Techno-economic and Environmental Analyses on Reduced Graphene Oxide modified Kapok Fiber as Oil Absorbent

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Abstract. The industrialization of synthetic fiber has resulted in an economic depression for both domestic and global kapok fiber industries as well as the farmers. On the other hand, the development of the oleochemical industry in Indonesia demands a separation process that is less cost- and energy-intensive. Supporting the sustainable development goals (SDGs) number 1, 8, 9, 12, and 13, in this study, the under-tapped kapok fiber has been utilized to show its potential value as an oil sorbent material. Despite having high oil sorption capacity and being biodegradable, the raw kapok fiber has low oil selectivity, low oil retention, and a fragile structure. The kapok fiber has been modified with reduced graphene oxide (rGO) to obtain hydrophobic-oleophilic absorbent with high absorption capacity, high oil selectivity, high oil retention, and strong structure to maximize the recovery yield. Modification has been done by soaking kapok fiber in GO supernatant and reducing them with ascorbic acid, then freeze-drying the fiber to get a robust superhydrophobic sponge. Techno-economic and life-cycle analyses have been conducted and the results indicate that rGO-KF aerogel is economically viable with a potential GPM greater than 36, 27%, and environmentally beneficial as it can potentially decrease product carbon emissions by 32.8 tons/ton recovered oil.

1. Introduction
Kapok (Ceiba pentandra) is one of the Indonesian commodities which market has been declining and dormant for more than half a century. In 1936/1937, Indonesia was the world's largest kapok fiber exporter accommodating about 85% of the global demand or about 28,400 tons. The industrialization of synthetic fibers and the global market competitions have turned down the economy of the kapok industry and farmers. In recent years, however, kapok fiber with its unique features attracts increasing attention, particularly in its utilization as an oil sorbent material [1]. Kapok fiber is hydrophobic, oleophilic, lightweight, and has a lumen (air cavity) in the middle of its fiber wall which makes it superior organic absorbent. Each gram of pristine kapok fiber can absorb approximately 40 grams of oil [2,3].

There are several interesting chemical dan physical modifications made on Kapok fiber. Chemical treatment with alkali/acid and acetylation as well as the simple blending with synthetic polymer (such as polyethylene) are among the oldest methods [2]. With technological advances and comprehensive knowledge of the chemical reaction mechanism, methods such as sol-gel mineralization [4,5], rGO-modified [6] as well as the use of ultrasonication in the process promote the advancement of the methods.
Table 1 summarizes the oil sorption capacity and reusability of some kapok fiber-based composite materials.

| Composite Material | Type of oil | Oil sorption capacity (g/g) | Reusability No. Cycle | Capacity reduction (%) | Ref. |
|--------------------|-------------|----------------------------|----------------------|------------------------|------|
| Pristine kapok     | Diesel      | 32                         | 1                    |                        | [3]  |
|                    | Soybean     | 50                         |                      |                        |      |
| Organo-silane      | Diesel      | 46.9                       | 8                    | ~ 20%                  | [4]  |
|                    | Soybean     | 58.8                       |                      |                        |      |
| rGO                | Palm oil    | 48.6                       | 10                   | 37.4%                  | [5]  |
|                    | Soybean     | 42                         | 8                    | ~ 6%                   | [6]  |

On the other hand, the growth of vegetable and essential oil industries in Indonesia increases the need for an effective and economical technology that can improve the quality as well as the yield of the produced oil and easily applied with low energy consumption levels without generating concerns over the possibility of becoming waste in the future. Palm oil is a key vegetable industry in Indonesia; crude palm oil (CPO) production in 2019 reached 42.9 million tons. About 0.6%wt. CPO has lost as palm oil mill effluent (POME) [7]. Reclaiming the oil content in POME enhances the yield production of the palm oil industry as well as reduces the BOD of the effluent. Oil recovery from POME using membrane faces a major drawback of fouling. Therefore, a pre-separation process that is less cost- and energy-intensive is desirable; and absorption material utilizing the long-forgotten commodity such as kapok fiber could be an option to address the needs.

Modification with rGO potentially strengthens the structural integrity, enhancing oil sorption capacity, reusability, and oil recovery of the kapok fiber without losing its affinity to oil and water repellency. In this study, rGO modified kapok fiber (rGO-KF) modification procedures have been formulated with considerations to the techno-economic feasibility and the environmental impacts through comprehensive literature reviews and simulations. Expectantly, the market of the long-forgotten commodity could revive with the positive impacts of this research.

