Extraction of *Calophyllum* oil as biodiesel raw material using a binary solvent

I Sailah¹, O T O Bernia¹ and I A Kartika¹,²

¹Department of Agroindustrial Technology, IPB University (Bogor Agricultural University), Dramaga Campus P.O. Box 220, Bogor 16680, Indonesia
²Surfactant and Bioenergy Research Center (SBRC), Bogor, Indonesia

E-mail: ikaamalia@ipb.ac.id

Abstract. The utilization of renewable raw material, low-cost feedstock, and efficient energy are the main parameters in sustainable biodiesel production. *Calophyllum* seeds are potential as a vegetable oil source for biodiesel production due to their high oil content and productivity. *Calophyllum* oil extraction is usually conducted by the mechanical press, but the yield and quality of oil produced by this method are very low. *Calophyllum* oil extraction using a binary solvent (a mixture of n-hexane and alcohol) was thus investigated to meet the aspects of sustainability and to solve the problem of mechanical extraction. The influence of extraction condition was examined to determine optimal oil yield and quality. The mixture of n-hexane and alcohol effectively extracts oil from *Calophyllum* seeds and simultaneously purified it from resin. The n-Hexane-to-alcohol ratio had a significant effect on oil recovery and its quality. The augmentation of the n-hexane-to-alcohol ratio from 1:1 to 2.5:1 increased oil yield. Acid value and density of oil improved as the n-hexane-to-alcohol ratio declined from 2.5:1 to 1:1. The n-Hexane-to-alcohol ratio of 2.5:1 has provided the best yield (88.0%) of oil extract at 40°C for 5 h. The oil present its best quality at 0.893 g/cm³ of density, 41.0 mPa.s of viscosity, 8.8 mg KOH/g of acid value, 88.3 g/100 g of iodine value, < 1% of moisture content and < 0.04% of ash content.

1. Introduction

In Indonesia, *Calophyllum inophyllum* plant has been extensively exploited for shipbuilding, fabrication of furniture, as a windbreaker, abrasion reduction, protection of coastal demarcation [1], and as a second-generation feedstock for biodiesel [2,3]. *Calophyllum* seeds are prospective for biodiesel raw material due to their high oil content (> 50%) compared to jatropha (< 40%) [4,5]. In addition, the oil extracted from *Calophyllum* seeds has antioxidant properties [6].

*Calophyllum* oil extraction is usually carried out mechanically using a screw press [7]. The quality of oil extract is very poor, as well as the yield. The oil is very viscous (> 90 mPa.s) and very acidic (> 45 mg KOH/g) because of its high resin content. Moreover, the acidic is difficult to remove from oil.
by using filtration. On the other hand, the solvent extraction of *Calophyllum* oil using *n*-hexane can result in better quality and yield up to 50% [8,9].

For the use of *Calophyllum* oil as a biodiesel feedstock, the resin, as well as free fatty acids must be removed from the oil by degumming and neutralization [10]. This oil refining, unfortunately, loses a lot of neutral oil (> 30%), and the consumption of water and chemicals is wasteful. On the other hand, the use of a mixture of *n*-hexane and methanol (3:1 v/v) for *Calophyllum* oil refining has succeeded in removing a large amount of resin from oil, and neutral oil loss was very low (< 2%) [11].

Based on these problems *Calophyllum* oil extraction using a binary solvent (a mixture of *n*-hexane and alcohol) was thus investigated to meet the aspects of sustainability and to solve the problem of mechanical extraction. The influence of extraction condition was examined to determine optimal oil yield and quality.

2. Materials and Methods

2.1. Materials

In this study, the Forest Research and Development Center (KHDTK Carita, Indonesia) supplied *Calophyllum* seeds, and BRATACO Chemical Ltd. (Indonesia) provided *n*-hexane, methanol, and ethanol. Merck and Sigma-Aldrich (Indonesia) supplied all chemicals and solvents in pure analytical grades.

