Two-stage continuous production process for fatty acid methyl ester from high FFA crude palm oil using rotor-stator hydrocavitation

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ABSTRACT

Two-stage continuous production process for fatty acid methyl ester (FAME) from crude palm oil was performed using the rotor–stator hydrocavitation reactor. The novel ABS filament printed rotor having spherical holes on the surface of the rotor which is an efficient, fast and cost-effective procedure, was installed in the stainless steel stator of hydrosonic reactor. The 3D printed hydrosonic reactor was used to treat the FFA-rich in MCPO by esterification and followed by transesterification to produce the methyl ester. The optimum conditions of both esterification and transesterification processes were determined using the response surface methodology (RSM). For the 1st step esterification, the conditions of methanol 17.7 vol%, sulfuric acid 2.9 vol%, 3000 rpm rotor speed, hole’s diameter and depth 4 and 6 mm, and 25 L/h MCPO, were used for decreasing the FFA from 11.456 and 1.028 wt% for the 2nd step, transesterification was employed with the optimal condition of 28.6 vol% methanol, 6.2 g/L of potassium hydroxide, 3000 rpm rotor speed, the dimension of the spherical holes on the rotor’s surface having diameter of 6.4 mm and 6.2 mm in depth, and esterified oil flow rate 25 L/h, for producing the methyl ester to over 99.163 wt%. Moreover, the purified biodiesel yields and the average energy consumption for the entire two-stage continuous process between hydrosonic and ultrasonic clamp reactors were compared. The results of purified methyl ester clearly indicate that the methyl esters of 99.163 wt% and 97.814 wt% were achieved from hydrosonic and ultrasonic clamp reactors, respectively, under the same optimized conditions. The maximum yields of purified biodiesel were 97.51 vol% and 88.69 vol% using hydrosonic and ultrasonic clamp reactors, respectively. The average energy consumption for the entire continuous two-stage process for both hydrosonic and ultrasonic clamp reactors were 0.049 and 0.056 kW h/L, respectively. For practical industrial processes, stainless steel rotors inside the stator was manufactured by CNC machine, which was also verified under the optimum conditions. The results showed that 1.07 wt% FFA and 99.221 wt% methyl ester of were obtained from first step and second step, respectively.

1. Introduction

The global warming and rapid rising the consumption of petroleum diesel are issues that are being addressed around the world today [1]. One of the main causes of these problems is the transportation role. In 2020, the world transportation sector liquid fuel consumption increases by 10.55 PWh; diesel and biodiesel-diesel blend are the largest growth about 3.81 PWh, jet fuel consumption increases 2.93 PWh, and gasoline and ethanol-gasoline blend increase by 2.64 PWh. Further expected that the increasing energy in the transport sector demand increased from 13.77 PWh in 2012 to 27.55 PWh in 2040 with an average annual increase of 2.5% for the region of non-OECD countries, due to the population growth [2]. The number of passenger vehicles manufacturing also increased from 62 million units in 2009 to 92 million units by 2019 [3]. It means that the annual fuel requirement is increasing year by year for transportation. A significant part of primary consideration is exhaust gases analysing such as sulphur dioxide (SO2), hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NOx), particular matter (PM), carbon dioxide (CO2) emissions were emitted from the combustion of diesel engines [4]. Therefore, the use of this petroleum diesel is the most relevant for air pollution [5]. On the other hand, biodiesel can be effectively substituted for petroleum-based diesel in transportation sector. Presently, the rate of biodiesel manufacturing is increasing all over the world due to its many benefits such as applying...
biodiesel in the transportation sector can reduce significantly toxic pollutants such as PM, CO, CO₂, HC, and SO₂ [6].

The vegetable oil or animal fat, which consists of the fatty acid ester's long chain, is the leading resource for the biodiesel production. [7]. The pure biodiesel (B100) and biodiesel-diesel blends can be applied in the conventional diesel vehicles with no modifications are required [8].

The biodiesel-diesel blends are also widely used in more than 60 countries including South America by country Argentina (B10), Brazil (B10), Colombia (B2 to B10), Asian by country Indonesia (B20), Malaysia (B10), Thailand (B10), and USA (B10), etc [9]. In the past decade reveal that the years from 2010 to 2019, the global demand for biodiesel soared from 19.5 to 43.5 billion liters, and the main applying regions are the United States, Canada, Latin American, Japan, Australia, and several Asian countries especially Malaysia, Indonesia, and Thailand [10]. Major biodiesel producing countries such as the United State, Brazil and Argentina are mainly using rapeseed, sunflower, coconuts, soybean, palm oil and jatropha as feedstocks. In Thailand, the fifth-largest biodiesel producing country, mainly use crude palm oil (CPO) as a feedstock [11]. Thailand produced approximately 2.78 million tons of CPO in 2018, and 1.2 million tons of CPO was applied for the biodiesel production sector. The production capacity per day was increased from 7.68 to 8.31 million liters during the period between 2018 and 2019. In Indonesia and Malaysia, a crude palm oil production rate is increasing according to their policy of promoting biodiesel blend B40 at the end of 2022 to recover the palm oil export suspension to European Union [11] and to supply regular incomes of the labour in the agricultural sector. Furthermore, many countries are planning to increase the biodiesel blending percentage such as France (B7 to B10), Italy (B8 to B9), Poland (B8 to B8.5) and Spain (B7 to B8.5). Other countries are also focusing on using more biodiesel blends such as Austria (B5.75 to B8.75), Finland (B18 to B20) and the Netherlands (B12.5 to B16.4) [12]. The disruption effect to all energy sectors due to the Covid-19 pandemic was worse than any other recent historical event. Because the current outbreak of COVID-19 has a devastating effect on the global economy [13]. This effect also has a significant impact on the global oil market. Because the international, national, local, and public transportations have been one of the hardest-hit sectors owing to the COVID-19 pandemic, due to lockdown and stay-at-home order by state in many countries [14]. Therefore, the price of petroleum fuel has fallen result in the delaying the blending of the mandated level of biodiesel and less economically attractive in higher blending fuel. For Asian countries, Malaysia announced that fully used B20 biodiesel across Malaysia was delayed by six months to early 2022, due to the COVID-19 economic recovery plan. In addition, their intention to use B40 will be postponed beyond the end of 2022 [15]. The Indonesian Palm Oil Association (IPOA) reported that the COVID-19 pandemic had also delayed biodiesel-related plans and the 40 biodiesel plants were still to undergoing testing on diesel engine [16]. In Thailand, biofuel consumption was targeted at 2.9 billion liters for biodiesel by 2036 for according to the renewable energy policy of Alternative Energy Development Plan (AEDP). Currently, Thailand has been commercially using B10 as a standard diesel type in Thailand for all gasoline stations since 1 October 2020 to support Thai government’s policy and oil palm farmers [17].

