g oil)	169.23
Saponification value (mg KOH/g oil)	246.17
Desirability	0.87

extraction yield of 57%. The team used a muffle furnace to ash cocoa pod and rice husks at 600 °C before characterizing them. Using Atomic Absorption Spectrometric analysis it was found that the metal constituents of the RHA were 1.748 ppm sodium, 3.24 ppm potassium, 0.053 ppm iron, 2.325 ppm calcium, 1.575 ppm magnesium and 0.009 ppm aluminium while CPA contained 6.65ppm sodium and 13.05 ppm potassium. The researchers conducted the transesterification experiments with various concentrations of RHA, CPA and KOH (ranging from 0.4-0.5%). The applied ratio of methanol-to-oil was 6:1. The authors obtained biodiesel yields of 88.85%, 98.61% and 99.94%, with 2% RHA, 4% CPA and 1% KOH catalysts respectively. The authors found out that all the obtained biodiesel fell within ASTM standard.

In another work, Awe et al. (2015) studied the inhibition of mild steel corrosion in 0.5 M sulphuric acid solution by ethanol extracts of parinari as an eco-friendly inhibitor at different temperatures by weight loss technique and linear polarization. The study showed that inhibition efficiencies increased as the concentration of the inhibitor increased. The researchers found the adsorption of the inhibitor on mild steel surface to be exothermic, spontaneous and best described by Freundlich and Temkim adsorption models. Tafel polarization analyses indicated that the studied plant extract is a mixed type inhibitor on the surface of mild steel. The adsorption characteristics of the inhibitor also favoured the mechanism of charge transfer from the charged inhibitor's molecule to the charged metal surface (Physical adsorption) and supported Freundlich adsorption model. Therefore, Awe et al. (2015) concluded that ethanol extract of parinari is a good adsorption inhibitor for the corrosion of mild steel in sulphuric acid.

More recently, Ogunkunle and Ahmed (2018) were interested in evaluating the performance of parinari oil biodiesel in a diesel engine. The duo extracted parinari oil via solvent extraction using potassium hydroxide as catalyst, obtained an optimum biodiesel yield of 94.6% and found that the properties of the biodiesel fell within ASTM D6751 standard specifications and thus can be used as an engine fuel. Performance evaluation tests were carried out on a stationary 5Hp diesel engine with loading conditions starting from 0 to 100%. The engine was operated both with diesel and four different blends of diesel and biodiesel. It was observed that higher load conditions led to increased exhaust gas temperatures and that the higher the biodiesel content in the blends, the higher the brake specific fuel consumption of the diesel engine became. The study also suggested that the performance of biodiesel blend, B5D95 is similar to that of biodiesels and therefore can improve the thermal efficiency of diesel engines. The recorded speed, torque, exhaust temperature, and fuel consumption rate for best engine performance for all blends were 2950 rpm, 8.50 Nm, 300 °C and 2.925×10^{-6} kg/s. Ogunkunle and Ahmed (2018) concluded that if the appropriate blending ratio is used, parinari oil biodiesel can burn well in diesel engines without any need to modify the engine.

Knowledge gaps and future perspectives

From the review of bio-product development from parinari, several observations were made. The catalysis of biodiesel production from parinari oil has been rarely studied as only Amos et al. (2016) did any work in this regard (used cocoa pod ash and rice husk ash as biodiesel catalyst). Research trends in recent times is to study, cheaper and efficient catalysts for the production of biodiesel from inedible oils. More work is recommended in the domain of parinari oil feedstock utilization. The study on optimization of parinari oil epoxidation will be an interesting avenue for research as parinari oil epoxidation has not been previously reported in literature. The design of processing machine for the oil extraction is also a challenge that needs to be tackled in order to effectively harness the relatively high oil yield. On thermochemical processes of parinari, it is recommended that other thermochemical methods such as gasification, co-gasification, and torrefaction be examined.

Currently, there are little or no reports on the financial advantage of using parinari feedstock over other feedstock for bio-product development. Therefore, a detailed techno-economic analysis of bio-product development from parinari is recommended. It is necessary to find more uses for parinari oil which is non-edible (Olatunji et al., 1996) since it will not compete with human consumption needs.

CONCLUSION

In this review, effort has been made towards understanding the composition, characteristics and utility potentials of parinari for chemical product development. A review of earlier works which indicated potentials of product development from parinari was presented. Research on the plant parts were mainly on seed oil characterisation, thermochemical processing, corrosion applications and biofuel applications. The prospects for future investigation suggests that the parinari plant is a promising bio-based feedstock.

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