

Biodiesel Production from Rambutan Seed Waste by Supercritical Ethanol: Economic Analysis

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The production capacity of rambutan (*Nephelium lappaceum* Linn.) in Thailand is approximately 0.3–0.4 million tons per year, and an average of 1,900 tons of rambutan seed is left as seed waste. This work pre-extracted rambutan seed oil using a single screw press machine to serve as feedstock for biodiesel production. However, the rambutan seed had a high lipid content of ~40%; the screw press machine was capable of extracting only 6–10% of the rambutan seed oil; in other words, ~24% of the residual oil remains in the seed cake. An ethanolic extraction was performed to recover the remaining lipids in the pressed seed cake. This work also aimed to use ethanol as a reactant for biodiesel production in supercritical conditions without removing the extracting ethanol. Ethanolic extraction and supercritical ethanol transesterification were collectively called the EE-SET process. The fatty acid ethyl esters (FAEE) content in the resultant biodiesel ranged from 40–60% because rambutan seed oil contained ~50% oleic (C18:1) and ~40% arachidic (C20:0) acids, which have higher molecular weights than common plant oil. Next, the experimental conditions were simulated in Aspen Plus V.12 software to estimate the mass and energy balances in the biodiesel production process. The results from computer simulations were applied to an economic analysis to assess the feasibility of the EE-SET process. Because the unique fatty acid profile of rambutan seed oil generated a lower FAEE content and consumed a large amount of energy for distillation, the process's complexity reduced the EE-SET process's profitability.

1. Introduction

Rambutan (*Nephelium lappaceum* Linn.) is an exotic fruit commonly found in Southeast Asia, especially Thailand. This fruit had a production capacity of approximately 0.3–0.4 million tons annually. Rambutan can be directly consumed or used as feedstock for canned fruit, one of the major export products of Thailand. During the production of canned fruits, a huge amount of seed waste was generated (1,900 tons per year). In previous work, the rambutan seed cultivated in Thailand had valuable compounds, such as polysaccharides, proteins, especially lipids around 40 wt% (Nilmat et al., 2024). The lipid content in rambutan seeds varies based on factors such as origin, environment, growing methods, and oil extraction techniques.

Table 1 shows the amount of seed oil in the tropical fruits extracted by various extraction techniques, such as solvent and mechanical extractions. Rambutan seed contains a higher lipid content compared to other seed wastes. Moreover, lipids in rambutan seed can be applied in many industries, including biorefinery. The high lipid content in rambutan seeds made it an interesting choice to use as the feedstock for biodiesel production. However, using seed waste as the feedstock for biodiesel production requires an oil extraction process to obtain seed oil. According to Table 1, solvent extraction is an effective method for extracting seed oil, as indicated by the highest yield of oil obtained.

Table 1: The amount of lipid content in various types of fruit by using different extraction techniques

Feedstock type	Extraction method	Lipid content	Reference
Guava seed	Solvent extraction (ethyl propionate)	24 wt%	(Veitía-de-Armas et al., 2024)
Papaya seed	Solvent extraction (<i>n</i> -hexane)	33.8 wt%	(Ezekannagha et al., 2023)
Muskmelon seed	Cold press extraction	35 wt%	(Al-Bawwat et al., 2024)
Rambutan seed	Solvent extraction (<i>n</i> -hexane)	34-40 wt%	(Wong & Othman, 2014)
Bitter Orange seed	Cold press extraction	38 wt%	(Almasi et al., 2023)
Tamarind seed	Mechanical extraction	35 wt%	(Sathish et al., 2024)

Ethanol was introduced as a green alternative in solvent extraction to minimize the environmental impact of toxic solvents. Unlike other solvents, ethanol is produced from the fermentation of biomass, which causes less impact on the environment (Tekin et al., 2018). According to the OECD-FAO Agricultural Outlook, Thailand is set to become the world's seventh-largest ethanol producer by 2024, leading to a decrease in ethanol prices in the country. Hence, using ethanol as the solvent for extracting rambutan seed oil can reduce the cost of processing and environmental impact. In conventional biodiesel production, the extracted seed oil is converted to biodiesel by a chemical reaction called transesterification, using methanol as the reactant under the presence of catalysts. Although ethanol yields less biodiesel and takes longer to react than methanol, many researchers still suggest using ethanol for biodiesel production due to its production sources, toxicity, and environmental concerns (Verma & Sharma, 2016).

