

# Microwave-Heated Tubular Reactor for Enhanced Biodiesel Transesterification Process

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Biodiesel is an important renewable fuel derived from bioresources that can help to mitigate climate change by significantly reducing carbon emissions from the transportation sector. The conventional batch reactor transesterification process to produce biodiesel is inefficient due to long production time and high energy consumption. In this study, transesterification of palm oil for biodiesel production is conducted using the combined technologies of tubular reactor and microwave-assisted heating method. Parameters investigated include the effects of microwave power, methanol to oil molar ratio, KOH catalyst concentration, and tube length, on FAME yield. Fatty acid methyl ester (FAME) yield of 96.5 % meeting the EN 14214 standard were obtained within the conditions where methanol to oil molar ratio was 8.5-10.0 and microwave power was 320 to 350 W. It was observed that FAME yield reduces when excess microwave power is provided to the reaction due to overheating of organic molecules and boiling of methanol. An average increase of around 10 % in FAME yield was found when the KOH catalyst concentration increases from 0.8 to 1.2 wt%. The results of this study provide insights into the optimisation of transesterification process for producing biodiesel using the combined microwave-assisted heating in tubular reactor method.

## 1. Introduction

The global pursuit of sustainable energy due to the urgent need to reduce greenhouse gas emissions and volatility in crude oil price and supply have led to significant research efforts in biomass-based fuels. For the transportation sector is liquid biofuels such as biodiesel, bioethanol and biojet fuels have emerged as viable substitutes for petroleum-based fuels for diesel engines, gasoline engines and jet engines. Within the context of biodiesel, various transesterification methods have been developed over the years with varying degrees of success, such as the use of micro-scale flow channels (Wen et al., 2009), jet-flow (Reyes et al., 2010), ultrasonic wave (Singh et al., 2007), transient Pareto approach (Wong et al., 2021), which generate turbulence flow environment at the micro-scale level. However, these approaches are not yet adopted by the industry, rendering the findings to have limited prospects for the end-goal of commercialisation.

The batch reactor method remains as the de facto method despite being less energy efficient, slow process and requires long separation time between product and by-products. The deficiencies are due to the sigmoidal biodiesel production's reaction curve which is formed by biphasic behaviour for the reactants, resulting in a slow and delayed reaction at the start of the reaction (Wong et al., 2019). As such, there are still ongoing research for more sustainable and efficient transesterification processes that can fundamentally improve the reaction kinetics, enhance mixing of reactants, and minimise energy consumption.

This study focuses on the enhancement of the biodiesel transesterification process using a microwave-heated tubular reactor for intensifying the mixing method, while also providing efficient heat transfers via a microwave for effective heating. The experimental approach to maximise biodiesel yield covers independent factors such as microwave power, methanol to oil molar ratio, KOH catalyst concentration, and tube length.

## 2. Experimental Procedures

The experimental procedures section covers the experimental rig set up, feedstock material, experimental test matrix and analysis of sample.

### 2.1 Experimental set up

Transesterification of palm oil was carried out in a single-mode microwave oven (SHARP R207EK) that has a maximum power output of 800 W. The microwave oven was modified to include an external twin timer relay (CIKACHI AH3D-D) which allows periodic microwave heating by setting the on-off time configuration using the timer interface. A 10 mm diameter hole was drilled through the top cover of the microwave oven to permit silicone tubes' entry into and out of the microwave oven. Silicone tubing (RUNZE Fluid) was coiled around the bottom of a 1 litre glass beaker (diameter = 111.6 mm) that was pre-wrapped with polyimide tape for thermal insulation. Silicone tubing with 1 mm internal diameter function as a continuous flow tubular reactor for transesterification. The complete setup of the experiment is shown in Figure 1.

