

A Full Factorial Analysis on One-Way Transient Transesterification Interactions Affecting Palm Biodiesel for Batch Reactor

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Biodiesel is commonly produced via the transesterification process, usually through the use of batch type reactor. There are significant gaps in batch reactor technologies, where the importance of these factors are often concluded based on the steady-state conditions, manifested in the form of the final yield. In this study, a comprehensive test matrix is setup using full factorial design of experiments, consisting of 4 factors and 2 levels. Four parameters of interest such as agitation speed (200-400 rpm), catalyst loading (0.5-1.5 wt%), methanol to oil ratio (3:1-6:1), and temperature (30-60 °C), were investigated to understand the interaction of these independent factors at the different stages of transesterification. To further investigate the effect of each factors on the transient process, one-way effect of these factors on the transient yield is investigated. Through the multi-factor analysis, the transesterification process can be segregated into 5 unique stages, as the standardised effect of these factors responded differently throughout. The results indicate that batch reactor transesterification performs better with low methanol-oil ratio at the beginning phase, and importance of methanol-oil ratio significantly increases over time. The methanol-oil ratio also become the most influential factor when steady-state is achieved, from a standardised effect magnitude of 0.38 to 14.21, representing an over 37-fold improvement. Agitation speed also showed a reduction of 37-fold in standardised effect throughout the transesterification process, where the effect reached plateau around mid-way of the reaction. Catalyst loading and temperature share similar trends, as they both influence the activation energy of transesterification. Although catalyst loading and temperature are highly influential throughout, a 1.88 and 1.78fold decrease in impact are observed. In conclusion, this study provides insights towards developing biodiesel production techniques, through better understanding of the cross-interactions between factors, and in terms of optimising transesterification dynamically.

1. Introduction

The production of biodiesel or as known as fatty acid methyl ester (FAME) has fostered the usage of cleaner energy due to its attractive properties, such as renewability, energy sustainability (Bokhari et al., 2014), biodegradability, and reduced emissions. However, although the production for FAME has escalated to more than 33.2 GL over the past decade (International Energy Agency, 2016), the industry have not been able to keep up with the demand, due to inefficiency in production methodology. In terms of biodiesel transesterification, key mechanism such as methanolysis has been widely accepted as it reflects the FAME sigmoid-like production curve. Besides batch mixing, intensification methods such as microwave irradiation, ultrasound and hydrodynamic cavitation has been widely adapted in current transesterification technology (Bokhari et al., 2016). During the initialisation of transesterification, the reactants behave as two distinct liquid-liquid phase with are partially miscible, as proposed by Nouredini and Zhu (1997), where there exist a mass transfer controlled phase and followed by a reaction controlled regime. The sigmoidal FAME trend is formed by the biphasic

behaviour between vegetable oil and alcohol, resulting a slow and delayed reaction at the beginning, and transitioned into a rapid one-phase reaction for FAME production (Csernica and Hsu, 2012).

With that in mind, optimisation of biodiesel transesterification processes had been attempted in many direction, particularly through statistical approach. From experimental design perspective, such as Box-Behnken which identifies and test individual reaction parameters (Dwivedi and Sharma 2015), to more advanced information processing systems such as artificial neural networks (ANN) (Dharma et al., 2017) to obtain optimum conditions. However, majority of the reported biodiesel related work does not represent the analysis at a standardised level for both dynamic and steady-state interactions in processing variables, resulting a less accurate interpretation of transesterification mechanism. In this work, a dynamic analysis for biodiesel transesterification is applied via Pareto study, to investigate both transient and steady-state of independent testing parameters in a batch reactor.

2. Experimental details

2.1 Materials used

The biodiesel is produced by Refined Bleach and Deodorised (RBD) palm olein sourced commercially. The standard biodiesel precursor, analytical grade methanol with 99.8% purity was obtained from Qrec, while potassium hydroxide (KOH) pallets >85%, and hydrochloric acid (HCL) 37% were obtained from Merck and VWR. Gas chromatography standard analytical reagent, methyl heptadecanoate was sourced from Sigma-Aldrich.

2.2 Experimental setup and sample characterisation

In this study, a comprehensive full factorial design of experiments (DoE) was setup as the test matrix, Table 1 summarises the testing parameters accompanied by their lower and upper testing limits. The DoE was constructed based on 4 factors and 2-level, resulting a 2^4 combination, equivalent to 16 unique experiments each accompanied with 10 sampling intervals for characterising the FAME yield curve.

