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Comprehensive analysis and process simulation of biodiesel production from biomass sources

Elavazhagan E[1], Sowmiya A[1] & Sivamani Sivalingam[2]*
[1]Department of Chemical Engineering, Sriram Engineering College, Perumalpattu, Chennai, Tamil Nadu 602 024, India
[2]Department of Chemical Engineering, Rajalakshmi Engineering College, Thandalam, Chennai, Tamil Nadu 602 105, India
*E-mail: sivamchem@gmail.com, sivamani.s@rajalakshmi.edu.in

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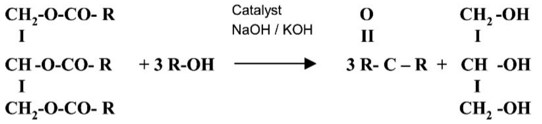
The present research work entails the process simulation of biodiesel production on a large scale using the ASPEN process simulator. Catalytic transesterification and non-catalytic supercritical mode of transesterification are simulated with experimental results and compared to determine the efficient mode of transesterification under different initial feedstock raw material conditions. It is found that the supercritical method (280°C; 276.4 atm; 42:1 for alcohol and oil ratio) is efficient in terms of cost and product quality for the feedstocks with high Free Fatty Acid (FFA) content. For feedstocks with a negligible amount of FFA, alkali-catalyzed homogeneous transesterification (60-65°C; 4atm; 6:1- alcohol: oil ratio) is efficient in terms of product quality and yield although the cost is similar to that of the supercritical mode of transesterification. Pre-treatment steps like simple esterification and glycerolysis for high FFA-contained feedstocks are studied using the ASPEN simulation to understand better the overall process by which the pre-treatment is carried out. Finally, the combustion characteristics of the biodiesel blend along with n-heptane (a surrogate for Petro-diesel) are studied using the Python scripted Cantera combustion chamber and it is found that the amount of soot and carbon monoxide emission is very less indicating complete and efficient combustion. This simulation study is carried out with the help of DWSIM simulation software.

Keywords: ASPEN software, Biofuels, Biodiesel, DWSIM, Simulation study

A recent study on global energy usage shows that a significant amount of energy comes from burning fossil fuels. Due to their innate physicochemical and combustion characteristics, liquid petroleum-based fuels make up most of the fossil fuel contributions. Unfortunately, the fossil fuel reserves especially the liquid fuels are finite and might run out in a few decades if they are not used wisely[1,2]. Throughout the world, efforts are being made to limit the usage of liquid petroleum fuels. There are two main strategies in use. The first step is to convert over alternate energy sources that are either abundant or easily replicated for the energy-consuming equipment. The second is to make combustion devices more effective[1,3]. Biofuels derived from biomass sources provide a better answer to this challenge. Bioethanol and Biodiesel are the potential substitute for petrol and diesel derived from crude oil, respectively. These biofuels are renewable, non-toxic, and biodegradable which can lead the world to sustainable development[3,4]. This work aims to produce biodiesel from various sources and explore possible methods. Direct usage and mixing, microemulsion, transesterification, and pyrolysis are some of the biodiesel production processes that have been introduced. Transesterification is the most extensively used process among these[5,6]. Synthesis of biodiesel from diverse biomasses like vegetable oils and fats, numerous catalytic and non-catalytic transesterification processes can be used[7,8]. Efforts are being made worldwide to limit the usage of liquid petroleum fuels due to cost and availability. In numerous applications around the world, traditional petroleum-based fuels are used as primary sources for energy generation. Excessive use of petroleum resources contributes to global warming, rapid depletion of petroleum reserves, and price volatility of petroleum-based hydrocarbon fuels. As a result, it is now more important than ever to adapt to sustainable alternatives.

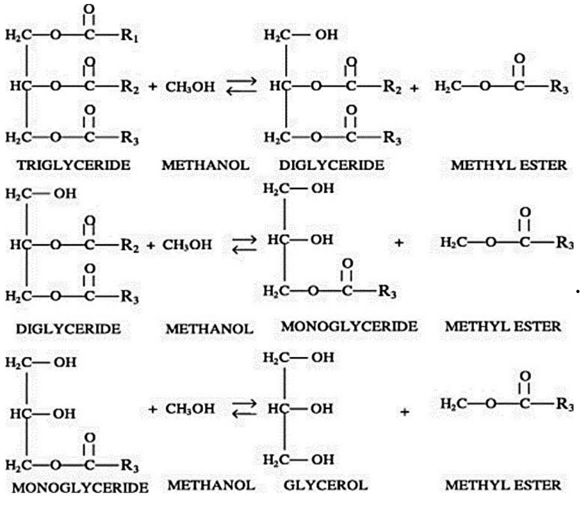
Biodiesel is a sustainable biodegradable fuel produced from used restaurant grease, animal fats, or vegetable oils. These biodiesel has been satisfying the standards for both the overall advanced biofuel and biomass-based diesel. Additionally, most diesel engines may utilize it without needing significant engine changes[1,6]. Biodiesel is a fuel that can be used in diesel engines as a substitute for diesel. In different combinations, plant oils including soybean, cotton seed, canola, and corn oils, repurposed cooking oils or greases like yellow grease, and animal fats like cow tallow and swine lard are used to make it[9,10]. Although they may contain animal fats, used cooking oils are primarily manufactured by plants. Those oils might come from recycled, environmentally friendly sources[11]. The ASTM specifications define biodiesel as a "fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100". Because of its significantly reduced viscosity, transesterified biodiesel can replace petroleum-based diesel in diesel engines.



$$\begin{array}{l}CH_2\text{-O-CO- R}\\ \text{I}\\ CH\text{-O-CO- R}\\ \text{I}\\ CH_2\text{-O-CO- R}\end{array} + 3\,R\text{-OH} \xrightarrow{\text{Catalyst NaOH / KOH}} 3\,R\text{-}\overset{\overset{O}{\text{II}}}{C}\text{-}R + \begin{array}{l}CH_2\text{-OH}\\ \text{I}\\ CH\text{-OH}\\ \text{I}\\ CH_2\text{-OH}\end{array}$$

… (1)

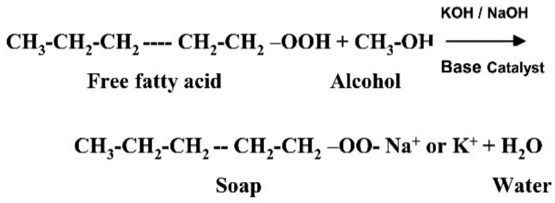
From Eq. (1), R is made up of a variety of fatty acid chains. Typically, methanol is utilized as the alcohol in the production of biodiesel where the R- corresponds to CH_3. So, fatty acids are contained in the glycerol backbone of a triglyceride molecule. This glycerol backbone contributes to the bound glycerol present in the oil/fat feedstocks. Apart from the triglycerides, partial reaction products like diglycerides and monoglycerides also contribute to the bound glycerol content of the initial feedstock. As per the standard specification of biodiesel prescribed by ASTM, the derived biodiesel should not contain more than 24 wt% of glycerol.



