

Fuel Properties of Pongamia (*Milletia pinnata*) Seeds and Pods Grown in Hawaii

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ABSTRACT: Pongamia, a leguminous, oilseed-bearing tree, is a potential resource for renewable fuels in general and sustainable aviation fuel in particular. The present work characterizes physicochemical properties of reproductive materials (seeds and pods) from pongamia trees grown in different environments at five locations on the island of Oahu, Hawaii, USA. Proximate and ultimate analyses, heating value, and elemental composition of the seeds, pods, and de-oiled seed cake were determined. The oil content of the seeds and the properties of the oil were determined using American Society for Testing and Materials and American Oil Chemist's Society methods. The seed oil content ranged from 19 to 33 wt % across the trees and locations. Oleic (C18:1) was the fatty acid present in the greatest abundance (47 to 60 wt %), and unsaturated fatty acids accounted for 77 to 83 wt % of the oil. Pongamia oil was found to have similar characteristics as other plant seed oils (canola and jatropha) and would be expected to be well suited for hydroprocessed production of sustainable aviation fuel. Nitrogen-containing species is retained in the solid phase during oil extraction, and the de-oiled seed cake exhibited enrichment in the N content, ~5 to 6%, in comparison with the parent seed. The pods would need further treatment before being used as fuel for combustion or gasification owing to the high potassium and chlorine contents.



1. INTRODUCTION

In 2017, biofuel accounted for about 1.0% of global total energy consumption.¹ Production and use of renewable alternative transport fuels, such as hydroprocessed esters and fatty acids (HEFAs), have grown significantly over the last 5 years. In 2017, HEFA accounted for approximately 6% of total biofuel production by energy content, contributed to in part by increased demand for sustainable aviation fuel.² The market for aviation fuel is unique from that of other transportation sectors, in that only alternative fuels qualified by the American Society for Testing and Materials (ASTM) D4054-19^{3,4} approval process can be substituted for the petroleum incumbent. In addition, there is no current opportunity for electrification, particularly for long haul flights.

Milletia pinnata, also called karanja or pongamia, is indigenous to the Indian subcontinent and Southeast Asia;⁵ it is a monotypic genus with a single known species.⁶ As a nitrogen-fixing and self-pollinating tree, pongamia can be cultivated easily, even in nonfertile lands and waste lands,⁷ and is often found in humid and subtropical environments^{8,9} with minimum mean monthly temperatures ranging from 10 to 50 °C. Optimal growth requires temperatures in the range of 16–40 °C.¹⁰ The plant has been introduced to humid tropical regions as well as parts of the United States.⁵ In general, the pongamia tree can grow to 15–25 m in height, commence flowering at 3–4 years of age, reach maturity in 4–5 years, and produce up to 90 kg of seeds per year.¹¹ The leaves, wood, and

seeds from pongamia trees have various value-added applications.^{7,11} Pongamia pods and seeds usually develop from flowering to harvest in 8–10 months in three stages: (i) early green immature pod stage; (ii) half brown pod stage; and (iii) late dark brown pod stage.¹² The oil content of the seeds increases with maturity stages and remains constant after full seed maturity is reached.¹² Additional information on cultural practices was reviewed by Morgan et al.¹³

Biofuels have been classified as first or second generation based on the feedstocks utilized for production (sugars, grains, or seeds (first generation) versus nonedible lignocellulose or vegetable oils (second generation)).^{14,15} Critical questions regarding energy crops considered for second generation feedstocks include ranges of yields, variation in the characteristics of the feedstock components, and their capacity to be productive in lower quality environments.¹⁵ Pongamia has also been recognized as a potential feedstock for second generation sustainable aviation fuel production due to the high oil content of its seed, 27–39%, and the presence of toxic and antinutri-

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tional compounds, such as pongamol, karanjin, and glabrin, which render it inedible.¹¹ Pongamia oil, generally yellowish orange to brown in color, has an energy content of 34–38.5 MJ/kg, similar to soybean oil, making it suitable for fuel production.¹⁶ In addition, the oil yields from pongamia trees are in the range of 2.0–4.0 Mg/ha/year,^{17,18} slightly higher than the inedible oil plant *jatropha* at 2.0–3.0 Mg/ha/year.

To date, research on pongamia oil has focused almost entirely on the production of biodiesel or direct combustion of the oil,^{5,7,11,16,17,19–25} with very few published studies on sustainable aviation fuel production.^{26,27} Klein-Marcuschamer et al. conducted a technoeconomic analysis of HEFA jet fuel from pongamia oil and found it would be competitive with petroleum jet fuel when the price of crude oil exceeded \$374/barrel.²⁶ The modeled price of pongamia seeds was ~\$590/Mg in 2013,²⁶ which is slightly higher than the market price of soybeans (average price for soybeans in 2013 was \$538/Mg).²⁸ Future technological improvements and an increased oil content in pongamia seeds reduced the price at which would be competitive with jet fuel to \$255/barrel of crude oil.²⁶ Cox et al. modeled the environmental impacts of producing aviation biofuel from pongamia oil and concluded that the pongamia pathway can realize 43% greenhouse gas abatement on a life cycle basis (reduction in emissions relative to the reference fossil fuel, aviation kerosene), avoid eutrophication, and reduce water use in comparison with sugarcane.²⁷

In the present study, pongamia trees grown at five locations on the island of Oahu in Hawaii were identified for investigation. The essential biomass properties, including seed oil content, proximate composition, heating value, iodine value, free fatty acid content, and nitrogen content of the oil, seed cake, and pods were measured. The seed oil was obtained through two different oil extraction methods, conventional solvent extraction and mechanical extraction. The oil properties, including the free fatty acid contents, fatty acid profiles, phase transition temperatures, iodine values, and H/C ratios, were determined and compared to that of commercial canola oil. The characteristics of oil extraction byproducts, i.e., pod and seed cake, were also determined to explore their potential coproducts.

2. MATERIALS AND METHODS

2.1. Materials. Pongamia seed pods were collected from five locations on Oahu: (1) Bachman Hall, University of Hawaii at Mānoa (21°17'49.60"N, 157°49'11.06"W); (2) Foster Botanical Garden (21°19'0.92"N, 157°51'31.94"W); (3) Ke'ehi Lagoon Beach Park (21°19'48.09"N, 157°53'52.42"W); (4) Hawaii Agriculture Research Center, Kunia, HI (21°22'58.9"N, 158°02'21.8"W) (TerViva Planting); and (5) TerViva Oahu orchard, Haleiwa, HI (21°34'28.7"N, 158°03'42.4"W). Pongamia seed pods from location (4) were provided by TerViva Inc. and collected from May 2016 to August 2018 with seven batches in total. The collected seed pods from locations (1)–(3) and (5) were oven dried at 35 ± 1 °C for 7 days. Afterward, pods and seeds were separated, followed by additional drying at 40 ± 1 °C for 7 days until the mass was constant. Note that the literature review revealed that there were no common agreements upon conditions for drying pongamia seed pods.¹³

Seed pods were hand harvested from trees at location (4) and then (1) soaked in a bleach/water solution for 1 min, (2) placed on a mesh screen and dried in full sun for 2–3 h, and (3) stored in an air conditioned room at ~21 °C in loosely woven mesh bags. The seed pods from location (4) were analyzed as received without further processing.

All the dried seeds were milled into fine powder at –196 °C using a cryogenic ball mill (Retsch Cryomill, Düsseldorf, Germany), and the dried pods were milled to a <0.2 mm particle size using an ultracentrifugal mill (Retsch ZM200, Düsseldorf, Germany). Canola oil (Wesson Foods, lot number: 2130532400X23:545, 1 gallon size) was purchased from a retail grocery. A summary of the sample preparation and oil extraction process is shown in Figure S1.