Table 1: Full factorial design of experiment using 4 factor and 2 level

Parameters	Unit	-1	+1
Agitation rate	rpm	200	400
Catalyst loading	wt% oil	0.5	1.5
Methanol to oil molar ratio	-	3:1	6:1
Reaction temperature	°C	30	60

The experiment was conducted using a 1 L cylindrical batch type reactor, with total volume of reactant set as constant of 600 mL throughout the test matrix. Test parameters such as methanol to oil molar ratio (3:1, 6:1), KOH catalyst loading (0.5 wt%, 1.5 wt%), agitation rate (200, 400 rpm), and reaction temperature (30 °C, 60 °C) were studied. Figure 1 shows the schematic drawing of the experimental setup, with agitation using an overhead stirrer, and temperature regulated by a heating jacket with PID controller.

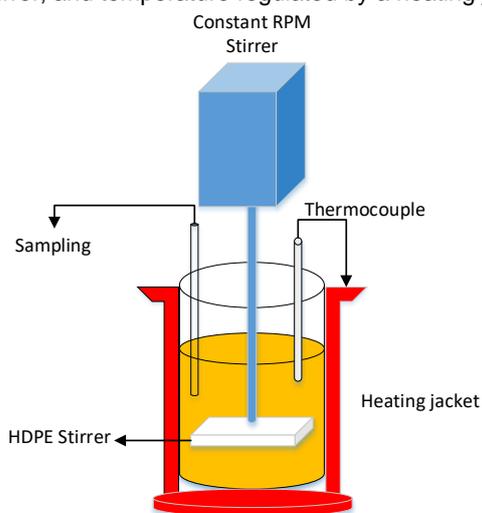


Figure 1: Schematic drawing of experimental setup of biodiesel batch type reactor.

Sampling was done using a mechanical pipette to extract reactants at 10 different intervals between 30 – 1,800 s, where the sampled reactants were immediately quenched via neutralisation of diluted HCL, which also simultaneously removes the excess methanol into the water phase of the quenching mixture. Table 2 summarises the resolution and uncertainty of instruments used in the experiment. The FAME content was characterised using an Agilent 7820A gas chromatograph system coupled with a flame ionisation detector (GC-FID), equipped with a capillary column (HP-INNOWax, 30 m x 0.25 mm, 0.25 µm). Analysis methodology was adopted based on EN 14103, with the FAME yield defined as the conversion of vegetable lipids to biodiesel, as the following equation:

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

where

$\sum A$: Total peak area from methyl ester in C₁₄ to that in C_{24:1}.

A_{EI} : Peak area corresponding to methyl heptadecanoate (C_{17:0}).

C_{EI} : Concentration (mg/mL) of methyl heptadecanoate solution.

V_{EI} : Volume (mL) of the methyl heptadecanoate solution.

m : Mass (mg) of the sample, synthesised biodiesel.

Table 2: Resolution and uncertainty of instruments.

Instrument	Measurement	Resolution	Uncertainty
Thermocouple (K-Type)	Reagent temperature	0.1 °C	± 2.2 °C
Constant stirrer controller	Revolution/min	1 rpm	± 1 rpm
Mechanical Pipette	Sample volume	0.1 mL	± 0.3% vol.
Silicon Heating Jacket	Temperature	0.1 °C	± 1.0 °C

3. Results and discussion

3.1 Pareto analysis

In this study, Pareto analysis was applied on the aforementioned sampling intervals using Minitab 18.0, which correspond to 10 Pareto charts of the standardised effect. Through combining the individual sets of Pareto analysis from different sampling time, results can be represented in a transient manner for each testing parameters. When moving from the lower testing limit (-1) to the higher testing limit (+1), the importance of each test parameters will be reflected by the magnitude of standardised effect, which is relative to a reference distribution fit line, that is defined as when effect is non-significant to the response, in this case the FAME yield. As the standardised effect crosses the reference line, the effect is considered to be statistically significant to the 0.05 level, as setup by the modelled terms. Since the effects from each testing parameter are standardised, they can be compared across the different stage of transesterification, which allows the generation of a dynamic study of factors affecting FAME yield.