2.2. Experimental

*Calophyllum* seeds with a moisture content of 2.43±0.40% and oil content of 66.16±5.39% were used in this study (Figure 1). 100 mL of alcohol and 100 g of seed were mixed and subsequently milled using an electric blender for 5 min. *n*-Hexane of 350-500 mL and 100-250 mL of extra alcohol, corresponding to 1:1-2.5:1 of *n*-hexane to total alcohol ratio (v/v), were then put into the mixture of seed and alcohol. The extraction was completed in a three-necked flask of 2000 mL equipped with a hot plate magnetic stirrer and a reflux system (Figure 2). Stirring speed, extraction temperature and time were set constant at 800 rpm, 40°C and 5 h, respectively.

![Figure 1. *Calophyllum* seeds used in oil extraction using a binary solvent](image)
After oil extraction was complete, the mixture was then cooled to ambient temperature. It was subsequently filtered using a vacuum filter to obtain a cake-free filtrate. The filtrate was left all night, and this allowed it to separate into two layers. The upper layer comprised of \( n \)-hexane and oil whereas the lower one constituted of alcohol and impurities (particularly resin). Oil and resin fractions were evaporated using a rotary evaporator to recuperate \( n \)-hexane and alcohol. The obtained oil and resin were then dried at 105 °C for 1 h. The dried oil and resin were weighed, and the oil yield and separated resin percentage were then calculated:

\[
\text{Oil yield(\%)} = \frac{\text{Mass of oil after drying (g)}}{\text{Mass of oil contained in seeds (g)}} \times 100
\]

\[
\text{Separated resin percentage(\%)} = \frac{\text{Mass of resin after drying (g)}}{\text{Mass of oil and resin after drying (g)}} \times 100
\]

All experiments were carried out in two replications. The effect of alcohol type and \( n \)-hexane to alcohol ratio on oil yield and its quality was examined using an experimental design of randomized factorial and an analysis of variance (ANOVA, \( F \)-test at \( p = 0.05 \)).

\[\text{Figure 2. Oil extraction of Calophyllum seeds using a binary solvent}\]

2.3. Analytical methods

The determination of moisture and oil contents of Calophyllum seeds was respectively conducted by the French standard of NF V 03-903 and NF V 03-908. The oil quality was examined by the analysis
3. Results and Discussion

Solvent extraction from oilseeds aims mainly to recuperate the triglycerides, and \( n \)-hexane is an effective solvent to retrieve them from various oilseeds. In solvent extraction of *Calophyllum* oil, the impurities such as resin are also extracted together with oil. For its application as biodiesel raw material, the oil must be free from these impurities because their presence will increase oil viscosity and acidity.

The resin extracted from *Calophyllum* seeds dissolves completely in alcohol [12]. On the other hand, triglycerides are completely soluble in \( n \)-hexane. This difference in solubility between triglycerides and resin can facilitate the separation of the resin from oil. A binary solvent consisting of \( n \)-hexane and alcohol may be a reasonable solution to recover triglycerides and to remove resin directly from them after oil extraction only with a decantation extra step because these two solvents are insoluble one another.

In this study, the ratio of \( n \)-hexane and alcohol added to *Calophyllum* seeds were various from 1:1 to 2.5:1 (volume/weight, expressed in mL/g) for all experiments, and the randomized factorial experimental design was conducted to comprehensively investigate the influence of alcohol type and \( n \)-hexane to alcohol ratio on oil yield and its quality. An enhancement in the ratio of \( n \)-hexane added to seeds will improve triglycerides extraction whereas an augmentation in the ratio of alcohol added to seeds will incline resin separation. Figure 3 showed that the oil yield improved as \( n \)-hexane to alcohol ratio increased from 1:1 to 2.5:1, and vice versa the separated resin percentage enhanced as \( n \)-hexane to alcohol ratio decreased from 2.5:1 to 1:1. The higher the \( n \)-hexane content, the more the oil yield; the higher the alcohol content, the more the separated resin. This phenomenon was observed for both alcohol types tested, i.e. methanol and ethanol. The results of variance analysis (\( F \)-test at \( p = 0.05 \)) showed that the \( n \)-hexane to alcohol ratio had more effect on oil yield than alcohol type (Table 1), meaning that methanol and ethanol had the same effectiveness to extract the oil from *Calophyllum* seeds. Both operating conditions significantly affect the separated resin percentage, and methanol was more effective to remove resin from the oil than ethanol as observed by Anggraini *et al* [11]. Due to its good polarity, the resin can be perfectly dissolved in methanol and ethanol.
**Figure 3.** Yield and separated resin percentage of oil extract (mean±SE, n=2) at different operating conditions (A1: alcohol type of ethanol, A2: alcohol type of methanol, B1: \( n \)-hexane to alcohol ratio of 1:1, B2: \( n \)-hexane to alcohol ratio of 1.3:1, B3: \( n \)-hexane to alcohol ratio of 1.8:1, B4: \( n \)-hexane to alcohol ratio of 2:1, B5: \( n \)-hexane to alcohol ratio of 2.5:1)