… (2)

The above Eq. (2) gives us a clear view of three-step transesterification to give out 3 moles of methyl esters and one glycerol molecule from one triglyceride molecule on reaction with 3 moles of alcohol in which the subsequent partial reaction products (di- and tri-glycerides) are being formed[12,13]. So, in some undesired cases, there might be the chance of failure in this complete reaction, and as we all know that every reaction in the chemical domain is an equilibrium reaction and we have to alter the reaction conditions such as temperature, pressure and composition of the reaction mixture according to Le-Chatelier's principle to shift the equilibrium to the desired direction (in this case- product formation). So, in general, the above-prescribed stoichiometry of (1 oil: 3 alcohols) will not be sufficient for the reaction to be favoured in the direction of methyl esters formation. So, in general, 60% to 100% of excess alcohol is added to arrive at our desired case of the efficient yield of methyl esters[3,14].

Small quantities of water and free fatty acids are frequently found in oils and fats. The lengthy carbon chains mentioned above that are severed from the glycerol backbone make up free fatty acids which are referred to as carboxylic acids at times[15,16]. The FFA present in the feedstock is the detrimental factor that can affect the quality and progressive nature of the reaction and further separations in post-reaction proceedings. The FFA on reaction with the mineral base (NaOH or KOH), yields salt (soap) and water as shown in Eq. (3).

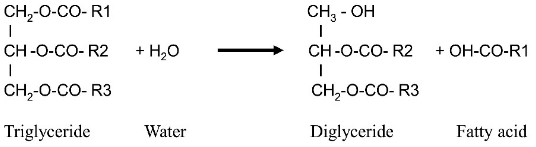


$$\underset{\text{Free fatty acid}}{CH_3\text{-}CH_2\text{-}CH_2\text{----}CH_2\text{-}CH_2\text{ –OOH}} + \underset{\text{Alcohol}}{CH_3\text{-OH}} \xrightarrow[\text{Base Catalyst}]{\text{KOH / NaOH}} \underset{\text{Soap}}{CH_3\text{-}CH_2\text{-}CH_2\text{ -- }CH_2\text{-}CH_2\text{ –OO- }Na^+\text{ or }K^+} + \underset{\text{Water}}{H_2O}$$

...(3)

This reaction is unfavourable because it binds the catalyst into a form that hinders the reaction's ability to proceed more quickly. Excessive soap content can prevent biodiesel from being processed subsequently, including glycerol separation and water washing. Additionally, the FFA will use the catalyst to create soap, preventing the major reaction on the catalytic surface between triglycerides and methanol. This accounts for the reason adding excess catalyst than the usual requirement in such a manner ensures the availability of the catalyst for the main reaction[17,18]. So, the amount of FFA content in the Oil/Fat feed stock should be determined by the acid value test and if the %FFA is less than 1% or more preferably less than 0.5% the FFA in the feedstock can be ignored, and if not, the feedstock should undergo the pre-treatment steps[6,19].

Another issue is water in the fat or oil. In the presence of water, especially at high temperatures, the triglycerides can hydrolyze to create diglycerides and a free fatty acid (Eq. 4). Free fatty acids will undergo the previously described process to produce soap in the presence of an alkali catalyst.



$$\begin{array}{llcll} CH_2\text{-O-CO-}R1 & & & CH_3\text{-}OH & \\ | & & & | & \\ CH\text{-O-CO-}R2 & +H_2O & \longrightarrow & CH\text{-O-CO-}R2 & +OH\text{-CO-}R1 \\ | & & & | & \\ CH_2\text{-O-CO-}R3 & & & CH_2\text{-O-CO-}R3 & \\ \text{Triglyceride} & \text{Water} & & \text{Diglyceride} & \text{Fatty acid} \end{array} \quad \ldots (4)$$

Water usually presents itself in a response by producing an excessive amount of soap. Due to the tendency of saturated fatty acid soaps to solidify at room temperature, an overabundance of soap in a reaction mixture can cause it to gel and create a semi-solid mass that is exceedingly challenging to remove. The main objective of this study is to analyze the different modes of biodiesel synthesis using a process simulator and conclude the best ones under different circumstances. Also, find efficient ways of treating the raw material for biodiesel synthesis with high FFA content and analyze the combustion characteristics of biodiesel blended with the conventional diesel (n-heptane).

Experimental Details

Materials

Vegetable oil (edible and non-edible), animal fat, and recycled grease, primary alcohol (Major feedstock), catalyst (Acid / Base) and neutralizer were used for biodiesel production

Typical proportion of ingredients for transesterification

1. 1: (4 to 6) ➔oil: alcohol mole ratio
2. Catalyst amount: (Base catalysis)- Generally used due to lower residence time

- If theFFA level in the oil is less than 1% (preferably less than 0.5%):
  a. NaOH = 1% of triglyceride (oil) weight.
  b. KOH = 1% of triglyceride (oil) weight.
  c. $NaOCH_3$ = 0.25% of triglyceride (oil) weight.
- If the FFA level in the oil is more than 1% up to (5-6%), an additional catalyst has to be added to account for what will be lost in forming soap. The amount of catalyst needed for such cases is
  a. NaOH = 1% of triglyceride (oil) weight + (%FFA * 0.144)
  b. KOH = 1% of triglyceride (oil) weight + (%FFA * (0.197/0.86))
  c. $NaOCH_3$ = 0.25% of triglyceride (oil) weight + (%FFA * 0.190)

Stages of the biodiesel production process

The following steps were used for biodiesel production.