Regarding transesterification process, this reaction is widely used in the biodiesel production. The glycerides will react with alcohol (typically methanol or ethanol) in the base-catalyst reaction for forming alkyl esters, for the base catalysts of KOH and CaO, respectively. At the optimal conditions was 6.1:1 and 10.9:1 methanol-to-oil ratio, 0.46 wt% and 0.96 wt% of KOH under 53.2 °C and 48.3 °C temperature, for the base catalysts of KOH and CaO, respectively. They reported that using KOH in the ultrasound-assisted transesterification process reduced mass transfer and expedited the chemical reaction between immiscible reactants resulting in the activation energy during the process to operate with a lower temperature. Furthermore, they mentioned that the potassium hydroxide catalyst condition delivers lower ratio of methanol-to-oil ratio values, reaction temperature, and energy demanding. [22], Besides, Yasvanthrajan et al. (2020) investigated the ethyl ester production from the waste cottonseed oil through transesterification using ultrasound. The horn of a probe-type ultrasonic processor having a diameter of 13 mm operating, 20 kHz frequency, 750 W ultrasonic power of ultrasonic horn, which was immersed into the reactant of mixture in a 500 mL glass reactor. The maximum yield 98.7% was obtained under the optimal condition of 4.5:1 ethanol-to-oil ratio, 5 wt% of enzyme catalyst loading, 6 hr reaction time, 45 °C reaction temperature, and the ultrasound pulsed at 15 s ON/15 s OFF. Many researches and publication papers have looked into the production of biodiesel using an ultrasound in a batch mode for the laboratory-scale [23]. Moreover, the ultrasonic intensity is significantly depended on the fixed frequency and acoustic power density in a batch ultrasonic reactor [24]. Therefore, the typical laboratory-scale ultrasound systems required high energy intensity, quite difficult for scaling up into industrial scale [25]. Because it is necessary to increase the acoustic energy density (AED) when the ultrasonic probe submerged into a large volume of liquid in the ultrasonic reactor [26]. Therefore, installing and maintenance cost are quite expensive to use ultrasound even in a laboratory to use even in laboratory scale [27]. On the other hand, several researchers have recommended that a hydrodynamic cavitation has many benefits compared to other traditional techniques. The hydrodynamic cavitation reactors have many advantages; the cheapest and energy-efficient methods for useful generating cavitation, simple equipment setup, less chemical consumption, less time required, and relatively easy to scale-up for commercial-scale [28,29,30]. Furthermore, the hydrodynamic cavitation can generate more cavities due to its configuration. The better cavitational results can be achieved and it is only depended on the geometry of cavitating devices [31]. Hydrodynamic cavitation has recently been widely used as a promising technique in many applications, such as industrial-scale applications of wastewater treatment, biofuel synthesis, and biogas production, etc [32,33]. The hydrodynamic cavitation can be generated by static elements and dynamic systems. For static elements, the flow velocity increases when the flow passes through the static elements of an orifice plate, a venturi tube, a throttle valve to create the hydrodynamic cavitation. For the dynamic systems, rotor–stator type generator provides high shear rate and high local energy dissipation [34]. This device delivers high mixing and high homogenization because it occupies a high shear, a high speed, and a higher power to develop the mixing energy, elongational stresses and shear, turbulence, and cavitation [34]. For the formation of cavitation on the rotor’s surface, the cavitation occurs in fluid because the pressure close to the surface of rotor drops into lower or equal to the vapor pressure of liquid when the surface velocity of fluid is too high [35].
Khan et al. (2020) proposed the converting Cannabis sativa oils to the ester with transesterification using hydrodynamic cavitation. Their hydrodynamic cavitation setup used the nozzle spray gun attached with the optimized geometry orifice plate with having 3 mm diameter for 7 holes to facilitate the dispersion of liquid into a spray, and a flow meter, a pressure gauge, control valves, a throttle valve, and a coupling to regulate and control the in-line flow. An AC induction motor was used to drive the pressure pumps. The methyl ester conversion of 97.5% was obtained under the optimal conditions of their results were 1 wt% KOH, 60 °C temperature, 6:1 M ratio of methanol-to-oil, and 20 min reaction time, at 3 bar upstream operation pressure [36]. Patil et al. (2020) investigated the biodiesel production with TiO₂ nanocatalyst transesterification using hydrodynamic cavitation from thumba oil. The static element of hydrodynamic cavitation of orifice plates was used as a cavitational device and the number of the holes of the orifice plate were varied such as 1, 10 and 20 holes. The optimized conditions; 2 mm of hole diameter, 20 number of holes, 80 °C reaction temperature, 1.6 wt% of TiO₂-CuO catalyst, 60 min reaction time, 6:1 methanol-to-oil ratio gave the maximum almost 65% of triglyceride [37]. Furthermore, a single hole orifice plate was used as a hydrodynamic reactor to produce biodiesel from waste cooking oil, which was described by Venkatachalam et al. (2020). The hydrodynamic cavitation was generated by static elements which composed with 2 mm diameter of single hole. They compared the hydrodynamic cavitation and ultrasonic cavitation. The transesterification process results using acoustic cavitation obtained 85% of methyl ester conversion after 40 mins under optimized conditions, whereas the results using hydrodynamic cavitation delivered 95% conversion within a short period. The optimization condition was 6:1 M ratio, 1 wt% of KOH, 60 °C of reaction temperature provided over 95% of methyl ester using the hydrodynamic cavitation. Many researchers have been reported using orifice plates and venturi tube as cavitational devices for biodiesel production. However, the major drawback of using orifice and venturi type is the high-pressure drop in pipes result in consuming more pumping power requirement [38,39]. For hydrodynamic cavitation, a hydrosonic reactor is composed with the rotating part of the rotor and stationary part of the stator. The benefits of utilizing this device are enhancing mixing intensity, mixing intensity, turbulent shear flow, and cavitation due to its high speed and high shear ability [34]. Inside the stator, a substantial region of cavitation formation occurs along the rotational direction and destroying the formed vapour bubbles formed by the high-velocity pressure at the same time. [34]. Samani et al. (2021) reported that biodiesel production from safflower oil using a rotor–stator reactor. Regarding, a transesterification process, the hydrodynamic cavitation device was set up with a stainless steel rotor with holes which was driven by an electric motor. The dimension of the stainless steel rotor was fixed with 4 mm in diameter. The reaction time, KOH loading, molar ratio of methanol to oil and rotor–stator gap were optimized to get the optimum combination for maximum yield. The maximum yield of 89.11% was obtained with the condition of 8.36:1 M ratio of methanol to oil, 0.94 wt% KOH, 63.88 sec reaction time [40]. Another research, biodiesel synthesis from refined palm oil by rotor–stator type hydrocavitation generator was described by Crudo et al. (2016). Their rotor–stator type of hydrocavitation reactor was purchased from Turin, Italy. Inside the reactor, the rotor was installed and aligned with the stator part which a rotor part was driven by an electric motor. The liquid was speed up in the radial direction and subjected to the atmospheric pressure to form cavitation. They varied three working temperatures, 55 °C, 45 °C, and 55 °C and two different flow rate 250 and 390 L/h. The residence time in the hydrocavitation reactor was fixed at approximately 10 s. Double step transesterification process dosing 75 vol % methoxide (CH₃OH) solution for the 1st step and the remaining 25% for the 2nd step was applied. In their study, the base catalyst transesterification process used sodium hydroxide (NaOH). They reported that over 99 wt% methyl ester was achieved at 55 °C reaction time and 390 L/h flow rate [41].

