

# Techno-Economic-Environmental Analysis of Sustainable Anionic Biosurfactant Production from Palm Fatty Acid Distillate

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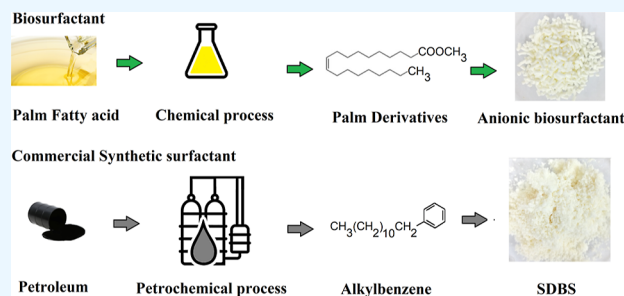


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Supporting Information

**ABSTRACT:** Currently, there is increased interest in biosurfactants as a substitute for surfactants synthesized from petroleum due to their superior properties and biodegradability. Palm oil derivatives, which can be converted to various products, were selected for biosurfactant synthesis. This paper simulated the biosurfactant production process from palm fatty acid distillate, that is, methyl ester sulfonate (MES), alkyl sulfate, alkyl phosphate, and alkyl carboxylate. Aspen Plus software was used to estimate the thermodynamic properties of intermediate aliphatic organic acids, e.g., methyl ester sulfonic acid, fatty alcohol sulfuric acid, and fatty alcohol phosphoric acid. The chemical process equipment was designed and evaluated to be used in techno-economic analysis, with comparison to petroleum source surfactant production, that is, sodium dodecylbenzenesulfonate (SDBS). The total production cost of each biosurfactant was expressed in terms of minimum selling price. The profitability of each project was determined and compared using three economic indicators: net present value (NPV), payback period, and internal rate of return (IRR). The life cycle assessment methodology was then used to evaluate the environmental impact of surfactant production. The results showed that all surfactant production processes, except for alkyl phosphate, were attractive alternatives as the project yielded a positive value of NPV. The highest NPV of 13.1 million USD was obtained from the MES production process, while the maximum IRR of 79.81% and payback period of 1.49 years were obtained from the alkyl carboxylate production process at a capacity of 1 ton/h. However, the sulfate production process caused more environmental impact than the other two surfactants (MES and carboxylate) due to more CO<sub>2</sub> emission per product unit at the level of 2.88 tons CO<sub>2</sub>/ton surfactant, which is also more than the SDBS surfactant production process that released 2.46 tons CO<sub>2</sub>/ton surfactant.



## INTRODUCTION

Surfactants are important chemicals in the chemical and petroleum industries due to their many applications, such as detergents, cleaners, food processing, and oilfield chemicals. In petroleum fields, surfactants are used to improve the amount of oil produced after the natural production phase, known as enhanced oil recovery (EOR). Waterflooding or water injection is the most widely used oil recovery process because it is effective and not too expensive for oil displacement from the reservoir, but nearly half of the reserved oil may remain in the pore if the rock wettability is not favorable. To address this, surfactant flooding is implemented to alter the reservoir rock and/or fluid properties, promoting more oil desorption by means of wettability alteration and reduction of interfacial tension (IFT).<sup>1</sup>

Generally, surfactants consist of two major functional groups: polar and nonpolar. The nonpolar functional group can be linear, branched, aromatic, or a combination of hydrocarbons. In the past, surfactants were synthesized from petroleum fractions, which were toxic and difficult to degrade.<sup>2,3</sup> For example, sulfonate surfactants were synthesized from alkyl aryl hydrocarbons, such as dodecylbenzene. Nowadays, the production of biosurfactants from agricultural

biomass or microorganisms is receiving more attention, as they are expected to substitute the usage of synthetic petroleum surfactants, such as sodium dodecylbenzenesulfonate (SDBS). These biosurfactants have a linear hydrocarbon structure with no aromatic moiety, resulting in a 3–8 day degradability compared to the 24 day degradability of synthetic petroleum surfactants.<sup>4,5</sup> However, the advantage of biosurfactants from agricultural biomass is their cost competitiveness over surfactants from microbials.<sup>4–6</sup>

The polar functional group can be divided into three main categories: anionic, cationic, and nonionic. Anionic surfactants are the most widely used due to their low cost of production and are used in detergents, soaps, cleaners, and cosmetics. Additionally, they are used in the EOR process for sandstone reservoirs because they have low adsorption on negatively

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**Table 1. Reactants and Raw Material Costs for Surfactant Synthesis**

raw materials/reactants	surfactant production	price (USD/kg)	references
palm fatty acid	MES/sulfate/phosphate/carboxylate	0.68	15
methanol	MES/sulfate/phosphate	0.42	16
fatty acid methyl ester (FAME)	MES	<sup>a</sup>	
hydrogen	sulfate/phosphate	3.50	17
fatty alcohol	sulfate/phosphate	<sup>b</sup>	
NaOH	MES/sulfate/phosphate/carboxylate	0.7	18
sulfuric acid	MES/sulfate	0.29	16
phosphoric acid	phosphate	0.815	18

<sup>a</sup>Produced by the esterification reaction of fatty acid and methanol. <sup>b</sup>Produced by the hydrogenation reaction of FAME and hydrogen.

**Table 2. Summary of Operating Conditions of Related Chemical Reactions in Producing Biosurfactants**

operating conditions of reaction	reaction pathway	temperature/pressure	catalyst	reactant molar ratio	reaction time	product yield (%)	refs
esterification	fatty acid + methanol → FAME + H <sub>2</sub> O	60 °C, atmospheric pressure	10 wt % bentonite	1:9 of fatty acid to methanol	3 h	82	22
sulfonation	FAME + sulfuric acid → methyl ester sulfonic acid + H <sub>2</sub> O	100 °C, atmospheric pressure		1:1.1 of FAME to sulfuric acid	3 h	84.9	23
hydrogenation	FAME + H <sub>2</sub> → fatty alcohol + methanol	250 °C, 40 bar	0.3 wt % CuCr	1:120 of FAME to hydrogen	3.33 h	97	24
sulfation	fatty alcohol + sulfuric acid → fatty alcohol sulfonic acid + H <sub>2</sub> O	90 °C, atmospheric pressure		1:1.1 of Fatty alcohol to sulfuric acid	8 h	83	25
phosphation	fatty alcohol + H <sub>3</sub> PO <sub>4</sub> → phosphate ester + H <sub>2</sub> O	150 °C, atmospheric pressure	10% mol MoOCl <sub>4</sub>	1:1 of fatty alcohol to phosphoric acid	6 h	61.84	26
saponification	fatty acid + NaOH → sodium carboxylate + H <sub>2</sub> O	80 °C, atmospheric pressure		1:1.1 of fatty acid to sodium hydroxide	35 min	86.5	27