3.2 Standardised effect of agitation rate

Preliminary studies for biodiesel transesterification was carried out to determine the range of agitation speed, with an increasing interval of 100 rpm, where above 400 rpm, the change in reaction speed plateau. The method was adopted from (Vicente et al., 2005), such that to avoid the laminar flow regime which can potentially cause swirling of fluid, resulting the mass transfer limitation between reactants (Darnoko and Cheryan, 2000). Thus, from the results in Figure 2, higher agitation for batch type transesterification was able achieve a standardised effect of 10.5 which is relatively significant. This is possibly due to more turbulence generated from the agitator resulted in increased effective contact area for reactants. Thus, more adequate mixing means that the forward reaction will be favored to produce more FAME. The effect of high rpm is more pronounced at the beginning of transesterification, particularly the physical-limiting regime, until 200 s into the reaction when the reaction enters reaction-limiting regime, where the standardised effect has reached the reference line. The standardised effect remained fairly consistent during the reactant limiting regime, plateaued at 0.45 when it reached the final yield point, equivalent to a 24-fold diminish in effect as compared to initialisation. This proposed that the reactants have achieved steady-state in terms of phase homogeneity, where increasing agitation does not provide any enhanced effect towards reaction. Therefore, it should be noted that although there are no significant differences for 200 rpm and 400 rpm beyond 200 s, results do not indicate if higher rpm causes a negative implication towards FAME yield by only using Pareto analysis.

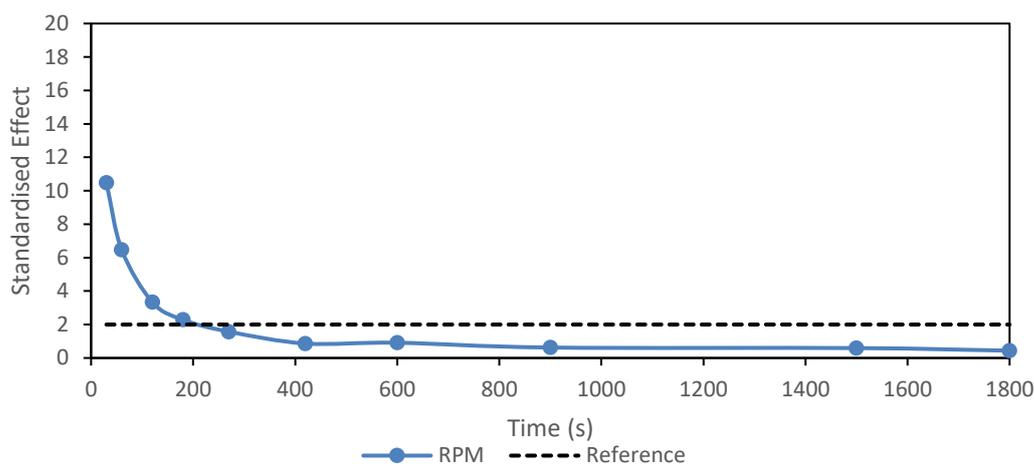


Figure 2: Pareto analysis of agitation rate from 200 rpm to 400 rpm

3.3 Standardised effect of catalyst loading

The results of catalytic loading from Figure 3 showed that the testing parameters have proven to be statistically significant throughout the experiment, when moving from 0.5 wt% to 1.5 wt% catalyst loading, as it lies above the reference line. During the initialisation, standardised effect has achieved a maximum of 16.1, which also surpasses other testing parameters. The result suggested that transesterification reacts more sensitive towards the significance of lowered activation energy, particularly when most triglycerides reacted to form FAME, as compared to other testing parameters. As the reaction transition from physical-limiting to reaction-limiting, another standardised effect localised peak of 13.6 is observed at about 200 s, which also coincide with agitation rate for crossing the reference line, and methanol to oil molar ratio for standardised effect valley. The phenomenon further highlights the capacity of increased catalyst loading, and also the physical-limiting regime which is less susceptible to agitation and mixing of excess methanol. Due to the role of catalyst which is responsible for the overall energy profile of the system. At the reaction-limiting regime, the standardised effect fluctuates minimally, and achieved 9.15 during steady-state, a 1.76-fold total decrement from the beginning of reaction.