As a new technology for biodiesel production, a 3D printing technology is used in many application such as a medical part, automotive part, robotic part, and soft sensor, etc [42], this technology is rarely used in both of methyl ester and ethyl ester productions with high levels of FFA of oils. Therefore, the main feature of this study is using cost and time effective 3D printed rotor in the hydrodynamic cavitation reactor. Although, there are many types of research about biodiesel production using various augmentation reactors and feedstocks. However, to our knowledge, there are no explicit reported the biodiesel synthesis from high FFA crude palm oil using a 3D printed rotor–stator hydrodynamic cavitational device with the two-stage continuous process. In the continuous stage of esterification, mixing reactants (MCPO, methanol, and sulfuric acid) were fed into a 3D-printed rotor–stator reactor. The first step’s optimal conditions (methanol 17.7 vol%, 2.9 vol % sulfuric acids, 3000 rpm rotor’s speed, 4 mm hole’s diameter, 6 mm hole’s depth) have been described earlier [43]. The goal of this current study to research the optimization of five-parameter; methanol, potassium hydroxide, hole’s diameter, hole’s depth, and rotor’s speed, in a continuous transesterification for methyl ester production to be the highest purity via the use of 3D-printed rotor–stator. Response surface methodology (RSM), a 5-level 2-factor central composite design, was used to investigate the effects of these parameters on the purities of methyl esters (CCI). Moreover, the yield for each step of biodiesel production, and the comparison of electricity usage for the entire process between hydrodynamic cavitation reactor and ultrasonic clamp reactor were also completed.

2. Material and methods

2.1. Material

In the second step transesterification process, the esterified oil from the first esterification process was utilized as the feedstock to achieve methyl ester, as shown in Fig. 1. The compositions in esterified oil consisted of 1.028 wt% free fatty acid (FFA), 5.138 wt% methyl ester (ME), 89.67 wt% triglyceride (TG), 4.061 wt% of diglyceride (DG), and 0.102 wt% of monoglyceride (MG). The density of esterified oil was 0.889 kg/L at 60 °C measuring by hydrometer. The commercial-grade of methanol 99.7% and of 98% of KOH were utilized for transesterification. Thin-layer chromatography with flame ionization detection (TLC/FID) was measured the FFA, ME, TG, DG, and MG. The residual methanol content was tested by a gas chromatography-flame ionization detector (GC-FID, model: GC 6850; Agilent Technologies; USA).