charged sandstone surfaces. The main functional groups for anionic surfactants are sulfonate (−SO<sub>3</sub>), sulfate (−SO<sub>4</sub>), phosphate (−PO<sub>4</sub>), and carboxylate (−COO).<sup>7</sup> Sulfonate surfactants are typically synthesized from a reaction between sulfuric acid and methyl ester, followed by neutralization. The conventional method for producing sulfate surfactants is the reaction between sulfuric acid and fatty alcohol, with sodium dodecyl sulfate (C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>Na) being the most common. The synthesis of phosphate surfactants is similar to that of sulfate surfactants as it is the neutralized salt of phosphoric acid, which is produced from the phosphate reaction of fatty alcohol. Lastly, carboxylate surfactants are produced from saponification or neutralization of fatty acid after hydrolysis of natural oil.<sup>2,3</sup> This surfactant type has the lowest cost at around 1.2 USD/kg, but their properties are sensitive to water salinity, as they form precipitates with hard water, containing high concentrations of divalent ions.<sup>8,9</sup> Additionally, methyl ester sulfonate (MES) is also an anionic biosurfactant that is produced commercially for detergent and personal care purposes.

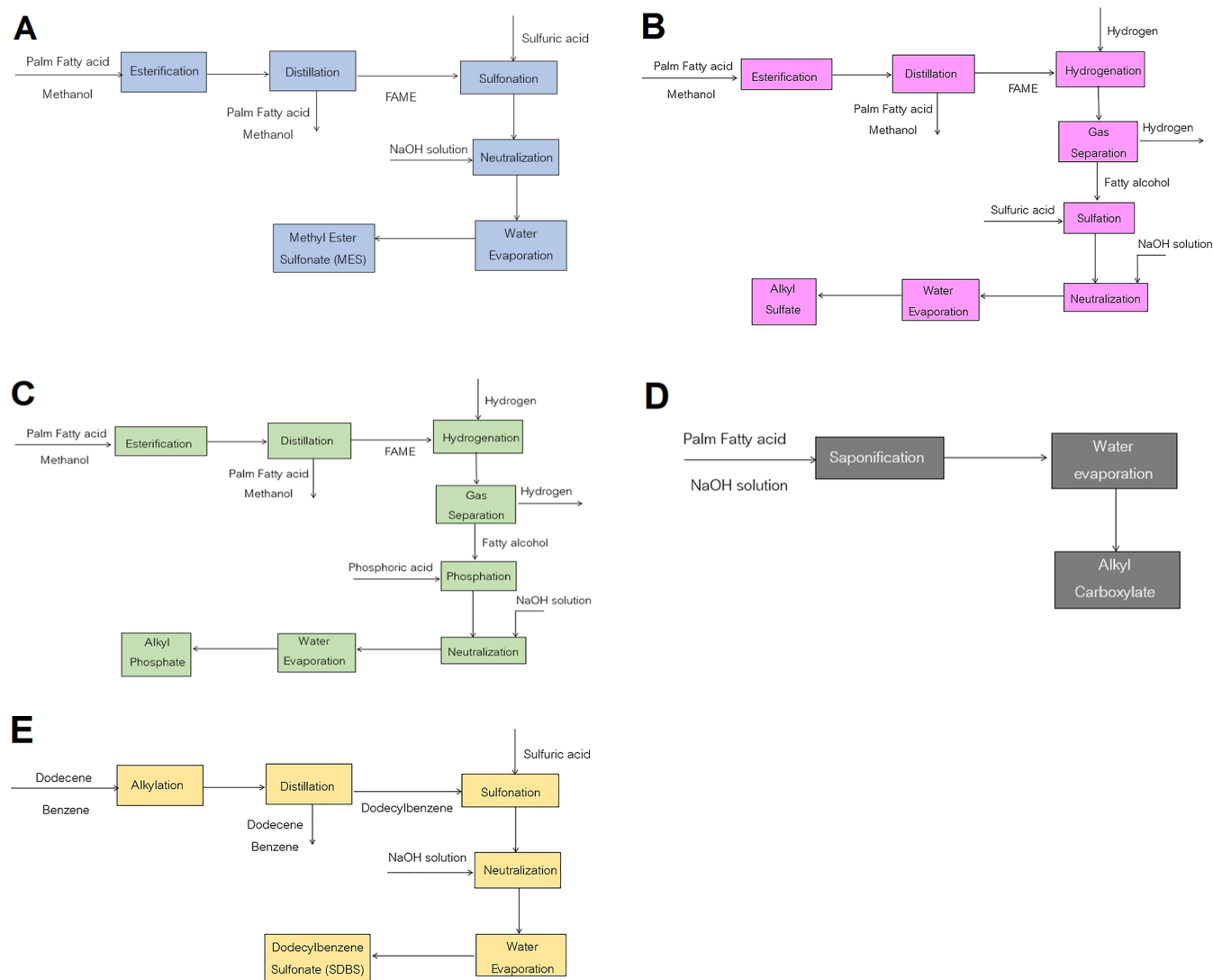
The hydrocarbon functional group is responsible for nonpolar interactions with surface-attached oil. Thus, the structure of the hydrocarbon chain in surfactants, including the chain length, affects the effectiveness of hydrocarbon recovery. Many studies have found that palm oil is a good candidate for biosurfactant production due to its suitable properties. For example, C<sub>16</sub>–C<sub>18</sub> chain length of palm oil derivatives was found to be more effective in altering the wettability of heavy oil reservoirs than C<sub>12</sub> chain length from coconut oil, as it has higher lipophilicity.<sup>10</sup> Additionally, the detergent and wetting characteristics of surfactants from palm methyl ester can be comparable to hydrocarbons from petroleum fractions, resulting in high effectiveness for IFT reduction.<sup>5,11</sup>

Although there had been a few studies on the production of biosurfactants from microbials,<sup>6,12</sup> this work aims to analyze and compare the economic indicators and environmental impact among different types of anionic biosurfactants produced from bio-oil, particularly from palm oil derivatives, as these surfactants had the advantage of cost competitiveness over surfactants from microbials with an acceptable level of degradability.<sup>4–6</sup> Thus, this paper designs the chemical processes used to convert palm fatty acid distillate (PFAD), a palm oil derivative, into four types of biosurfactants: MES, alkyl sulfate, alkyl phosphate, and alkyl carboxylate. The economic analysis of these surfactant production processes will be performed to offer profitable and cost-competitive alternatives for biosurfactant synthesis. Additionally, the environmental impact of each surfactant production process will be assessed in terms of CO<sub>2</sub> emission to estimate the carbon footprint of different biosurfactants, with comparison to a surfactant from a petroleum source, that is, SDBS. The economic and environmental analyses will be used to judge the attractiveness of biosurfactant production from palm derivatives that could potentially be used for various purposes instead of the surfactant from petroleum sources, which is toxic to the environment in terms of degradability.

