

Energy and Economic Analysis of In Situ Biodiesel Production from Microalgal Biomass

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Increasing energy consumption across the globe has gained the researcher's attention to the search for renewable fuels such as biodiesel. The present work focuses on energy and economic analysis of biodiesel synthesis from dried microalgal biomass through in-situ transesterification (i.e. single stage extraction-transesterification). An entire process has been developed and simulated using Aspen plus V11. Furthermore, mass and energy balances have been investigated. The process is developed assuming the biodiesel plant capacity of ~1500 kg/h. The overall cooling duty and heating duty for the entire process were found to be -6.874 MW and 4.567 MW, respectively. Moreover, the total capital expenditure (CAPEX) and total operating costs (OPEX) were estimated to be \$6.534 million and \$45.104 million, respectively. Additionally, biodiesel production cost and total outcome was found to be \$3.75 per kg and \$5.11 per kg respectively. Therefore, net profit was calculated as \$1.36 per kg.

Keywords: in-situ transesterification, process simulation, biodiesel, microalgal biomass, Aspen plus

Introduction

In recent years, the scarcity of crude petroleum sources and environmental concerns have led to the use of renewable fuels such as biodiesel. The immense increase in fossil fuel consumption has led to an alarming situation¹. Consequently, several countries such as the United States of America (USA), Brazil, Italy, France, and Malaysia have commenced the industrialization and commercialization of biodiesel production². The conventional method of biodiesel production involves the transesterification of triglycerides into fatty acid methyl esters (FAME), as depicted in Fig.1. The transesterification reaction can be accomplished using alcohol

with or without suitable catalyst³. The oil acquired from the food crops such as mustard, sunflower, safflower, soybean, and rapeseed are utilized for biodiesel production. However, route is a major concern worldwide because it eventually causes the food crisis and perturbs the economies. Therefore, the non-edible feedstocks like jatropha, karanja, mahua, rice bran, tobacco seed, rubber seed, waste and animal fats are considered as suitable raw materials for the biodiesel synthesis^{4,5}. However, their availability is also uncertain and processing is difficult. On the other hand, the microalgae are unicellular eukaryotes that can grow in any ecosystem on earth and offers several benefits in terms of high biomass

productivity, fast growth rate, and high photosynthetic efficiency. Furthermore, it has the highest oil yield over other traditional terrestrial crops (i.e. 10,000 gallons of oil/acre of land)⁶. Hence, the algae biomass is regarded as a potential feedstock for the biodiesel production⁷.

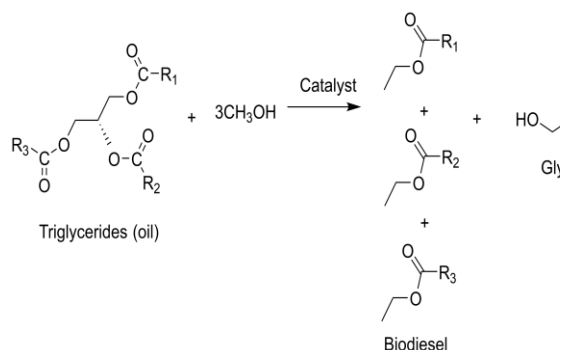


Fig. 1. Transesterification of triglycerides (oil) to biodiesel. R₁, R₂, & R₃ are alkyl groups⁸.

A few notable investigations considering the process simulation and economic assessment of biodiesel production from several edible or non-edible oil have been reported⁹⁻¹⁴. A very detailed economic study to produce biodiesel with alkaline catalyst was estimated for a complete entire plant using a commercial process simulator⁹. West et al.¹⁰ reported the economy of biodiesel plant producing 8000 ton per year of biodiesel from waste cooking oil (WCO). Four processes using Aspen Hysys were evaluated. These processes are supercritical process, homogeneous alkali-catalyzed process, homogeneous acid-catalyzed process and heterogeneous catalyzed process. The results presented that the heterogeneous catalyzed process was found to be most effective in terms of economics and profitability. In another study Zhang et al.¹¹ reported a technical and economic study on biodiesel synthesis from waste cooking oil using an acid catalyst. Both

the process overview and economic analysis were discussed in detail and additional costs were included while Marchetti et al.¹² designed and simulated continuous biodiesel plant of capacity 36036 ton/year using Super pro designer. A supercritical transesterification was used to produce biodiesel from waste cooking oil. Three continuous biodiesel production process were simulated by Lee et al.¹³ The authors analyzed different processes like alkali catalyzed process and supercritical process. The results showed that the supercritical process was the most profitable overall. Sanchez et al.¹⁴ demonstrated the simulation of continuous biodiesel production from microalgal oil with acid catalyst using Aspen Plus simulator 2006.5.