2.2. Oil Extraction Methods. Pongamia oil was extracted from the seeds by conventional solvent extraction (CSE) and mechanical extraction (ME). CSE was conducted using milled pongamia seeds and hexanes as solvents. The milled sample (20–25 g) was mixed with 250 ± 5 mL of hexane (boiling point 65.5–68.3 °C) in a 500 mL flat bottom boiling flask. The mixture was boiled with vapor reflux on a water bath at 80 °C with a stirring bar at 300 rpm for 60 ± 1 min. The supernatant was separated from the residues by filtration under a vacuum (filter paper pore size, 25 μm), and the solvent was then evaporated at 70 °C with a rotary evaporator under a vacuum to obtain oil samples. ME was conducted using a manual oil expeller (Piteba, The Netherlands) for which the whole seeds from location (1) were first size-reduced using a food processor and then fed into the expeller heated with an alcohol lamp. The oil obtained from the expeller was filtered with a 0.45 μm syringe filter (MilliporeSigma SLHV033NS) to exclude seed particles.

2.3. Oil Fatty Acid Profile. The oil samples were converted to their corresponding fatty acid methyl esters (FAMES) by KOH-catalyzed transesterification. Oil samples (40 μL) were dissolved in a mixture of 4 mL of hexane and 4 mL of KOH–methanol solution (0.5 mol/L) and vortexed for 5 min.^{29,30} After 5 min, 12 mL of saturated NaCl was added to the mixture and vortexed for 1 min. The resulting mixture was centrifuged for 5 min at 4000 rpm. The ~2 mL upper phase of the liquid mixture was filtered with a 0.45 μm PTFE syringe filter and transferred to a 2 mL vial. This sample was analyzed using a Bruker 436-GC gas chromatograph and SCION-MS select and single quadrupole mass spectrometer (Bruker Corp., Billerica, MA). The gas chromatograph was equipped with a 60 m Agilent DB1701 column (low/mid polarity (14%-cyanopropyl-phenyl)-methylpolysiloxane) with a 15 m guard column before the back flush valve and operated at a helium flow rate of 1.5 mL/min. A reference standard containing 10 mg/mL each of palmitic acid methyl ester, linolenic acid methyl ester, stearic acid methyl ester, methyl *cis*-9-octadecenoate, linoleic acid methyl ester, methyl *cis*-9-hexadecenoate, and myristic acid methyl ester was purchased (AccuStandard, New Haven, CT) and used for chemical identification and quantification.

2.4. Property Determination. **2.4.1. Proximate Analysis.** The milled pongamia seeds, pods, and de-oiled seed cake were subjected to proximate analysis using a macro thermogravimetric analyzer (TGA801, LECO Corporation, St. Joseph, MI) based on ASTM E1756,³¹ E872,³² and E1755³³ for moisture, volatile matter, and ash content determination, respectively. The instrument has the capacity to analyze batches of 19, ~1 g samples in individual ceramic crucibles. Details on the TGA measurement process were included in the Supporting Information. Note that this study reports the amounts of ash, volatile matter, and fixed carbon on a dry basis. The fixed carbon content was calculated by subtracting the ash and volatile matter contents from 100%.

2.4.2. Ultimate Analysis. A LECO CHN628 with sulfur module (LECO Corp., St. Joseph, MI) was employed to determine the carbon, hydrogen, nitrogen, and sulfur contents of

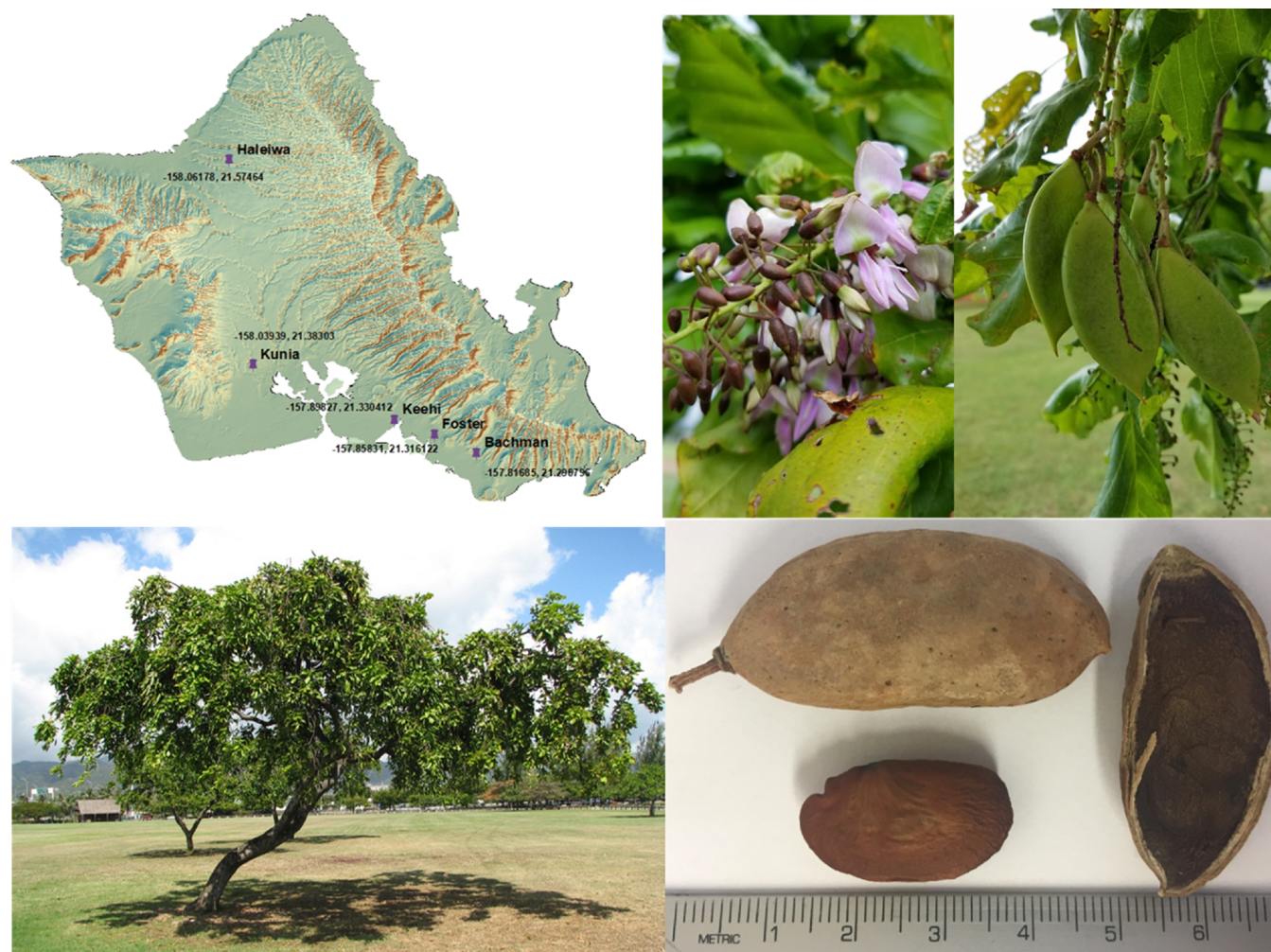


Figure 1. Pongamia tree, flower, seed, pod, and sampling location on Oahu, HI, USA.

pongamia seeds, pods, oils, and seed cake. The furnace and afterburner temperatures of the CHN628 system were set at 950 and 850 °C, respectively. For solid phase samples, approximately 50 mg of sample was placed in tin foil and sealed. For liquid oil samples, ~50 mg of sample was placed in a tin foil cup and then covered with ~200 mg Com-Aid (>99% Al_2O_3 , LECO Corp., part no. 501-427) and sealed. The sulfur content of the solid samples was measured with the sulfur module with the furnace temperature set at 1350 °C. The solid sample (~100 mg) was placed into a crucible and covered with ~1 g of Com-Cat (>95% tungsten(VI) oxide, LECO Corp., part no. 501-321). Sulfur analysis was not performed on the oil samples.