## METHODOLOGY

**Design Basis.** The raw material mass flow rate was based on 1000 kg/h for surfactant production. Because the surfactant is used in oilfield chemicals, the produced surfactant is of regular or industrial grade. The maximum impurity of the produced biosurfactant must not exceed 20 wt %, as per the product specification of the commercial MES surfactant.<sup>13</sup>

**Raw Materials.** Due to its availability and cost, palm oil and its derivatives are the major raw materials used in biosurfactant production. The production rate of palm oil is



**Figure 1.** General block flow diagrams of (A) MES production process, (B) alkyl sulfate production process, (C) alkyl phosphate production process, (D) alkyl carboxylate production process, and (E) SDBS production process.

around 2.5 million tons per year in Thailand.<sup>14</sup> PFAD is a palm oil derivative selected as a raw material in this paper because it is a remaining product from the palm oil refinery, which cannot be used in the food industry. Therefore, the conversion of PFAD into a biosurfactant is expected to add value to this selected raw material. The composition of PFAD, which is used in the simulation of the surfactant production process, is composed of 36.3 wt % palmitic acid, 45.4 wt % oleic acid, 10.7 wt % linoleic acid, and 7.6 wt % stearic acid.<sup>4</sup> Other raw materials depend on the types of anionic polar groups in the biosurfactant; for example, sulfuric acid and NaOH are reactants for MES surfactant synthesis. The costs of raw materials used in economic analysis are presented in Table 1.<sup>15–18</sup> Moreover, the utility costs used in process equipment are based on Ulrich and Vasudevan<sup>19</sup> and Turton et al.,<sup>20</sup> as shown in Table S1 in the Supporting Information.

**Simulation.** A surfactant synthesis process could be designed after gathering data on raw material composition, including the chemical reaction yield and operating conditions, which are shown in Table 2. The operating conditions for the related chemical reactions were selected based on conditions that utilized palm oil derivatives as the reactant. In cases where

data for these specific reactions were not available, the operating conditions would be chosen by referencing reactions that involved a reactant with the same functional group as palm oil derivatives and considering that the hydrocarbon length of the reactant was close to the  $C_{16}$ – $C_{18}$  range, which is the typical hydrocarbon chain length of palm fatty acid. Then, the estimation of properties of components not available in the Aspen Plus Simulation database was implemented by constructing the molecular structure of those components. The Joback method was selected as the estimation methodology for boiling point and heat capacity, while the Benson method was selected as the estimation methodology for standard heat of formation due to its lowest error in calculation compared to other methods.<sup>21</sup> The calculated values of the related properties used in process simulation, including the estimation methodology, are expressed in Tables S2–S4 in the Supporting Information. Additionally, the electrolyte-NRTL thermodynamic model was applied to the overall simulation environment due to the involvement of both nonpolar and polar compounds in the process, as well as the presence of electrolytes such as sulfuric acid and sodium hydroxide.

After estimating the properties of substances not available in the simulation databank, the production process of each surfactant was designed based on the collected reaction information and operating conditions. Figure 1 represents the process flow diagram of all of the studied surfactant production processes, and the description of the production process for each surfactant is provided below:

**MES Production.** The feed stream containing PFAD with 36.3 wt % palmitic acid, 45.4 wt % oleic acid, 10.7 wt % linoleic acid, and 7.6 wt % stearic acid, along with methanol, was preheated before being fed to the esterification reactor (R-101) at a molar ratio of 1:9. The kinetic model used for the esterification reaction, which was studied by Supardan and Satriana,<sup>22</sup> is expressed in eq 1.

$$R_{\text{esterification}} = 0.02177C_{\text{FA}}C_{\text{MET}} - 0.00384C_{\text{ME}} \quad (1)$$

where  $R_{\text{esterification}}$  is the rate of esterification reaction in units of mol/min,  $C_{\text{FA}}$  is the concentration of fatty acid,  $C_{\text{MET}}$  is the concentration of methanol, and  $C_{\text{ME}}$  is the concentration of methyl ester

At a temperature of 60 °C and atmospheric pressure, the yield of methyl ester was 82% when bentonite clay was used as a catalyst and the residence time in the reactor was 3 h, with the liquid volume at 80%. The aqueous phase was separated from the reactor outlet stream by the decanter (D-102), reducing the water content to below 0.1% wt. Methanol was then separated from a mixture by a distillation column (C-101) with 13 equilibrium stages in a tower at a condenser temperature of 47.7 °C and a pressure of 0.49 atm, together with a reboiler temperature of 203.6 °C and a pressure of 0.83 atm. FAME was further separated from fatty acid by a second distillation column (C-102) with 88 equilibrium stages at a condenser temperature of 131.0 °C and a pressure of 0.26 atm, together with a reboiler temperature of 331.5 °C and a pressure of 0.60 atm. Additionally, the fatty acid stream was recycled to the esterification reactor (R-101), as illustrated in Figure S1 in the Supporting Information. After separation, a FAME stream and sulfuric acid were mixed and preheated before being fed to the sulfonation reactor (R-102) at a molar ratio of 1:1.1. The kinetic model used for the sulfonation reaction that was fitted by the experiment of Mungpayaban and Ma et al.<sup>23,28</sup> is expressed in eq 2.

$$R_{\text{sulfonation}} = 0.101C_{\text{H}_2\text{SO}_4}C_{\text{ME}} - 0.00113C_{\text{MES}} \quad (2)$$

where  $R_{\text{sulfonation}}$  is the rate of sulfonation reaction in units of mol/min,  $C_{\text{ME}}$  is the concentration of methyl ester,  $C_{\text{H}_2\text{SO}_4}$  is the concentration of sulfuric acid, and  $C_{\text{MES}}$  is the concentration of methyl ester sulfonic acid.

The residence time in the sulfonation reactor was 3 h, yielding 84.9% methyl ester sulfonic acid at a temperature of 100 °C and atmospheric pressure. The reactor outlet stream was then cooled to separate the acidic aqueous phase by the decanter (D-106) before mixing with 50% NaOH solution at a molar ratio of 1:1.1 and feeding to the neutralization reactor (R-103) at a temperature of 40 °C with a reaction time of 65 min. The kinetic model used for the neutralization reaction, as described by Martinez et al.,<sup>4</sup> is expressed in eq 3.

$$R_{\text{neutral}} = 0.15C_{\text{NaOH}}C_{\text{MES}} \quad (3)$$

where  $R_{\text{neutral}}$  is the rate of neutralization reaction in units of mol/min,  $C_{\text{MES}}$  is the concentration of methyl ester sulfonic acid, and  $C_{\text{NaOH}}$  is the concentration of sodium hydroxide.

The neutralized product, MES, was first separated from the recycled organic phase. To reduce the moisture content of sulfonate to below 0.4 wt %, water was evaporated at a temperature of 110 °C in a flash separator (F-101). This process is illustrated in Figure S2 in the Supporting Information, and the details and conditions of each unit operation used in MES are shown in Table S5 in the Supporting Information.