1. Raw materials treating (pre-treatment)
2. Mixing of Alcohol with catalyst
3. Chemical reaction (transesterification)
4. Separating the products
5. Purifying the products (post-treatment)

Techniques to treat high FFA feedstocks

To determine the required FFA amount the Acid value titration has been used with a given biomass feedstock.

1. Analysis of the Enzymatic technique
2. Analysis of Glycerolysis
3. Analysis of Acid catalysis
4. Analysis of Acid catalysis with alkali catalysis.

Simulation software

ASPEN: ASPEN is a powerful software program for process simulation in the industry. ASPEN uses mathematical models to forecast the performance of the process in the presence of a process design and an acceptable choice of thermodynamic models. The design may then be improved using this knowledge in an iterative method. To effectively separate non-ideal mixtures, correct thermodynamic property modeling is crucial, and ASPEN contains a vast database of regressed parameters. ASPEN is capable of managing a wide range of extremely complex processes, including chemical reactors, multiple-column separation systems, the distillation of chemically reactive substances, and even electrolyte solutions like mineral acids and sodium hydroxide solutions.

The process is not created by ASPEN. It uses a design that the user provides and simulates how the process outlined in that design would run. Therefore, it is essential to have a firm grasp of the fundamental concepts of chemical engineering to provide appropriate input parameter values and assess the acceptability of the outcomes. Before attempting to utilize ASPEN, for example, a user needs to have some understanding of how columns behave. At present frequently utilize ASPEN PLUS, a steady-state process simulator, to mimic the biodiesel manufacturing process. Different methods employed to achieve the goal of biodiesel fulfilling ASTM criteria were investigated and provided as formal flow sheets with the corresponding results in the current context.

For the combustion characteristic of biodiesel produced along with the Petro diesel, we used DWSIM (also a process simulator) to arrive at the desired results.

ASPEN PLUS methodology production can proceed with the following steps,

1. In the process flow sheet, locate the unit activities and the procedure streams that flow to and from them. All streams should be given names and connected to the unit operation models.
2. Characterize the ASPEN PLUS databank's substance columns or identify them there and then.
3. Find the thermodynamic models ASPEN PLUS has integrated to measure the physical characteristics of the components and mixtures concurrently.
4. Determine the thermodynamic circumstances and the information streams' portion stream rates.
5. Determine the operational conditions for the unit.

DWSIM: For the combustion characteristic of biodiesel produced along with the Petro diesel, we used DWSIM (also a process simulator) to arrive at the desired results. This is the open-source software available in the market mainly for students/academicians. We used the DWSIM python-scripted Cantera combustion chamber to study the combustion characteristics of biodiesel as a blend with conventional hydrocarbon diesel. The various steps involved in the simulation using DWSIM are as same as that stated for the ASPEN technology simulation software.

Simulation design developments

(a) Production paths adapted to simulate biodiesel production using the ASPEN simulator:
- Alkali catalyzed homogeneous transesterification
- Non-catalytic supercritical transesterification
- Pre-treatment cum simulation for high FFA contents:
  a) Acid-catalyzed esterification
  b) Glycerolysis-transesterification

(b) Combustion characteristic of biodiesel-petro diesel blend using python scripted Cantera combustion chamber in DWSIM process simulator.

Results and Discussions

Homogeneous base catalysis in biodiesel synthesis[9]:[Modeling tool: ASPEN PLUS]

Step 1: Adding the components[21]

OIL (TG+DG+MG), Primary Alcohol, Fames, Glycerol, Water. Table 1 describes the composition of the raw palm oil taken into consideration for the homogeneous base catalysis transesterification. It can be noticed that various components are present in the palm oil (composition profile) which could be used[20,21].

Step 2: Method (Thermodynamic Model): UNIF-DMD

The UNIFAC approach is a semi-empirical method for forecasting non-electrolyte activity in unworkable

Table 1 — Components in alkali-catalyzed transesterification in conventional type

Component Id	Component Name	Alias
METH+F3:F31ANOL	Methanol	CH_4O
OOO	Triolein	$C_{57}H_{104}O_6$
MMM	Trimyristin	$C_{45}H_{86}O_6$
METHYL-O	Methyl-Oleate	$C_{19}H_{36}O_2$
GLYCEROL	Glycerol	$C_3H_8O_3$
NAOH	Sodium-Hydroxide	NaOH
WATER	Water	H_2O
H3PO4	Orthophosphoric-Acid	H_3PO_4
NA3PO4	Trisodium-Phosphate	Na_3PO_4
PPP	Tripalmitin	$C_{51}H_{98}O_6$++
METHYL-P	Methyl-Palmitate	$C_{17}H_{34}$O2-N1
PPS	Tag-Pps	$C_{53}H_{102}O_6$-13
PPO	Tag-Pop	$C_{53}H_{100}O_6$-5
POS	Tag-Pos	$C_{55}H_{104}O_6$-3
MMP	Tag-Mmp	$C_{47}H_{90}O_6$-10
PPLI	Tag-Plip	$C_{53}H_{98}O_6$-5
POO	Tag-Poo	$C_{55}H_{102}O_6$-6
PLIO	Tag-Plio	$C_{55}H_{100}O_6$-7
OOS	Tag-Oos	$C_{57}H_{106}O_6$-4
OOLI	Tag-Ooli	$C_{57}H_{102}O_6$-5
MPLI	Tag-Mlip	$C_{51}H_{94}O_6$-3
METHYL-M	Methyl-Myristate	$C_{15}H_{30}O_2$-N1
METHYL-S	Methyl-Stearate	$C_{19}H_{38}O_2$-N1
METHY-LI	Methyl-Linoleate	$C_{19}H_{34}O_2$
1-M	1-Monomyristin	$C_{17}H_{34}O_4$
1-P	1-Monopalmitin	$C_{19}H_{38}O_4$
1-S	1-Monostearin	$C_{21}H_{42}O_4$
1-O	Monoolein	$C_{21}H_{40}O_4$
1-LI	1-Monolinolein	$C_{21}H_{38}O_4$-1
MM	1,3-Dimyristin	$C_{31}H_{60}O_5$-1
PP	1,3-Dipalmitin	$C_{35}H_{68}O_5$-1
OO	1,2-Diolein	$C_{39}H_{72}O_5$-2
PO	Sn-1-Palmito-3-Olein	$C_{37}H_{70}O_5$-3
PLI	Sn-1-Palmito-3-Linolein	$C_{37}H_{68}O_5$-3
MP	Sn-1-Myristo-3-Palmitin	$C_{33}H_{64}O_5$-7
PS	Sn-1-Palmito-3-Stearin	$C_{37}H_{72}O_5$-7
OS	Sn-1-Oleo-3-Stearin	$C_{39}H_{74}O_5$-4
LIO	Sn-1-Linoleo-3-Olein	$C_{39}H_{70}O_5$-8
MLI	Sn-1-Myristo-3-Linolein	$C_{35}H_{64}O_5$-3