2.4.3. X-ray Fluorescence Analysis. Quantitative element analysis of the solid seeds, pods, and CSE residues (seed cake) was performed using a Bruker S8 TIGER X-ray Fluorescence (XRF) spectrometer (Bruker Corp., Billerica, MA) to determine the ash-forming and nutrient elements (e.g., Na, Mg, Al, Si, P, S, K, Ca, Mn, and Fe) and environmentally important elements (e.g., S, Cl, Ti, Pb, Cd, As, and Hg). The pellets for XRF were prepared by: (1) mixing 4–5 g of milled sample (<200 μm in diameter) with 1–2 g of Hoechst wax C powder (Bruker AXS, ethylene bis(stearamide), $\text{C}_{38}\text{H}_{76}\text{N}_2\text{O}_2$, with a grain size of approximately <10 μm); (2) pressing the mixture using an Angstrom model 4451AE Briquet Press (Bellefonte, MI USA) with 40 mm steel die and a stable, applied pressure of 345 MPa held for 30 s.^{34–36} The pellets obtained were mechanically

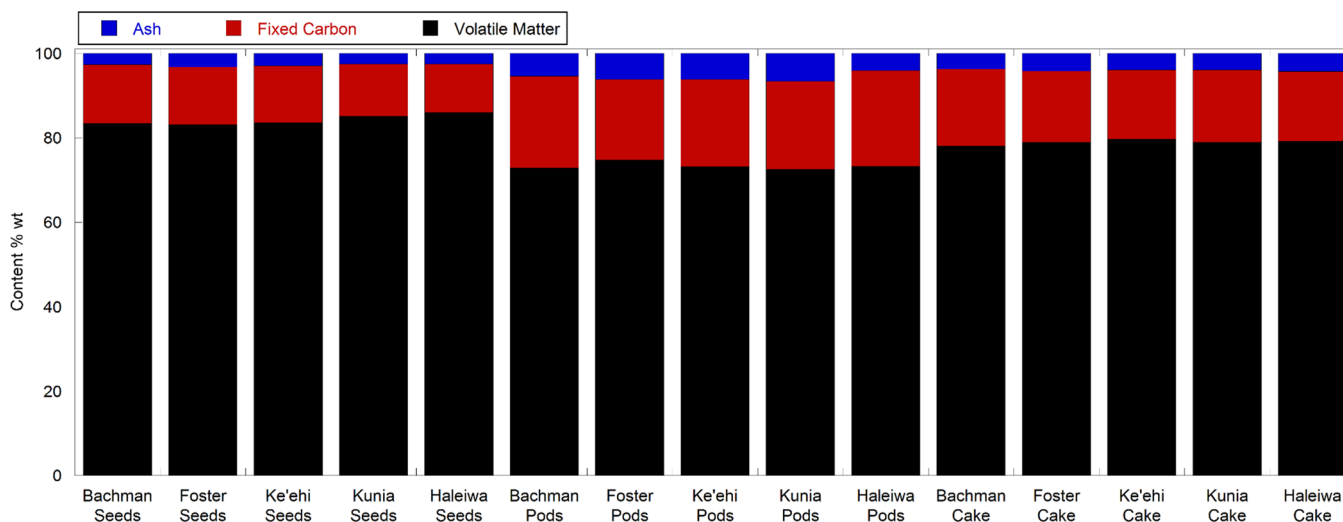
stable, with 40 mm in diameter and 4–5 mm in height, and stored in a desiccator until analyzed. The Bruker S8 TIGER XRF uses a 4 kW (limited to 3 kW for this analysis) water-cooled X-ray tube with an Rh anode, a 75 μm Be window, and a 60 kV maximum acceleration voltage. Spectrum recording and evaluation were performed with QuantExpress software using the best detection mode (Bruker AXS). The instrument and method have been described in detail in a previous study.³⁴

2.4.4. Other Physicochemical Properties.

1. A Parr 6200 Isoperibol calorimeter (Parr Instrument Company, Moline, IL) was used to measure the heat of combustion based on ASTM D4809³⁷ and reported as the higher heating value (HHV).
2. A Setaflash Series 8 closed cup flash point analyzer (model 82000-2 U) was used to measure the flash point of oil samples according to the ASTM D3828 method³⁸ (hot wire ignition).
3. The free fatty acid contents (FFAs) and iodine values (IVs) of the pongamia oils were determined using American Oil Chemist's Society (AOCS) methods Ca 5a-40³⁹ and Cd 1d-92,⁴⁰ respectively.
4. Differential scanning calorimetry (DSC) analyses were conducted using a TA Q2000 system (TA Instruments, New Castle, DE) equipped with an RCS90 temperature control, which permits operation over the temperature

Table 1. Environmental Factors at the Five Locations of Pongamia Trees on Oahu, HI, USA

location	elevation (m)	soil type	mean annual rainfall (mm)	annual supplemental irrigation water (mm)	solar insolation ($\text{kWh m}^{-2} \text{d}^{-1}$)	mean annual temperature ($^{\circ}\text{C}$)	tree age (years)
Bachman	21	Makiki stony clay loam	931	972	5.2–5.8	23.5	63
Foster	6	Ka'ena clay	833	1737	5.2–5.8	23.8	>47
Ke'ehi	1	fill land, mixed	695	1862	5.2–5.8	23.7	>35
Kunia	72	Moloka'i silty clay loam	621	1321	5.2–5.8	23.3	<5
Haleiwa	208	Wahiawa silty clay	1050	1321	5.2–5.8	22.3	<5

**Figure 2.** Proximate analysis results of pongamia seeds, pods, and de-oiled cake; x axis labels refer to locations in Figure 1.**Table 2. Properties of Pongamia Seeds, Pods, and Seed Cake after Conventional Solvent Extraction with Soybean Seed Cake Data Shown for Comparison^a**

location	seed			pod		cake	
	H/C	XRF ash wt %	oil content (%)	H/C	XRF ash wt %	H/C	XRF ash wt %
Bachman	1.81	3.12 ± 0.22	24.82 ± 1.09	1.68	5.64 ± 0.06	1.76	3.24 ± 0.01
Foster	1.88	3.44 ± 0.28	22.26 ± 2.34	1.74	6.01 ± 0.01	1.77	4.63 ± 0.13
Ke'ehi	1.85	2.84 ± 0.16	19.65 ± 1.56	1.71	6.61 ± 0.02	1.77	3.39 ± 0.03
Kunia	1.92	N/A	26.86 ± 1.86	1.80	6.23 ± 0.80	1.95	4.17 ± 0.19
Haleiwa	1.85	N/A	32.45 ± 0.27	1.65	3.88 ± 0.06	1.89	4.76 ± 0.04

^a(1) XRF ash wt % values are calculated with the $\text{C}_6\text{H}_{10}\text{O}_5$ matrix as the mean ± standard error of six analyses (3 pellets and 2 sides); (2) XRF analysis was not conducted for Kunia and Haleiwa seeds due to high oil contents; and (3) the Kunia values are averages of seven sample batches.

range of -90 to 400 $^{\circ}\text{C}$. The DSC measurement method has been described in detail in a previous publication.⁴¹ The cooling scan was analyzed to determine the crystallization onset temperature (FO) and the crystallization peak temperature (FP), which reflect the low-temperature quality of the oils.