**Alkyl Sulfate Production.** In the process of alkyl sulfate synthesis, a feed stream of fatty acid and methanol was fed into the equipment set, where an esterification reaction occurred until the FAME was separated from fatty acid by a second distillation column (C-102), as shown in Figure S1 in the Supporting Information. The mixture of methyl ester was then pumped and preheated before being mixed with hydrogen gas at a molar ratio of 1:125 and entering the hydrogenation reactor (R-102) at the reaction conditions. The kinetic model used for the hydrogenation reaction, proposed by Simasatitkul,<sup>24</sup> is expressed in eq 4.

$$R_{\text{hydrogenation}} = 0.03197P_{\text{ME}}P_{\text{H}_2} \quad (4)$$

where  $R_{\text{hydrogenation}}$  is the rate of hydrogenation reaction in units of kmol/s,  $P_{\text{ME}}$  is the partial pressure of methyl ester, and  $P_{\text{H}_2}$  is the partial pressure of hydrogen gas.

The vapor residence time in this reactor was 113.3 s. At a temperature of 250 °C and a pressure of 40 bar with CuCr as the catalyst, the yield of fatty alcohol was 97%. The cooling process of the reactor outlet stream can be divided into two stages. First, the outlet stream was cooled down to 100 °C in a flash separator (F-101) to separate the gas phase, which contains H<sub>2</sub> and methanol. Then, hydrogen gas was separated from methanol at 30 °C by another flash separator (F-102) for recycling. Additionally, the liquid stream pressure was reduced to atmospheric pressure before being reacted with sulfuric acid at a molar ratio of 1:1.1. The kinetic model used for the sulfation reaction, which was fitted by the study of Gill et al.,<sup>25</sup> is expressed in eq 5.

$$R_{\text{sulfation}} = 0.0556C_{\text{H}_2\text{SO}_4}C_{\text{FAL}} - 0.00293C_{\text{FAS}} \quad (5)$$

where  $R_{\text{sulfation}}$  is the rate of sulfation reaction in units of mol/min,  $C_{\text{FAL}}$  is the concentration of fatty alcohol,  $C_{\text{H}_2\text{SO}_4}$  is the concentration of sulfuric acid, and  $C_{\text{FAS}}$  is the concentration of fatty alcohol sulfuric acid.

The residence time in the sulfation reactor was 12 h, with a yield of fatty alcohol sulfuric acid of 83% at a temperature of 90 °C and atmospheric pressure. The outlet stream from the reactor was then cooled down to separate the aqueous phase by the decanter (D-106) before mixing with a 50% NaOH solution for neutralization at a temperature of 40 °C. Finally, the neutralized product, alkyl sulfate, was separated from the recycled organic phase and the moisture content was reduced at a temperature of 110 °C in a flash separator (F-103), as illustrated in Figure S3 in the Supporting Information. The details and conditions of each unit operation used in alkyl sulfate are provided in Table S6 in the Supporting Information.

**Alkyl Phosphate Production.** The process of phosphate synthesis was similar to that of the production of sulfate surfactant. A feed stream of fatty acid, methanol, and hydrogen gas was fed into the equipment set where esterification and hydrogenation reactions occurred until the liquid product (fatty alcohol) stream was separated from the gas phase using two flash separators (F-101 and F-102), as shown in Figure S4



in the Supporting Information. The fatty alcohol stream was then heated to the reaction temperature before being reacted with phosphoric acid at a molar ratio of 1:1. The kinetic model used for the phosphate reaction, which was fitted by the experiment of Sakakura et al.,<sup>26</sup> is expressed in eq 6.

$$R_{\text{phosphation}} = 0.0529C_{\text{H}_3\text{PO}_4}C_{\text{FAL}} - 0.0141C_{\text{FAP}} \quad (6)$$

where  $R_{\text{phosphation}}$  is the rate of phosphation reaction in units of mol/min,  $C_{\text{FAL}}$  is the concentration of fatty alcohol,  $C_{\text{H}_3\text{PO}_4}$  is the concentration of phosphoric acid, and  $C_{\text{FAP}}$  is the concentration of fatty alcohol phosphoric acid.

This reactor had a residence time of 13 h and a liquid volume of 80%. Pyridine was used as a catalyst to produce a phosphate ester yield of 61.8% at a temperature of 150 °C and atmospheric pressure. The reactor outlet stream was cooled to separate the aqueous phase by a decanter (D-106) before mixing with a 50% NaOH solution for neutralization, which was divided into two stages. The first stage was partially neutralized to a level of 50% at a temperature of 65 °C for phosphoric acid separation.<sup>29</sup> The second stage was to react with the remaining phosphate ester at a temperature of 40 °C. The residence time in the neutralization reactor was 65 min. The neutralized product, which is alkyl phosphate, was then separated from the recycled organic phase, and water was evaporated at a temperature of 110 °C in a flash separator (F-103) as illustrated in Figure S4 in the Supporting Information. The details and conditions of each unit operation used in alkyl phosphate production are provided in Table S7 in the Supporting Information.

**Alkyl Carboxylate Production.** The feed stream, a mixture of PFAD and a 50 wt % NaOH solution at a molar ratio of 1:1.1, will be preheated to the reaction conditions before entering the saponification reactor. The kinetic model used for the saponification reaction, proposed by Protasova et al.,<sup>27</sup> is expressed in eq 7.

$$R_{\text{sapon}} = 0.0478C_{\text{NaOH}}C_{\text{FA}} \quad (7)$$

where  $R_{\text{sapon}}$  is the rate of saponification reaction in units of mol/min,  $C_{\text{FA}}$  is the concentration of fatty acid, and  $C_{\text{NaOH}}$  is the concentration of sodium hydroxide.

The residence time in this reactor was 35 min, with the liquid volume at 80%. At a temperature of 80 °C and atmospheric pressure, the conversion of fatty acid into alkyl carboxylate was 86.5%. The neutralized product, alkyl carboxylate or soap, was then cooled for separation from the recycled organic phase by a decanter (D-101). Again, the water content was then reduced at a temperature of 110 °C in a flash separator (F-101), as illustrated in Figure S5 in the Supporting Information. The details and conditions of each unit operation used in alkyl carboxylate production are shown in Table S8 in the Supporting Information.