2.2. Procedure

2.2.1. Experimental setup of hydrosonic reactor

The experimental setup of the two-stage continuous process for hydrodynamic cavitation was shown in Fig. 2. The important component of the continuous two-stage process is the hydrosonic reactor. The dimensions of hydrosonic reactor have been described in a previous paper of [43]. The use of hydrosonic reactor in the first stage esterification process for reducing FFA in MCPO was already presented in previous paper of [43]. In this study, the two continuous hydrosonic reactors were used as the cavitational devices; the first reactor was for the FFA reduction from MCPO using acid-catalyzed esterification. The second step was used to continuously produce methyl ester from the esterified oil using a base-catalyzed transesterification process. The details of preparing, manufacturing the 3D printing process, and dimensions of the holes on the rotor’s surface for the 3D printed rotor of both the first and second steps were the same a first step. For the physical dimensions of rotors, the ABS filament printed rotor having diameter in 60 mm, length in 46 mm. The stator was manufactured with the SUS304 stainless steel material and applied as a stationary component of the rotating unit. The dimensions of stator having 80 mm in inner diameter, and 90 mm in outer diameter. For the second step of the transesterification procedure, the dimensions of holes on the rotor’s surface
4 of diameter and depth differed according to the design of experiments. The real prototypes of 3D printed rotor and stainless steel rotor of hydrosonic reactor were described in Fig. 3. The hydrosonic reactor was composed of a 3D printed rotor which had 80 spherical holes on the rotor’s surface and was driven by a mechanical shaft and electric motor (Grundfos, model: MG112MC). In order to adjust the speed of the rotor inside the reactor, an inverter (Emerson, model: M201) was used to control the electric motor.

2.2.2. Experimental procedure of hydrosonic reactor

The detailed procedures of the first step esterification were described in the earlier paper [43]. The outcome products (esterified oil mixed with generated wastewater) from the first step esterification process were separated using the separator tank (T4) by the gravity method, as shown in Fig. 2. After separating, the esterified oil overflowed continuously into the tank (T5), prepared to start up for the second stage. This esterified tank oil (T5) was the primary raw material for the trans-esterification in the second stage. After that, first-step esterified oil was started to heat up to 60 °C using an immersion heater (HT2) and circulate to get the uniform temperature in the tank (T5) using circulating pump (P5, SANSO, model: PMD-371). For preparing the potassium methoxide solution (CH₃OK), the KOH loading predetermined required ratios were dissolved with methanol in the potassium methoxide tank (T6). For the second stage continuous transesterification process, the esterified oil and potassium methoxide (CH₃OK) solution, which is the solution of KOH dissolving in methanol, were fed into the second step hydrosonic reactor using a digital dosing pump (P6, Grundfos alldos, model: DME 48–3) at 25 L/h, and a chemical resistant pump (P7, Grundfos alldos, model: DDC 15–4), respectively. For mixing esterified oil and potassium methoxide solution, the motor was then switched on to rotate the 3D printed rotor. The mixtures inside the hydrosonic reactor were run for 20 sec residence time to get the equilibrium reaction. At the outlet sampling ports, the samples were kept three times per one condition in 30 mL sampling glass bottle with 20 sec interval time for each, thereafter immediately cool it in water to stop a reaction. All samples were then cleaned with warm water to eliminate the impurities in the crude biodiesel for the last purification process. For the analyzing step, the thin layer chromatography and flame ionization detection technique (TLC/FID) was used to investigate the compositions of purified biodiesel: methyl ester, FFA, MG, DG, and TG in the weight percentage. The optimum condition was modelled and optimized the independent and dependent variables using the response surface methodology (RSM) technique.

Fig. 1. Production steps of methyl ester production using the rotor–stator hydrodynamic cavitation reactor (A) mixed crude palm oil at 32 °C, (B) esterified oil and wastewater after first step esterification, (C) crude biodiesel and glycerol after second step transesterification, and (D) purified biodiesel after washing process.

Fig. 2. Diagram of two-stage continuous process for hydrocavitation. (P1: MCPO pump, P2: methanol pump, P3: sulfuric acid pump, P4: MCPO circulating pump, P5: esterified oil circulating pump, P6: esterified oil pump, P7: potassium methoxide pump, T1: MCPO tank, T2: methanol tank, T3: sulfuric acid tank, T4: separator, T5: esterified oil tank, T6: potassium methoxide tank, M: motor, SP: sampling port, HR: hydrosonic reactor, RO1: 3D-printed rotor for first step, RO2: 3D-printed rotor for second step, C: flexible shaft coupling, SH: mechanical shaft, B: high speed bearing, F: flange, and ST: stator).
Fig. 3. The real 3D printed and stainless steel rotors of hydrodynamic cavitation; (A) and (B) are the optimized stainless steel rotors of first and second step, respectively; (C) and (D) are optimized 3D printed rotors of first and second step, respectively.

Fig. 4. Machining of stainless steel rotor and filling filament of 3D printed rotor; (A) stainless steel rotor was machined by the CNC manufacturing process, and (B) 3D printed rotor was employed 100% filling filament by 3D printer.
2.2.3. Experimental procedure of ultrasound clamp

The experiments were conducted with ultrasonic clamp reactor to compare the results using the hydrosonic reactor. The comparison of the results between hydrosonic and ultrasonic reactors is a part of the objectives of this study. For the ultrasonic clamp reactor, the continuous transesterification process was executed with total ultrasonic power of 6400 W (16 unit × 400 W per ultrasonic clamp) at 20 kHz, and the ultrasonic clamps were arranged 100 mm along the reactor length. The details of the experimental setup were described in a previous paper of [44]. For comparison the results with hydrodynamic cavitation reactor (HC), the ultrasonic clamps were tested under the optimal condition of both first step esterification and second step transesterification when obtained from the optimizing results through the hydrosonic reactors. All experimental setup and procedure such as feeding oil and chemicals into the ultrasonic clamp reactor were the same as the procedures of hydrosonic reactors. The only difference is the cavitation reactor which was changed to ultrasonic clamp reactor. For the first step, crude palm oil, methanol, and sulfuric acid have been continually pumped into the ultrasound clamp reactor. The samples of esterified oils were taken out from each 100 to 900 mm in the length of ultrasonic clamp to check the FFA conversions. In the second step methyl ester production, the mixtures (esterified oil and mixed with generated wastewater) from optimal outlet port of first step ultrasonic clamp reactor were collected and then kept it into separation tank. After complete separation, the esterified oil was mixed with potassium methoxide solution inside the second step of ultrasonic clamp reactor. The collection of finished products of the second step were taken at the outlet port and immediately stop reaction, as the same as the first step. The purification and analyzing processes were carried out as the same as the two-stage continuous process for hydrosonic reactor.