combinations (UNIQUAC Functional-group Activity Coefficients). UNIFAC uses the functional groups of the molecules that make up the liquid mixture to determine the activity coefficients[22]. The parameters are given in Table S1 (Supplementary Information). The Redlich-Kwong-Soave (RKS) property method was used[22,23] for all thermodynamic characteristics other than liquid molar volume. The general model for real components and the API method for liquid molar volume of fictitious components were used.

Biodiesel uses the Dortmund-adapted UNIFAC property technique. This is appropriate for introductory work. Although an estimate of NRTL binary interaction parameters is required, NRTL would likely produce more accurate findings. The new biodiesel databank presently has tri-, di-, and mono-glyceride thermo-physical property model parameters available. This includes the following terms: vapour pressure, the heat of vapourization, ideal gas heat capacity, liquid heat capacity, liquid molar volume, and liquid viscosity. The literature has provided in-depth details for the creation of these thermo-physical property models[10].

Step 3: Simulation

Triglycerides (TG) like OOO, PPP, and MMM are all included in vegetable oil[21]. We assume that the palm oil feedstock used in this biodiesel model has a composition profile given by CheMan's research[20]. The flow sheet is based on information reported by Zhang et al.[9]. The vital operations in the alkali catalyzed transesterification are given in Table S2.

Reactions: Transesterification kinetics- Palm oil

Table S3 presents the reactions predicted to be taken place in the reactor based on the experimental analysis[9]. These kinetic reactions have been intruded into the simulation data manually in the reactor kinetic module.

Catalyst Removal

$$3\,NaOH + H_3PO_4 \text{ ----> } Na_3PO_4 + 3\,H_2O \qquad \ldots (5)$$

The kinetic parameters for reactions 1 to 96 can be seen in Table S4 which are derived from the work of Narvaez[24] in 2007. The power expression used for the rate-controlled transesterification reactions is given in Eq. 6.

$$r = k\left(\frac{T}{T_0}\right)^n \exp\left(\frac{-E}{RT}\right)\prod_{i=1}^{N} C_i^{ai}\left(\frac{1}{T}-\frac{1}{T_O}\right) \qquad \ldots (6)$$

Where, r = Rate of reaction, T = Absolute temperature, k = Pre-exponential factor, E = Activation energy,^{o} T = Reference temperature, n= Temperature exponent, R = Universal gas constant, Ci= Concentration of component I, N= Number of components in the reaction, a_i= the reaction equation's component i's stoichiometric coefficient.

Table S5 depicts the unit operations and corresponding equipment selected as the simulation module tool to simulate the homogeneous base catalysis biodiesel simulation in the ASPEN PLUS simulator. The simulation module of homogeneous catalysis cum biodiesel production and the main segments involved in the production are highlighted in Fig. 1.

Results from the Simulation

We could able to observe the key results of homogeneous base catalysis transesterification from Table 2, which includes the product fraction and its purity. Note that if we follow the exact washing and neutralization as suggested in the process, anyone can get purer products.

Biodiesel Composition

The composition of the biodiesel processed from palm oil is shown in Table 3. The density of the biodiesel is found to be 873.6 kg/m^3 (at 15°C) which are similar to that of the commercial petro-diesel at the same temperature. As the conversion is good for the suggested process, 99.7% of FAME (biodiesel) has been obtained with only a trace amount of partially converted products.

Recycled oil composition

Table S6 shows the composition of unconverted oil in the process which is recycled back to the reactor. This table classifies the composition of recycled oil in terms of monoglycerides, diglycerides, triglycerides, and FAMEs percentage. The total mass flow of the recycled oil is found to be 41.57 kg/h.

Supercritical method for biodiesel synthesis[8].[TOOL: ASPEN PLUS]

Step 1: Select the components for the simulation

The sample raw material oil with the following composition is taken for the simplified analysis of the BD production using the supercritical method. The components in SC transesterification, conventional type is given in Table S7.

Step 2: Method (Thermodynamic Model) [7]

Chemical species' properties in the liquid and vapour phases were predicted using ASPEN plus's NRTL-Redlich-Kwong property approach. This is

