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A first report on biodiesel production from *Aglaia korthalsii* seed oil using waste marine barnacle as a solid catalyst

Intan Shafinaz Abd Manaf[a], Mohd Hasbi Ab. Rahim[a,b], Natanamurugaraj Govindan[a], Gaanty Pragas Maniam[a,b,c,*]

[a] *Faculty of Industrial Sciences & Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia*
[b] *Earth Resources & Sustainability Centre, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia*
[c] *Central Laboratory, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia*

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ABSTRACT

Feedstock cost is one of the main considerations in biodiesel production and researchers intensively searching for a low cost feedstock in order to make the process viable. This study reports the use of *Aglaia korthalsii* seed oil as a potential feedstock for biodiesel production using waste marine barnacle as a solid catalyst. *A. korthalsii* with oil content of 16.2 ± 0.18 wt.% was subjected to transesterification using barnacle (a source of CaO) as a solid base catalyst. The catalyst was characterized using TGA, XRD and FESEM; upon calcination $CaCO_3$ turned into CaO, the species that catalyze the transesterification reaction. Parametric optimization under Central Composite Design revealed that the optimal reaction conditions are as follow: 12.2:1 MeOH:oil molar ratio and 4.7 wt.% catalyst at 65 °C, 3 h reaction duration, under which *A. korthalsii* oil was successfully converted into methyl ester (ME) with highest conversion of 97.12 ± 0.49%. The catalyst could be reused for four times, maintaining methyl ester content at 95.83% and the product meets the key specifications for biodiesel.

1. Introduction

Need to act now, if intend to counter the current deteriorating state of the environment. As diesel engines stand at one-third of the entire US transportation, EPA regulates the amount of sulfur in diesel fuel as the sulfur content is directly linked to the amount of pollution produced (United States Environmental Protection Energy (EPA), 2018). Feedstock cost is one of the main factors in dictating the biodiesel production cost. Continuous and extensive efforts are being taken to set the feedstock cost as minimal as possible (Kamel et al., 2018; Alves et al., 2016; Embong et al., 2016; Maniam et al., 2013). Numerous reports on the utilization of plant-based oil in the production of biodiesel have been reported (Silitonga et al., 2017; Damanik et al., 2017; Kusumo et al., 2017; Silitonga et al., 2016). Biofuel feedstock is exclusive as compared to other renewable sources in its ability to produce solid, liquid and gaseous fuels (Igathinathane and Sanderson, 2018). Developing non-food feedstock for renewable energy, that can be cultivated in non-cropped marginal and waste lands, is the current focus in maintaining the food security (Xiong et al., 2018). There are few fundamental aspects to be considered before claiming a process to be sustainable or otherwise. As to sustain the biodiesel production, serious attention must be given to the concept of biorefinery, in which multiple high-value coproducts can be produced along with biodiesel. Depending only on biodiesel market will not promise the industry's viability for a longer term; instead integrating current plant design into a number of biorefineries that allows the production of value-added products will ensure the market competitiveness (Monteiro et al., 2018; Gutierrez et al., 2017; Budzianowski, 2017). For instance, glycerol, a co-product from biodiesel industry, is used to prepare monoacetin, in turn producing solketalacetin (a green fuel additive) upon reacting with acetone (Ghaziaskar and Gorji, 2018). Alternatively, glycerol can be a starting material for glycerol carbonate synthesis (Zuhaimi et al., 2015) and many more. Such initiatives readily create demand for glycerol; hence, become a driving force for the viability of biodiesel industry.

Another aspect is the life cycle assessment (LCA) from which an overall profile of cost, energy and waste of a particular process is derived. Conventional LCA usually found to be, for a certain extent, inaccurate, uncertain and arbitrary. As to understand the overall impact on environment, LCA that is equipped with new approaches, beyond the conventional models, is crucial (Rosen, 2018; Yang, 2017). Additionally, emergy evaluation is necessary too, to study the synergies between industry and nature and their impact on surroundings. Emergy

* Corresponding author at: Faculty of Industrial Sciences & Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300, Gambang, Kuantan, Pahang, Malaysia.

E-mail address: gaanty@ump.edu.my (G.P. Maniam).

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evaluation is essential to provide key information on various ecosystem services. Studies proved that biodiesel industry performing well in term of air quality but improvements needed for carbon sequestration and water provisioning services. Nevertheless, continuous efforts have been taken to cater those shortfalls, for instance by utilizing treated wetland water for manufacturing purposes (Saladini et al., 2018). The other important concerns pertaining to biodiesel in fueling diesel engines are the engine performance and the exhaust emissions. Most of the documented data on engine function and emission are under the steady-state conditions rather than the actual conditions. As such, test on real-world conditions is necessary for much realistic data (Rajaeifar et al., 2017).

Renewable energy initiatives need various feedstock distributed across the landscape locally as well as regionally. Preferably, bioenergy crop production should not compromise environment quality but rather enrich ecosystem services such as nutrient cycling, carbon storage and wildlife habitation and pollinators (Igathinathane and Sanderson, 2018). European Union Directive underlined that biofuels must be produced in a sustainable manner by utilizing sustainable feedstock (such as lignocellulose, non-edible crops, urban waste and algae) and creating benefits to local communities in term of job creation, food availability, preserve biodiversity and the quality of water and soils; in addition to lesser waste generation (European Union, 2009).