2.3. CNC machining of a stainless steel rotor

In our previous paper, the 3D printed rotor was filled an acrylonitrile butadiene styrene (ABS) filaments with a Flashforge Creator3 [43], as shown the processing step in Fig. 4. The main purposes of using 3D printed rotors for the esterification and transesterification reactions were to reduce the manufacturing cost due to its cost-effectiveness and less time-consuming construction. All the experimental preliminary studies used 3D printed rotors varying the depth of hole and diameter of the hole on the rotor’s surface according to RSM method to determine the optimal condition. For practical industrial process, a computer numerical control (CNC) machine was applied to manufacture long-life stainless steel rotors having many holes on its surface. The CNC stainless steel rotor, having dimensions of 60 mm diameter of rotor, 46 mm height of rotor, hole’s diameter 6.4 mm, hole’s depth 6.2 mm were used as the rotating cavitation for hydrosonic reactor. These dimensions of the holes were obtained from the optimum conditions for continuous methyl ester production with 3D printed rotors by response surface methodology (RSM). The stainless steel rotor was machined by the CNC manufacturing process, as shown in Fig. 4. Before running the CNC machine, the prepared drawing of the rotor model was extracted the part of geometry, and applied digital programming code which can control the CNC machine. For the CNC machining operation, CNC milling machine (OKUMA, model: LB3000) was used to create and shape the smooth surface rotor, and remove the unneeded material’s part from the workpiece. The stainless steel grade 304 (SUS304) was used for creating methyl ester production using the second step transesterification process (Fig. 3A) and methyl ester production using the second step transesterification process (Fig. 3B).

2.4. Experimental design

Experimental conditions for the optimization of methyl ester purifying were fitted by the response surface methodology (RSM). Multiple regression analysis model was executed to predict the methyl ester value and searching the optimal conditions after the transesterification process using hydrosonic reactor. Consequently, a second-order polynomial model was built to response for the methyl ester purity.

For the methyl ester producing ester from esterified oil, Y is the response (ME, wt%), the five independent variables: methanol (5–17 vol %), potassium hydroxide (2–10 g/L), speed of the rotor (1000–5000 rpm), the diameter of hole (3–7 mm), and depth of the hole (4–10 mm) were varied to validate the optimal condition for the production of methyl ester using hydrosonic reactor. In this study, the levels of five varying variables of −2, −1, 0, +1, and +2, were optimized and the ranges of parameters were described in Table 1.

3. Results and discussion

3.1. Experimental results

Thirty experimental conditions of five parameters (methanol, potassium hydroxide, diameter of the hole, depth of the hole, and speed of rotor) were varied with the design of the experiment. Table 2 showed the results of methyl ester production from the transesterification by a hydrosonic reactor. Results of the predictive model and statistical analysis were described in the next section.

3.2. Response surface model of results and statistical analyses

Response surface methodology (RSM) was used to evaluate the fitted regression model for the production of methyl ester (ME) from continuous transesterification process using hydrosonic reactor. The second-order multiple polynomial regression functional equation was represented in Eq. (1). The coefficients and p-values of fitted predictive model were listed in Table 3. The predictive model was archived with the coefficient of determination ($R^2$) of 0.987, and the adjusted determination coefficient ($R^2_{\text{adj}}$) of 0.981. Table 4 showed an analysis of variance (ANOVA) of each response surface model term corresponding to the continuous transesterification process.

$$ ME = \beta_0 + \beta_1M + \beta_2S + \beta_3D_s + \beta_4C + \beta_5M^2 + \beta_6C^2 + \beta_7D_s^2 + \beta_8S^2 $$

(1)

where ME is methyl ester (wt%), M is methanol (vol%), C is potassium hydroxide (g/L), $D_s$ is the diameter of hole (mm), $D_h$ is the depth of the hole (mm), $S$ is the speed of the rotor (rpm), and $\beta$ is fixed coefficient.

For the predictive model, the satistic importance of regression coefficient in each term depends on the p-values. At 95 percent confidence level, the p-values smaller than 0.05 have strong significance results. The detailed list of p-values observed for each parameter is described in Table 3. The smaller significance of p-values were found in the terms of $\beta_1M$ and $\beta_2M^2$. Therefore, the methanol influenced by the term of $\beta_1M$ and $\beta_2M^2$ had the highest level of significance. Therefore, the methanol had a large impact on producing high purity of methyl ester. The smallest p-values, and these parameters are the most essential for considering to produce methyl ester with continuous transesterification process.