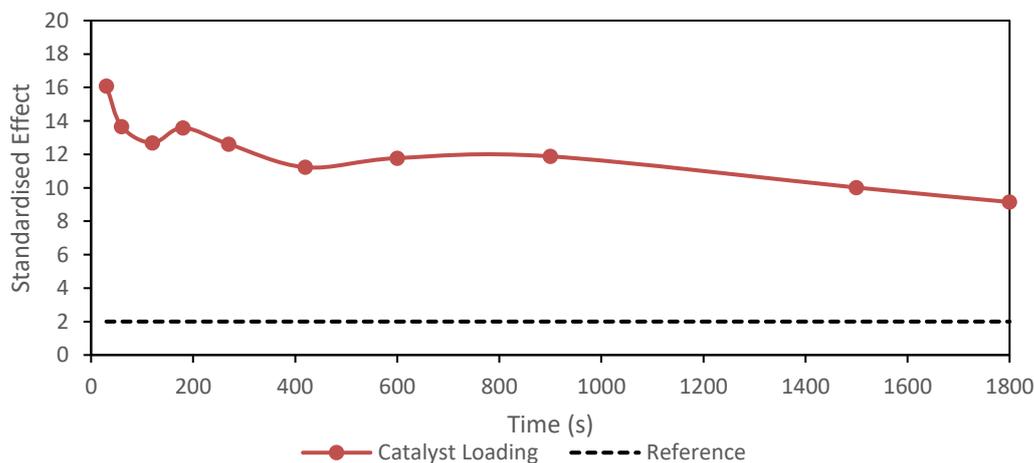


Figure 3: Pareto analysis of catalytic loading with 0.5 wt% to 1.5 wt% oil

3.4 Standardised effect of methanol to oil molar ratio

Standardised effect of molar ratio exhibits interesting observations, as it exists at both extreme of significance and non-significance from transient to steady-state.

Figure 4 showed that during the initialisation of transesterification, higher molar ratio has proven to be more advantageous in terms of FAME production, as excess methanol can potentially reduce the mixing length and

improve contact surface between both the reactants and catalyst for adsorption. The initial standardised effect of 13.3 rapidly plummeted to 0.38 from 30 s to 200 s, which suggested that using high molar ratio condition prolonged the existence of the two-phase behaviour of oil and methanol, as FAME produced is more likely to diffuse into excess methanol than the oil. As the transition from physical-limiting to reaction-limiting, standardised effect of molar ratio ascended from non-significant to significant in several second, and progressed to become the most important among all testing parameters from transient to steady-state, achieving a standardised effect of 14.2 at 1,800 s, reflecting a 37.4-fold improvement as compared to transition. This is supported by the fact that methanol exists as a limiting factor for the reaction during reaction-limiting regime, to convert the remaining of oil into FAME for a high final yield.

