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# Reaction Parameters and Energy Optimisation for Biodiesel Production Using a Supercritical Process

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Biodiesel has been proven to be the best reliable alternative for petroleum diesel. Besides, being renewable, it is biodegradable and non-toxic fuel. This paper aimed to study the production of this green fuel using industrial, competitive techniques; base-catalysed transesterification and supercritical methanol transesterification. The research involved techniques for reaction parameters optimisation and thus embedded optimum values into a simulation-based design procedure for overall energy optimisation/integration and emissions reduction.

Literature experimental reaction data for the two technologies conduct an optimisation for biodiesel production. The state-of-the-art process flowsheets for the two processes were used for the study. This optimisation was done for the most affecting parameters on the production processes. The experimental results from the literature for the two techniques were optimally analysed using parameters analyse carried out using Pareto chart, contour plot methodology, and surface plot methodology. The research study revealed that the key process variable for the base-catalysed process was the catalyst loading. On the other hand, for the supercritical methanol process, the most prominent variable was the methanol to oil ratio. The optimal process conditions were used to build an ASPEN HYSYS rigorous simulation model for the previous techniques. The supercritical based-process was chosen for further studies for its better economic performance.

Pinch Analysis principles through ASPEN Energy Analyser software were employed to analyse the energy performance of the overall optimum model obtained from ASPEN HYSYS. The energy targets were calculated for biodiesel production using supercritical methanol approach. Composite curves resulted in 3.4 and 3.7 MW for heating and cooling requirements, respectively compared with 4.4 and 4.7 MW for the original process. Finally, a heat exchanger network was developed to accomplish the energy targets proposed by the composite curves. The resulting integrated process flowsheet has better energy saving opportunities. The energy consumption of the optimum case has been reduced by 25 %, and thus substantial cut in the CO<sub>2</sub> emissions. Utility curves were also generated to determine the loads of hot utilities to be produced by the proposed energy integration.

## 1. Introduction

Biodiesel is defined as the monoalkyl esters of long chain fatty acids to be used in compression ignition engine. The term biodiesel usually refers to an ester made from the oil and methanol (fatty acid methyl ester - FAME). Biodiesel is considered as the 'green fuel' of choice, this mainly returns to its renewable source and lower emissions. Commonly, it is prepared by reacting the triglycerides in vegetable oils with alcohol; this reaction is called the transesterification reaction.

### 1.1 Basics of transesterification process and process variables

The transesterification process can be defined as the chemical modification applied to the oil to produce biodiesel. Transesterification is the crucial, vital process used to produce cleaner and environmentally safer fuel from triglycerides that exist in vegetable oils (Meher et al., 2006). Chemically, transesterification is similar to hydrolysis, except that alcohol is used instead of water to be displaced from an ester by another (Meher et al., 2006). Commonly, the high viscosity of triglycerides is reduced by the mean of this process.

The transesterification reaction depends on some process variables or reaction parameters. Optimisation of these variables and identification for the optimal conditions greatly affect the yield and purity of biodiesel. The main common popular variables are the type of feedstock, type of catalyst, catalyst loading, alcohol to oil molar ratio, reaction temperature, and reaction time.

### 1.2 Base-catalysed transesterification approach

Base-catalysed transesterification is the process at which the triglycerides reacted with an anhydrous alcohol in the presence of an alkaline catalyst. In the biodiesel reactor the final mixture is stirred vigorously for 3 h at 65 °C. A successful transesterification reaction produces two liquid phases: ester and crude glycerin. After 10 min the phase separation is obviously noticed and can be completed within 2 h of settling. After complete settling, water is stirred with the mixture for 5 min and the glycerine is allowed to settle again.

(Vicente et al., 2007) developed experimental results for this technique. The results shows that the conversion of triglycerides to biodiesel is correlated with the temperature of the reaction, the catalyst loading and methanol to oil molar ratio. The time of reaction was fixed at 3 h. The optimum conditions were found to be at 25 °C for the temperature, 1.3 % for catalyst loading and 6:1 methanol to oil molar ratio.

### 1.3 Supercritical methanol transesterification approach

Supercritical transesterification is a possible alternative to the typical catalytic routes. Supercritical methanol transesterification shows nearly a complete conversion in a relatively short period (2-8 min) (Warabi et al., 2004) for the reaction to take place high temperatures and large alcohol to oil ratios are employed to achieve the high levels of conversion. The operating temperature could reach 350 °C and the alcohol to oil ratio is about 42:1 (Kusdiana et al., 2001).