Table 1 Ranges of independent variables.

| Independent variable | Varying level          |
|----------------------|------------------------|
|                      | -2 | -1 | 0 | +1 | +2 |
| M Methanol (vol%)    | 10 | 15 | 20 | 25 | 30 |
| C Potassium hydroxide (g/L) | 2 | 4 | 6 | 8 | 10 |
| D_s Diameter of hole (mm) | 3 | 4 | 5 | 6 | 7  |
| D_h Depth of hole (mm)  | 2 | 4 | 6 | 8 | 10 |
| S Speed of rotor (rpm) | 1000 | 2000 | 3000 | 4000 | 5000 |
As seen in Table 2, the analysis of variance (ANOVA) was applied to the set of data to solve the independent variables of methanol (M), potassium hydroxide (C), the diameter of hole (D_i), depth of the hole (D_e), and speed of the rotor (S) and build a regression model Eq. (1) to investigate the optimal conditions for continuous methyl ester production. The results showed that the set point of 99.55 wt% methyl ester for hydrosonic reactor was reached at an optimized condition of 28.6 vol% methanol, 6.2 g/L of KOH, hole’s diameter 6.4 mm, hole’s depth 6.2 mm, and 3000 rpm of rotor’s speed by the predictive model. Moreover, the methyl ester was verified with the both of 3D printed and stainless steel rotors inside the hydrosonic reactor with the actual experiment under the optimum condition. The results showed that 99.163 wt%, 99.221 wt% methyl ester purities were achieved with the 3D printed and stainless steel rotors. This methyl ester contents in the biodiesel were very close to 99.55 wt% as predicted by the predictive model. For the ultrasonic clamp reactor, the ester purities were 96.734 wt%, 97.117 wt%, 97.789 wt%, 97.814 wt%, 97.434 wt%, 97.420 wt%, 97.434 wt%, 97.334 wt%, 97.322 wt% at 100–900 mm apart from 100 mm each other in the length of ultrasonic clamp reactor, respectively. Thus, the methyl ester reached the acceptable equilibrium after 400 mm in length. Therefore, the methyl ester purity at 400 mm in length of ultrasonic clamp reactor is enough to distribute the equilibrium in the high purity of methyl ester under the same optimized conditions as hydrosonic reactor. The energy consumption of the hydrosonic and ultrasonic clamp reactors will be compared under the same reaction condition in the section of electricity consumption for two-stage continuous process.

### 3.4. The optimum condition for the purity of methyl ester

The completed experimental conditions, as well as the testing results, are described in Table 2. Microsoft’s Excel solver function was applied to analyze the set of data to solve the independent variables of methanol (M), potassium hydroxide (C), the diameter of hole (D_i), depth of the hole (D_e), and speed of the rotor (S) and build a regression model Eq. (1) to investigate the optimal conditions for continuous methyl ester production. The results showed that the set point of 99.55 wt% methyl ester for hydrosonic reactor was reached at an optimized condition of 28.6 vol% methanol, 6.2 g/L of KOH, hole’s diameter 6.4 mm, hole’s depth 6.2 mm, and 3000 rpm of rotor’s speed by the predictive model. Moreover, the methyl ester was verified with the both of 3D printed and stainless steel rotors inside the hydrosonic reactor with the actual experiment under the optimum condition. The results showed that 99.163 wt%, 99.221 wt% methyl ester purities were achieved with the 3D printed and stainless steel rotors. This methyl ester contents in the biodiesel were very close to 99.55 wt% as predicted by the predictive model. For the ultrasonic clamp reactor, the ester purities were 96.734 wt%, 97.117 wt%, 97.789 wt%, 97.814 wt%, 97.434 wt%, 97.420 wt%, 97.434 wt%, 97.334 wt%, 97.322 wt% at 100–900 mm apart from 100 mm each other in the length of ultrasonic clamp reactor, respectively. Thus, the methyl ester reached the acceptable equilibrium after 400 mm in length. Therefore, the methyl ester purity at 400 mm in length of ultrasonic clamp reactor is enough to distribute the equilibrium in the high purity of methyl ester under the same optimized conditions as hydrosonic reactor. The energy consumption of the hydrosonic and ultrasonic clamp reactors will be compared under the same reaction condition in the section of electricity consumption for two-stage continuous process.

### 3.5. Effect of the hole dimensions and methanol content on the methyl ester

In this study, the methanol content was the most significant effect on the production of the high purity of methyl ester according to the statistical analysis. The methanol content was varied in the range of 10 to 30 vol% for second stage transesterification. The effects of methanol (M) on the depth (D_e) and diameter (D_i) of the holes on the purity of methyl ester show in the Fig. 5F and Fig. 5I. The highest methyl ester of 99.5 wt% occurred when the diameter of hole was varied in the range of 5.5 to 7 mm and methanol was between 25 and 30 vol%. The purities of methyl esters were getting lower when the methanol content was less than 25.5 vol% and diameter of hole was less than 5.5 mm. According to Fig. 5I, a higher value of methyl ester of 99 wt% was obtained when the methanol was in the range of 25.5 to 30 vol% and the D_e was between 6 and 9 mm. When the M was less than 20 vol% and De was lower than 6 mm, the purity of methyl ester decreased. Fravardin et al. (2019) reported that the methyl ester producing from unused cooking oil with combined hydro- and ultra-cavitation system. They used RSM to optimize the independent variables such as residence time, methanol and potassium hydroxide to get the high methyl ester. Their study showed the methanol to oil ratio was one of the highest significance according to the results of statistical analysis for increasing the methyl ester yield using transesterification. [45]. Kolhe et al. (2017) concluded that the production of biodiesel from a raw material of waste frying oil by hydrocavitatio.
Fig. 5. Contour plots of two-stage continuous process (A, B and C) effects of hole depth and potassium hydroxide, rotor speed and hole diameter; (D, E and F) effects of hole diameter and potassium hydroxide, rotor speed and methanol; (G, H and I) effects of methanol and potassium hydroxide, rotor speed and hole depth; (J) effects of rotor speed and potassium hydroxide on the methyl ester purities.
Their results showed that methanol to oil molar ratio was the one of the considerations for high methyl ester production. The methanol to oil ratios; 3:1, 4.5:1 and 6:1 delivered the methyl ester value 54, 93.86 and 95.4 wt% respectively [46]. The independent parameters for the diameter and depth of the hole were also one of the most considerations for high methyl ester production. The methanol to oil molar ratio was the one of the considerations for the production of high methyl ester because the cavitation conditions and efficiency are directly related to the operating parameters and the geometries of the cavitation devices (eg. size and shape of the hole). Moreover, the formation of various flow conditions which can be caused. Because, the variation of the configuration cavitation devices could also effect the purity of methyl ester. [31].