5. An Anton Paar SVM3000 Stabinger viscometer (Anton Paar USA Inc., Ashland, VA) was used to measure the viscosity and density of the pongamia oil samples at temperatures according to the ASTM D7042 method.³

The instruments and methods for the above mentioned analysis have been described in detail in previous studies.^{42,43}

3. RESULTS AND DISCUSSION

3.1. Pongamia Seeds and Pods. The pongamia pods contained one or two seeds and were collected from five locations on Oahu, Hawaii (shown in Figure 1) after reaching stage (iii), i.e., the late dark brown pod stage, after naturally

falling from the tree. The size of the pods and seeds varied, but the lengths of the pods and seeds were typically in the ranges of 4–6 and 2–3 cm, respectively. It should be noted that pods with two seeds usually have a one bigger seed (2–3 cm long) and one smaller seed (0.5–1 cm long).

The five sites are within 25 km radius and have similar mean annual temperature and solar insolation, while the other growing conditions are different (see Table 1). Locations (1) and (2) have only a single tree, whereas locations (3)–(5) have 13, 49, and 7976 trees, respectively. The pongamia trees at locations (1), (2), (4), and (5) are planted in relatively deep productive soils, whereas the soil at location (3) is a mixed fill land located within 100–150 m from a brackish water estuary and ~ 1 m above sea level.⁹ Tree ages vary from <5 years at the Haleiwa location to 65 years for the Bachman tree. Ages at the Foster and Ke'ehi locations are minimums based on available records. The combined total of rainfall and mechanically applied irrigation water ranges from 1900 to 2500 mm per year, with the Bachman and Kunia locations at the lower end of the range and the

remaining three sites toward the upper end. Yellowed leaves are often apparent on trees at location (3), possibly due to heat, drought, or salt stress.⁹

Figure 2 presents the proximate analysis results of the seeds and pods; data and error estimates are presented in Tables S1 and S2. The values reported for location (4) are averages of seven batches; data for individual batches are included in the Supporting Information. The slightly higher volatile matter of the seeds from locations (4) and (5) compared to locations (1)–(3) results from their higher oil content, all >25 wt % (see Table 2 and Table S8). Materials from trees under stress at location (3) had comparable proximate analysis results to those collected from locations (1) and (2). As expected, the fixed carbon content of the pods are all higher than the seeds, ~6–11 wt % (absolute), and the values from all locations differ by <3% (absolute). In general, the VM/FC ratio is regarded as an indicator of the reactivity or combustibility of biomass. The VM/FC ratios of the seeds from locations (1)–(5) are approximately 100% (relative) greater than those of the pods from the corresponding locations. This higher reactivity results from the volatile/combustible oil present in the seeds.⁴⁴

The ash content of the pod samples was ~2–3% (absolute) higher than the seed samples at all locations. This is consistent with the lower energy content of the pods (shown in Figure 3)

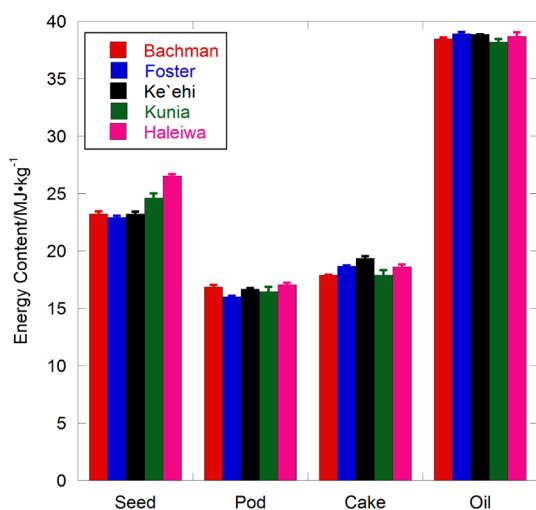


Figure 3. Energy content analysis results of pongamia seeds, pods, de-oiled cake, and oil; legend labels refer to locations in Figure 1.

compared to the seeds. A similar trend was observed when the mass fractions of the oxide forms of the elements identified by XRF are summed (listed in Table 2). The greater ash content of the pods compared to the seeds is associated with the significantly increased amounts of several elements, i.e., sodium (Na), chlorine (Cl), potassium (K), calcium (Ca), and silicon (Si) shown in Tables S3 and S4. The pods collected from location (5) have a slightly lower ash content in comparison with other four locations, which may be associated with tree age or increased water supply (rainfall + irrigation). Prasad et al.⁴⁵ also conducted a proximate analysis on pongamia pods collected from New Delhi, India (see Table S2). Although the volatile matter and fixed carbon content of the pod samples reported by Prasad et al.,⁴⁵ 80.13 and 13.42%, respectively, are different from the values obtained in this study, the ash content of the pod samples, 6.45%,⁴⁵ is within the range of the values obtained in this study, i.e., 4.09–6.67 wt %. The energy content (HHV) of

the pods reported by Prasad et al.,⁴⁵ 16.81 MJ/kg, is comparable to the values of the pods collected at sites (1), (2), (3), and (5). Location (4) was slightly lower, 16.01 MJ/kg.

Proximate analysis results obtained from macro thermogravimetric analysis were in good agreement with the results obtained from conventional methods, see Figure S1. The root mean square deviation between the TGA and conventional measurements is 1.21%. This confirms the interchangeability of the automated LECO TGA method and the manual ASTM method for determining proximate analysis.

Ultimate analysis results of seeds and pods are shown in Figure 4A–C; complete data and error estimates are presented in Tables S1 and S2. The seed samples generally have a higher carbon content and hydrogen content in comparison with the pod samples (shown in Figure 4A). The carbon and hydrogen contents of the seeds from locations (3) and (4) are higher than that of the other locations due to the higher oil content of the seeds. As observed in the proximate analysis, the carbon and hydrogen contents of the pod samples did not show significant differences that could be attributed to tree locations. The H/C ratio calculated from the ultimate analysis (listed in Table 2) is an indicator of the combustibility of the fuel,⁴⁶ and the greater H/C ratios of the seeds in comparison with pods agree with the trends predicted by the VM/FC ratio.

The nitrogen contents of the seeds and pods vary with the sampling location (shown in Figure 4B). Overall, the nitrogen contents of the seed samples are at least three times greater than that of the corresponding pod samples, indicative of a higher seed protein content.⁴⁷ The highest nitrogen contents of seeds were from location (3), the site with the most severe environmental conditions. Location (2) has the highest pod nitrogen content of the five locations, but all were in a range from 0.7 to 1.2 wt %. Figure 4C displays the sulfur content of the pongamia seeds and pods. Similar to the nitrogen content, the sulfur content of the seeds from all five locations is at least twice that of the corresponding pods. Seeds and pods from location (4) have the highest sulfur contents, 0.25 and 0.12 wt %, respectively. Although clean wood fuels typically contain <0.1 wt % sulfur, the sulfur content of pongamia seeds and pods is still far lower than coal.

Figures 5 and 6 present the XRF analysis results of the pongamia seeds and pods, respectively (data and error estimates presented in Tables S3 and S4). The limit of detection (LOD), defined as the minimum detectable concentration of an element in a matrix, is also included. The LOD value is the average based on all the measurements on the seed, pod, and de-oiled cake materials in the wax pellets/matrix. Samples with element concentrations higher than the LOD are reported in tables. The XRF system background was determined by analyzing blank samples, i.e., Hoechst wax C powder binder. Results indicate that the XRF system background has trace amounts of Ru (21.6 ± 1.2 ppm), Fe (8.4 ± 0.6 ppm), and Cu (4.9 ± 0.7 ppm). XRF limits of quantification (LOQ) four times of the LOD were used for this study. The LOQ is the minimum concentration that the system can quantify accurately. XRF analysis was not conducted on seeds from locations (4) and (5) because their high oil content prevented the formation of a stable pelleted sample.