(Kusdiana et al., 2001) obtained experimental data for supercritical methanol transesterification. They correlated the conversion of triglycerides into biodiesel with the reaction time in minutes and the methanol to oil molar ratio. The optimum conditions, that achieve almost complete conversion was found to be at 8 min and 42:1 methanol to oil molar ratio.

## 2. Parameter optimisation and rigorous HYSYS model simulation of base-catalysed transesterification technique

### 2.1 Pareto chart

Pareto chart for this approach is presented in Figure 1. It is clear from the figure that the factors affect the yield of biodiesel the most are mainly B (catalyst loading) followed by AB (catalyst and temperature). So, we can conclude that the catalyst loading is the most affecting parameter that highly influencing base-catalysed transesterification, which agrees with the analysis of (Vicente et al., 2007).

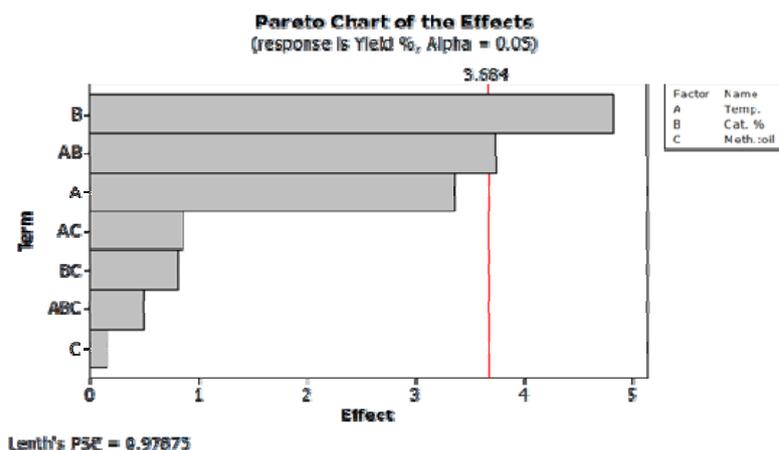


Figure 1: Pareto chart for base-catalysed transesterification

### 2.2 Contour plot methodology

Contour plots are used to investigate the potential relationship between three variables (while holding other variables constant if any). Contour plots present the 3-dimensional relationship on x-y coordinates. Predictors (variables) are plotted on x- and y-scales and response is displayed by contours.

Further, Figure 2 shows the effect of catalyst loading (y) and temperature (x) on the yield (contours) of the produced biodiesel. The darker regions identify higher z-values. The contour levels show a peak on the L.H.S at 0.5 % (Catalyst loading) and 25 °C (Temperature). Quality scores in this region are greater than 98 %.

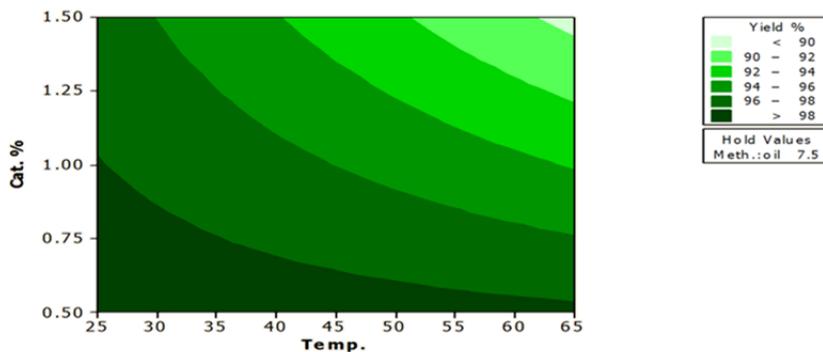


Figure 2: Biodiesel yield contour plot for the effect of temperature (°C) and catalyst loading

**2.3 Surface plot methodology**

Figure 3 describes the temperature and catalyst loading effect on the biodiesel yield, while holding the third parameter at 7.5:1.

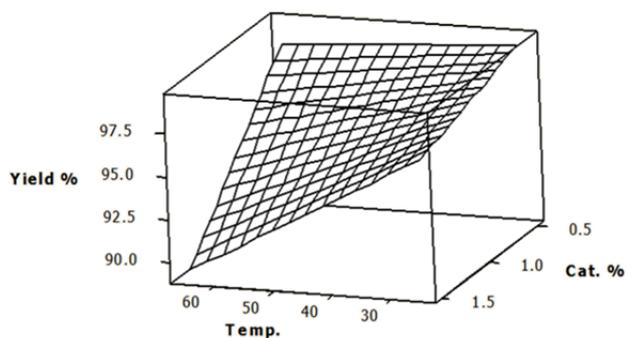


Figure 3: Biodiesel yield surface plot with temperature (°C) and catalyst

**2.4 HYSYS simulation**

HYSYS simulation model for the biodiesel production from waste vegetable oil using NaOH as an alkaline catalyst is developed. Figure 4 illustrates the model for this approach.