There are no earlier studies on process simulation and economic assessment of biodiesel production from dried microalgae biomass of *Chlorella* sp. MJ 11/11 has not been yet investigated. Therefore, the present work develops and simulates a biodiesel plant based on the experimental work reported by Ghosh et al.¹⁵ to produce biodiesel through in-situ transesterification process (i.e. single stage extraction-transesterification). Moreover, a steady state process simulation was performed to examine the feasibility of biodiesel production using Aspen plus simulator. Furthermore, in this simulation study, in-situ transesterification process is represented by a continuous stirred tank reactor (CSTR). In the subsequent part, the effect of important process parameters such as reactor temperature and residence time was investigated. The energy and economic analysis were also carried out in this study.

Process simulation and design

This section describes the methods used to conduct the process simulation and design.

Process simulation:

Aspen plus V11 process simulator was employed to model the homogeneous acid catalyzed in-situ transesterification of microalgal biomass for biodiesel production. The process developed and simulated in this work is based on the experimental study carried out by Ghosh et al.¹⁶ for the biodiesel production through in-situ process. In-situ transesterification is represented by a continuous stirred tank reactor (CSTR) and RADFRAC (which performs rigorous equilibrium calculations) columns are used to represent the distillation operations. The steps for accomplishing the process simulation involved specifying: i) the chemical components for the process and ii) selection of the thermodynamic property model. Moreover, input and operating conditions, plant capacity and unit operations were also specified.

Chemical components:

The Aspen plus databases have an in-built information for the following components which were utilized in the process: methanol, sulphuric acid, tripalmitin, tristearin, triolein, trilinolein, trilinolenin, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, methyl linolenate, phenylalanine,

sucrose, glycerol, water, calcium oxide and calcium sulphate. Additionally, calcium oxide and calcium sulphate were selected to carry out the neutralization of acid because of their inorganic property.

Thermodynamic model:

The polar nature compounds such as glycerol and methanol were employed in the process. Therefore, the non-random two liquid (NRTL) thermodynamic property model was chosen as the base property method to estimate the activity coefficient of the liquid phase in the simulation¹³.

Plant capacity, unit operations and operating conditions:

The plant capacity was assumed to be 1500 kg/h biodiesel (FAME) synthesis. The required amount of raw materials was calculated based on the Ghosh et al.¹⁵. The amount of microalgal biomass, methanol, sulphuric acid and calcium oxide is 2575 kg/h, 10197.9 kg/h, 2781 kg/h and 1591.3 kg/h respectively. The equipment's employed in the process were: mixer, reactor, component separator, distillation column, pumps, neutralization tank, heater and cooler.

Process design:

The detailed process flowsheet of biodiesel production from dried microalgal biomass is depicted in Fig. 2.