As observed in the ash content from the proximate analysis, the total mineral content of pods is much higher than the corresponding seeds from locations (1)–(3). Of the elements quantified with XRF, potassium is present in the highest concentrations in both seeds and pods, ranging from 0.9 to 1.2 and 1.8 to 3.4 wt %, respectively. Phosphorus (P) and Ca are

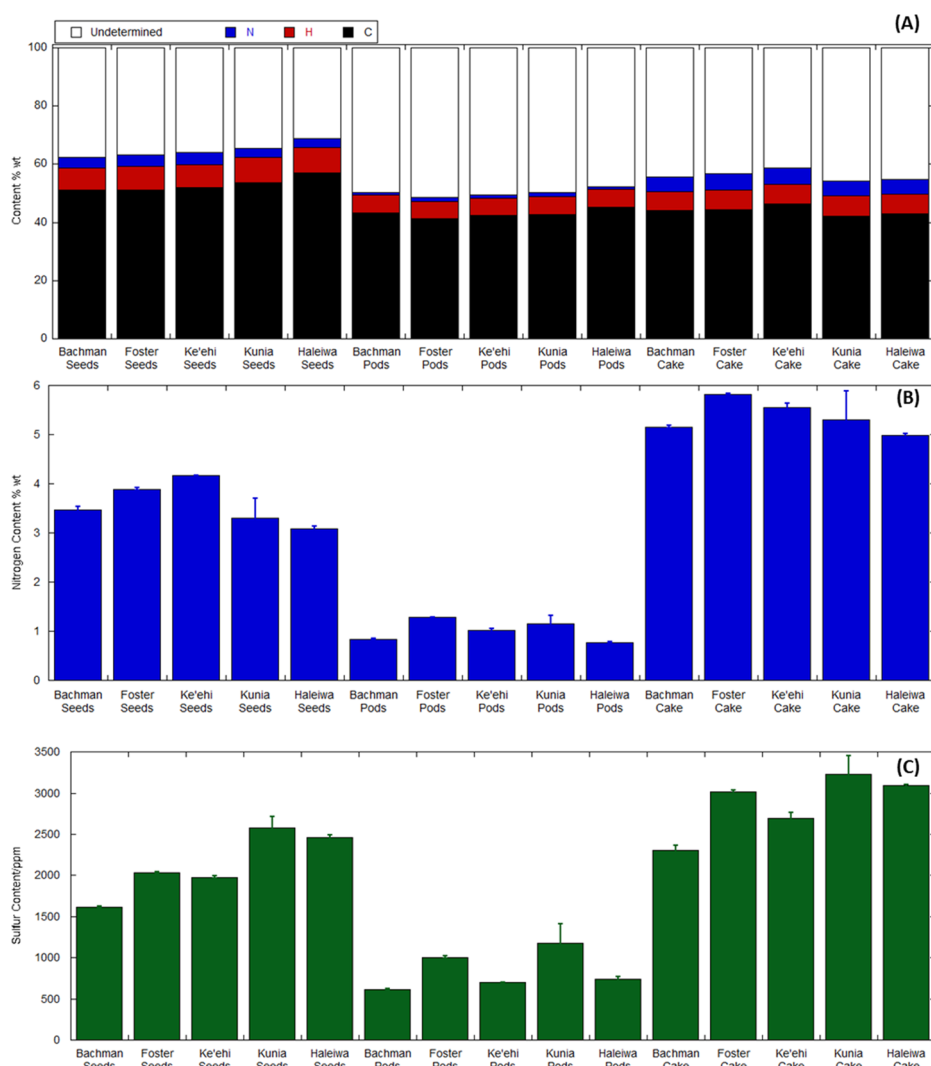


Figure 4. Ultimate analysis results of pongamia seeds, pods, and de-oiled cake: (A) summary of C, H, and N analysis; (B) nitrogen content analysis; and (C) sulfur content analysis: x axis labels refer to locations in Figure 1.

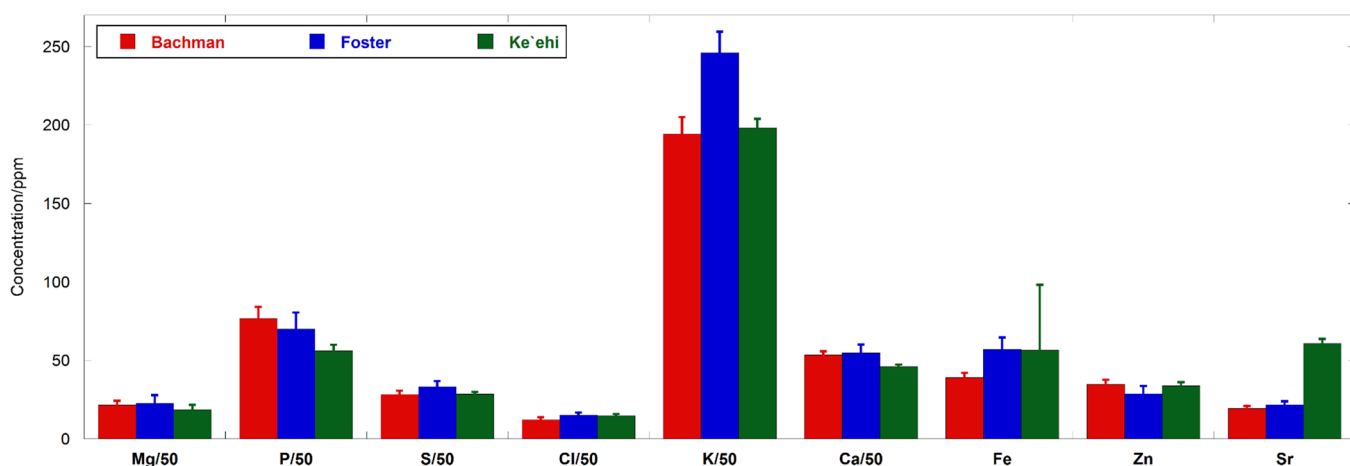


Figure 5. XRF elemental analysis results of pongamia seeds; legend labels refer to locations in Figure 1. XRF analysis of seeds from other two locations was not conducted because their oil content prevented the formation of a stable pelleted sample.

both present in roughly equal concentrations, 0.25 to 0.35 wt % in the seed. Ca occurs in a wider range of concentrations in the pod, 0.4 to 1 wt %, but P is reduced to levels of 200–500 ppm. Magnesium and sulfur are present at levels above 1000 ppm in

the seed with the remaining elements present at concentrations below this benchmark.

The Na content of the pods is approximately six times higher than that of seeds from locations (1) and (2), and over 12 times

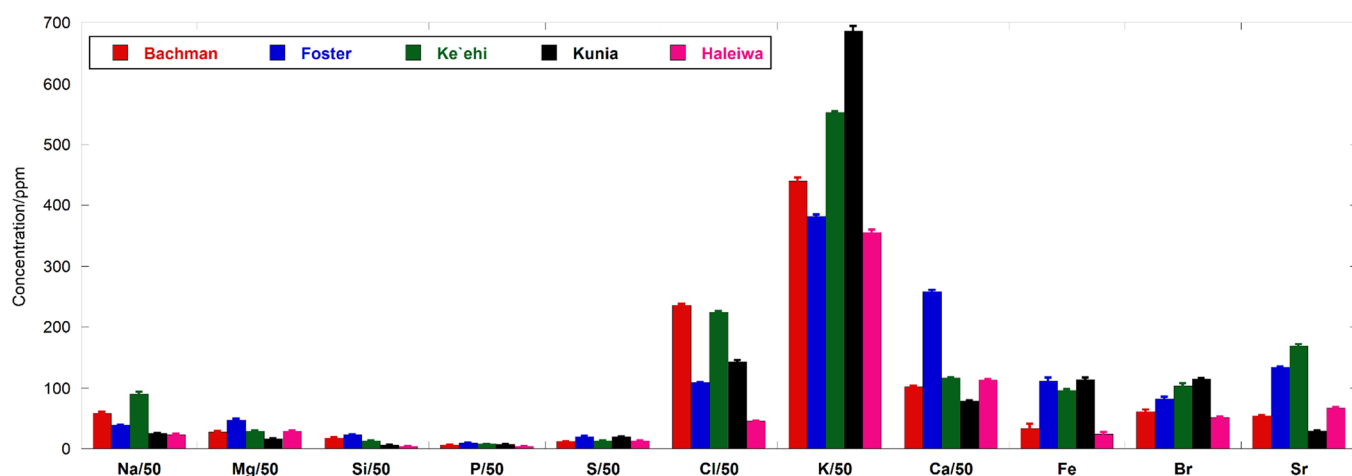


Figure 6. XRF elemental analysis results of pongamia pods; legend labels refer to locations in Figure 1.