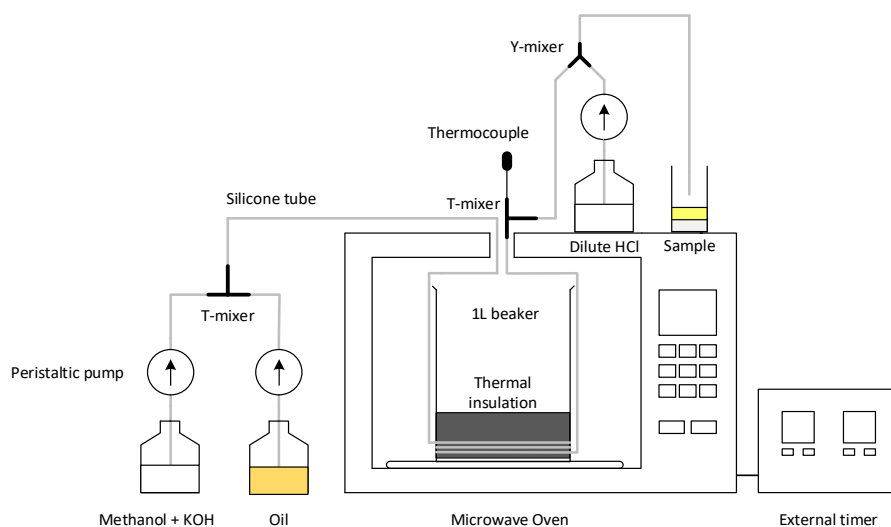


Figure 1: Experimental set up for the microwave-assisted transesterification in a tubular reactor.

Every apparatus inside the microwave oven has low dielectric constants to reduce heating up due to microwave irradiation. The dielectric constant the key materials are shown in Table 1.

Table 1: Dielectric constants of materials inside the microwave oven.

Apparatus	Material	Dielectric constant	References
Silicone tube	Silicone rubber	< 4.5	(Ghost et al., 2001)
Glass beaker	Glass	3.6	(Letz, 2017)

The outlet of the silicone tubing was connected to a digital dual channel K-type thermocouple thermometer to measure the temperature of reactants flowing out of the microwave oven. Two peristaltic pumps (ODM 312) were used to pump palm oil and methoxide as reactants for transesterification. The two reactants meet head on at a polyethylene T-mixer (RUNZE FLUID, ID: 1 mm). A T-mixer was used because it allowed more efficient mixing through the dispersion of reactants when they collide head on at the T-mixer junction. The mixture of reactants flows out of the T-mixer to the silicone tube inside the microwave oven. Product of transesterification was quenched by dilute HCl using a third peristaltic pump (KAMOER) where they meet at a polyethylene Y-mixer (RUNZE FLUID, ID: 1 mm).

A microwave leakage detector (HTi HT-M2) was used to check for microwave leakage around the perimeter of the microwave oven. A leakage not exceeding 5 mW/cm<sup>2</sup> was required to ensure safe operation of the experiment. Three layers of copper mesh with an aperture of 1.27 mm and wire diameter of 0.457 mm were used as a shield to prevent microwave from leaking to the surrounding.

## 2.2 Feedstock material and catalyst

Methanol and potassium hydroxide (KOH) pellets from Qrec were used in this experiment. Refined bleach deodorised (RBD) palm olein was used as the triglyceride feedstock, while methanol was selected as the alcohol reactant. To vary the methanol to oil molar ratio, oil and methoxide pump were set at specific individual flow rates while maintaining a total flow rate of 1.6 mL/min.

## 2.3 Experimental test matrix

In this experiment, microwave power, methanol to oil molar ratio, KOH concentration and tube length were varied to study how these parameters affect fatty acid methyl ester (FAME) yield. Two experiment models were set up in this study. The first model involves two factors: microwave power (320, 400, 533.3 W) and methanol to oil molar ratio (5.96, 9.03, 12.05), with tube length was fixed at 2.0 m and KOH concentration at 1.0 wt%. The second model is a 3<sup>3</sup> full factorial model with methanol to oil molar ratio, KOH concentration and tube length as variables and microwave power set at 400 W (refer to Table 2).

Table 2: Factors and levels of varied parameters of the full factorial model.

Factor	Level (low)	Level (mid)	Level (high)
Methanol to oil ratio	5.96	9.03	12.05
KOH concentration (wt%)	0.8	1.0	1.2
Tube length (m)	1.0	1.5	2.0

These four factors were selected to be used in both models because they are the main parameters of microwave-assisted transesterification (Günay et al., 2019). Tube length instead of flow rate was used as a parameter to control residence time.

## 2.4 Sample analysis

After the sample was collected for 10 minutes, it was given 6 hours for complete sedimentation. The upper layer of FAME was then extracted with a syringe and put into an oven at 80 °C for 30 minutes to remove excess methanol. Tap water was added to sample drop-by-drop using a syringe to wash the sample. The washed sample was put into the oven at 110 °C for another 30 minutes to remove moisture.