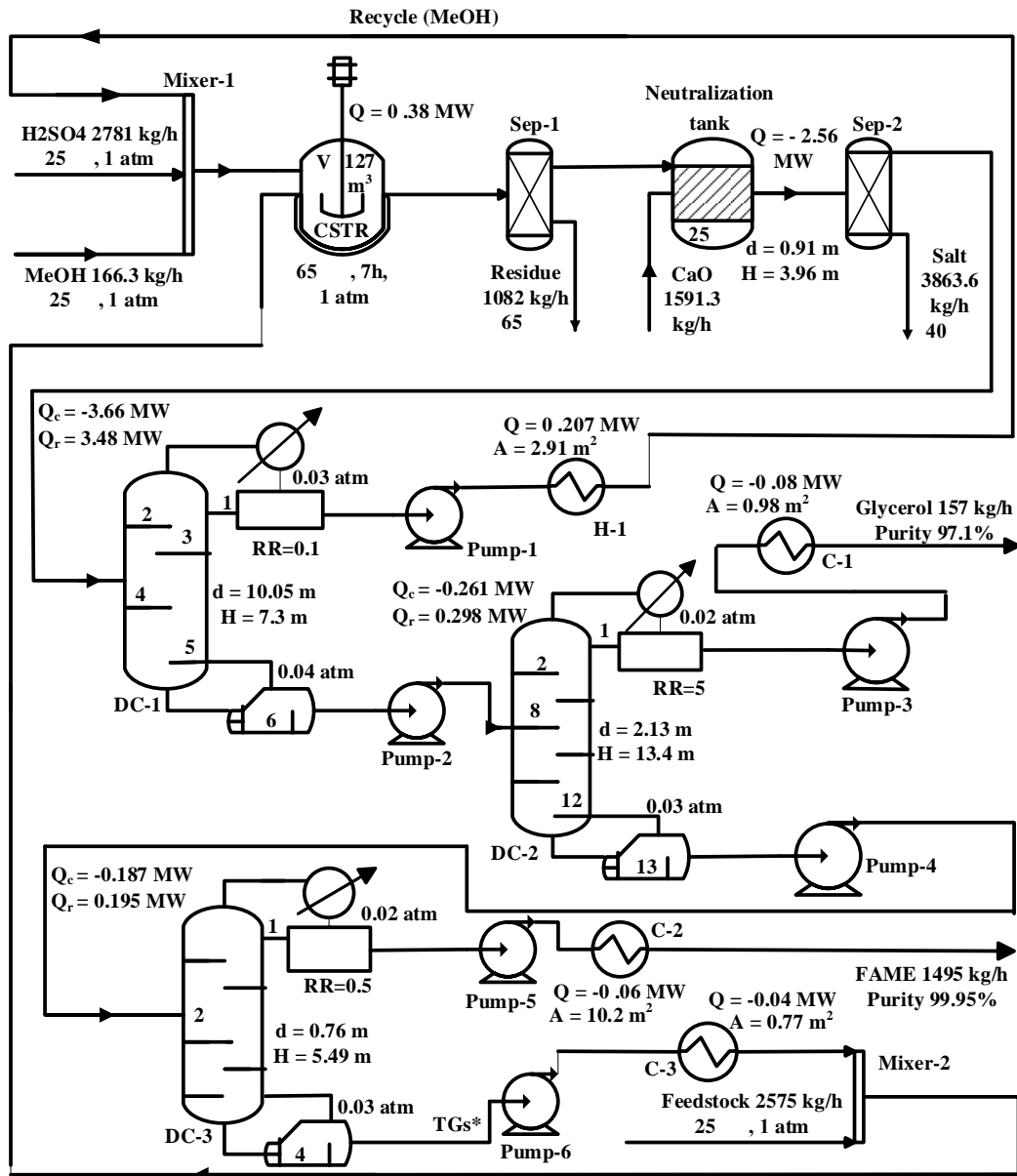


Fig. 2. Schematic process flow diagram of direct biodiesel production from microalgae biomass

In-situ transesterification in a CSTR

Transesterification involves three moles of alcohol and one mole of oil to form three moles of alkyl esters and one mole of glycerol. Generally, the excess of alcohol drives the reaction towards the products' side.

Likewise, alkali, acid or enzyme catalyst can be used to catalyze the transesterification⁸.

In-situ transesterification is a single-stage process, integrates both oil extraction and transesterification to produce biodiesel. Thus, this method reduces the unit operations such as extraction and purification. Therefore,

the equipment requirements, solvent usage, and energy consumption are get decreased. In the present work, in-situ transesterification process is used for the biodiesel synthesis from dried *Chlorella* MJ 11/11 microalgae biomass. The microalgae used in this study contained 58% lipids on dry weight basis¹⁶. The fraction of the remaining components was not mentioned in the base reference. Hence, remaining fraction was equally distributed among carbohydrates and proteins. The dried microalgae biomass was directly charged into the CSTR along with the mixture of methanol and acid catalyst. An acid catalyst, i.e. sulphuric acid, was used because microalgal biomass contains high free fatty acids. In this study, excess of methanol was supplied. Methanol also acts as an extracting solvent. The reactor temperature and reaction time were fixed to 65 °C and 7 h, as per the study by Ghosh et al¹⁵.