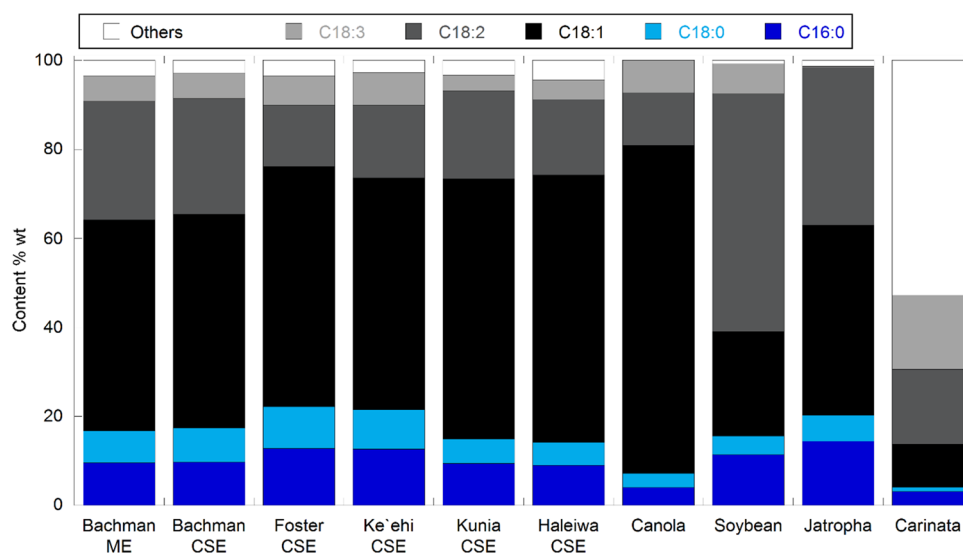


Figure 7. Fatty acid profile of pongamia oils in comparison with that of canola, soybean,⁵⁴ jatropha,⁵⁴ and carinata oil.⁵⁵ x axis labels refer to locations in Figure 1; CSE and ME are conventional solvent and mechanical extraction, respectively

higher for location (3). The Na contents of seeds from all three locations are similar, <0.05 wt %, whereas the Na content of the pods from location (3) is ~1.5 to 4 times higher than the other four locations. The Cl content of pods was also elevated compared to seed values. The molar ratio of Na:Cl for the seed and pods varied from 0.70 to 1.19 and 0.27 to 0.79, respectively. The elevated concentrations in the pods and the molar ratio values suggest origins resulting from dry and wet deposition of both elements on the external surface of the pod due to proximity (~100 m to 3 km) to the ocean. The water table at the Ke'ehi Lagoon location (100–150 m from the ocean) is tidally influenced,⁴⁸ indicating that pongamia is to some degree salt tolerant.⁴⁹ Salinity measurements at nearby monitoring wells recorded salinity levels of 0.5%, a sevenfold dilution compared to seawater.⁴⁸

Sulfur concentrations in the seeds and pods at the five locations were determined by both LECO CHN628 sulfur module (Tables S1 and S2) and Bruker XRF (Tables S3 and S4), except for seeds from locations (4) and (5). The two measurement methods are in general agreement, with most of the differences falling within the levels of the reported measurement error for the pods. The LECO S values for the

seeds were consistently higher than the XRF values, and the differences ranged from 200 to 550 ppm, 1.7 to 9.4 times the value of the corresponding XRF measurement error.

Required plant micronutrients include Fe, Zn, Mn, Mo, Cu, and B. Fe was quantified in both the seed and pods at concentrations of 40–60 and 25–115 ppm, respectively. The higher concentrations of the pods may be due to soil dust deposited on their external surfaces. Zinc present at concentrations of ~30 ppm was measured in the seed samples but were below the LOQ or undetectable in the pods. Mn was only present above the LOQ in the Haleiwa pod material. Mo was detected in all pod samples but only locations (3) and (4) contained amounts greater than the LOQ. Copper was detected in all seed and pod samples but was only slightly (<3 ppm) above the LOQ in two samples. Boron was not detected in any of the samples.

Strontium (Sr) was detected in both seed and pod materials, in ranges from 19 to 61 and 30 to 170 ppm, respectively. Basalt lava, Asian dust, and rainfall (ocean derived) are the three main sources of Sr in Hawaii.⁵⁰ Although the origin of the Sr was not determined in these pongamia samples, Sr quantified in leaf

Table 3. Summary of Measured Properties of Pongamia Oil from Trees in Five Locations on Oahu and Commercial Canola Oil (Shown for Comparison)^a

properties	Bachman-ME	Bachman-CSE	Foster-CSE	Ke'ehi-CSE	Kunia-CSE	Haleiwa-CSE	canola oil
C wt %	77.2 ± 0.24	77.28 ± 0.20	77.24 ± 0.15	76.88 ± 0.19	76.31 ± 0.30	76.45 ± 0.14	77.37 ± 0.22
H wt %	11.4 ± 0.03	11.55 ± 0.05	11.78 ± 0.04	11.78 ± 0.10	11.78 ± 0.10	11.98 ± 0.01	12.41 ± 0.05
O wt %	11.2 ± 0.21	11.17 ± 0.24	10.97 ± 0.19	11.33 ± 0.21	11.91 ± 0.31	11.57 ± 0.15	10.13 ± 0.20
FFA %	0.92	0.63	2.67	0.57	0.71 ± 0.06	0.37 ± 0.02	0.10 ± 0.00
iodine value	93.9 ± 0.3	85.0 ± 0.5	72.94 ± 0.23	71.5 ± 1.2	51.8 ± 13.6	44.6 ± 1.2	114.4 ± 2.7
H/C	1.78	1.79	1.83	1.83	1.85	1.88	1.93
<i>T</i> _{onset} /°C	4.05	5.35	15.49	15.16	1.37 ± 0.25	6.88	−22.59
<i>T</i> _{peak} /°C	2.98	4.47	15.13	14.34	0.25 ± 0.63	4.7	−58.39
HHV MJ kg ^{−1}	35.18 ± 0.12	38.50 ± 0.09	38.93 ± 0.14	38.85 ± 0.00	38.20 ± 0.28	38.71 ± 0.32	39.31 ± 0.09

^a(1) Iodine value is the mean ± standard error for three analyses; (2) FFA values for Bachman, Foster, and Ke'ehi Lagoon and all oil flash point values are reported from a single measurement due to limited sample mass; the flash point standard error is the system analysis uncertainty, 2 °C; (3) *T*_{onset} and *T*_{peak} values are determined from a single analysis; and (4) the Kunia values are averages of seven sample batches.

tissue samples of *Metrosideros polymorpha*, an 'ōhi'a lehua tree endemic to Hawaii, was determined to be of soil origin.