### 3.6. Yield of each product of the two-step process

The verification of optimized condition for the production of methyl ester by hydrosonic and ultrasonic clamp reactors was analyzed using TLC/FID. The optimum condition for the purities of methyl ester values can convert to 9.163 wt% for hydrosonic reactor and 97.814 wt% for ultrasonic clamp reactor. Moreover, the purity of methyl ester was also verified with the stainless steel rotor which was manufactured by CNC machine inside the hydrosonic reactor under this optimum condition. The purity of methyl ester value 99.221 wt% was obtained with the stainless steel rotor hydrosonic reactor. This methyl ester value was very close to the purity of methyl ester using 3D printed rotor hydrosonic reactor.

The yields of each product of the two-step process were calculated relative to 100 vol% based original MCPO, as listed in Table 5. The yields of purified biodiesel after the purification process of 97.51 vol% and 88.69 vol% were obtained from hydrosonic and ultrasonic clamp reactors under the optimized condition, respectively. Fig. 1C shows the completely separated condition of the crude biodiesel and glycerol. The separation time took 4 hrs to settle down the glycerol (dark brown phase) to the bottom of the sampling bottle and separate the crude biodiesel (yellow phase) as an upper layer. Fig. 1D showed the purified biodiesel after the separation process, the crude biodiesel was purified using warm water to eliminate residual impurities. After the purification process, the average values of 97.51 vol% and 88.69 vol% yields of the purified biodiesel from the continuous two-stage process were achieved from hydrosonic and ultrasonic clamp reactors, respectively. Thus, a 9.47% increase in yield of biodiesel was obtained under the optimal condition when using the hydrosonic reactor.

For the consideration of the residual methanol before the purification process, a gas chromatography (GC) was used to analyze the residual methanol in the crude biodiesel phase and the glycerol phase. Because the excess methanol in the transesterification was suspended between the intermediate and final product and glycerol [47,48]. The results showed that the residual methanol in the glycerol was high at 10.87 vol%. This residual methanol in glycerol can be reused for another reaction process for the recovery of chemical consumption cost [48]. For this issue, similar report was described by Kiss et al. [42] who proposed the dividing-wall column (DWC) which is a developed intensification method for the trilateral separation process. The DWC consisted a pre-fractionator and the main distillation column. The main purpose of this process was to recover the methanol in the glycerol byproduct, residual water in product after washing process, and FFA pretreatment steps through biodiesel production using transesterification. They recommended that this DWC technology be applied as a novel application to recover methanol and separate glycerol for industrial skill biodiesel production. [48]. Moreover, the residual methanol content of 14.47 vol % was founded in crude biodiesel after complete second step. This residual methanol contents will be eliminated with warm water in the purification process before applying to the diesel engine [49].

### Table 5

| Composition, yield<sup>a</sup>, and residual methanol | MCPO<sup>[43]</sup> | Esterified oil<sup>HC</sup> | Biodiesel<sup>b</sup> | US<sup>c</sup> |
|---|---|---|---|---|
| Composition | Free fatty acid, FFA (wt%) | 11.46 | 1.028 | 0.794 |
| | Methyl ester, ME (wt%) | 5.138 | 10.70 | 10.70 |
| | Triglyceride, TG (wt%) | 77.88 | 24.53 | 24.53 |
| | Diglyceride, DG (wt%) | 10.35 | 3.16 | 3.16 |
| Density | at 60 °C (kg/L) | 0.883 | 0.883 | 0.883 |
| | at 32 °C, room temperature (kg/L) | 0.91 | 0.943 | 0.943 |
| Yields<sup>d</sup> | For first step of esterification | 96.07 | 96.07 | 96.07 |
| | Esterified oil (vol%) | 89.24 | 89.24 | 89.24 |
| | Generated wastewater (vol %) | 24.53 | 24.53 | 24.53 |
| For second step of transesterification | Biodiesel (vol%) | 97.51 | 97.51 | 97.51 |
| | Glycerol (vol%) | 88.69 | 88.69 | 88.69 |
| Residual methanol |
| For first step of esterification | Residual methanol in esterified oil (vol %) | 1.383 | 1.383 | 1.383 |
| | Residual methanol in generated wastewater (vol %) | 8.305 | 8.305 | 8.305 |
| For second step of transesterification | Residual methanol in crude biodiesel (vol %) | 14.47 | 14.47 | 14.47 |
| | Residual methanol in glycerol (vol %) | 10.87 | 10.87 | 10.87 |

**Note:**

<sup>a</sup> The yields are relative to 100 vol% of initial MCPO.

<sup>b</sup> HC is the hydrosonic reactor.

<sup>c</sup> US is the ultrasound clamp.

### Table 6

| Continuous process steps | Electricity (kW h) |
|---|---|
| Start up | Process |
| Hydrocavitation |
| For first-step of esterification | 25 L of MCPO was preheated to 60 °C within 15 min | 0.56 |
| | Three dosing pumps: MCPO, MeOH and H₂SO₄ | 0.034 |
| | Motor for hydrocavitation | 0.569 |
| | Total | 0.569 |
| | For second-step of transesterification | 25 L of esterified oil was preheated to 60 °C within 15 min | 0.56 |
| | Two dosing pumps: esterified oil, CH₂K₂O | 0.025 |
| | Motor for hydrocavitation | 0.569 |
| | Total | 0.569 |
| | Total for two-step process of hydrosonic reaction | 1.12 | 1.197 |
| | Ultra cavitation |
| For first-step of esterification | 25 L of MCPO was preheated to 60 °C within 15 min | 0.56 |
| | Three dosing pumps: MCPO, MeOH and H₂SO₄ | 0.034 |
| | 2400 W<sup>4</sup> ultrasound clamps | 0.512 |
| | Total | 0.546 |
| | For second-step of transesterification | 25 L of MCPO was preheated to 60 °C within 15 min | 0.56 |
| | Two dosing pumps: esterified oil, CH₂K₂O | 0.025 |
| | 3200 W<sup>4</sup> ultrasound clamps | 0.683 |
| | Total | 0.708 |
| | Total for two-step process of ultrasound clamp | 1.12 | 1.254 |

**Note:**

<sup>a</sup> The ultrasonic power was operated at 6 unit × 400 W (2400 W).