FAME yield (%) for samples were identified using an Agilent 7820A gas chromatography (GC) with flame ionization detector. The GC was equipped with a HP-INNOWAX capillary column (0.25 µm × 0.32 mm × 30 m) for FAME analysis. FAME analysis was performed based on the EN 14103:2003 standard, and calculated based on the following equation:

$$C = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100 \% \quad (1)$$

where  $C$  denotes the ester content,  $\sum A$  is the total peak area from methyl ester in  $C_{14}$  to  $C_{24:1}$ ,  $A_{EI}$  is the peak area of methyl heptadecanoate,  $C_{EI}$  denotes the concentration of methyl heptadecanoate (mg/mL),  $V_{EI}$  represents the volume of methyl heptadecanoate (mL) and  $m$  is the mass of sample (mg).

## 3. Results and discussions

### 3.1 Effects of microwave power

Samples achieving the EN 14214 standard of 96.5 % FAME yield were obtained within the conditions where methanol to oil molar ratio was from 8.5 to 10 and microwave power 320 to 350 W. Figure 2 shows that FAME yield increases to a peak value before dropping when methanol to oil molar ratio increased from 6 to 12. An increase in microwave power raised the dipolar polarisation duration of methanol molecules, which resulted in greater amount of heat generated. A general trend of net decrease in FAME yield with increase in microwave power from 320.0 to 533.3 W is observed for all methanol to oil molar ratios. Total drop in FAME yield from 320.0 to 533.3 W for methanol to oil molar ratios 5.96, 9.03 and 12.05 are 6.46 %, 9.46 % and 5.8 %. The decrease in FAME yield can be explained by the superfluous amount of energy absorbed by reactants at high levels of microwave power (Deghan et al., 2019). Organic molecules such as triglycerides would hydrolyse into fatty acids at high microwave power. It is postulated that high microwave power can cause overheating which destroy some organic molecules in FAME.

Temperature with respect to time were recorded during the experiments. It was observed that the average temperature of reactants was approximately 80 °C when microwave power is set at 533.3 W. The temperature

exceeds the boiling point of methanol (64.7 °C) at atmospheric pressure. The decrease in FAME yield is attributed to the boiling of methanol at temperatures higher than its boiling point. The rapid movement of methanol molecules during boiling reduces contact between methanol and oil, complicating the transesterification reaction (Deghan et al., 2019). Boiling of methanol also reduces the amount of liquid methanol available for transesterification to take place (Ding et al., 2018). When temperature exceeds 90 °C, FAME content is postulated to decrease due to the loss of methanol to boiling, cracking and oxidation of FAME.

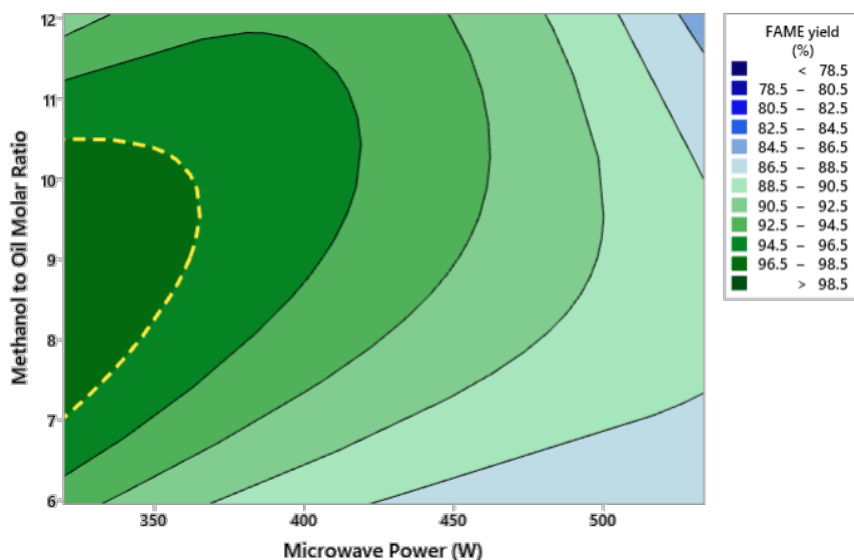


Figure 2: Contour plot of FAME yield when microwave power and methanol to oil molar ratio are varied with tube length is fixed at 2 m and potassium hydroxide concentration at 1.0 wt%.