**SDBS Production.** This type of surfactant is not a biosurfactant produced by palm oil derivatives; however, it is used as a reference in economic and environmental assessments, because it is synthesized from petroleum fractions, which are widely used in EOR. The production of SDBS surfactant involves the following steps: the feed stream, which contains dodecene ( $\text{C}_{12}\text{H}_{24}$ ) and benzene ( $\text{C}_6\text{H}_6$ ), was preheated before being fed to the alkylation reactor (R-101) at a molar ratio of 1:6. The kinetic model used for alkylation reaction, which was studied by Aslam et al.,<sup>30</sup> is expressed in eq 8.

$$R_{\text{alkylation}} = 0.0459C_{\text{DODEC}}C_{\text{BEN}} \quad (8)$$

where  $R_{\text{alkylation}}$  is the rate of alkylation reaction in units of mol/min,  $C_{\text{DODEC}}$  is the concentration of dodecene, and  $C_{\text{BEN}}$  is the concentration of benzene.

At a temperature of 120 °C and atmospheric pressure, the yield of dodecylbenzene was 80.6% when mordenite was used as the catalyst. The residence time in the reactor was 63 min, with the liquid volume at 80%. The remaining reactants, dodecene and benzene, were separated from the reactor outlet by a distillation column (C-101) with 11 equilibrium stages in a tower. The condenser temperature was 30.9 °C and pressure was 0.16 atm, while the reboiler temperature was 295.4 °C and pressure was 0.50 atm. The separated reactants were then recycled to the alkylation reactor (R-101), as illustrated in Figure S6 in the Supporting Information.

After separation, a bottom stream containing dodecylbenzene and a trace of reactants was mixed with sulfuric acid and preheated before being fed into the sulfonation reactor (R-102) at a molar ratio of 1:1.1. The reaction in the sulfonation reactor took place at a temperature of 100 °C and atmospheric pressure with a residence time of 3 h, and the product yield of 85%. The reactor outlet stream was then cooled to separate the acidic aqueous phase by the decanter (D-104) before being mixed with 50% NaOH solution at a molar ratio of 1:1.1 and fed to the neutralization reactor (R-103) at a temperature of 40 °C with a reaction time of 65 min. The neutralized product, SDBS, was first separated from the recycled organic phase, and water was evaporated at a temperature of 110 °C in a flash separator (F-101). The details and conditions of each unit operation used in SDBS production are shown in Table S9 in the Supporting Information.

**Techno-Economic Analysis.** The simulation results were used to analyze the economic feasibility of each surfactant production process. Profitability was a key factor in determining the type of attractive palm biosurfactant on the market. The costs of raw materials used in the economic analysis are presented in Table 1, while the selling prices of SDBS/MES, alkyl sulfate, alkyl phosphate, and alkyl carboxylate were 1.8, 2.0, 1.9, and 1.2 USD/kg, respectively.<sup>16,18</sup> The equipment costs were calculated using the bare module approach.<sup>20</sup> Additionally, the project components were evaluated by using the operational premises,<sup>31</sup> which are shown in Table S10 in the Supporting Information.

The project had a life of 10 years, and a discounted rate of 15% was assumed to determine the net present value (NPV). In addition to three economic indicators (NPV, payback period, and internal rate of return (IRR)), the minimum selling price was also determined to compare the total production cost of each type of surfactant, which accounted for not only raw material and utility costs but also capital and all indirect costs. The selling price was used to indicate the competitiveness of the biosurfactant to the petroleum source surfactant, SDBS, as this price will be the expense for oil fields when performing EOR processes.

**Life Cycle Assessment.** The environmental impact of the biosurfactant production processes was assessed and compared to that of surfactant from petroleum fraction, that is, SDBS. A cradle-to-gate approach was implemented, which considered agricultural processes, raw material extraction, and processing until the synthesis of the product, as the raw materials for production of biosurfactant and surfactant from petroleum are different. The main impact category was global warming

**Table 3. Input and Output Raw Materials and Energies in the Surfactant Production Process Based on the Product Unit of 1000 kg**

input/output	unit	surfactant production				
		SDBS	MES	sulfate	carboxylate	phosphate
fatty acid	kg		794.1	784.9	924.9	784.8
methanol	kg		95.1	94.0		94.0
methyl ester	kg		828.1	818.6		818.6
dodecene	kg	483.2				
benzene	kg	224.19				
dodecyl benzene	kg	707.36				
hydrogen	kg			11.7		11.7
sulfuric acid	kg	364.4	328.9	376.3		
phosphoric acid	kg					455.6
sodium hydroxide	kg	142.1	128.3	226.0	180.1	235.4
natural gas (heating)	kW	819.1	1380.3	2818.6	259.1	2934.1
cooling media	kW	1454.8	1751.4	2819.0	140.9	2762.0

potential (GWP) or CO<sub>2</sub> emission, as the major reactant was fatty acid, mainly composed of hydrocarbon functional groups. Additionally, the energy sources from cold and hot utilities also had an impact in this category. The environmental impact for synthesizing palm fatty acid and alkylbenzene was obtained from de Faria et al.<sup>32</sup> and Forman et al.<sup>33</sup> respectively, due to the complex processing of these two raw materials. The LCSof v6.2 program was used to assess the environmental impact from the chemical process for producing the surfactants, including the related chemical reactions, e.g. esterification, sulfonation, and neutralization, and the separation of products from reactants by distillation. The functional unit was defined as 1000 kg of produced surfactant, and the material and energy input and output inventories were obtained using the simulation results from Aspen Plus software.

**Sensitivity Analysis.** Sensitivity analysis was conducted to study the effect of fluctuations in both raw material costs and utility costs on the minimum selling price of biosurfactant. A 20% cost increment from the base price (as shown in Table 1) was applied to the purchasing cost of raw materials (palm fatty acid, methanol, hydrogen gas, sulfuric acid, phosphoric acid, and sodium hydroxide) and the hot/cold utility cost. The results of sensitivity analysis will be used to estimate the palm biosurfactant price when raw material and utility costs fluctuate within a 20% range from the base price.