**Table 1.** \( F \) value obtained from the analysis of variance for *Calophyllum* oil yield and its quality

| Source of variation              | \( F \) value for oil yield | \( F \) value for separated resin percentage | \( F \) value for density | \( F \) value for viscosity | \( F \) value for iodine value | \( F \) value for acid value | \( F \) value at \( p = 0.05 \) |
|----------------------------------|-------------------------------|---------------------------------------------|---------------------------|----------------------------|-------------------------------|----------------------------|-----------------------------|
| Alcohol type (A)                 | 4.32                         | 6.94*                                       | 8.05*                     | 6.66*                      | 0.26                          | 28.38*                     | 5.32                        |
| \( n \)-Hexane to alcohol ratio (B) | 77.87*                      | 28.71*                                     | 18.69*                    | 1.11                       | 1.93                          | 15.84*                     | 4.07                        |
| Interaction of \( AB \)          | 11.00*                       | 1.21                                        | 0.55                      | 0.29                       | 1.19                          | 1.22                       | 4.07                        |

*Significant.

The best oil yield of 87.04\% and 88.02\% were respectively obtained with methanol and ethanol at 2.5:1 of \( n \)-hexane to alcohol ratio, 40°C for 5 h of extraction time. At this process condition, the separated resin percentage was 11.89\% for methanol and 10.72\% for ethanol, and oil had thus a clear yellow color. For comparison, the best oil yield notified in previous studies [9,13] was comparable (80-90\%), but it was obtained under longer extraction time (16-48 h versus 5 h), higher \( n \)-hexane to alcohol ratio (3:0 versus 2.5:1), and oil had a greenish-yellow color due to its resin content. On the
other hand, compared with oil extraction using screw press [7], the oil yield obtained from this study was superior (87-88% versus 38%) even though its extraction temperature was lower (40°C versus 45°C) and its seeds moisture content was higher (2.43% versus 1.7%). This showed that the oil extraction from *Calophyllum* seeds using the solvent was more efficacious than the mechanical press, as described in earlier studies [9,13]. Moreover, the application of lower temperature and shorter time in oil extraction from *Calophyllum* seeds using this binary solvent should reduce the cost production of this process, and it should support the aspects of sustainable biodiesel production, i.e. low-cost feedstock, efficient energy and renewable raw material.

For each extraction condition tested, the extracted oil was quite good in quality. The density (0.893-0.900 g/cm$^3$), viscosity (41.0-52.1 mPa.s), acid (less than 22 mg KOH/g) and iodine values (85-89 g iodine/100 g) were acceptable. Besides, it had very poor moisture (less than 1%) and ash (less than 0.04%) contents. The oil obtained in this study was of superior quality than that obtained in a precedent study [8]. It had a lower acid value (less than 20 mg KOH/g versus 24 mg KOH/g), a lower density (less than 0.90 g/cm$^3$ versus 0.94 g/cm$^3$) and a lower viscosity (≤ 52 mPa.s versus ≥ 56 mPa.s). It was also of better quality than the oil produced by mechanical pressing [7,10], with an acid value < 20 mg KOH/g versus > 48 mg KOH/g, a density ≤ 0.900 g/cm$^3$ versus ≥ 0.904 g/cm$^3$, a viscosity ≤ 52 mPa.s versus ≥ 94 mPa.s, an iodine value ≤ 89 g iodine/100 g versus > 90 g iodine/100 g, and an ash content < 0.04% versus 0.26-0.31%. Furthermore, its quality was comparable to the oil refined by degumming and neutralization, especially for density, iodine value and ash content, and for viscosity, it was better. The impurities (resin and free fatty acids in particular) content of oil extracted in this study was, therefore, lower, and its utilization as a biodiesel feedstock will be more favorable. This is supported by the appropriate properties of *Calophyllum* oil a biodiesel source, i.e. high calorific value (9392 cal/g), low cloud point (13°C), high flash point (234°C), low water and sediment content (< 0.05%), low phosphor content (0 mg/kg), low sulfated ash content (< 0.014%) and low sulfur content (< 0.03%) [10]. In addition, the coumarins and xanthones contents in *Calophyllum* oil demonstrated antioxidant properties to protect the oil oxidation [14]. Furthermore, *Calophyllum* oil composed of saturated (31.4%) and unsaturated (68.6%) fatty acids [5], and these fatty acids composition was favorable in biodiesel production, especially associated with flow properties of biodiesel [2].
Figure 4. Acid value of oil extracted (mean±SE, n=2) at different operating conditions (A1: alcohol type of ethanol, A2: alcohol type of methanol, B1: n-hexane to alcohol ratio of 1:1, B2: n-hexane to alcohol ratio of 1.3:1, B3: n-hexane to alcohol ratio of 1.8:1, B4: n-hexane to alcohol ratio of 2:1, B5: n-hexane to alcohol ratio of 2.5:1)