### 3.2 Effects of tube length

In this study, tube length was used to control residence time. Residence times for tube lengths of 1.0, 1.5 and 2.0 meters were 29.5, 44.2 and 58.9 s, with a constant flow rate of 1.6 mL/min. Figure 3(a) shows that the highest FAME yield of 94.4 % was achieved with 5.96 methanol to oil molar ratio, 1.2 wt% KOH concentration and 2.0 m tube length. None of the results from methanol to oil molar ratio of 5.96 gave FAME yield that met the minimum EN 14214 standard biodiesel yield of 96.5 %. There is a general trend of increase in FAME yield when tube length increases. From tube length of 1.0 to 2.0 meters, FAME yield increased from 77.7 to 86.0 % when KOH concentration 0.8 wt%, 83.6 to 89.2 % when KOH concentration was 1.0 wt% and 87.6 to 94.4 % when KOH concentration was 1.2 wt%. Increase in FAME yield was due to longer residence time with increase in tube length. Longer residence time increases predisposition of methanol and oil to react due to collision between molecules.

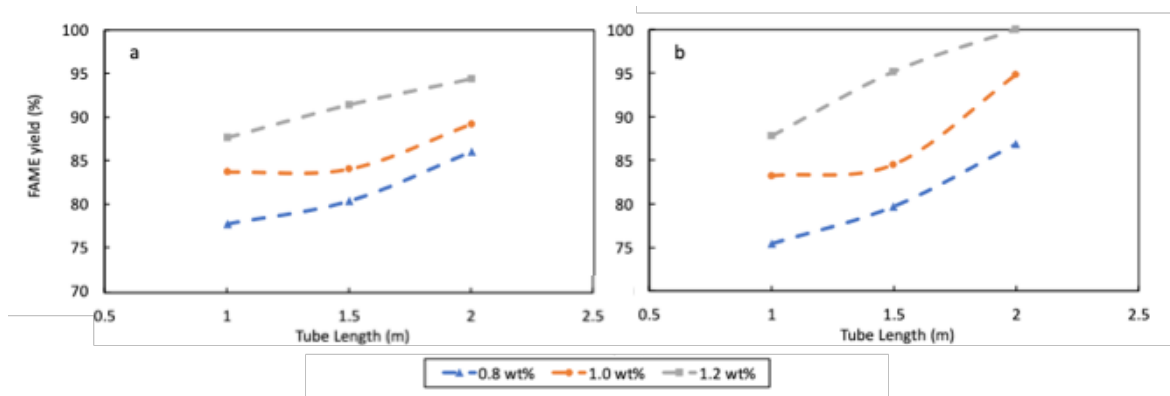


Figure 3: FAME yield from tube length of 1.0 to 2.0 meters at potassium hydroxide concentrations of 0.8, 1.0 and 1.2 wt% when methanol to oil molar ratio is (a) 5.96 and (b) 9.03.

The same trend can be seen in Figure 3(b) with the exception that significantly higher yields were achieved for tube length of 1.5 to 2.0 m with KOH concentration of 1.2 wt% (95.2 and 100.0 %) and tube length of 2.0 m with KOH concentration of 1.0 wt% (94.8 %). FAME yield meeting the EN 14214 requirement was achieved when 9.03 methanol to oil molar ratio, 1.2 wt% KOH concentration and 2.0 m tube length was used. All three cases of KOH concentration when methanol to oil molar ratio is 9.03 show similar net increase in FAME, averaging at 11.6 %, due to the use of higher methanol to oil molar ratio. The highest FAME yield of 100 % was achieved in 58.9 s with the condition set of methanol to oil molar ratio, potassium hydroxide concentration, tube length and microwave power were 9.03, 1.2 wt%, 2.0 m and 400.0 W.