Laboratory scale reaction conditions, such as 1:5 (wt./vol) algal biomass to methanol ratio, 65 °C temperature and 7 h reaction time, were considered as operating conditions in this process¹⁵. The variation in FAME concentration was measured. A graph between temperature and rate constant (k) was plotted by varying the temperature in the range from 35 °C to 75°C. A linear plot was obtained, showing first order transesterification reaction. Therefore, it is evident from the results presented in Ghosh et al.¹⁵ that the transesterification reaction follows first-order kinetics with frequency factor and activation energy of 3.22 min⁻¹ (which was converted to second⁻¹ as per the requirement of Aspen Plus software) and 22.828 kJ mol⁻¹, respectively. In this study, the simulation was performed considering the reaction of five triacylglycerols with methanol to produce the corresponding five FAMEs and glycerin. All

reactions were assumed to follow the same kinetics. After the biodiesel was produced through in-situ transesterification reaction, product biodiesel was separated and purified in the downstream. The downstream processing involved residue separation, methanol recovery, catalyst removal, biodiesel purification and glycerin separation.

Catalyst removal

Calcium oxide (CaO) was supplied to neutralize the acid catalysts that form calcium sulphate (CaSO₄). The reaction for the neutralization is shown below as:



The precipitate (calcium sulphate) was removed using a separator and then the desired product (FAME) and the by-product (glycerol) were separated through a series of distillation columns.

Methanol recovery

Selected algal biomass to methanol ratio was 1:5 (wt./vol) which is higher as compared to the stoichiometry of the reaction and therefore the excess methanol must be recycled into the process. This was carried out using a vacuum distillation column to overcome the degradation of biodiesel and glycerol. Methanol is the distillate product with a purity of 100%. The number of stages in the column was chosen based on the required purity and amount of methanol to be distilled while minimizing the reboiler duty. Column with more than six stages and reflux ratio over 0.1 was found to have insignificant effect on methanol purity and recovery. The recovered methanol is heated before being reused and mixed with a fresh stream of methanol prior to entering the reactor. The bottom product comprised of the main mixture of methyl esters, unreacted triglycerides (TGs*), and glycerol at 269 K.

Glycerol separation

Glycerol is recovered using a distillation column having 13 stages. The feed enters on the eighth tray and a reflux ratio of 5 is specified. The glycerol leaves from the top of the column with 97.11% purity (mass basis) and the bottom stream comprising of FAME and unreacted triglycerides was sent to another distillation column for further separation.

Biodiesel separation

Biodiesel-glycerol separation is an essential part of biodiesel synthesis. Biodiesel with a high level of glycerol causes several issues such as storage problem, fuel injector clogging and emission of aldehydes¹⁷. Few studies have been reported for the separation of biodiesel and glycerol mixture by washing with the aid of water^{9,10,18} or gravity settling^{10,12,19}. It was found by Zhang et al.¹¹

Results and discussion

Comparison of simulation results

The simulated process has been validated with previously reported simulation work as well as experimental study. The comparison between the findings of Olivieriet al.²⁰ and the current simulation study is shown in Table 1. These outcomes are in good agreement with each other. However, the wet microalgal biomass was chosen as feedstock by Olivieriet al.²⁰. Moreover, the present findings match well with the experimental study reported by Ghosh et al.¹⁶. Triglycerides conversion of 93.74% [(wt. of lipids- wt. unreacted lipids/wt.) of lipids] and a biodiesel yield of 54.4% (wt. of FAME/wt. of dry biomass) are obtained in this study, which are consistent with Ghosh et al.¹⁵. Therefore, the modelled in-situ process for biodiesel production is consistent since its findings are in

Table 1. Comparison of simulation results

Parameters	Results of this work	Results reported ²⁰
Purity of glycerol (molar %)	98.70	93.92
Purity of FAME (molar %)	98.50	96.80
Conversion of triglycerides (%)	93.77	97.80
Methanol recovery (%)	99.98	92.00

that the desired separation could not be acquired by gravity settling only. Therefore, in this study, biodiesel was separated using a distillation column having four trays. The biodiesel obtained from the top of the column with high purity and unreacted triglycerides in bottom stream was recycled back after cooling down to room temperature.

good agreement with data reported in the literature. Furthermore, sensitivity analysis was performed to analyze the effect of operating parameters such as reaction temperature and reaction time on the process indicators such as biodiesel yield and conversion. An increase in the FAME production was observed when the reaction time was increased beyond 6 h. The reason is being most of the lipids (triglycerides) were already converted in 6 h.