These preliminary property analysis results indicate that *Milletia pinnata* seeds are a source of protein, and the pods have potential use as energy or byproduct feedstock. The seeds have a comparably high protein content, 17–21% (based on nitrogen content analysis and a Jones factor of 5.18 for seeds and nuts),⁴⁷ and the nitrogen concentration of the seeds and pods do not appear to be significantly affected by adverse growing conditions, as demonstrated at location (3).

As fuels considered for thermochemical energy conversion, the pods have desirably low sulfur and nitrogen contents. The elevated K and Cl concentrations, however, will require attention if pods are considered for combustion and gasification applications.^{51,52} Their concentrations in the fuels range from 1.3 to 2.6 kg (Na₂O + K₂O) GJ^{−1} and 0.13 to 0.7 kg Cl GJ^{−1}. Prior experience indicates that ash from fuels with values of >0.33 are almost certain to produce fouling and slagging without active management. Miles et al.⁵³ reported a K concentration of ~27,000 ppm in almond hulls and found K-enriched deposits accumulated on simulated boiler tubes under combustion conditions. More than 80% of the potassium and 100% of the chlorine present in almond hulls were water-soluble. Opportunities to improve fuel properties of pongamia pods that should be explored as post-harvest processing techniques are developed. Fuel additives, advanced reactor designs, and conversion system operating strategies can also contribute to controlling impacts.

3.2. Pongamia Oil. Table 2 lists the oil content of the seeds from locations (1)–(5) using the conventional solvent extraction (CSE) method. The seeds from location (3) were found to have the lowest oil content, which may result from its more severe growth condition.⁹ The seeds from the younger trees at locations (4) and (5) exhibited a higher oil content compared to the older trees at locations (1)–(3). Figure 7 shows the fatty acid composition of the pongamia seed oils (data and error estimates are presented in Table S5) along with that of canola, soybean,⁵⁴ jatropha,⁵⁴ and carinata oil.⁵⁵ The fatty acid profile of pongamia oil varies with location, but the major acid is oleic (C18:1) in all cases, 47.4–60.1 wt %. This is consistent with the 41.4 to 71.3% range of the C18:1 content in pongamia oil reported in the literature.^{13,16} The major difference between the profiles is the linoleic acid (C18:2) content. In location (1), its concentration is approximately 30–100% (relative) higher than that from other four locations. The fractions of unsaturated fatty acid present in oil from location (1), 82.61 and 82.09 from

the CSE and ME processes, respectively, are similar to the values obtained from locations (4) and (5) but approximately 5% (absolute) higher than that from locations (2) and (3).

The overall fatty acid profile of the pongamia oil is somewhat similar to canola and jatropha oils (Figure 7) for which the major fatty acid is also C18:1, 73.7, and 42.8 wt %, respectively, followed by C18:2, 11.8, and 35.4 wt %, respectively. The unsaturated acid fraction of pongamia oil (77.0–82.6 wt %) is closer to the values of soybean and jatropha oils, 83.57 and 78.48 wt %, respectively,⁵⁴ than to the canola oil, 92.85 wt %. *Brassica carinata*, a promising oil crop for the southeastern and northern United States, however, exhibits a significantly different fatty acid profile in comparison with soybean, jatropha, and pongamia,⁵⁵ and over 40% of the fatty acid profiles are heavy erucic acid (C22:1). Note that HEFA jet fuel typically contains C8 to C19 hydrocarbons.⁵⁶

The physicochemical properties of pongamia seed oil obtained from CSE and ME methods and commercial canola oil were measured; results are presented in Table 3. In general, the presence of free fatty acids (FFAs) in vegetable oils is associated with cells in the parent seed tissue damaged during the harvesting, storage, transportation, or initial processing. Up to 5% FFA may be found in crude vegetable oils.⁵⁷ The FFAs of the oils from all five locations were found to be of a normal level (i.e., <5%) and within the range reported by Gaurav and Sharma,¹⁶ 2.53–20%. It should be noted that the FFAs of oil from locations (1)–(3) were only measured once without repetition due to sample limitation. Seeds from location (1) were extracted using both ME and CSE processes, and oil from the former was found to have a slightly higher FFA content. This may result from the alcohol lamp used to heat the expeller during the ME process, as cell damage can occur under elevated temperature conditions,⁵⁷ or it may be due to a less effective extraction resulting in only partial recovery of oil components. The FFA of commercial canola oil is much lower, only 0.1%, in comparison with the pongamia oil obtained in this study (0.57–2.67%), as most of the FFAs in commercial canola oil have been removed in the refining process.⁵⁸ The HHVs of the pongamia oil obtained from the five locations are very similar and close to that of commercial canola oil. The iodine values of the oils extracted from locations (1)–(3) are all close to the literature reported range for pongamia oils, 85–110,^{59,60} and lower than that of canola oil, which is consistent with the fatty acid profile analysis results shown in Figure 7. The iodine values of oil from locations (4) and (5), however, are significantly lower than that from other three locations, even though their unsaturated fatty

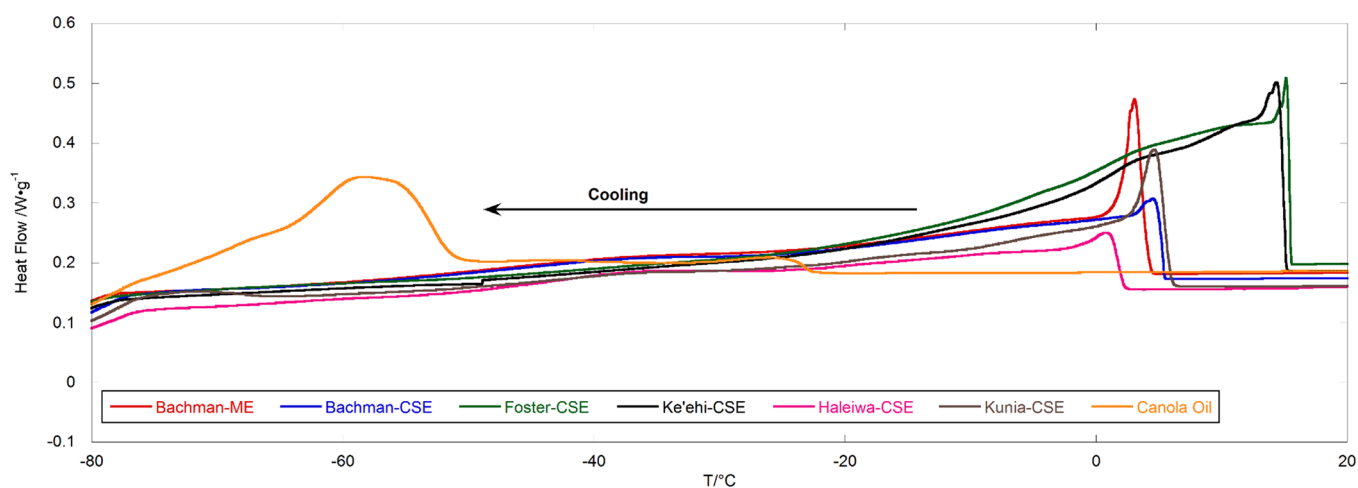


Figure 8. DSC cooling curve of pongamia oils: legend labels refer to locations in Figure 1; CSE and ME are conventional solvent and mechanical extraction, respectively.