A positive decreasing trendline is observed from FAME yield results when KOH concentration was 1.2 wt% for the two methanol to oil molar ratio. The positive decreasing trendline is an indication that FAME yield is approaching its peak. At higher KOH concentration, FAME yield starts peaking at shorter tube lengths. In the cases where KOH concentration was 1.2 wt% for methanol to oil molar ratio of 5.96 and 9.03, FAME yield was already peaking within the 1.0 to 2.0 m tube length range. As such, it is predicted that further increase in tube length would increase FAME yield, but not significantly as FAME yield is approaching its peak.

### 3.3 Effects of reactant and catalyst

Figure 4 shows that FAME yield increases from less than 88.5 % to more than 94.5 % for all levels of methanol to oil molar ratio. An increase in KOH concentration from 0.8 to 1.2 wt% gives an average net increase in FAME yield of 10 %. The presence of KOH as the catalyst of the reaction accelerates the reaction. KOH forms alkoxide ion when they dissolve in methanol. When oil is mixed with methoxide, reaction between triglyceride (TG) and alkoxide ion forms a tetrahedral intermediate. This tetrahedral intermediate reacts with methanol molecules to form alkoxide and a different intermediate which rearranges to give ester and diglyceride (DG). DG reacts with another alkoxide ion to form monoglyceride (MG) and ester, and in the same manner MG to ester and glycerol. An increase in KOH concentration increases the concentration of alkoxide ions, which in turn accelerates rate of reaction because more alkoxide ion are present to react with TG, DG and MG (Nayak et al., 2019).

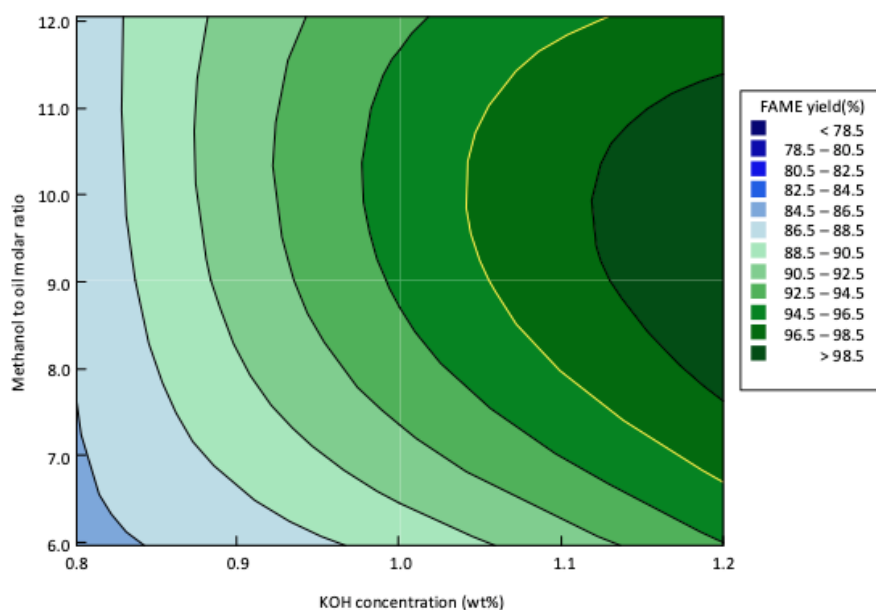


Figure 4: Contour plot of FAME yield when methanol to oil molar ratio and potassium hydroxide are varied, microwave power is fixed at 400 W and tube length at (a) 1.0 m and (b) 2.0 m.

FAME yield peaks at methanol to oil molar ratio of 8.0 to 11.0 and KOH concentration of 1.1 to 1.2 wt% in the 2.0 m tube, achieving FAME yield which meets the EN 14214 standards of exceeding 96.5 % yield. FAME yield in both 1.0 and 2.0 m tube peaks at the higher extreme end of the KOH concentration range of 1.1 to 1.2 wt%. Conversely, FAME yield does not peak at an any extreme end of the methanol to oil molar ratio range used in this experiment. Instead, FAME yield rises and drops within the methanol to oil molar ratio of 6 to 12.

The peaking of FAME yield can be explained by a few reasons. Stoichiometric methanol to oil molar ratio in the transesterification process is 3:1. Transesterification is a reversible reaction, causing reaction to cease when the reactants and products reach dynamic equilibrium. A higher than stoichiometric methanol to oil molar ratio

is used so that excess methanol can drive the reaction in the direction of products according to Le Chatelier's principle. An increase in methanol to oil molar ratio ensures that more products formed. This leads to a rise in FAME yield with increasing methanol to oil molar ratio.