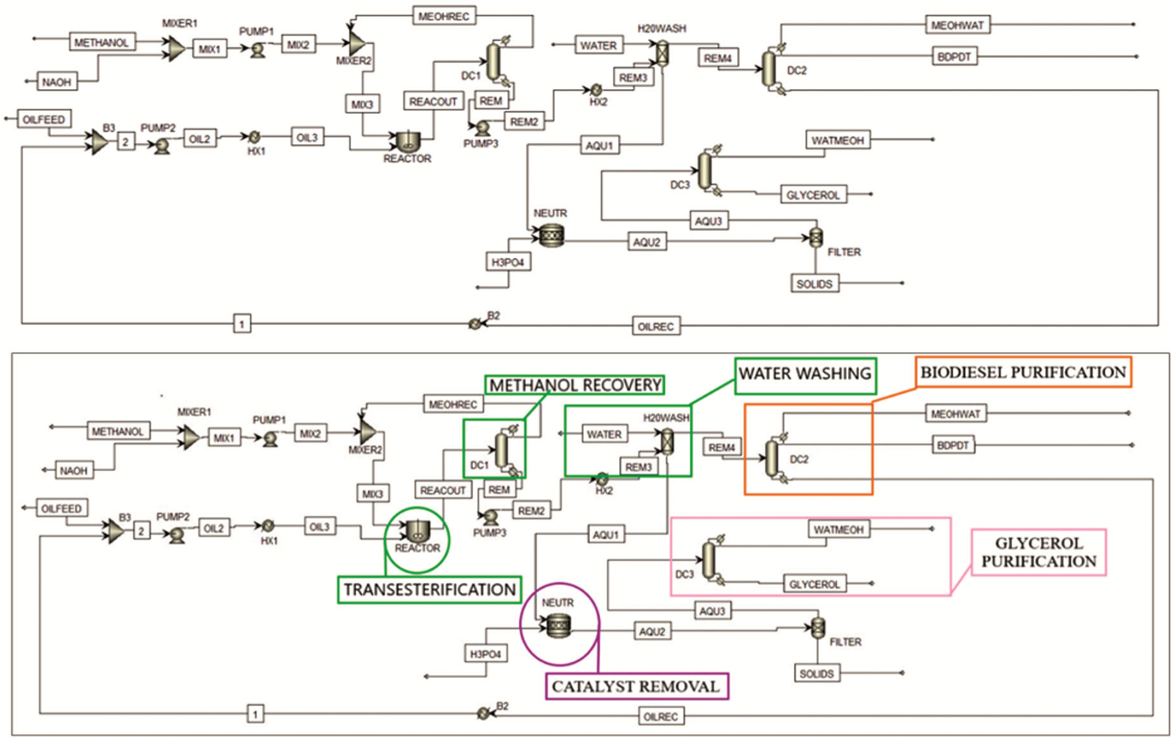


Fig. 1 — Alkali homogeneous catalysis transesterification

Table 2 — Key results of the simulation

S. No	Result	Value	Unit
1	Plant capacity (pure FAME)	9.19	MM kg/yr
2	Oil feed	1050	kg/h
3	Methanol feed	127.1	kg/h
4	Catalyst feed	50	kg/h
5	H_3PO_4 feed	40.8	kg/h
6	Cleaning of Water feed	50	kg/h
7	Biodiesel composition of transesterification reactor	0.756	Mass fraction
8	Transesterification reactor oil conversion	0.98	1 h
9	Product FAME purity	0.997	Mass fraction
10	Product Glycerol purity	1	Mass fraction

Table 3 — Composition of Biodiesel obtained from the simulation

S. No	Constituent in the Biodiesel	Value
1	Methyl-O	37.82wt%
2	Methyl-P	49.33wt%
3	Methyl-M	2.15wt%
4	Methyl-S	2.82wt%
5	Methyl-Li	7.58wt%
6	TOTAL FAME	99.7wt%
7	Monoglycerides	0.27wt%
8	Diglycerides	Trace
9	Triglycerides	Trace
10	Density at 15°C	873.6 kg/m^3

because it has been shown that the Redlich-Kwong model is adequate for forecasting chemical species' vapour-liquid equilibria under supercritical and subcritical conditions, whilst the NRTL activity coefficient model is adequate for predicting such equilibria at moderate settings. The triolein triglyceride molecule used in this study was modeled using actual data on the subcritical lipid hydrolysis of triolein and kinetic models of the supercritical oleic acid esterification and supercritical transesterification reactions to create methyl oleate[25]. The VLE and LLE of highly non-ideal solutions can be described by the NRTL model. An activity coefficient is calculated using the non-random two-liquid (NRTL) model to account for non-ideality in the liquid phase.

Step 3: Simulation

This basic model explores the transesterification of oil containing a single triglyceride composition (Triolein) with methanol as per the experimental results reported[7,8,26]. At very high pressure and temperature (i.e., above the critical point, the fluid tends to enter the supercritical range where the fluid can exhibit an unusual behaviour of both liquid and gas. Both the liquid phase and gas phase tends to coexist. In this study cum simulation, methanol (primary alcohol) for transesterification exhibits the supercritical nature when appropriate temperature and pressure are maintained above the critical points. The high methanol-to-oil ratio is another inevitable requirement of this supercritical process. According to an experimental study by Onyiah (2015)[7], the rate constant of the supercritical transesterification process was reported as 280°C of operating temperature, 42:1 for the molar ratio of methanol to triglyceride, and 28 MPa pressure.

$$\text{TAG} + 3\text{MeOH} \rightarrow 3\text{FAME} + \text{Glycerol} \quad \dots (7)$$

$$r_{sp} = \frac{-dC_{TAG}}{dt} \cong k_{sp}C_{TAG} \quad \dots (8)$$

$$k_{sp} = 141.796\ e^{-(56000/RT)} \quad \dots (9)$$

where C_{TAG} is the concentration of triglyceride in asupercritical transesterification reaction, k_{sp} is the rate constant of supercritical transesterification in s^{-1}, the constant value 141.796 is the pre-exponential constant in s^{-1}, the constant value 56,000 is the activation energy in kJ/kmol, R is the universal gas constant 8.314 kJ/kmol. K and T are the temperatures in K.

Table S8 depicts the unit operations and corresponding equipment selected as the simulation module tool to simulate the supercritical mode of biodiesel production in the ASPEN PLUS simulator. The ASPEN PLUS simulation module of supercritical biodiesel production and the main segments involved in the production are highlighted with the help of the below depicted in Fig. 2.

Results from the simulation

Table 4 shows the key results of a supercritical mode of biodiesel production simulation module and it is apparent that a large quantity of methanol is used in this simulation under a non-catalytic route with set reaction parameters (temperature=280°C, pressure=28 MPa and oil: methanol= 1:42).

Biodiesel composition

Table 5 is the composition profile of biodiesel obtained from the supercritical mode of transesterification and the product purity is about 93.8%.