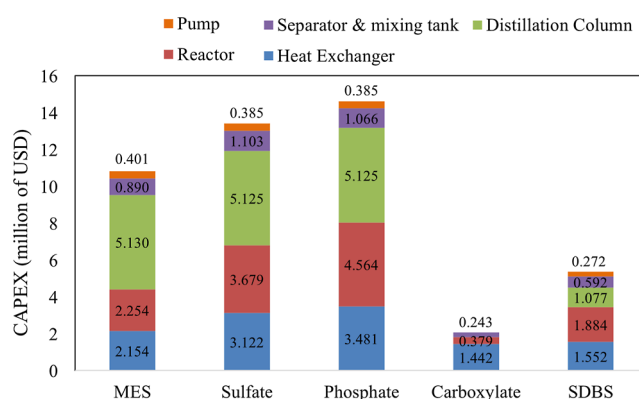
## RESULTS AND DISCUSSION

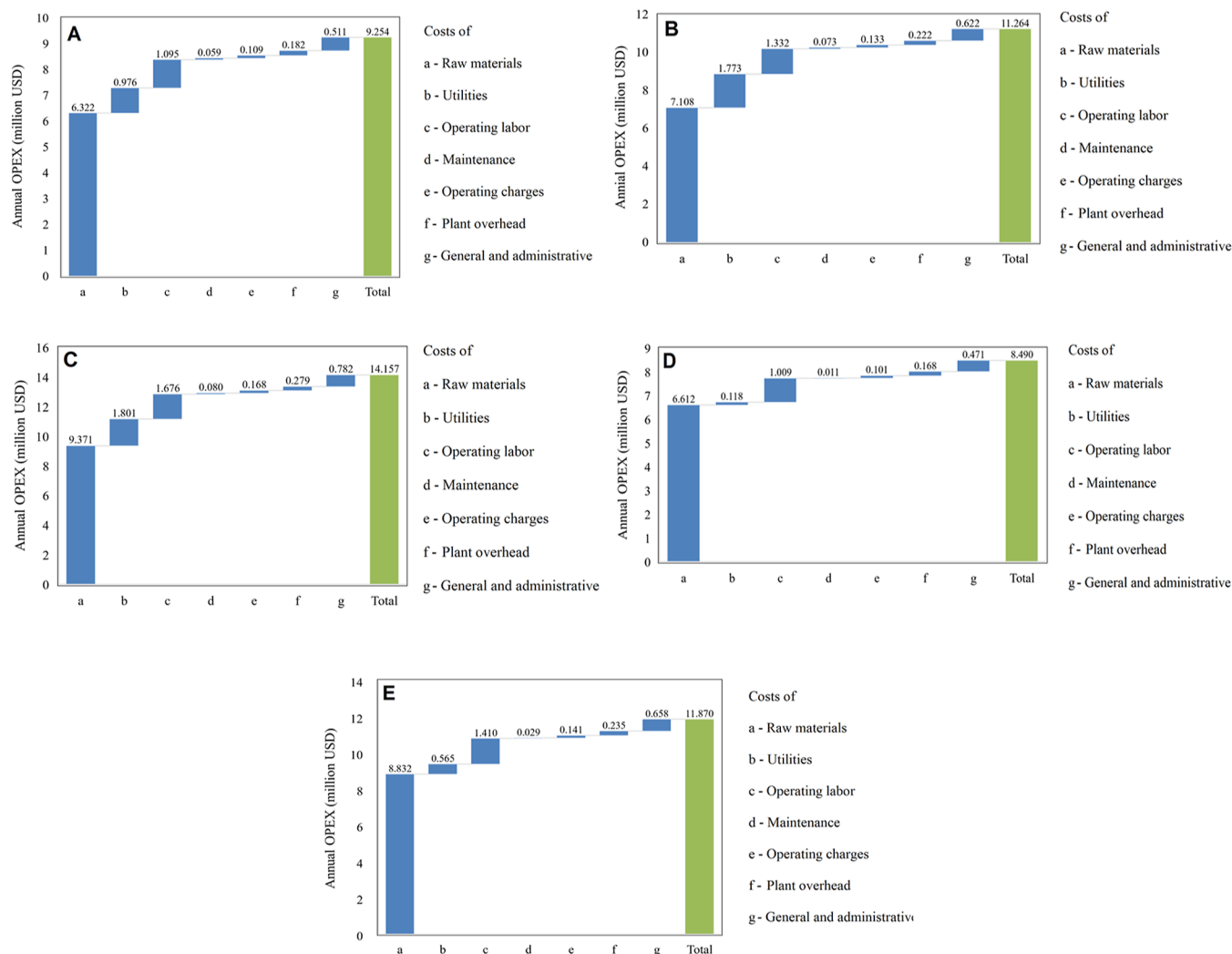
**Simulation Results.** From the process design and simulation results, Table 3 shows the mass flow rate of each reactant based on 1000 kg/h of each biosurfactant product. It was found that the final product purity could reach the commercial surfactant specification of 80 wt % or above from the design of production processes. The product stream of the alkyl carboxylate production process was composed of 95 wt % active matter, while the purity of the final product of other surfactants (MES, alkyl sulfate, and alkyl phosphate) was around 82–83 wt %. To improve the surfactant purity, advanced solid purification processes or the separation of remaining acidic reactants before neutralization would be required; however, this would mean higher capital and operating costs.<sup>34</sup>

The energy consumption for alkyl phosphate production was the highest, with 2934.1 kW h/ton surfactant for heating and 2762.0 kW h/ton surfactant for cooling, as shown in Table 3. It was followed by heating and cooling energies of alkyl sulfate

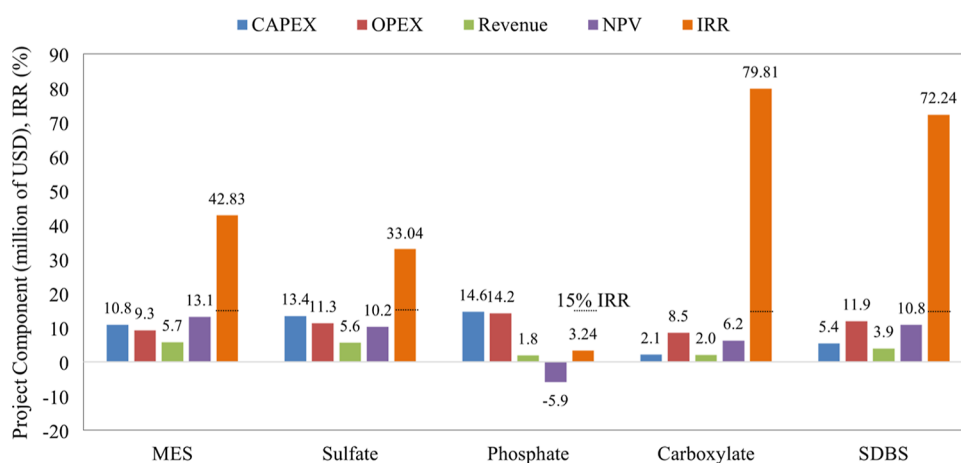
and sulfonate surfactants, respectively. The main energy consumption was in the condenser and reboiler of the distillation column, and also in the unit operation of the reactor, due to the high temperature (250 °C) required for the hydrogenation reaction. The lowest energy consumption was in carboxylate production, with 259.1 kW h/ton surfactant for heating and 140.9 kW h/ton surfactant for cooling, as the major equipment was the reactor for the saponification (neutralization) reaction, which did not require a distillation column.

**Profitability Analysis.** The project expenses consist of two major components: the capital cost (CAPEX) and the operating cost (OPEX). CAPEX was mainly from the cost of the processing unit operations, which consisted of five categories: distillation column, reactor, heat exchanger, pump, phase separator, and mixing tank. The cost of distillation columns in most biosurfactant production processes was the highest, except for carboxylate production, as there was no column. This cost accounted for 35–47% of total CAPEX, followed by reactors (21–31% of CAPEX), heat exchangers (20–24% of total CAPEX), and other equipment, as illustrated in Figure 2. The annual operating costs from the surfactant production process are shown in Figure 3, and the project economic indicators, including the CAPEX, annual OPEX, annual revenue, NPV, and IRR, are shown in Figure 4. The results indicated that all alternatives, except for phosphate surfactant production, yielded a positive value of NPV,

**Figure 2.** Equipment cost distribution of surfactant production processes.



**Figure 3.** Annual OPEX distribution of (A) MES production process, (B) alkyl sulfate production process, (C) alkyl phosphate production process, (D) alkyl carboxylate production process, and (E) SDBS production process.