Applying green technology in biodiesel production is the alternative route to manage the biodiesel production process to become more environmentally responsible. Supercritical fluid technology is one of the green technologies that can be used in biodiesel production. Compared to conventional biodiesel production, supercritical fluids technology can promote the chemical reaction without requiring catalysts and make the reaction time shorter (Wen et al., 2009). Although supercritical fluid technology can reduce the amount of chemical usage in the process, the cost of production in the process is still a concern.

Techno-economic analysis (TEA) is a crucial tool used to evaluate the possibility of the production process. TEA is widely used to assess economic performance and evaluate the impact of technology on production costs in biodiesel production processes. For example, the effects of the methanol-to-oil molar ratio on profitability were estimated by TEA (Sakdasri et al., 2018). The biodiesel production from different feedstocks, waste cooking oil, and virgin soybean oil and the various types of catalysts applied TEA to evaluate the economic performance of the process (Al-Sakkari et al., 2020). Green extraction and supercritical fluid technology could produce biodiesel from rambutan seeds; however, further research is necessary to explore and validate this approach, especially the profitability. This study focuses on designing the process simulation and estimating the economic feasibility of biodiesel production from rambutan seed using ethanolic extraction and supercritical ethanol transesterification, which is called the EE-SET process hereafter. The biodiesel production plant was simulated based on the preliminary study of rambutan seed oil extraction and biodiesel production from rambutan seed oil via supercritical ethanol. TEA was used to evaluate the net present value (NPV), internal rate of return (IRR), and the payback period of the EE-SET process.

2. Materials and Methods

2.1 Experimental data used in process simulations

The preliminary experimental showed that the rambutan seed oil yield obtained from a single screw press was around 10 wt%. Oleic acid (C18:1) and arachidic acid (C20:0) are the primary fatty acids found in rambutan seed oil, comprising approximately 50 wt% and 40 wt%, respectively (Nilmat et al., 2024). Biodiesel production from rambutan seed oil using supercritical ethanol was performed in a 4.5-mL batch reactor to find the optimal conditions for maximizing FAEE concentration in the biodiesel sample. The results showed that the maximum ester content in the biodiesel sample was ~50 wt% when operated at the reaction temperature of 350 °C, ethanol to oil molar ratio of 30:1, and pressure of 15 MPa. All the experimental data was used to simulate the biodiesel production from the rambutan seed in a computer simulation program.

2.2 Process simulations

Biodiesel production from rambutan seed with EE-SET plant was simulated by Aspen Plus® V.12. Rambutan seed is set as a non-conventional compound which the proximate analysis data was based on the previous study (Nilmat et al., 2024). For the enthalpy and density model, HCOALGEN and DCOALIGT were chosen. The main fatty acid in rambutan seed oil (Oleic acid) was used to represent the oil that reacts with the solvent in triolein (C₅₇H₁₀₄O₆). For biodiesel production, UNIQUAC was chosen as the thermodynamic model for the

transesterification reaction. For the simulated product, ethyl oleate ($C_{20}H_{38}O_2$) represents the FAEE produced from rambutan seed oil and glycerol, the by-product of the transesterification reaction. The amount of rambutan feedstock was set at 100 kg/h, an average amount of rambutan seed generated in Thailand. The data obtained from the process simulation, such as material balance, energy usage in unit operation, and equipment size, will be used to estimate the economic feasibility of the process.

2.3 Process Description

The biodiesel production from rambutan seed using the EE-SET process diagram is shown in Figure 1. The fresh rambutan seed that contains moisture at 43 wt% was sent to the dryer to remove the moisture in the seed. Dried rambutan seed was fed into a single screw press machine to pre-extract the rambutan seed oil at 10 wt%. The seed cake was separated from the screw press machine and used as feedstock to extract the remaining oil (~25 wt%) by soaking with ethanol in an extractor with the extractable ethanol to oil mass ratio at 30:1. Since ethanol can be used as the extracting solvent and reactant, the mixture of rambutan oil and ethanol was directly fed into the EE-SET reactor. After removing the defatted seed cake from the extracting unit, the ethanol-oil mixture, the extracted rambutan seed oil from the pre-extracting unit, and the unreacted oil were pressurized to 15 MPa. The high-pressure mixture was pre-heated in a heat exchanger and then fed into the reactor to produce biodiesel under supercritical conditions. According to the preliminary experiment, the maximum ester content in biodiesel was 50 wt%. The product mixture consisted of excess ethanol, biodiesel, glycerol, and unreacted rambutan seed oil. The high-temperature product line was used as the heating source to preheat the pressurized mixture through the heat exchanger. After cooling down the product line, the trotting valve was used to depressurize the product line to atmospheric pressure. The product line was sent to the distillation unit to separate components. The excess ethanol was recycled back to the extracting unit to reduce the required amount of solvent in the process. The unreacted rambutan seed oil was sent to mix with the extracted rambutan seed oil in a pre-extracting unit. The biodiesel and glycerol products were separated by a decanter in a separating unit before being sold as products.

