Determination of the potential of *Albizia lebbeck* and *Albizia saman* as biodiesel feedstock

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Abstract. Sustainability of supply, biodegradability and non-toxicity are three of the most important criteria being considered in the selection of the most appropriate alternative to fossil fuels to ensure the reduction of CO_2 emission in the atmosphere. Biodiesel, defined as a mono-alkyl esters that comes from of vegetable oils, animal fats or other related materials and composed largely of triglycerols is by far the most promising among the identified alternative for non-renewable fossil fuels. This piece of work aims to contribute to the body of known information about the list of potential biodiesel feedstock by profiling the fatty acid contents of two (2) leguminous tree species widely distributed in the Philippines.

Seeds of *A. lebbeck* and *A. saman* were collected from Mt. Makiling, UP Los Banos and UP Diliman grounds, respectively. Although the two species are related, it was evident that they vary in seed production with *A. saman* being more prolific and with available seeds all year round hence much easier to collect as compared to *A. lebbeck.*

Fatty acid profiling using Gas Chromatography-Mass Spectrometry (GC-MS) revealed that the most prominent fatty acid common to both species is linoleic acid followed by palmitic and oleic acids for *A. lebbeck* and *A. saman*, respectively. This indicates that the two species are similar in unsaturated fatty acid content but not with the saturated fats present. With regards to its oil content, initial weighing of seeds prior to extraction revealed that *A. lebbeck* contains only 1% of oil while *A. saman* produced only about 5.2% rendering them both not a good candidate as biodiesel feedstock. In addition, the two species also contain considerable amount of cyclic fatty acids most notably coronaric acid (2-4%), vernolic acid and 9,10-epoxy-octadecanoic acid, which are classified as leukotoxins among humans, hence, it can seriously affect health once ingested.

Key Words: biodiesel, fatty acid profile, methyl ester, coronaric acid, leukotoxins

1. INTRODUCTION

The demand for alternative source of fuel for transportation is undoubtedly one of the critical issues of the present era. The continuous increase in human population has led to serious demands for a more sustainable source of materials to run major transportation system in a global scale. In the last 20 years or so, numerous efforts have already been done to identify possible alternatives to petroleum fuels however, only biodiesel satisfied the minimum requirements such as non-toxicity, superior lubricity and biodegradability (Razon, 2009). Defined as the mono-alkyl esters of vegetable oils, animal fats or other triacylglycerol containing materials, biodiesel is derived from a variety of feedstocks mostly coming from both animal and plant species (Knothe, 2013). But inspite of the promising features, biodiesel was not successfully legislated due to the unresolved issue on plant use either as food vs. biodiesel. As such, some commodity crops that contain considerably high amount of oil cannot be recommended as alternative feedstock like olive oil and avocado (Knothe, 2013). This situation therefore implied that the search is not yet over for the most feasible alternative crop as biodiesel feedstock.

Realizing the need to look for more appropriate alternative, this piece of work aims to contribute the current list of potential feedstock by determining the oil content of two species of *Albizia* widely distributed in the Philippines. A member of the Fabaceae (formerly *Leguminosae*) family of plants and the *Mimosaceae* subfamily, *Albizia* comprises about 150 species, mainly shrubs and trees (Prinsen, 1986). *Albizia lebbeck* (L.), popularly known as Indian siris is a medium to large tree, of multi-stemmed and may exhibit widespread canopy when grown in the open reaching 30 meters in diameter. Height can reach a maximum of 20 meters with rough bark and with flat oblong pods (120-350 mm x 30-60 mm) that is stiff-papery when ripe producing 3-12 seeds per pod. In terms of distribution, although it originates in Indian continent, it spreads throughout Southeast Asia particularly in areas with marked dry season. This species is mainly use as fodder crop with its foliage of high quality for animal nutrition.

As nitrogen-fixers, *A. lebbeck* can also increase soil fertility which will favor the growth of its neighboring species (Prinsen, 1986). The extensive, shallow root system also makes it a good soil binder and suited to soil conservation and erosion control (Lowry *et al.*, 2007). Matured individuals can also withstand grass fire of considerable intensity. Seed production is not a major problem since *A. lebbeck* can produce seed annually. As with many legumes, there is no need to wait until pods are dry to harvest seed. Pods are mature when they have turned light yellow and should be harvested when the last patches of green are disappearing (Larbi, *et al.* 1996).