Developing simulation model for pre-treatment of high FFA contained feedstock

Esterification serves to be the efficient pretreatment step for high FFA-contained feedstock. These stocks have to be treated since the FFA has a high potential

Table 4 — Key results of SC transesterification

S. No	Result	Value	Unit
1	Oil feed	1050	kg/h
2	Methanol feed	1595.7	kg/h
3	Transesterification reactor biodiesel composition	0.37768	Mass fraction
4	Transesterification reactor oil conversion	0.8947	Fraction
5	Product FAME purity	0.9383	Mass fraction
6	Product Glycerol purity	0.9675	Mass fraction
7	Reactor heat duty (RSTIOC)	198872.135	cal/sec

Table 5 — Biodiesel composition from SC Trans, Mass fraction unit

S. No.	Constituent in the biodiesel	Value
1	Methyl-O	0.9383
2	Triolein	0.061005
3	Methanol	2.55E-30
4	Glycerol	0.00067

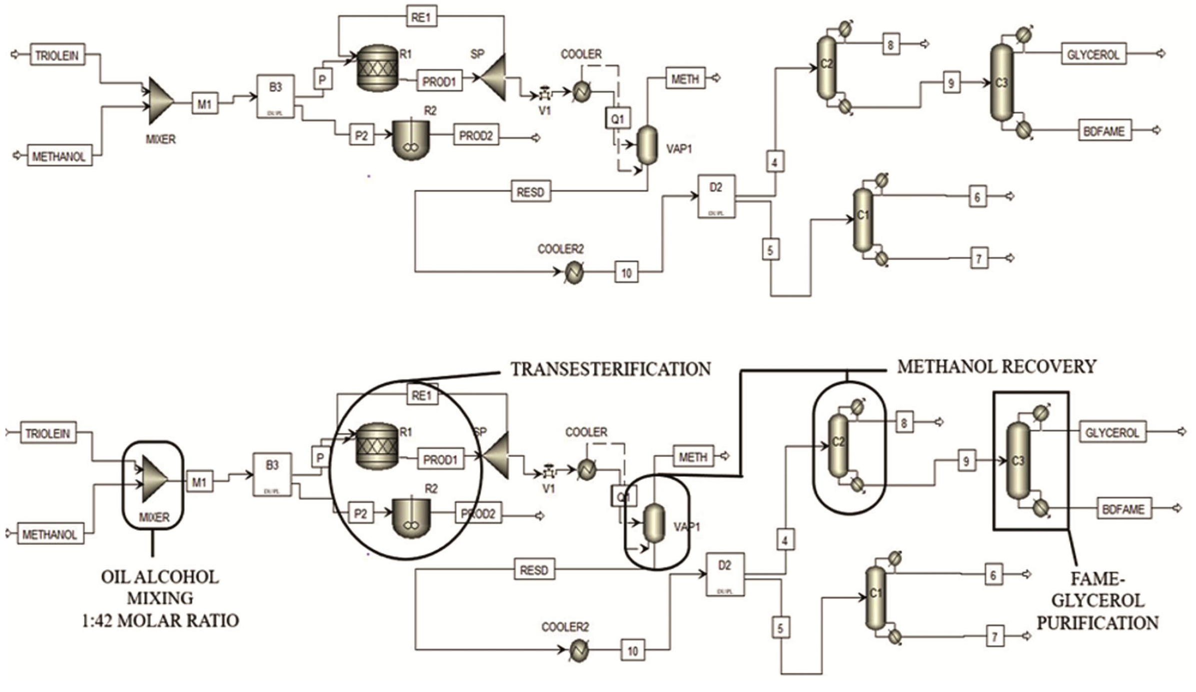


Fig. 2 — Supercritical biodiesel synthesis main PFD

of forming soap on reacting with the alkali in base-catalyzed transesterification which is the widely adopted method of BD production. The acid catalyst can enhance the rate of esterification to yield methyl esters and water as the product. Alcohol and the FFA-containing feedstock react in the presence of an acid catalyst to produce esters and water. Generally, acid-catalyzed transesterification is a very slow process but can help us in converting the high FFA-contained feedstocks to the potential feedstock with lesser /no FFA for further transesterification. The simple esterification reaction is modeled using theASPEN HYSYS simulation tool.

***Step 1: Select the components for the simulation*:**

A simple component set comprising of oleic acid, methanol, methyl oleate and water is selected to study the simple esterification reaction.

Step 2: Selecting the thermodynamic fluid package

PRSV fluid package is selected for this Hysys work. The PRSV model is a two-part modification of the Peng-Robinson equation of state that allows the original Peng-Robinson technique to be applied to somewhat non-ideal systems. This EOS is proven to match pure component and mixture vapour pressure curves more precisely than the PR approach, particularly at low vapour pressures. It has been effectively extended to handle non-ideal systems, yielding results that are comparable to those obtained using excess Gibb's energy functions such as the Wilson, NRTL, or UNIQUAC equations.

***Step 3: Simulation*:**

The simple esterification equilibrium reaction set is defined as given below,

$$\text{FFA} + \text{Methanol} \rightarrow \text{Methyl oleate} + H_2O \qquad \dots (10)$$

Once the reaction set is properly specified, then the set is connected to the flow process. For the esterification, an equilibrium reactor is used. The feed is specified with the conditions as oleic acid fraction=0.40 M, methanol fraction=0.40 M, temperature=60°C, pressure=101.3 kPa and molar flow rate = 100 kmol/h.

Then the reaction set is specified, and the reaction is carried out to yield vapour and liquid products. The results suggest that the methanol and water formed during the reaction are obtained as the overhead product and the methyl oleate along with the unreacted oil, methanol, and water is obtained as the bottom liquid product.

Fig. 3 represents the simple esterification reactor module in the ASPEN HSYS simulator which results in a liquid methyl ester product following the above stated reaction of FFA with the primary alcohol (i.e. methanol here)

Results of the Simulation

Table 6 shows that some amount of FFA content can be pretreated by esterification to tackle the high FFA content of the feed raw material oil. The methyl ester from the liquid stream can be separated using any of the separators and the remaining can be re-esterified to obtain more conversion. The resultant can be used as the feedstock to the transesterification by base catalysis.

Glycerolysis

The high FFA concentration of the feedstock is used in this method to make mono- and di-glycerides by allowing them to react with glycerol at a high temperature (200°C) in the presence of a catalyst (Zinc chloride, ZnCl). The user-specific glycerolysis model representing the general process design of biodiesel is developed using ASPEN PLUS.

Step 1: Selecting the components

In this study case, the feed is made in such a manner to contain oleic acid which is converted to MONOOLEIN and DIOLEIN with the help of the glycerolysis process as the pre-treatment step. The components in glycerolysis simulation are given in Table S9.