2. Methodology

This research focuses on the techno-economic analysis and life-cycle assessment of the rGO-KF aerogel. Figure 1 shows the framework of this research started from literature study at stage 1 to the process innovation at stage 2, case study at stage 3, and techno-economic analyses and life cycle assessment at stage 4. The techno-economic analyses have been carried out based on the implementation scenario of crude palm oil (CPO) reclamation from palm oil mill effluent (POME). Process material and energy requirements are simulated using Aspen Hysys V.8. Assumptions taken in the rGO-KF aerogel production process simulation and assessment are summarized in Table 2. Life cycle assessment (LCA) has been conducted based on the acid and carbon emissions of rGO-KF aerogel in comparison to the synthetic polypropylene absorbent.
Figure 1. Research framework.

Table 2. Assumptions taken for the rGO-KF aerogel production process simulation and assessment.

| Assumptions                        | Value                   |
|------------------------------------|-------------------------|
| Raw kapok fiber                    | 1000 ton/year           |
| Production rate rGO-KF aerogel     | 1133 ton/year           |

Product specifications

| Assumptions                        | Value                   |
|------------------------------------|-------------------------|
| rGO:kapok fiber (mass)             | 3:20                    |
| Oil sorption capacity              | min. 46 g oil/g absorbent |
| Number of cycles                   | 5                       |
| Capacity reduction                 | max. 10%                |

Operational cost (Aspen Hysys simulation)

| Assumptions                        | Value                   |
|------------------------------------|-------------------------|
| Raw materials and chemicals        | Price (million IDR)    |
| Kapok fiber (per year)             | 2,705                   |
| Chemicals (per year)               | 122,820                 |
| Energy (per year)                  | 21,317                  |
| Utility (per year)                 | 7,313                   |
| Recovered oil (per ton)            | 7.5                     |

3. Results and Discussion

Prior to the techno-economic analyses, the process flow diagram of rGO-KF aerogel production should be determined. Figure 2 displays the process flow diagram of rGO-KF aerogel production. Prior to the modification processes, the raw kapok fiber was separated from seeds and cleaned from dust by aeration then oxidized by sodium chlorite (5%wt. NaClO₂) under acid condition (pH 4.5, temperature 80°C) to eliminate the waxy layer from the kapok surface exposing the hydroxyl group on the cellulosic material [5].

The Marcano method can be utilized to oxidize the graphite into graphite oxide. This method uses a mixture of sulfuric acid (H₂SO₄) and phosphoric acid (H₃PO₄) without using sodium nitrate (NaNO₃); thus, the production of acid waste can be reduced and the toxic gases (i.e., NO₂ and N₂O₄) can be eliminated from the synthesis process [8]. The graphite oxide could be exfoliated into graphene oxide
through ultrasonication [9]. Kapok fiber bundle is added into the GO solution (1g/L) with a weight ratio of 20:3; the modification has been carried out for 2 hours with stirring at room temperature. Reduction takes place at 95°C for 1 hour with 1 M sorbic acid (1/10 v/v GO solution) instead of hydrazine to reduce the formation of unwanted chemical waste [10]. After reduction, the rGO is neutralized with aqua demin at room condition. Lastly, the rGO-KF aerogel is made from freeze-drying 2 %wt. suspension rGO-KF in the aqua demin at 0.1 mbar, -55°C for 72 hours [6].

Figure 2. Process flow diagram of rGO-KF aerogel production.

Techno-economic and life cycle assessments have been carried out to evaluate the feasibility of rGO-KF process production as well as its utilization for CPO reclamation from POME. The economic analysis carried out in this report is limited to the gross profit margin (GPM) of the product while the revenue comes from the sales of the reclaimed oil. Conventional palm oil mill lost about 0.6%wt. of its CPO production during condensate disposal of boiling stations and clarification stations [11]. Taking Indonesian CPO production in 2019, the amount of prospectively reclaimable CPO is about 264 thousand tons/year. Therefore, the reclamation potentially achieves revenue of IDR 1.98 trillion/year. Figure 3 displays the GPM assessment against the value of %-oil recovery from the utilization of rGO-KF aerogel. Based on CSI Market 2020, the average GPM value of the chemical industry in Q1 2020 is 36.27%; this value is used as a benchmark for the economic feasibility of rGO-KF aerogel utilization for CPO reclamation from POME. Based on the graph, with only 17%-oil recovery, the sorbent is economically viable with a potential GPM greater than 36,27%.
The utilization of rGO-KF aerogel in oil reclamation from POME is expected to support sustainable development goals (SDGs) number 1, 8, 9, 12, and 13. To assess whether the rGO-KF aerogel meets the expectations as environmentally friendly oil absorbents, LCA has been carried out. There are four stages in the LCA manufacturing process as stipulated in ISO 14040 and ISO 14044: identification of the definition of purpose and scope; inventory analysis; LCIA (life cycle impact analysis); and data interpretation. In the context of products from natural biomass, LCA is used to compare the environmental effects between biomass products and products from synthetic fibers [12]. The approach used is cradle-to-grave, which is the analysis of products from the production of raw materials to the end of product life. The inventory analysis of the rGO-KF aerogel production is summarized in Table 3.