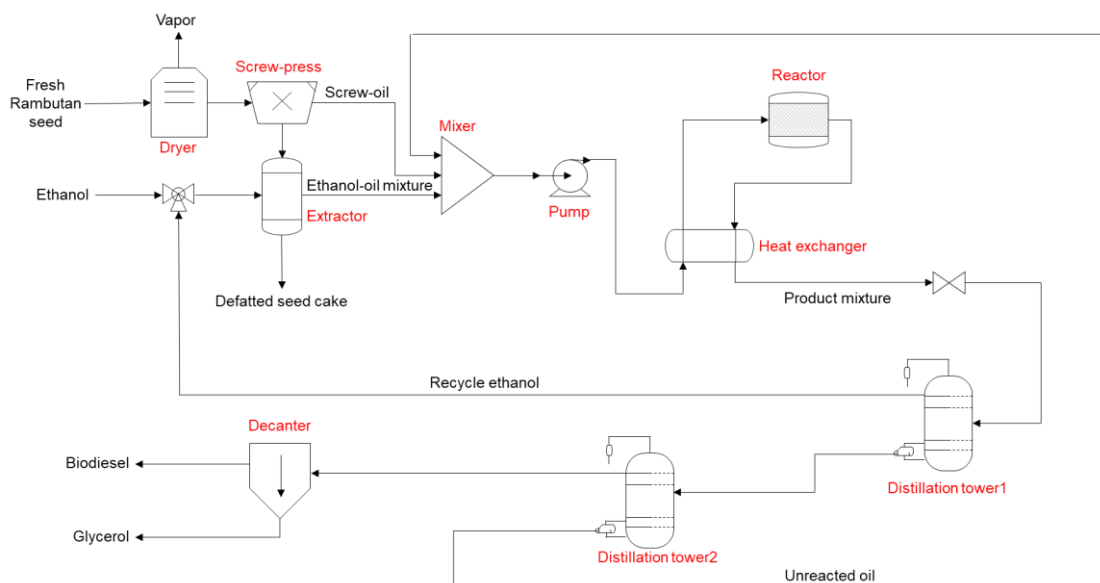


Figure 1. Process diagram of biodiesel production from rambutan using EE-SET.

2.4 Techno-economic analysis

EE-SET was applied as the Pissanumhon Food Products Co., Ltd. extension process for the assumption. The production plant was located in Chumphon province, Thailand. The labor cost was based on Thailand's regulations, which depend on the province. The equipment price was estimated by CAPCOST MS-excel add-in and chemical engineering plant cost index (CEPCI). The electricity cost was based on the rate price for a small-scale factory regulated by the Metropolitan Electricity Authority of Thailand. Metropolitan Waterworks Authority of Thailand was assigned the price for the water cost. The project life plan was set for 20 years with the taxation rate at 35%, annual interest rate at 10%, and inflation rate at 2%, based on the Revenue Department, Ministry of Finance, Thailand. Since rambutan is the seasonal fruit cultivated for 8 months, the operating days in the production plant were set at 240 days with working hours at 24 h. All the calculation methods for the cost of

production were adapted from the methods in the literature (Turton et al., 2008). The economic indicators for predicting the profitability of the EE-SET plant are NPV, IRR, and payback periods.

3. Results and Discussion

3.1 The material balance and energy consumption of EE-SET

The material balance in the biodiesel production plant using EE-SET is shown in Table 2. Annually, the amount of rambutan seeds required in the simulation was higher than the generated waste seed in a small factory. Because fresh rambutan seeds have a high moisture content of 43 wt%, a dryer requires much energy to remove the excess moisture. Consequently, the extracted oil yields were lowered, especially based on the weight of the fresh rambutan seeds.

Table 2: Material balance in biodiesel production from rambutan seed oil by EE-SET.

Feedstock	Flow input (kg/h)	Flow input (Ton/year)	Product	Flow (kg/h)	outputFlow output (Ton/year)
Fresh rambutan seed	100.00	576.00	FAEE	9.69	55.81
Dried rambutan seed	57.00	328.32	Glycerol	0.96	5.52
Rambutan seed cake	51.30	295.49	Unreacted seed oil	9.31	53.63
Ethanol	40.03	8.55	Defatted seed cake	51.70	297.79

Note: Material balance is based on the production plant's annual operation.