Energy analysis

Condenser and reboiler heat duties of recovery columns along with the energy consumed in each unit operation are shown in Fig. 3). The methanol recovery column for the recovery of excess methanol has a high condenser and reboiler heat duty as compared to the other recovery columns. This excessive amount of heat duty in the distillation column is mainly due to the large amount of methanol to be recycled. Heat was required to elevate the temperature of distillate product from methanol recovery column so that it could be mixed with fresh stream whereas cooling of main product and by-product, i.e. biodiesel and glycerol were done after recovery from distillation column. The overall cooling duty and heating duty of this in-situ process are calculated to be -6.874 MW and 4.567 MW respectively. These duties are relatively small (but significant) as this process considers dried microalgal biomass as a feedstock. Heating duty would be much higher if the energy required for the drying of biomass was to be considered.

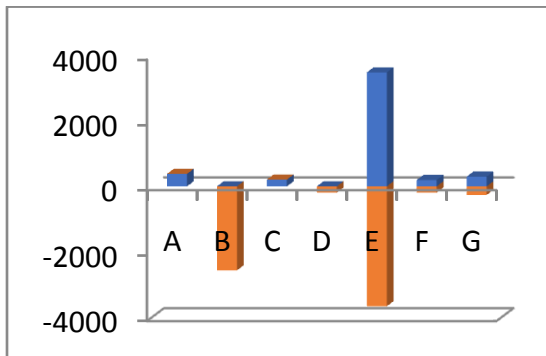


Fig. 3. Energy consumption in each unit [A- CSTR; B- Neutralization tank; C- Heaters; D- Coolers; E- Methanol recovery tower; F- Biodiesel separation tower; G- Glycerol purification tower.

Economies of the process

In general, Lang factor method or bare-module concept was used for the economic estimations^{10,11,13}. These concepts reveal approximate cost estimation and have relatively lower accuracies. Consequently, Aspen in-built economic analyzer was chosen for economic assessment in this work, since it has been employed for over 40 years in commercial plants and process engineering designs, and reveals more accurate cost estimation. Aspen in-built economic analyzer provides economic data and specifications for thorough design and estimation. It allows sensitivity analysis and quick adjustments of the process equipments¹³. Moreover, operating costs, capital costs and the equipments' costs were evaluated using Aspen Economic Analyzer V.11. Figure 4 shows the share of raw material cost and utility cost in the total operating cost. It can be observed that the cost of raw materials (i.e. dried microalgae and chemicals: ~79%) outweighs the cost of utilities and other costs. Since, the utility cost for the drying of wet microalgae has not been considered in this study and also due to high feedstock cost.

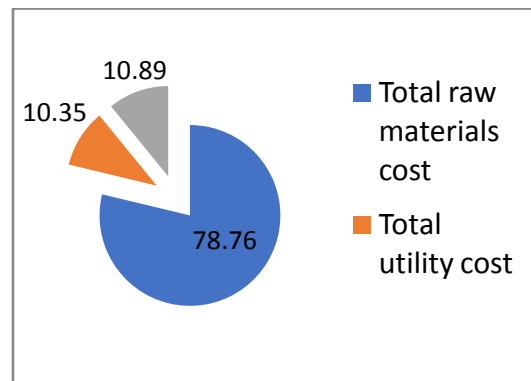


Fig. 4. Share of raw material cost and utility cost in the total operating cost [other costs- labor cost, etc.

Table 3. Comparison between a conventional process and in-situ synthesis process.