Albizia saman, on the hand, is a large tropical tree capable of producing a wide canopy hence, it is always recommended for landscaping activities. The evergreen leaves are alternate, bipinnate, 25–40 cm long, with 2–6 pairs of pinnae, each of which bears 6–16 paired stalkless leaflets, with a glandular dot between each pair (National Tropical Botanical Garden website). *A. saman* is also known by other names including raintree, due to its folding of leaves during rainfall, and monkeypod (Ishimaru, 2012). And like most other trees from the Mimosaceae (Fabaceae) family, this is an important honey plant, producing sweet substance that attracts several insects.

Fatty acid content of *A. lebbeck* has already been reported in several studies but there seems to be inconsistencies in the average amount probably due to the difference in the geographical location of the seed source (Knothe, 2014).Hence, this study aimed to shed a new light to the issue. In addition, the present work was the first report on the presence of epoxy or other cyclic moieties particularly coronaric acid in *A. lebbeck* and *A. saman* species, which was originally detected among representatives of Asteraceae (Compositae) family.

Besides epoxy fatty acids, other fatty acids with cyclic moieties are those containing cyclopropene and cyclopropane rings, most notably malvalic (8,9-methylene-8-heptadecenoic), sterculic (9,10-methylene-9-octadecenoic) and dihydrosterculic (9,10-methylene octadecanoic) acids. For species of the *Malvaceae* family, seed oils have often been shown to exhibit the “biogenetic oddity” of containing both cyclopropene and epoxy fatty acids (Wilson *et al.* 1969). It is possible that similar to a previous work done with *Acacia Arabica*, cyclopropene fatty acid might also be available among *Albizia* species.

Although the primary goal of this work is to produce an updated fatty acid profile of the two *Albizia* species, a novel discovery on the presence of coronaric acid was likewise generated and established.

2. METHODOLOGY

Collection of specimen

Albizia lebbeck and *Albizia saman* are both tropical tree species that can be found anywhere in the Philippines. However, the latter is more common as it is usually used as landscape material due to its shading effect.

Seeds of *A. lebbeck* were collected inside University of the Philippines Los Baños in the month of January during most of the pods are already matured while that of *A. saman* were obtained from pods fallen on the grounds of University of the Philippines in Diliman, Quezon City, Philippines. Collection of *A. lebbeck* wasproven to be more challenging than that of *A. saman* since the sampled trees were located along the creek hence fallen pods goes with the water. As for the few pods collection, high level of insect infestation were evident by the presence of the holes in the different parts of the seeds, hence resulting in a small amount of seeds collected.

Fatty acid profiling

Seeds were first washed to remove all the debris present afterwhich it was airdried. It was proven that the seeds contain less than 1% (*A. lebbeck*) and approximately 5.2% (*A. saman*) oil as determined by weighing the seeds prior to and after extraction. Seeds were then grinded in a coffee grinder and extracted with hexane in a Soxhlet extractor for 6 h (*A. lebbeck*) or 24 h (*A. saman*). After their transesterification to fatty acid methyl esters (FAMEs), the fatty acid profile of the oils was analyzed utilizing a Perkin-Elmer (Norwalk, CT, USA) Clarus 580 gas chromatograph equipped with a flame ionization detector and an HP-88 ((88% cyanopropyl) methylarylpolysiloxane) column (30 m x 0.25 mm ID x 0.20 µm film thickness) from Agilent Technologies (Santa Clara, CA, USA). The temperature program was an initial temperature of 100°C held for 15 min, increased to 210°C at 2°C/min then 50°C /min to 220°C held for 25 min with H_2 as carrier gas at 9.6 mL/min. The injector and detector temperatures were 240°C and 280°C, respectively. Gas chromatography-mass spectrometry was carried out under the same conditions and using the same type of column with an Agilent 6890N gas chromatograph and 5973N mass selective detector in electron ionization mode. Retention times were verified against authentic samples of individual pure FAMEs.