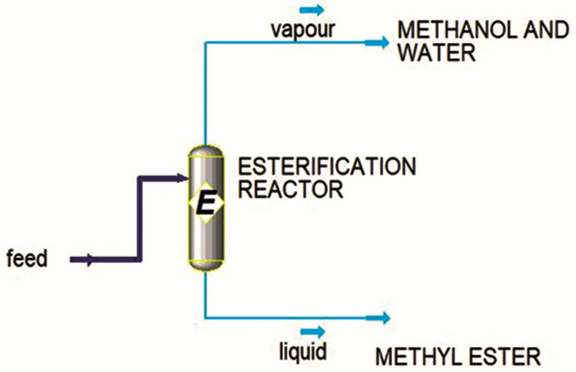


Fig. 3 — Simple esterification

Table 6 — Results of esterification

Component	Methanol and Water (vapour)	Methyl ester (Liquid)
	Molar fraction	Molar fraction
Methyl oleate	0	0.1124
Methanol	0.9113	0.4875
Water	0.0887	0.1124
Oleic acid	0	0.2875

Step 2: Method (Thermodynamic Model)

A semi-empirical method for predicting non-electrolyte activity in impractical mixtures is the UNIFAC method (UNIQUAC Functional-group Activity Coefficients). Activity coefficients are determined by UNIFAC using the functional groups of the molecules that make up the liquid mixture.

Step 3: Simulation (Process Design Model)

This process involves the sequel of steps as, pretreatment Glycerolysis, Transesterification followed by FAME and Glycerol Purification. The process flow model has been developed to understand the above-stated processes and the user design flow sheeting model is developed using ASPEN PLUS and they are depicted in Fig. 4.

Process Description

Glycerolysis is carried out for the feedstock with high FFA content (under a high temperature of 200℃). The glycerol obtained from the transesterification can be purified and used for the above-stated process. As the result of carrying out glycerolysis, we end up obtaining mono and diglycerides of corresponding FFA's present in the feedstock. The resultant product of the glycerolysis is fed as feed to the transesterification process where the feed reacts with primary alcohol to yield the biodiesel (FAME) and glycerol byproduct. The excess primary alcohol is recovered and reused along with fresh alcohol. The products formed are properly treated before they were dispatched to the market. Fig. 4 is the main simulation module design of glycerolysis and the resultant di/monoglycerides are treated with methanol in further steps to obtain the biodiesel product.

Studying the combustion characteristics of biodiesel using DWSIM simulation tool

Step 1: Selecting the Components

Table S10 shows the components involved in this combustion characteristic study of biodiesel blend using the DWSIM PROCESS SIMULATOR.

Step 2: Selecting Thermodynamic Model: Raoult's Law

In this study cum analysis Raoult's law is chosen as the thermodynamic package considering the whole blend to be the ideal kind of the mixture. The phase rule shows that the two phases at a specific T and P are not independent when an ideal solution and a perfect gas are thought to be in equilibrium. According to Raoult's Law, species are distributed between the liquid and gas phases.

$$p_i = y_i P = x_i p_i^o \qquad \ldots (11)$$

Step 3: Simulation

The combustion characteristics of the biodiesel blend along with the conventional diesel (n-Heptane) have been studied using the Python-scripted Cantera combustion chamber in the DWSIM simulation tool. In this mere study concerning the model tutorial of DWSIM, methyl decanoate is considered to be the FAME. It is mixed along with air and n-heptane in the mixer block and further admitted to a python-scripted combustion chamber. The temperature of FAME, n-heptane, and the air are maintained at 1000K under atmospheric conditions. After undergoing the combustion in the Cantera chamber, the products of the

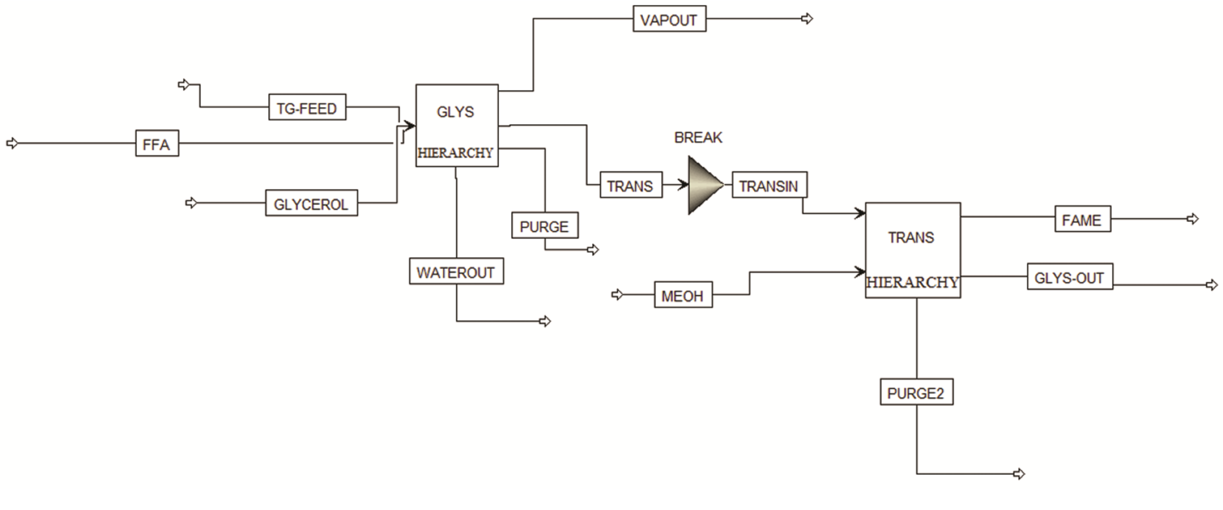


Fig. 4 — Overall process flow design of glycerolizes cum transesterification

combustion are analyzed with the help of separation columns as shown in the PFD to arrive at the results (Fig. 5).

Results of the combustion characteristics

Table S11 represents the mass and energy balance of the Python-scripted Cantera combustion characteristic study done with the help of DWSIM. The Cantera combustion chamber model PFD is shown in Fig. 6.