Authors	Feedstock	Process	Plant Capacity (kt per year)	TMC (\$ millions)	Product cost (\$/kg)
Mohammadsh irazi et al. ³⁰	Waste cooking oil	Conventional	2000 L	not reported	1.06
Patle et al. ²⁸	Wet microalgae biomass	In-situ	20	11.3	3.13
Heo et al. ²⁹	Wet microalgae biomass	In-situ	0.48	2.08	7.62
This work	Dry microalgae biomass	In-situ	12	6.534	3.75

The total capital expenditure, total utility cost, total raw materials cost, total product sales and total operating cost of the process are presented in Table 2. It has been assumed that the plant producing biodiesel will be installed and operated in Malaysia. The calculated costs of each parameters and also the price of raw materials is considered in US dollars. The price of biodiesel (\$1.464 per kg), methanol (\$0.28 per kg), sulphuric acid (\$0.4 per kg) & calcium oxide (\$0.12 per kg) and biomass (\$1.2 per kg) are obtained from previously reported literature²¹⁻²⁴, whereas costs of residue (\$0.3 per kg), calcium sulphate (\$0.4 per kg), steam (\$1.2 per kg) and cooling water (\$0.4 per kg) are taken from²⁵. Cost of glycerol i.e. \$1.1 per kg is taken from²⁶. Lastly, price of electricity (i.e. 0.06\$ per kWh) is obtained from Lee et al.²⁷. For the biodiesel production, total operating costs and total product sales were M\$ 45.10 and M\$ 61.35 respectively. According to the findings of this work, overall biodiesel production cost was \$/kg 3.75 and the total income was found out to be \$/kg 5.11. Based on these findings net profit was calculated as \$/kg 1.36.

Table 2. Economies of the process

Parameters	Values (\$)
Total capital cost	6.3049*10 ⁶
Equipment cost	1.7981*10 ⁶
Total installed cost	5.3431*10 ⁶
Total raw materials cost	35.5198*10 ⁶
Total product sales	61.3553*10 ⁶
Total operating cost (annually)	45.1037*10 ⁶
Total utility cost (annually)	4.6683*10 ⁶

Comparison with wet microalgae-based in-situ transesterification process

Recently, Patle et al.²⁸ developed and simulated the in-situ biodiesel synthesis from wet microalgae using Aspen plus V8.8 simulation package. The feedstock used in this work was wet "Nannochloropsis sp." microalgae at a mass flowrate of 50322 kg/h. This microalgae feedstock has 27% lipid content on dry cell weight basis. Based on our research group, Patle et al.²⁸ reported the capital cost of the developed in-situ biodiesel synthesis process is about 2.5 to 4 times

higher than the conventional two-step process. However, the former process is better in terms of processing equipments and kinetics of the reaction. For homogeneous catalyzed in-situ biodiesel synthesis, Patle et al.²⁸ reported a total module cost of \$ 11.3 million for a plant producing 20 kt biodiesel annually. Patle et al.²⁸ and in the present study same operational time i.e. 8000 h was considered. In the present work, 20.6 kt of dried microalgae biomass was processed and using Aspen economic analyzer, the total capital cost (i.e. a total module cost was found by multiplying the installed cost by 1.18) of \$6.534 million is obtained. Patle et al.²⁸ reported a production cost of \$3.13 per kg of biodiesel from wet microalgal biomass through in-situ process. This value is low as compared to the production cost (\$ 3.75/kg) of biodiesel obtained in the present study. These differences in costs are because of the following reasons: type of feedstock, the lipid content of microalgae, amount of chemicals, cost of feedstock, costing procedures and their correlations. Finally, the comparison between various routes producing biodiesel is presented in Table 3. It can be seen from the table that the obtained cost of biodiesel is consistent with the biodiesel costs reported by other researchers²⁸⁻³⁰.

Conclusions

In this paper, process development and simulation of the biodiesel production from dried microalgal biomass through in-situ transesterification with acidic catalyst was performed using Aspen plus V11. From a technical standpoint, this process seems to be viable as it produces a high purity biodiesel product which can be employed in blends with petro-diesel. Consequently, microalgal biodiesel production through in-situ

transesterification method could be commercialized if microalgae strain with high oil content and reactants proportion, co-solvents, catalysts and operating conditions such as temperature, pressure are optimally selected. Furthermore, the overall cooling duty and heating duty of the entire process were found to be -6.874 MW and 4.567 MW, respectively. Moreover, the total capital investment and total operating costs were calculated to be \$6.534 million and \$45.104 million, respectively. These numbers denote a significant investment. Moreover, the biodiesel production cost and total outcome was found to be \$ 3.75 per kg and \$ 5.11 per kg respectively. Therefore, net profit was estimated as \$ 1.36 per kg.

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