**Table 3.** Inventory analysis of the rGO-KF aerogel production.

| Activity                          | Input                                      | Output                                      |
|-----------------------------------|--------------------------------------------|---------------------------------------------|
|                                   | **Type (unit)** | **Amount** | **Type (unit)** | **Amount** |
| Kapok plantation                  | Water (kg)      | 41,43      | Kapok fiber (kg) | 1          |
|                                  | Fertilizers (kg)| 9,19×10^-2 | CO₂ eq. (kg)     | 0,12       |
|                                  | Energy (MJ)     | 0,30       | CO₂ (kg)         | 1624,83    |
|                                  | CO₂ (kg)        | 1624,83    |                 |            |
| Transportation                    | Diesel (L)      | 2,30×10^-2 | CO₂ eq. (kg)     | 8,04×10^-4 |
| Graphite production               | Energy (MJ)     | 163        | Graphite (kg)    | 1          |
|                                  |                |            | CO₂ eq. (kg)     | 14,74      |
| Graphene oxide production         | Enegri (MJ)     | 1,70       | GO (kg)          | 1,90       |
|                                  | H₂SO₄ (kg)      | 12,67      | SO₂ eq. (kg)     | 12,93      |
|                                  | H₃PO₄ (kg)      | 1,29       | CO₂ eq. (kg)     | 0,33       |
|                                  | Graphite (kg)   | 1          |                 |            |
| rGO-modified Kapok fiber production | Kapok Mentah (kg)| 0,95        | Absorbent (kg)   | 1          |
|                                  | rGO (kg)        | 0,05       | CO₂ eq. (kg)     | 14,93      |
|                                  | Energy (MJ)     | 76,19      |                 |            |
| Waste burning                     | Absorbent (kg)  | 1          | Energy (MJ)      | 12,08      |
|                                  |                |            | CO₂ eq. (kg)     | 1,09       |
The LCA in this report aims to compare the environmental impacts of two types of oil absorbents: rGO-KF aerogel and polypropylene oil boom [13]. The scope of comparison is the greenhouse gas and acid emissions in units of kg of CO₂ equivalent and kg of SO₂ equivalent, respectively. Table 4 summarizes the comparative LCA between rGO-KF aerogel and synthetic PP oil boom. Based on the value of carbon gas emissions from LCA, it shows that the utilization of the rGO-KF aerogel is beneficial for the environment because it reduces CO₂ gas emissions by 32.8 tons/ton absorbed oil.

Table 4. Comparative LCA between rGO-KF aerogel and synthetic PP oil boom.

| Comparative factors         | rGO-KF aerogel | Synthetic PP [13] |
|-----------------------------|----------------|-------------------|
| Oil sorption capacity (kg)  | 1000           | 1000              |
| Required absorbent (kg)     | 21.46          | 68.83             |
| Emission (kg eq. CO₂)       | -32814.89      | 536.37            |
| Energy consumption (MJ)     | 1575.41        | 1863.49           |
| Acidification (kg eq. SO₂)  | 13.89          | 3.34              |

4. Conclusion
rGO strengthens the structural integrity of the kapok fibers, enhancing its oil selectivity, retention, and recovery of the fiber while kapok fiber reduces the acid and other unwanted chemical wastes generation caused by the production of pure rGO aerogel. rGO is chemically compatible with the surface of oxidized kapok fiber; thus, to achieve homogeneous coverage, pretreatment of kapok fiber with a strong oxidation agent (e.g., NaClO₂) is necessary. Modified Hummer method (Marcano method) to oxidize graphite and ascorbic acid to reduce graphene oxide potentially reduce the acid waste and eliminate the toxic gases (i.e., NO₂ and N₂O₅) as well as hydrazine footprint from the rGO synthesized process. With 17% oil recovery, the rGO-modified kapok fiber is economically viable with a potential GPM greater than 36.27%. Furthermore, the use of rGO-KF aerogel can reduce CO₂ gas emissions in the environment by 32.81 tonnes / 1 ton of absorbed oil.

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