**Figure 4.** Economic indicators of the surfactant production processes. The dashed line corresponds to the minimum rate of return at 15%.

meaning that the return rate was greater than 15%. The production process of methyl sulfonate (MES) surfactant resulted in the highest NPV of 13.1 million USD due to the highest annual revenue of 5.7 million USD. In contrast, the NPV of phosphate production process was negative due to both the highest value of OPEX (14.2 million USD) and

CAPEX (14.6 million USD), although the selling price of alkyl phosphate surfactant was the highest. However, the IRR of 42.8% for methyl sulfonate production was lower than the return rate of the carboxylate production process (79.8%), and the payback period of 1.49 years for carboxylate production was lower than the payback period of the MES production

process (2.98 years). This was because the CAPEX of MES production was significantly higher at 10.8 million USD, compared to the carboxylate production CAPEX of 2.1 million USD. Taking into account the NPV as the most important indicator,<sup>35</sup> MES surfactant production is the most profitable alternative. However, when considering the overall production cost of surfactants, the minimum selling price of carboxylate surfactant was the lowest at 1.02 USD/kg, followed by MES (1.41 USD/kg), SDBS (1.49 USD/kg), alkyl sulfate (1.70 USD/kg), and alkyl phosphate (2.08 USD/kg), as shown in Table 4, due to an increased trend of capital costs. Therefore, it

**Table 4. Economic Indicator and Minimum Selling Price of Each Surfactant Production Process**

economic indicator	surfactant production process				
	sulfonate	sulfate	phosphate	carboxylate	SDBS
NPV (million USD)	13.13	10.18	-5.91	6.23	10.78
payback period (year)	2.98	4.00	>10	1.49	1.66
IRR (%)	42.83	33.03	3.24	79.81	72.24
minimum selling price (USD/kg)	1.407	1.699	2.075	1.023	1.494

can be concluded that only MES and alkyl carboxylate biosurfactants are competitive with synthetic surfactants due to their lower selling prices than SDBS.

**LCA of the Production Process.** The input and output inventories of raw materials and energies for each biosurfactant production process are shown in Table 3. The difference between each surfactant production process is the type and amount of raw material used in a chemical reaction. For example, carboxylate surfactant production required the highest amount of fatty acid (924.9 kg of fatty acid per ton of surfactant); however, there was no input of inorganic acid solution, that is, sulfuric acid or phosphoric acid. On the other hand, the energy consumption for each process depends on the complexity of the unit operations. The sulfate and phosphate surfactant production process required around 2800 kW•h of energy, which was significantly higher than the other two surfactants due to the high temperature and pressure conditions (250 °C and 40 bar) of the hydrogenation reaction for converting FAME into fatty alcohol. The amount of CO<sub>2</sub> emission from each type of input during the production process is presented in Table 5.

The results indicated that the amount of CO<sub>2</sub> released during alkyl phosphate surfactant production was the highest at 2.98 tons CO<sub>2</sub>/ton surfactant product, followed by alkyl sulfate (2.89 tons CO<sub>2</sub>/ton product), dodecylbenzenesulfonate (2.46 tons CO<sub>2</sub>/ton product), MES (2.33 tons CO<sub>2</sub>/ton product), and alkyl carboxylate (1.39 tons CO<sub>2</sub>/ton product). The CO<sub>2</sub> emission from sulfate and phosphate was higher than that of the synthetic surfactant (SDBS) due to the higher proportion of CO<sub>2</sub> emission from energy usage during heating and cooling in a larger number of unit operation equipment, even though the emission from raw material processing was lower than that of dodecylbenzenesulfonate. If environmental concerns are taken into account, only MES and carboxylate surfactants have a lower global warming impact than the petroleum-based surfactant, SDBS.

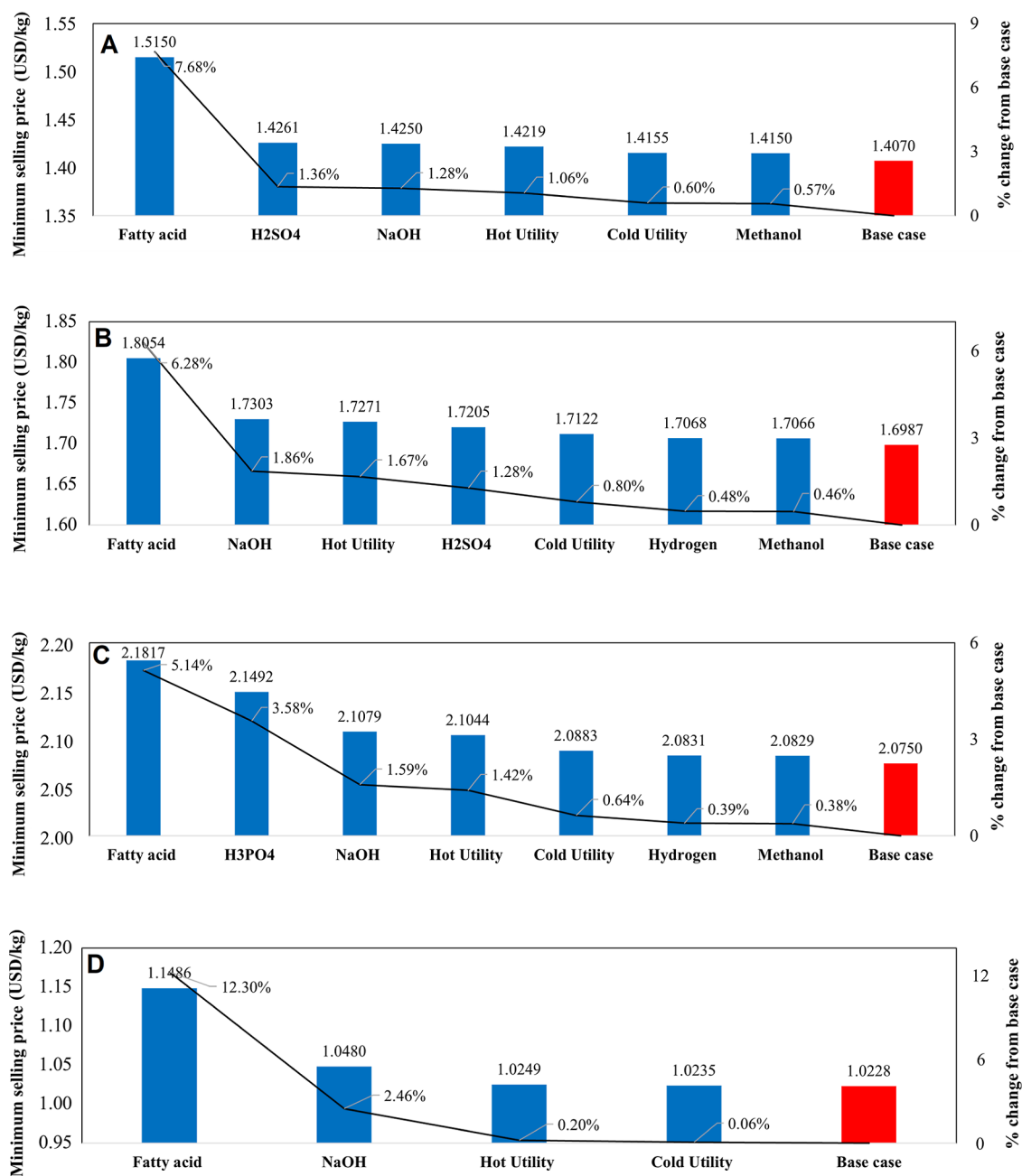
**Sensitivity Analysis.** The results of sensitivity analysis of raw material and utility costs on the value of the minimum selling price are shown in Figure 5. Figure 5A illustrates the effect of various costs on the minimum selling price of MES. The purchasing cost of palm fatty acid had the greatest impact when compared to other raw materials, resulting in a 7.68% increase of the minimum selling price from 1.407 to around 1.515 USD/kg when the palm fatty acid cost was increased by 20%. This was followed by sulfuric acid, sodium hydroxide, and methanol prices, respectively, due to the mass input proportion of each raw material, as shown in Table 3. The increase of the minimum selling price from these following raw material costs was around 0.57–1.36%. Additionally, when considering the effect of utility cost, the rise of hot utility cost would increase the minimum selling price to 1.422 USD/kg, or 1.07%, while the rise of cold utility cost would increase the price to 1.416 USD/kg, or 0.64%. The greater impact from the hot utility cost was due to the high-temperature condition of the distillation column reboiler (more than 200 °C), resulting in a higher total energy cost of hot utility (70.8 USD/ton surfactant) than cold utility (40.5 USD/ton surfactant), although the amount of energy from heating was lower than energy from cooling, as found in Table 3.