3. RESULTS AND DISCUSSION

Results of the fatty acid profiling reveals that the most prominent fatty acid in the two *Albizia* species investigated here is linoleic acid (Table 1). However, in *A. lebbeck*, the second most prominent fatty acid is palmitic (hexadecanoic) acid followed by oleic acid while in *A. saman*, the second most prominent fatty acid is oleic acid followed by docosanoic (behenic) acid. Thus, the two *Albizia* species studied here largely have similar amounts of unsaturated fatty acids but most notably differ in the amounts of saturated fatty acids.

The range of saturated fatty acids in *A. lebbeck* is greater than that of *A. saman*, beginning at C14. Both seed oils contain trace amounts of saturated long-chain fatty acids up to C26 (Table 1). To the best of our knowledge, this is the first report on the presence of cyclic fatty acids present among *Albizia* species. In particular, considerable amount of coronaric acid was detected in both *Albizia* seed oils investigated. Besides coronaric acid, minor amounts of vernolic acid and 9,10-epoxy-octadecanoic acid were observed with methyl vernolate eluting just before methyl coronarate.

Other components. Minor amounts of additional oxygenated fatty acids may be present in the seed oil of *A. saman* as two minor peaks with methyl ester retention times beyond those of methyl coronarate were observed (apparent M^+ at *m/z* 310) but no definitive structures are assigned. Epoxy fatty acids appear to be the only (or by far the most common) fatty acids with cyclic moieties in *Albizia* species based on the results of this study.

Potential biodiesel properties. To the best of our knowledge, no report yet exists on the production and properties of biodiesel (as FAMEs) from any *Albizia* species. Due to the low oil content of the seeds, this implied that *Albizia* seed oils a less attractive source of biodiesel. The results further implied that the biodiesel from the seed oils of both *Albizia* species would likely possess poor cold flow properties. In the case of *A. lebbeck*, the high content of methyl palmitate (melting point 28.5°C) together with methyl stearate (melting point 37.7°C) and lesser amounts of methyl eicosanoate (m.p. 46.4°C) and methyl docosanoate (m.p. 53.2°C), totaling more than 30% saturated fatty acids could possibly cause a cloud point well over 10°C, if not above 15°C.

On the other hand, the saturated esters in biodiesel from *Albizia* species would also likely account for high cetane numbers exceeding 60 (Knother, 2014).

Finally, with regards to lubricity, it proved to be not a problem since the oil can be classified neat biodiesel and thus it can be assumed that it would not be an issue with biodiesel produced from *Albizia* seed oils (Knothe, 2014).

4. CONCLUSION

The fatty acid profiles of *Albizia lebbeck* and *Albizia saman* (monkeypod) seed oils were determined. While linoleic and oleic acids are the most prominent fatty acids in these oils, they also contain significant amounts of saturated fatty acids.

Coronaric acid in the range of 2-4% of the fatty acid profiles was detected, accompanied by minor amounts of vernolic and 9,10-epoxyoctadecanoic acids which are reported for the first time in *Albizia* species, as well as minor amounts of saturated odd-numbered fatty acids. With coronaric acid now identified in *Albizia* species besides *Acacia* species, the presence of this acid (and other epoxy fatty acids in minor amounts) may be a distinguishing feature of the seed oils of plants of the *Fabaceae* family.

5. ACKNOWLEDGEMENT

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Table 1. Fatty acid profiles of *Albizia lebbeck* and *Albizia saman* seed oil investigated in the present work. Fatty acids given in order of elution as methyl esters.

Fatty acid	***Albizia lebbeck***	***Albizia saman***
14:0	0.5	---
15:0	0.2	---
16:0	22.9	4.8
16:1 Δ9	2.2	0.2
17:0	0.2	tr
17:1 Δ9	0.1	tr
18:0	7.0	5.3
18:1 Δ9	15.7	15.9
18:1 Δ11	1.6	1.5

18:2 Δ9,Δ12	31.8	41
18:3 Δ9,Δ12,Δ15	1.9	tr
20:0	4.0	6.3
20:1 Δ9	0.8	0.5
20:1 Δ11	0.4	1.1
21:0	0.3	0.1
22:0	3.5	13.6
23:0	0.2	0.3
24:0	0.5	2.3
9,10-Epoxystearate	0.3	0.6
Vernolic	0..2	0.4
25:0		tr
Coronaric	2.3	3.6
26:0	0.1	tr
Other [a)]		

a) tr = trace (fatty acids present in amounts < 0.1%).

b) Includes the fatty acids whos