Figure 5. Density of oil extracted (mean±SE, n=2) at different operating conditions (A1: alcohol type of ethanol, A2: alcohol type of methanol, B1: n-hexane to alcohol ratio of 1:1, B2: n-hexane to alcohol
ratio of 1.3:1, B3: n-hexane to alcohol ratio of 1.8:1, B4: n-hexane to alcohol ratio of 2:1, B5: n-hexane to alcohol ratio of 2.5:1)

![Figure 6. Viscosity of oil extracted (mean±SE, n=2) at different operating conditions (A1: alcohol type of ethanol, A2: alcohol type of methanol, B1: n-hexane to alcohol ratio of 1:1, B2: n-hexane to alcohol ratio of 1.3:1, B3: n-hexane to alcohol ratio of 1.8:1, B4: n-hexane to alcohol ratio of 2:1, B5: n-hexane to alcohol ratio of 2.5:1)](image)

The application of variance analysis (F-test at p = 0.05) on the oil quality data showed that the effect of extraction conditions on oil quality, especially density, viscosity and acid value, was significant (Table 1). An increase in both acid values (from 13.3 to 21.9 mg KOH/g for ethanol and from 8.8 to 16.5 mg KOH/g for methanol) (Figure 4) and density (from 0.894 to 0.900 g/cm³ for ethanol and from 0.893 to 0.898 g/cm³ for methanol) (Figure 5) were observed when n-hexane to alcohol ratio increased from 1:1 to 2.5:1. The acid value and density of oil extracted by n-hexane and ethanol mixture were higher than those extracted by n-hexane and methanol mixture. This confirmed that the impurities content (i.e. resin and free fatty acids) of the oil extracted by n-hexane and ethanol mixture was higher than that extracted by n-hexane and methanol mixture because methanol could remove resin from oil better than ethanol (Figure 3). With regard to oil viscosity, its value was significantly affected only by alcohol type. Oil extracted by n-hexane and ethanol mixture had a higher viscosity than that extracted by n-hexane and methanol mixture (Figure 6). Again this proof that the impurities content (particularly resin) of oil extracted by n-hexane and ethanol mixture was higher than that extracted by n-hexane and methanol mixture. Furthermore, the extraction conditions had no effect...
on iodine value, moisture and ash content. Indeed, they remained relatively stable as the n-hexane to alcohol ratio increased for each alcohol type tested.

4. Conclusions

A binary solvent has successfully extracted oil from Calophyllum inophyllum seeds and it has directly removed resin from oil. The influence of n-hexane to alcohol ratio was most significant on oil yield and its quality, and enhancement of n-hexane to alcohol ratio inclined the oil yield and its quality. The best oil yield of 88.0% and 87.0% were respectively obtained with ethanol and methanol at an n-hexane to alcohol ratio of 2.5:1, 40°C for 5 h. The oil quality was comparable to the oil refined by degumming and neutralization, so its utilization as a biodiesel feedstock is very favorable.

Acknowledgments

The authors gratefully acknowledge the funding from the KEMENRISTEKDIKTI Republic of Indonesia through National Competitive Grant (Applied Research) with contract no. 4297/IT3.L1/PN/2019.

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