Table 7 shows the results of the combustion and it is found that the combustion of the biodiesel blend with the petro-diesel resulted in a significant reduction in the waste and partial reaction product.

Table 8 describes the comparison of results obtained from the homogenous base catalysis module and supercritical transesterification module.

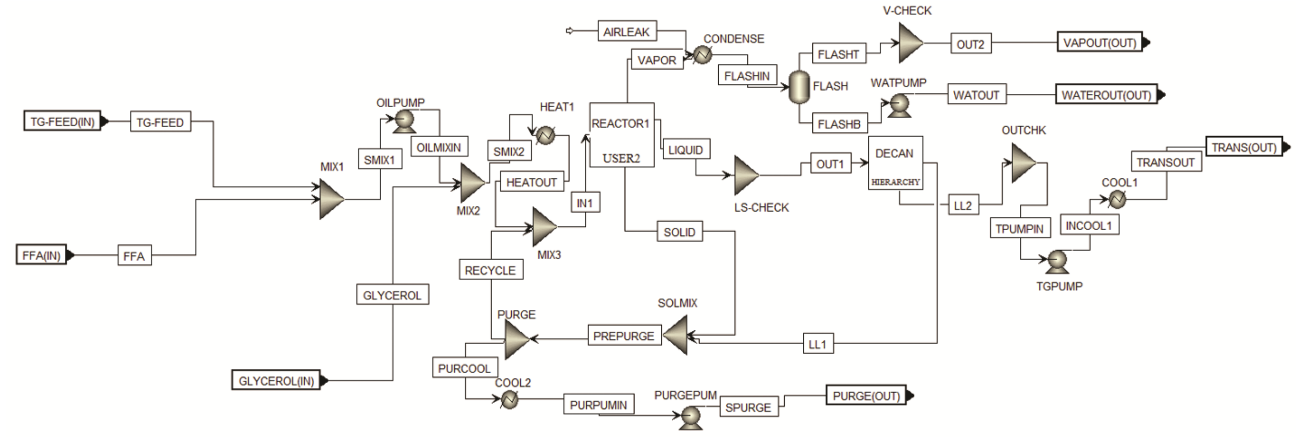


Fig. 5 — Detailed PFD of GLYS hierarchy block

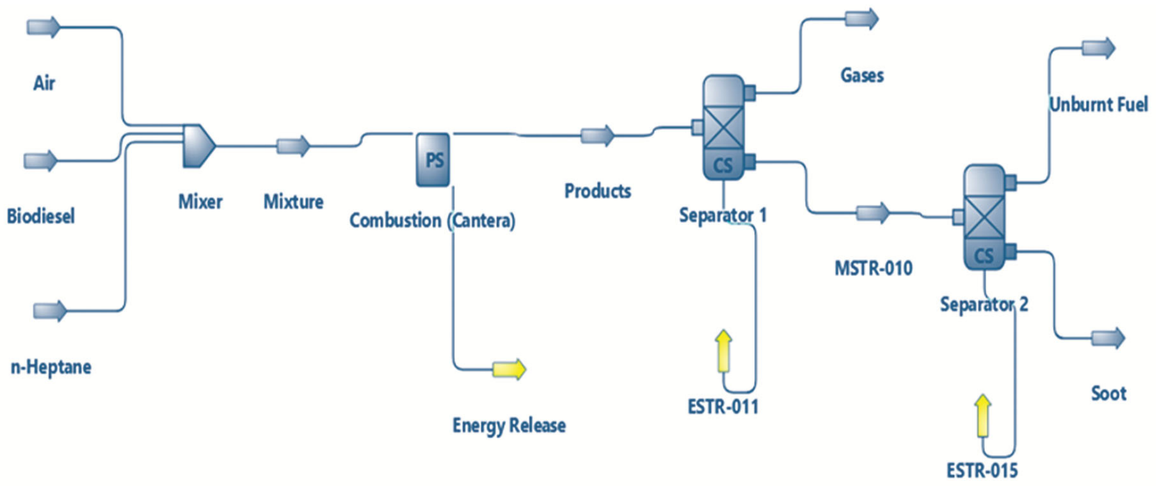


Fig. 6 — Cantera combustion chamber model PFD

Table 7 — Results on combustion

	Combustion results		Units
Energy Release	Energy Flow	350330	kW
Biodiesel	Mass Flow	10	kg/s
Soot	Mass Flow	3.11E-81	kg/s
Unburnt Fuel	Mass Flow	5.32E-48	kg/s
Products	Mass Flow (Mixture) / Carbon monoxide	8.40E-09	kg/s
Products	Mass Flow (Mixture) / Carbon dioxide	26.2939	kg/s
Air	Mass Flow	125	kg/s

Table 8 — Comparative results of alkali-catalyzed and supercritical transesterification simulations

Parameters/results	Conventional homogenous catalysis	Supercritical transesterification	Units
Feed input	1050	1050	Kg/hr
Methanol input	127.1	1593	Kg/hr
Feed: methanol ratio	01:06	01:42	Mole ratio
Temperature (in the reactor)	60	280	°C
Pressure (in a reactor)	400000	28000000	Pa
Biodiesel molar flow	0.001041395	0.000815479	Kmol/sec
Glycerol	0.000344369	0.000177596	Kmol/sec
Catalyst feed	50	No catalyst	Kg/hr
Reactor	Cstr	Stoichiometric reactor	No unit
Energy	2.99e+05	1.68e+06	Watt
Energy savings	19.63	36.47	%
Capital cost	541310072.5	468795588.3	Rupees
Utility cost	8025276.58	6566644.74	Rupees/yr.

Conclusion

The harmful emission level of biodiesel is very much lesser than that of conventional petroleum sources as proven by the DWSIM analyzing work. For feeds with high amounts of FFA content, a proper pretreatment step was done, and further transesterification process proceeded. From the obtained results, it is apparent that the supercritical process is highly energy-consuming and they can be adopted with proper heat integration, thus utilizing the energy generated within the process as a potential source in other units involved which as a whole results in an overall reduction in energy consumption. Although the supercritical method is a highly energy-consuming process in terms of cost, homogeneous catalyst-based transesterification is costlier than supercritical transesterification due to the requirement of in-process water washing and neutralization steps to enhance product purity.

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Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789.

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