Figure 5B–D shows the effect of various variables on the minimum selling price of alkyl sulfate, phosphate, and carboxylate, respectively. The results indicated that the most impacted variable was also the cost of fatty acid, as it is a major reactant for biosurfactant production. This was followed by the cost of sodium hydroxide, inorganic acid (sulfuric/phosphoric acid), and other raw materials. The increases in the minimum selling prices of alkyl sulfate, phosphate, and carboxylate due to the rise of palm fatty acid were 6.28, 5.14, and 12.30%,

**Table 5. CO<sub>2</sub> Emission from Each Inventory of the Surfactant Production Process Based on the Product Unit of 1000 kg**

inventory	CO <sub>2</sub> emission (kg)				
	SDBS	MES	sulfate	carboxylate	phosphate
methyl ester		1714.17	1694.50		1694.50
dodecyl benzene	2003.95				
fatty acid				1309.01	
hydrogen			108.29		108.29
sulfuric acid	99.65	89.95	102.92		
phosphoric acid					173.08
sodium hydroxide	0.32	0.29	0.51	0.41	0.53
natural gas (heating)	186.59	314.44	642.07	59.02	668.39
cooling media	174.18	209.69	337.44	16.86	330.69
total	2464.69	2328.54	2885.73	1385.30	2975.48





**Figure 5.** Effect of utility and raw material prices on (A) MES minimum selling price, (B) alkyl sulfate minimum selling price, (C) alkyl phosphate minimum selling price, and (D) alkyl carboxylate minimum selling price.

respectively. The highest degree of incremental selling price was observed for carboxylate, as the ratio of carboxylate raw material cost to the overall operating cost (OPEX) was around 79%, while this ratio of other biosurfactants was around 65%, as shown in Figure 3. The utility costs also had a slight impact on the surfactant minimum selling prices of surfactants at around 1% change, with more influence from hot utility cost, similar to the result from high-temperature conditions of both the distillation column and hydrogenation reactor.

## CONCLUSIONS

The techno-economic analysis of anionic biosurfactant production from palm fatty acid revealed that all biosurfactant production processes without phosphate would earn more than 15% annually. The most profitable process was found to be

methyl sulfonate surfactant synthesis, with the greatest value of project NPV, although the payback period was not the best due to a higher capital investment than carboxylate surfactant production. Sensitivity analysis showed that the raw material cost of fatty acid had the most impact on the change of palm biosurfactant minimum selling price, from 5 to 12%, when this raw material price was increased by 20%. Additionally, the rise of hot utility cost resulted in a greater increment of selling price, as the total energy cost from heating was higher than the cold utility cost. From an environmental impact perspective, phosphate and sulfate surfactant production processes would result in higher CO<sub>2</sub> emissions than petroleum source surfactants due to high-energy usage in unit operations. Thus, from both techno-economic and environmental points, MES and carboxylate production processes are attractive

projects due to their high profitability, lower carbon emissions, and cost-competitiveness with synthetic surfactants from petroleum products. However, if more energy efficient techniques were developed, sulfate surfactant production could also be a viable option and could potentially replace petroleum-based surfactant production.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c06777>.

Description of utility cost, estimated properties of nondatabank substances in the production process, process flow diagram, and description of unit operations in the process (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ NOMENCLATURE

### Symbols

CO <sub>2</sub>	carbon dioxide
–COO	carboxylate

C <sub>6</sub> H <sub>6</sub>	benzene
C <sub>12</sub> H <sub>24</sub>	dodecene
C <sub>12</sub> H <sub>25</sub> SO <sub>4</sub> Na	sodium dodecyl sulfate
C <sub>16</sub>	sixteen carbon chain length
H <sub>2</sub> SO <sub>4</sub>	sulfuric acid
H <sub>3</sub> PO <sub>4</sub>	phosphoric acid
NaOH	sodium hydroxide
–PO <sub>4</sub>	phosphate
–SO <sub>3</sub>	sulfonate
–SO <sub>4</sub>	sulfate

### Abbreviations

CAPEX	capital expenditure
EOR	enhanced oil recovery
FAME	fatty acid methyl ester
GWP	global warming potential
IFT	interfacial tension
IRR	internal rate of return
LCA	life cycle assessment
MES	methyl ester sulfonate
NPV	net present value
NRTL	nonrandom two-liquid
OPEX	operational expenditure
PFAD	palm fatty acid distillate
SDBS	sodium dodecylbenzenesulfonate

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