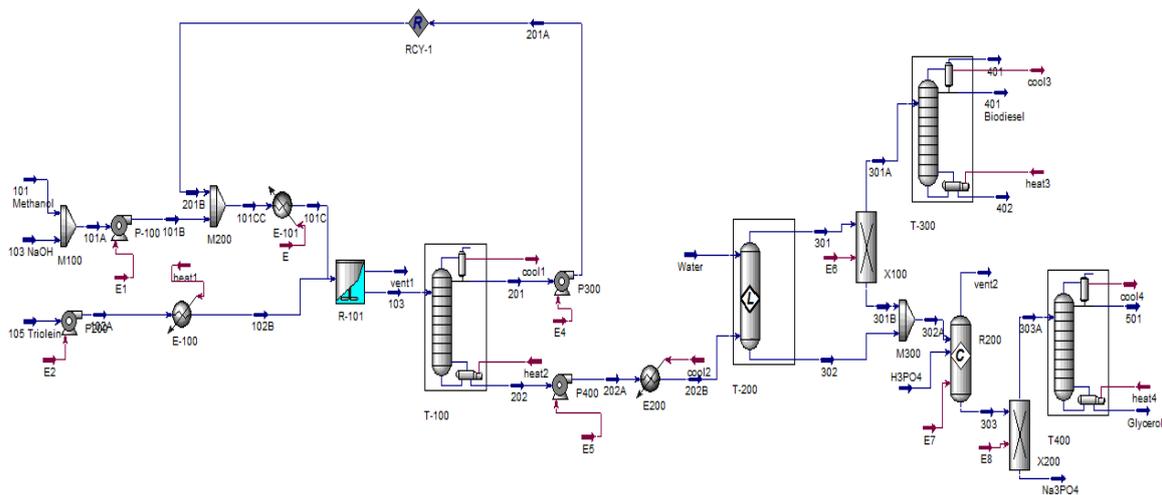


Figure 4: HYSYS model for base-catalysed process

### 3. Parameter optimisation and rigorous HYSYS model simulation of supercritical methanol transesterification technique

#### 3.1 Pareto chart

Similar analysis is performed for this technique; the chart describes the importance of each of methanol to oil ratio and time of reaction on the biodiesel conversion. It is conducted that the alcohol molar ratio with oil is the controlling parameter for supercritical methanol transesterification, and hence any change in methanol to oil molar ratio will greatly affect the conversion.

#### 3.2 Contour plot methodology

The contour plot for this technique was developed similarly previous but using the data related to this process. The contour plot describes the relationship between the time (y) and the molar ratio of methanol to oil (x) affect the conversion (contours) of biodiesel. The contour levels reveal a peak at the top R.H.S in almost 8 minutes (time) and 42:1 (Meth: oil).

#### 3.3 Surface plot methodology

The supercritical methanol transesterification is mainly influenced by: methanol to oil ratio, reaction time, and reaction temperature of the methanol entering. The surface plot for this process shows the relation between the response, biodiesel conversion, and two independent variables; methanol ratio with oil and time while the inlet methanol stream temperature is held on 350 °C.

#### 3.4 HYSYS simulation

HYSYS model for the production of biodiesel from WVO using supercritical methanol was also developed to simulate the actual process mechanism similarly as we have done in the previous approach.

## 4. Energy integration and targeting

### 4.1 Composite curve

Plot between temperature and enthalpy using a minimum temperature difference ( $\Delta T_{\min}$ ) of 10 °C was developed as shown in Figure 5. A minimum temperature of 10 °C was selected as such a value is mostly relevant for chemical and petrochemical plants; however, capital-energy trade-off is suggested for overall optimum solutions (Klemeš, 2013). In the composite curve the two streams are overlapping together at the middle of the graph, this region highlights the quantity of heat to be recovered for the process. For this process the possible amount of heat to be recovered ( $Q_{\text{REC}}$ ) is about 1 MW. The rest of the two streams cannot be heated or cooled by integrating energy between them. But to satisfy their energy requirements, either heating or cooling, utilities should be supported for both cold and hot streams, respectively. For this process, the minimum requirement for the hot utility is denoted as ( $Q_{\text{Hmin}}$ ) and has the value of 3.8 MW and the minimum requirement for the cold utility ( $Q_{\text{Cmin}}$ ) has a value of 3.7 MW (Smith, 2005).