The decrease in FAME yield with further increase in methanol to oil molar ratio can be attributed to the diminishing KOH concentration with respect to methanol and change in flow regime of reactants. The concentrations of KOH used in this experiment are based on the weight of oil. When methanol to oil molar ratio increases, concentration of KOH with respect to the volume of methanol decreases, minimising the catalytic effect of KOH at the interfacial area between methoxide and oil in the tubular reactor.

It is postulated that methanol to oil molar ratio and KOH concentration are not independent in a tubular reactor. Higher methanol to oil molar ratio undermines KOH as catalyst in the transesterification process at low tube lengths where FAME yield has not reach steady state.

#### 4. Conclusions

In conclusion, this study offers valuable insights into accelerating the transesterification process to produce fatty acid methyl ester (FAME) using a microwave-assisted heating method and tubular reactor. The study investigated the effects of various parameters, including microwave power, methanol to oil molar ratio, KOH catalyst concentration, and tube length, on FAME yield. The results show that using an optimal KOH concentration and a moderate microwave power can lead to improved FAME yield. Conversely, an excessively high microwave power reduces the FAME yield. The study also found that the flow regime and tube length play significant roles in determining the FAME yield. Overall, the findings of this study can be useful in providing a starting point to further optimise the transesterification process for efficiently producing biodiesel using the combined technologies of microwave-assisted heating and tubular reactor. These findings have significant implications for the development of a more sustainable and carbon neutral biofuel for use in the transportation sector.

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#### References

- Deghan L., Golmakani M.-T., Hosseini S.M.H., 2019, Optimization of Microwave-Assisted Accelerated Transesterification of Inedible Olive Oil for Biodiesel Production, *Renewable Energy*, 138, 915 – 922.
- Ding H., Ye W., Wang Y., Wang X., Li L., Liu D., Gui J., Song C., Ji N., 2018, Process Intensification of Transesterification for Biodiesel Production from Palm Oil: Microwave Irradiation on Transesterification Reaction Catalyzed by Acidic Imidazolium Ionic Liquids, *Energy*, 144, 957 – 967.
- Ghosh A., Naskar A.K., Khastgir D., De S.K., 2001, Dielectric Properties of Bends of Silicone Rubber and Tetrafluoroethylene/Propylene/Vinylidene Fluoride Terpolymer, *Polymer*, 42, 9849 – 9853.
- Günay M.E., Türker L., Tapan N.A., 2019, Significant Parameters and Technological Advancements in Biodiesel Production Systems, *Fuel*, 250, 27-41.
- Letz M., 2017, Microwave Dielectric Properties of Glasses and Bulk Glass Ceramic, Chapter in: Sebastian M.T., Jantunen H., Ubc R., *Microwave Materials and Applications 2V Ser, I&II*, John Wiley & Sons, 345-354.
- Nayak S.N., Bhasin C.P., Nayak M.G., 2019, A Review on Microwave-Assisted Transesterification Processes using Various Catalytic and Non-Catalytic Systems, *Renewable Energy*, 143, 1366 – 1387.
- Reyes J.F., Malverde P.E., Melin P.S., De Bruijn J.P., 2010, Biodiesel Production in a Jet Flow Stirred Reactor, *Fuel*, 89, 3093 – 3098.
- Singh A.K., Fernando S.D., Hernandez R., 2007, Base-catalyzed Fast Transesterification of Soybean Oil using Ultrasonification. *Energy Fuels*, 21, 1161 – 1164.
- Wen Z., Yu X., Tu, S.-T., Yan J., Dahlquist E., 2009, Intensification of Biodiesel Synthesis using Zigzag Micro Channel Reactors, *Bioresource Technology*, 100, 3054 – 3060.
- Wong K.Y., Ng J.-H., Chong C.T., 2019, A Full Factorial Analysis on One-Way Transient Transesterification Interactions Affecting Palm Biodiesel for Batch Reactor, *Chemical Engineering Transactions*, 72, 349 – 354.
- Wong K.Y., Ng J.-H., Chong C.T., Lam S.S., Chong W.T., 2021, Pareto-hierarchical Clustering Framework for Biodiesel Transesterification, *Sustainable Energy Technologies and Assessments*, 45, 101160.