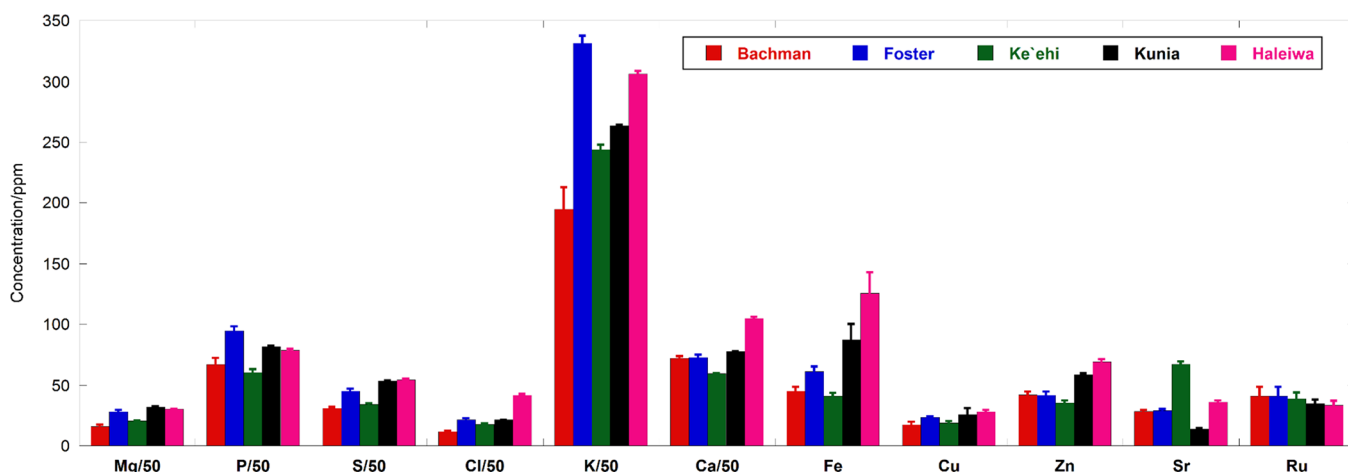


Figure 9. XRF elemental analysis results of de-oiled seed cake; legend labels refer to locations in Figure 1.

acid fraction is similar to that from location (1). The pongamia oil obtained from the ME process in location (1) was also subjected to flash point, kinematic viscosity, and density measurements. The flash point of the oil from location (1), 210 ± 2 °C, is within the range reported by Gaurav and Sharma,¹⁶ 205–270 °C, and much lower than that of canola oil, 315 ± 2 °C, whereas the kinematic viscosity ($46.764 \text{ mm}^2 \text{ s}^{-1}$ at 40 °C) and density (0.9415 g cm^{-3} at 15 °C), are slightly higher than the reported ranges, $27.84\text{--}38.2 \text{ mm}^2 \text{ s}^{-1}$ at 40 °C and $0.912\text{--}0.940 \text{ g cm}^{-3}$ at 15 °C, respectively.⁸

The ultimate analysis results of the pongamia oil obtained in this study and commercial canola oil are listed in Table 3. The nitrogen content of all the oil samples was not included, as the values were below the detection limit (<200 ppm based on the ~ 50 mg sample used for analysis, LECO CHN628 system N detection limit: 0.01 mg). The oxygen content was calculated by subtracting the carbon and hydrogen contents from 100. The carbon contents of the oil samples are tightly grouped, whereas canola oil possesses a slightly higher hydrogen content, which results in its slightly higher HHV (also shown in Figure 1) and H/C ratio.

The low-temperature properties of pongamia oil obtained from the five locations and two extraction methods were investigated using DSC, and the results were compared with

those for canola oil. Figure 8 presents the cooling scan of the oil samples. Oils with a higher degree of unsaturation usually have lower solid–liquid phase transition temperatures. The results confirm this, as the CSE pongamia oil from locations (1), (4), and (5) exhibited lower crystallization onset temperatures, 5.35, 1.37, and 6.88 °C, respectively, in comparison with that from locations (2) and (3), 15.79 and 15.16 °C, respectively, consistent with the fatty acid profile. Owing to its higher fraction of unsaturated fatty acids, the crystallization onset temperature of canola oil, -22.59 °C, is significantly lower than that of pongamia oils. As expected, the oils obtained from ME and CSE processes have similar low-temperature properties, i.e., the crystallization onset temperatures from location (1) are 4.05 and 5.35 °C, respectively.

3.3. De-oiled Pongamia Seed Cake. The characteristics of the de-oiled pongamia seed cakes obtained from CSE were determined and compared with that of a soybean cake.⁶¹ Similar to the seeds, the pongamia cake from locations (1)–(5) have a similar volatile matter, ash, and fixed carbon content (shown in Figure 1), and the results are consistent with literature values.⁶² The pongamia cake samples exhibited slightly higher ash and fixed carbon contents in comparison with the corresponding seed samples due to the removal of the volatile organic oil

fraction from the seeds. In addition, pongamia cake possesses a lower ash content than that of a soybean cake, 6.14 wt %.⁶¹

The ultimate analysis of the cake samples in Figure 4A shows that the soybean cake has a lower H/C ratio, 1.41,⁶¹ than the pongamia cakes (listed in Table 2) owing to the higher carbon content in soy meal. The soybean cake, however, exhibited a greater heat of combustion, 23.23 MJ/kg,⁶¹ than that of the pongamia cake (shown in Figure 3). The HHVs of pongamia cakes from location (3) are slightly higher than those from other four locations, although the HHVs of the seed from location (5) are the highest. Similar to the fixed carbon content obtained from proximate analysis in Figure 1, the pongamia cake samples were also found to have higher nitrogen (Figure 4B), sulfur (Figure 4C), and metal (i.e., Na, Mg, P, Cl, K, and Ca shown in Figure 9) contents in comparison with the corresponding seed samples (Figure 5), as the oil samples are mainly composed of hydrocarbons. The de-oiled seed cake exhibited enrichments in N and S compared to the parent seed, indicating that nitrogen and sulfur are retained in the seed cake during oil extraction. Thus, the seed cake may serve as a source of protein, 17–21% protein content (based on nitrogen content analysis and a Jones factor of 5.18 for seeds and nuts).⁴⁷

4. CONCLUSIONS

Seeds and pods collected from pongamia trees grown in five different locations on the island of Oahu in Hawaii were studied. The physicochemical properties of the seeds, pods, oils, and the de-oiled seed cakes were determined and compared with those from pongamia trees grown in South Asia and other oil plants. The oil content of pongamia seeds was found to range from 19 to 32.5% with younger trees producing higher oil concentrations. Although the fatty acid profiles of the extracted oils varied with collection location, oleic (C18:1) and linoleic (C18:2) acids were present in the highest concentrations in all samples. The qualities of the pongamia oil are similar to those of jatropha and canola oils in groups that also included soybean and carinata. The pongamia seed cakes after oil extraction were found to have a nitrogen content of ~5 to 6%, which may be used as a protein source. The pods contained high concentrations of potassium (~1 to 3%) coupled with elevated chorine contents and will require management to avoid deposition and fouling at temperatures typical of combustion and gasification conditions. Future research on pretreatment and thermochemical conversion of aged trees removed from production and residues derived from pongamia seed processing, such as pods and seed cakes, should be pursued.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c00635>.

LECO TGA801 System Program for Proximate Analysis; properties of pongamia seeds (Table S1); properties of pongamia pods (Table S2); summary of XRF results for pongamia seeds (Table S3); summary of XRF results for pongamia pods (Table S4); fatty acid composition of pongamia oil (Table S5); properties of pongamia cake obtained through conventional solvent extraction (Table S6); summary of XRF results for pongamia seed cakes (Table S7); properties of seven batches of pongamia seeds from location (4) (Table S8); properties of seven sample batches of pongamia pods from location (4)

(Table S9); summary of XRF Results for seven batches of pongamia pods and cakes from location (4) (Table S10); properties of pongamia oil obtained from seven batches from location (4) seed (Table S11); fatty acid composition of seven batches of pongamia oil from location (4) (Table S12); properties of seven batches of pongamia seed cake from location (4) (Table S13); schematic of sample preparation and oil extraction process (Figure S1); comparison of the proximate analysis results (Figure S2); and DSC of pongamia oil obtained from seven sample batches from location (3) (Figure S3) (PDF)

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Notes

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