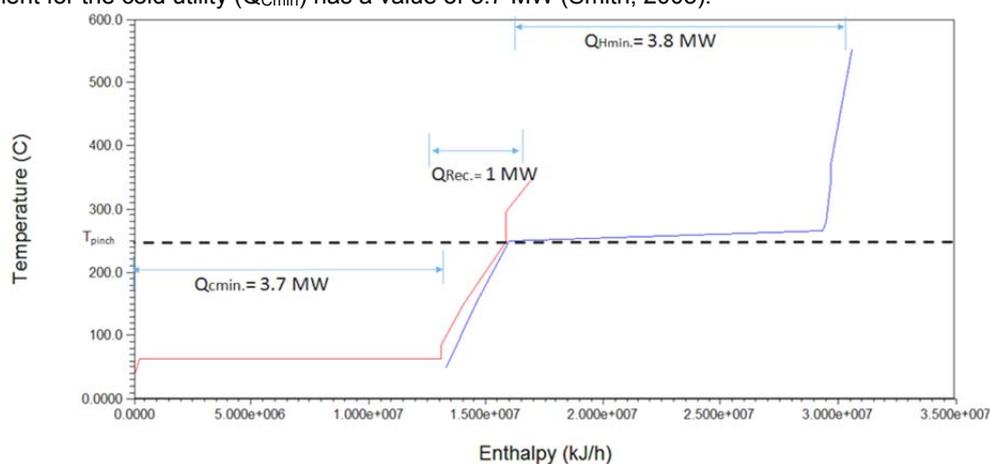


Figure 5: Composite curve for supercritical methanol process

### 4.2 CO<sub>2</sub> emissions

Carbon dioxide emissions are one of the main and critical emissions that must be estimated for any process. These emissions are emitted due to burning some kinds of fuels to produce sufficient heat that would satisfy the heating requirements of the desired process (biodiesel production process). Commonly, the fuels used for this purpose is either natural gas or heavy fuel oil.

(Gadallah et al., 2006) derived an equation to calculate the emissions of carbon dioxide. Carbon dioxide emissions are estimated for both the original process and the integrated one. Table 1 obviously shows that the emissions of the integrated process are lower than the original process upon using both kinds of burning fuels. The percentage reduction of carbon dioxide emissions was found to be almost 21 %.

Table 1: CO<sub>2</sub> emissions for the original and integrated processes using natural gas and heavy fuel oil, t/h

	Original process emissions	Integrated process emissions
Heavy fuel oil	1.53	1.03
Natural gas	1.213	0.815
% Reduction	21 %	20.7 %

#### 4.3 Heat exchanger network design (HEN)

Heat exchanger network analysis identifies both the hot streams and the cold streams from the mass and energy balance stand points. Consider a heat source and a heat sink with supply temperature and target temperature and enthalpy change for both streams. Steam is available at 180 °C and cooling water is at 30 °C. Consequently, heating the cold stream by steam and cooling the hot stream by cooling water is possible. However, recovering the heat between the process streams is preferable as it would save an excessive energy cost. Figure 6 shows the proposed HEN for the production of biodiesel using supercritical methanol approach. This HEN shows how the integration between hot and cold streams would happen to achieve the energy targeting and the possible heat recovering. Table 2 shows, in details, every heat exchanger, its cold stream, its hot stream and the duty required for each exchanger.