In this production, the EE-SET process was designed to use ethanol as an extracting solvent and reactant, which requires a large amount of ethanol compared to conventional biodiesel production. To reduce the amount of chemicals in the process, ethanol obtained from the distillation unit was returned to the extraction unit as the recycling solvent. Because the main fatty acids in rambutan seed oil are ~50% oleic (C18:1) and ~40% arachidic (C20:0) acids, the produced FAEE had similar LHV to the conventional biodiesel (Mehta & Anand, 2009). However, the FAEE content obtained from EE-SET was 40–60%, which contaminated unreacted oil in the product line. Triglyceride in unreacted oil had a higher molecular weight than FAEE, making the distillation unit require more energy than separating pure FAEE. Further study on increasing the ester content in product lines can reduce the complexity and energy required of the process.

3.2 The economic feasibility of the process

The summarization of TEA on annual cost in the biodiesel production from rambutan seed oil using EE-SET is shown in Table 3. Biodiesel and glycerol are the main products sold during this process. The price of biodiesel is based on the Department of Alternative Energy Development and Efficiency, Thailand, at 1,163 USD/ton. In contrast, the glycerol selling price is based on the average glycerol price in Southeast Asia at 680 USD/ton (www.businessanalytiq.com). The total product sale revenue in the process is 68,665.08 USD.

Table 3: The annual cost of production of biodiesel production plant using EE-SET

Cost category	Item	Cost (USD)
Direct manufacturing cost	Raw material cost	8,752.90
	Waste treatment cost	10,648.21
	Utility cost	7,407.36
	Labor cost	60,604.62
Fixed cost of production	Plant overheard	21,989.94
	Taxes and Insurance	15,850.73
	Administration cost	8,137.73
General manufacturing expenses	Distribution and selling costs	17,467.93
	Research and development	7,939.97
Total cost of production		158,799.38

Compared to the total cost of biodiesel production, the revenue from selling products is lower than 40%, making the net annual profit negative at -90,134.30 USD. At the end of the project life plan, the NPV of the project becomes negative at -1,156,680 USD. Due to the negative values of NPV, the IRR and payback period cannot

be calculated. This value can indicate that the EE-SET process cannot make the process profitable within the project life plan. A key contributor to the high total production cost is the direct manufacturing expense, which includes the costs of raw materials, waste treatment, utilities, and labor involved in the process. Figure 2 shows the subfactor's contribution to the process's direct manufacturing cost.

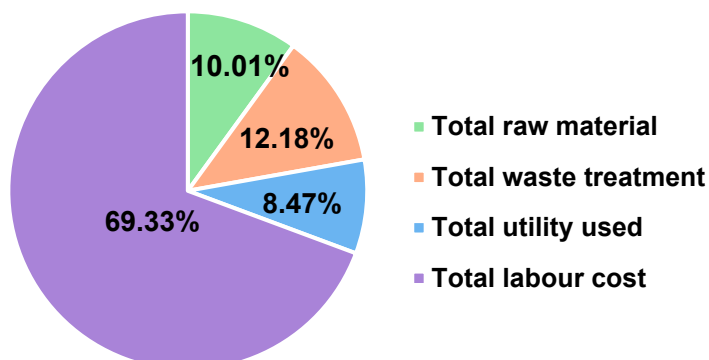


Figure 2. The contribution of the direct manufacturing cost in biodiesel production from rambutan seed oil

The labor cost is the most contributing factor to direct manufacturing costs. Since this process was used in a small factory, the maximum production capacity was low, while the amount of labor was high. Increasing the production capacity will make the project more profitable while using the same labor cost. However, there are limitations to the labor cost adjustment, such as the safety of the production and the regulations. Waste treatment costs are another factor affecting the distribution of direct manufacturing costs. The defatted rambutan seed cake is the only waste generated during production. This waste is categorized as non-hazardous waste. According to the waste management cost, defatted rambutan seed cake costs 36 USD/ton (Turton et al., 2008). To reduce the direct manufacturing cost, the cost of waste treatment must be adjusted. Using defatted rambutan seed cake as the feedstock for producing new products can increase the project's revenue, making the process more economically viable. Moreover, decreasing the waste generated from the process reduces the waste treatment cost and environmental impact. Examining the value-added potential of defatted rambutan seed cake can effectively reduce production costs.