In a broad sense, oil from non-food crop source is preferred for biofuel production, accordingly *A. korthalsii* was utilized in this work. *Aglaia* is one of the leading genus, subtropical and tropical angiosperm families *Meliaceae* (mahogany family, order *Sapindales*) and mainly found in many tropical countries (Pannell, 1992). The habitats usually live at forests, peat swamp riverine, on clay, sandstone, limestone and loam. The seeds are 1–1.5 cm wide and 1.5–2 cm long (Floral Malesiana, 2017). On the other hand, catalysts from waste sources, especially from the shells (source of calcium oxide) have advantages in the aspect of supply, ease of product-coproduct separation, reusable, less corrosive, cost effective and environmental friendly. In addition, heterogeneous catalysts are recoverable as such generation of large volume of wastewater is greatly reduced, hence, minimizing the energy requirement and treatment cost. To the best of our knowledge, there is no previous report on *A. korthalsii* seed oil as a feedstock for biodiesel production. This study reports the use of *A. korthalsii* seed oil as a potential feedstock catalyzed by waste marine barnacles for biodiesel production.

2. Methods

2.1. Materials

The *A. korthalsii* seeds were collected from Kelantan, Malaysia. Waste marine shells (barnacle) were collected at Pantai Gelora beach Pahang, Malaysia. Methyl heptadecanoate of chromatographic grade, obtained from Sigma–Aldrich (Switzerland), was utilized as an internal standard for methyl ester content determination, whereas potassium hydroxide, methanol and *n*-hexane of analytical grade were purchased from Bendosen Laboratory Chemicals (Norway).

2.2. Feedstock preparation

The *A. korthalsii* seeds were collected and washed using warm water to remove the dirt. *A. korthalsii* seeds then were dried in an oven at 105 °C till constant weight. Subsequently, the dried seeds were crushed using grinder and sieved to obtain smaller particles. The oil was extracted by using the Soxhlet extraction method with *n*-hexane in a reflux system for 6 h (Lim et al., 2009). The extracted oil was separated from the solvent using a rotary evaporator at 65 °C and 85 rpm. The yellow-brown supernatant was collected then the process was repeated five times and the oil content was calculated using the following formula:

$$\text{Oil content (\%)} = M_1/M_0 \times 100$$

where M_1 and M_0 are the masses of the accumulated oil and *A. korthalsii* seed in g, respectively.

2.3. Catalyst preparation and characterization

Barnacles shell was cleaned using warm water to remove dirt, fibrous matters and proteins. Then the shells were dried in the oven at 105 ± 2 °C until constant weight. The shells were then roughly crushed by mortar and further crushed finely using a dry-mill grinder through 100 μm mesh. The powder was then calcined to remove the remains of carbon and other impurities, as reported elsewhere (Maniam et al., 2015). The catalyst active ingredients were identified by X-ray diffraction (Rigaku MiniFlex II) with Cu Kα X-ray as a source. The catalyst was examined for thermal stability through thermogravimetric analysis (TGA) using Mettler Toledo TGA/DTA (851e instrument), from 25 to 900 °C with 10 °C/min heating rate. The size and morphology of the catalyst were identified by FE-SEM (JEOL JSM-7800 F).

2.4. Transesterification and methyl ester analysis

Transesterification reactions were performed in a 25 mL 2-neck glass reactor with a condenser, immersed in water bath. In a typical reaction, 5 g of oil was added onto the mixture of calcined catalyst (900 °C, 2 h) and methanol. The contents were refluxed under magnetic stirring at varied methanol to oil molar ratio (9:1, 12:1 and 15:1) as well as varied catalyst amount (2, 4 and 6 wt.%.) at 65 °C reaction temperature for 3 h reaction. After completion, the reaction mixture was allowed to cool, resulting in the glycerol being separated by gravity. Centrifugation was used to further separate the layers (methyl ester, glycerol, and catalyst) and the residual methanol in the methyl ester layer was evaporated out using a rotary evaporator, operated at 80 °C, then washed with warm water, to obtain a pure methyl ester. The methyl ester content was determined using gas chromatography-flame ionization detector (GC-FID) (Agilent 7890 A) using capillary DB-Wax column (length 60 m x internal diameter 0.25 mm x film thickness 0.25 μm). The methyl ester content of biodiesel was calculated by following EN14103 procedure and using methyl heptadecanoate as an internal standard. The ME content was calculated using the following formula:

$$\text{Methyl ester content (\%)} = \frac{A_{total} - A_{ISTD}}{A_{ISTD}} \times \frac{C_{ISTD} \times V_{ISTD}}{W_{sample}} \times 100\%$$

where, A_{total} is the total area of ME from $C_{16:0}$ to $C_{18:2}$
A_{ISTD} is the area of methyl heptadecanoate
C_{ISTD} is the concentration of methyl heptadecanoate in mg/ml
V_{ISTD} is the volume of methyl heptadecanoate in ml
W_{sample} is the weight of sample in mg

2.5. Parameter optimization

Parametric optimization was conducted using Design-Expert 11 (Stat-Ease, Inc., Minneapolis USA) under the Central Composite Design with 4 factorial points, 4 axial point (alpha value at ± 1.41) and 5 centre points. MeOH:oil molar ratio was varied at 9:1, 12:1 and 15:1 whereas the catalyst amount at 2, 4 and 6 wt.%.

3. Results and discussion

3.1. Catalyst characterization

TGA/DTA result shows a major decomposition at 560–770 °C where the weight loss is accounted for 42% (Fig. 1). The decomposition is attributed to the evolvement of CO_2 as the weight loss is matched with the stoichiometric weight loss of CO_2 to form CaO from $CaCO_3$ (Boey