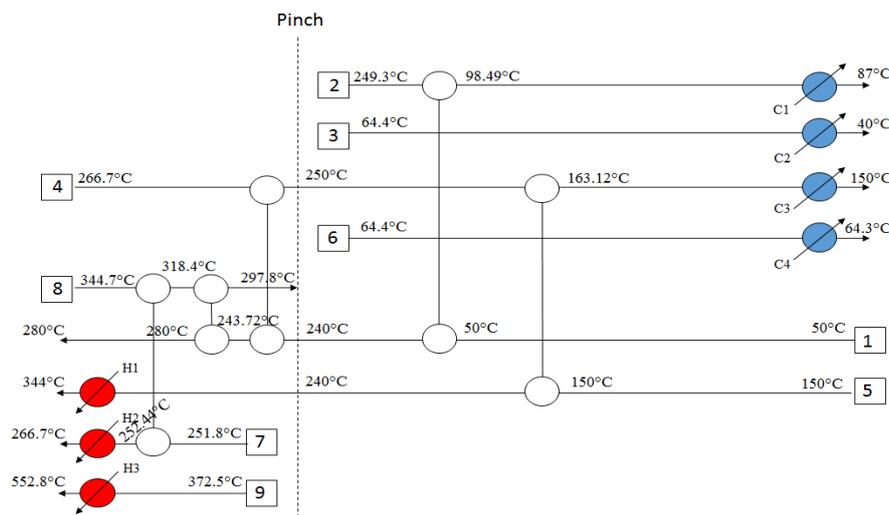


Figure 6: Heat Exchanger Network (HEN) for supercritical methanol process

Table 2: Heat exchangers duties and connections

Equipment	Cold stream	Hot stream	Duty (kW)
Hex-1	2	1	641.82
Hex-2	4	1	12.56
Hex-3	8	1	122.56
Hex-4	4	5	65.38
Hex-5	8	7	156.50
C1	2	-	48.93
C2	3	-	66.47
C3	4	-	9.87
C4	6	-	3566.67
H1	-	5	75.55
H2	-	7	3477.62
H3	-	9	241.42

The following Table 3 concludes the energy requirements for the process before and after integration to be compared with the expected requirements from composite curve.

Table 3: Cooling and heating requirements for the original process, integrated process and composite curve

	Original process	Composite curve	Integrated process
Cooling requirements (MW)	4.7	3.7	3.69
Heating requirements (MW)	4.8	3.8	3.79

#### 4.4 Integrated process flowsheet

The following process flowsheet is developed to show the energy integration by implementing the HEN on the designed process. The flowsheet represented in Figure 7 achieves the proposed energy target for minimising the total heating and cooling energy requirements.

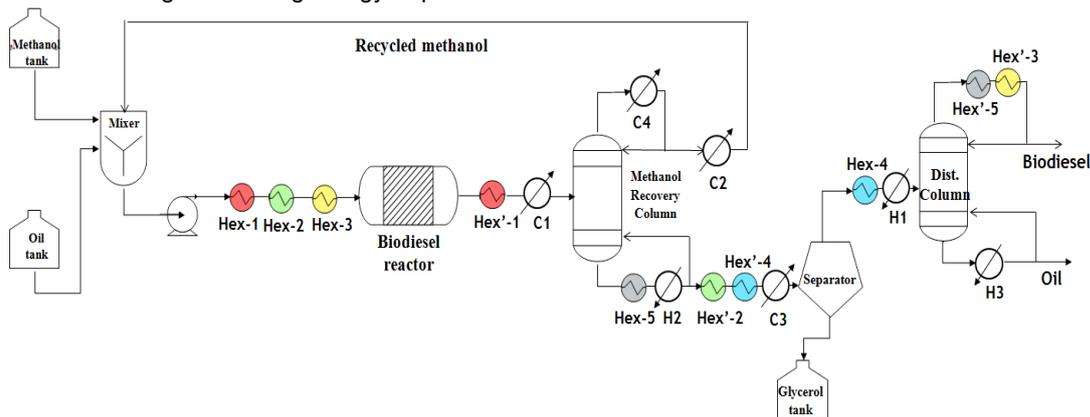


Figure 7: Integrated process flowsheet

## 5. Conclusions

The results conducted showed an optimisation for biodiesel production using base-catalysed and supercritical methanol processes. The experimental results that were discussed were validated using parameter analysis that was carried out using Pareto chart, contour plot methodology, and surface plot methodology. It was found from the thesis that the most affecting process variable for the base-catalysed process was the catalyst loading and the optimum conditions were found to be at 25 °C, 1.3 % NaOH and 6:1 M/O molar ratio. While, for the supercritical methanol process the most affecting variable was the M/O molar ratio and the optimum conditions were found to be at 8 min and 42:1 M/O molar ratio. The results illustrated focused on the energy requirements for biodiesel production using supercritical methanol approach. Composite curve was used to determine the minimum energy requirements for the process that were found to be 3.4 and 3.7 MW for heating and cooling requirements, respectively. The energy consumption of the base case has been reduced by 25 %, thus substantial cut in the CO<sub>2</sub> emissions. Finally, heat exchanger network was developed to accomplish the energy minimisation target proposed from the composite curve.

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