4. Conclusions

The EE-SET process was suitable for application in larger-scale canned fruit factories. This process can reduce the amount of rambutan seed waste and make it more valuable. However, there were limitations on the biodiesel production from rambutan seed oil, such as the need to balance the amount of feedstock with the required quantity, the low ester content in biodiesel products, and the large amount of waste generated in the process. The EE-SET process did not render the biodiesel production process profitable during the project's life. Effective waste management is crucial for boosting efficiency and reducing environmental impact. Additionally, exploring ways to increase the conversion of rambutan seed oil and utilizing defatted rambutan seeds as feedstock for valuable product production can enhance profitability. Presently, subcritical water is utilized for polysaccharide extraction from defatted rambutan seeds, and the extracted seeds are further used for hydrochar production.

Nomenclature

EE-SET – Ethanolic extraction and supercritical ethanol transesterification
 FAEE – Fatty acid ethyl ester
 OECD – Organization for Economic Co-operation and Development
 FAO – Food and Agriculture Organization of the United Nations

TEA – Techno-economic analysis
 NPV – Net present value
 IRR – Internal rate of return
 CEPCI – Chemical Engineering Plant Cost Index
 LHV – Low Heating Value

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References

- Al-Bawwat, A.a.K., Gooma, M.R., Cano, A., Jurado, F., Alsobou, E.M., 2024. Extraction and characterization of Cucumis melon seeds (Muskmelon seed oil) biodiesel and studying its blends impact on performance, combustion, and emission characteristics in an internal combustion engine. *Energy Conversion and Management*: X, 23, 100637.
- Al-Sakkari, E.G., Mohammed, M.G., Elozeiri, A.A., Abdeldayem, O.M., Habashy, M.M., Ong, E.S., Rene, E.R., Ismail, I., Ashour, I., 2020. Comparative Technoeconomic Analysis of Using Waste and Virgin Cooking Oils for Biodiesel Production. *Frontiers in Energy Research*, 8.
- Almasi, S., Najafi, G., Ghobadian, B., Ebadi, M.T., 2023. Waste to fuel: biodiesel production from bitter orange (*Citrus aurantium*) seed as a novel bio-based energy resource. *Biomass Conversion and Biorefinery*, 13, 6543-6552.
- Ezekannagha, C.B., Onukwuli, O.D., Obibuenyi, J.I., Udunwa, D.I., 2023. Kinetic modeling of papaya seed triglyceride transesterification catalyzed by calcined banana peel ash in methyl ester production. *Chemical Engineering Research and Design*, 200, 256-265.
- Mehta, P.S., Anand, K., 2009. Estimation of a Lower Heating Value of Vegetable Oil and Biodiesel Fuel. *Energy & Fuels*, 23, 3893-3898.
- Nilmat, K., Hunsub, P., Ngamprasertsith, S., Sakdasri, W., Karnchanatat, A., Sawangkeaw, R., 2024. Effects of Defatting Pretreatment on Polysaccharide Extraction from Rambutan Seeds Using Subcritical Water: Optimization Using the Desirability Approach. *Foods*, 13.
- Sakdasri, W., Sawangkeaw, R., Ngamprasertsith, S., 2018. Techno-economic analysis of biodiesel production from palm oil with supercritical methanol at a low molar ratio. *Energy*, 152, 144-153.
- Sathish, T., Giri, J., Saravanan, R., Zairov, R., Hasnain, S.M.M., 2024. Nano-fuels of Al₂O₃/SiO₂/MgO/tamarind seed oil biodiesel for CI engines: An evaluation of combustion consumption and emission performance. *International Journal of Thermofluids*, 23, 100815.
- Tekin, K., Hao, N., Karagoz, S., Ragauskas, A.J., 2018. Ethanol: A Promising Green Solvent for the Deconstruction of Lignocellulose. *ChemSusChem*, 11, 3559-3575.
- Turton, R., Bailie, R.C., Whiting, W.B., Shaeiwitz, J.A. 2008. *Analysis, synthesis and design of chemical processes*. Pearson Education.
- Veitía-de-Armas, L., Reynel-Ávila, H.E., Bonilla-Petriciolet, A., Jáuregui-Rincón, J., 2024. Green solvent-based lipid extraction from guava seeds and spent coffee grounds to produce biodiesel: Biomass valorization and esterification/transesterification route. *Industrial Crops and Products*, 214, 118535.
- Verma, P., Sharma, M.P., 2016. Comparative analysis of effect of methanol and ethanol on Karanja biodiesel production and its optimisation. *Fuel*, 180, 164-174.
- Wen, D., Jiang, H., Zhang, K., 2009. Supercritical fluids technology for clean biofuel production. *Progress in Natural Science*, 19, 273-284.
- Wong, C., Othman, R., 2014. Biodiesel production by enzymatic transesterification of papaya seed oil and rambutan seed oil. *International Journal of Engineering and Technology*, 6, 2773-2777.