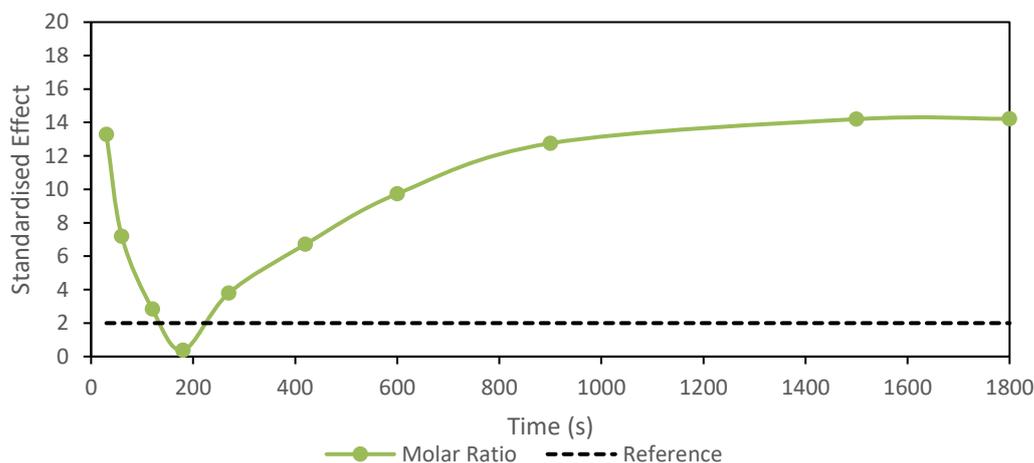


Figure 4: Pareto analysis of methanol to oil molar ratio from 3:1 to 6:1

3.5 Standardised effect of reaction temperature

The increase in reaction temperature has shown consistent positive effect, with minimal fluctuation towards transesterification, as reflected by the standardised effect. Figure 5 showed that during the physical-limiting regime, a peak has been observed at about 60 s, with a standardised effect of 7.66. Since increasing temperature contributes towards increasing the energy level of the system, the trend of effect is comparable with catalyst loading, as they are closely related. When both are studied concurrently, the trend is almost identical, with magnitude of standardised effect offset by about 6, compared to catalyst loading, and also advanced by 120 s in terms of the peak. The sudden spike in effectiveness could be due to the increase in temperature, improving the solubility and diffusivity between oil and methanol. Temperature's effect in terms of reaction kinetic is governed by the Arrhenius equation, thus, the steady and consistent outcome of results is expected.

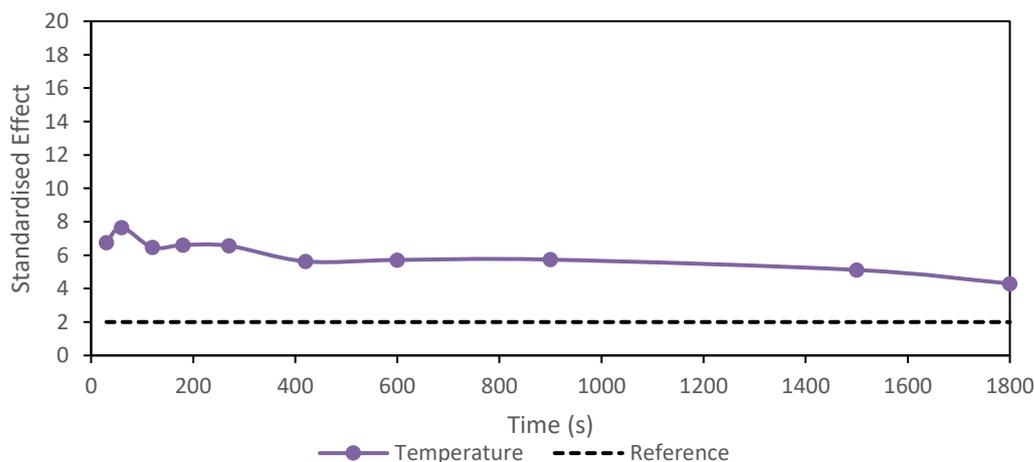


Figure 5: Pareto analysis of reaction temperature from 30 °C to 60 °C

During the reaction-limiting regime, the standardised effect hovers at about 5.7, then gradually decrease to 4.3 at steady-state. However, although it is obvious that higher temperature is easily achievable along with significant effect on transesterification, but due to the low boiling point of methanol, optimisation for temperature has a natural boundary.

4. Conclusions

From the Pareto analysis, the effect of elevated agitation rate provided a temporary positive influence, particularly at the physical limiting regime achieving up to 10.5 for standardised effect, therefore optimisation with rpm needs to be accounted by the follow up effect during reactant-limiting regime, as it becomes non-relevant to FAME yield, this is most likely due to the mixture achieving a one-phase homogeneous state, resulting physical agitation to diminish in effect. Increasing catalytic loading and reaction temperature both showed promising results for FAME yield, as the standardised effect are both significant and consistent throughout, since both test parameters are responsible to interact with activation energy of the transesterification mechanism, with catalyst loading standing out with a standardised effect of 16.1. Methanol to oil molar ratio on the other hand, showed a non-conventional trend, when used in excess. The results are counterintuitive considering that excess methanol as reactant should promote forward reaction due to chemical equilibrium, therefore this suggest that two-phase fluid can behave differently since product miscibility has to be taken into account. Nevertheless, increased molar ratio did promote FAME yield, but at the reaction-limiting regime, where other testing parameter has achieved an equilibrium, leaving molar ratio as the sole factor for achieving high final FAME yield. Evidently, the transition of methanol standardised effect from valley to peak coincide with the diminishing agitation effect, which further supports that miscibility of mixture plays a key role in transesterification, as outline in Figure 2 and 4 at 200 s. The final standardised effect of 14.2 for molar ratio is the highest, which is highest when compared against other test parameters at steady-state. In all, this study has demonstrated the capacity of transient analysis from a statistical perspective, to describe transesterification and its independent factors via a dynamic approach, hence highlighting the gap in understanding transient transesterification behaviour for improving reaction efficiency and efficacy.

Acknowledgments

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