<sup>b</sup> The ultrasonic power was operated at 8 unit × 400 W (3200 W).
3.7. Electricity consumption for two-stage continuous process

The comparison of energy demanding for the entire system between the hydrosonic and ultrasonic clamp reactors described in Table 6. The average electricity usage was measured by the digital power meter. For the hydrosonic reactor, the details of the total electricity consumption for the first step esterification process have described in an earlier paper by Oo et al. (2021) [43]. For the second step transesterification process, the preparation for the preheating esterified oil from first step esterification process to 60 °C, and controlling the stable temperature in the tank consumed 0.56 kW h. The hydrosonic reactor required the electricity consumption of 0.569 kW h to operate a rotor on the process. The esterified oil and potassium methoxide solution were supplied into the hydrodynamic reactor by using two digital pumps, which required the electricity usage of 0.025 kW h. The hydrosonic reactor for the second step transesterification process consumed 0.594 kW h. The total electricity consumption for the entire two stages continuous esterification and transesterification process, excluding start-up preparation, was 1.197 kW h to produce the purified biodiesel of 24.37 L/h. Therefore, two stages process required the average energy usage of 0.049 kW h/L for the whole completed continuous process utilizing a hydrosonic reactor.

For the ultrasonic clamp reactor, the electricity consumption for the start-up preparation and using digital dosing pumps for the first and second steps were the same as the hydrodynamic cavitation process. The only different thing is the ultrasonic input power. The electricity consumption for first step esterification process consumed 0.512 kW h which is calculated based on the required ultrasonic input power 2400 W (6 × 400 W) within 300 mm of ultrasonic clamp reactor to reduce the FFA value of 1.070 wt%. For the second step transesterification process, the ultrasonic clamp reactor consumed 0.683 kW h which is calculated based on the required ultrasonic input power 8 × 400 W (3200 W) within 400 mm of ultrasonic clamp reactor to reach equilibrium in the methyl ester purity. The whole process for both esterification and transesterification using ultrasonic clamp reactor needed 1.254 kW h excluding start-up preparation to get the purified biodiesel of 22.17 L, which calculated based on initial MCPO flow rate (25 L/h). Thus, the average energy usage for the whole completed biodiesel synthesis using ultrasonic clamp reactor was 0.056 kW h/L. For the comparison of average energy demanding for the entire process between the hydrosonic and ultrasonic clamp reactors, the hydrosonic reactor consumed lower than the ultrasonic clamp reactor. The percentage difference of average energy consumption between the hydrosonic and ultrasonic clamp reactors was 13.3%. The hydrodynamic cavitation reactor gave 1.369 wt% methyl ester higher than acoustic cavitation reactor. Related similar description was explored by Ghayal et al. (2013) who optimized the methyl ester production from consumed frying oil with hydro-cavitation reactor using transesterification process. They reported that the methyl ester conversion comparison between hydro- and ultrasound cavitation under the same optimized conditions. The methyl ester conversion 88% was obtained after 40 min of reaction time using acoustic cavitation while using hydrodynamic cavitation delivered more than 95% of the methyl ester conversion within 10 min. The hydrodynamic cavitation reactors gave 11.1% methyl ester higher and 3 times of reaction time less than acoustic cavitation reactor [50]. Another research to support the results of this study was described in hydrodynamic cavitation for sonochemical effect by Moholkar et al. (1999). They compared the energy efficiency between hydro- and ultrasound cavitation based on the yield decomposition and the actual energy input into the system. Moreover, the hydrodynamic cavitation delivered a higher cavitation intensity result in the energy efficiency was 2 times more than ultrasound cavitation. Because hydrocavitation provided a large number of pressure pulses with small magnitudes for achieving the oscillation of the cavity in hydrodynamic cavitation, while acoustic cavitation was performed with a single pulse using high magnitude [51]. In the current research, those researches proved that hydrodynamic cavitation is a more efficient and promising selection for the biodiesel production than acoustic cavitation [50,51].

4. Conclusions

A novel cost-effective ABS filament printed rotor–stator hydrocavitation reactor provides an efficient way for FAME production from high FFA content of crude palm oil using a continuous two-stage process. The optimum conditions; 28.6 vol% methanol, 6.2 g/L of KOH, 6.4 mm diameter of hole, 6.2 mm depth of hole, and 3000 rpm of rotor speed were obtained according to the response surface methodology (RSM). These optimal conditions delivered the purities of methyl ester of 99.163 wt% and 97.814 wt% using hydrosonic and ultrasonic clamp reactors. The maximum yields of purified biodiesel after the purification process of 97.51 vol% and 88.69 vol% were achieved using hydrosonic and ultrasonic clamp reactors. The average energy demanding for two-stage continuous biodiesel production at the constant flow rate of 25 L/h MCPO by the hydrosonic and ultrasonic clamp reactors were 0.049 kW h/L and 0.056 kW h/L of MCPO, respectively. The hydrodynamic cavitation process indicates conspicuously, according to all experimental results, that it can be a better choice for the two-stage continuous biodiesel production process from MCPO. The energy consumptions for continuous process of the hydrodynamic cavitation reactors for esterification and followed by transesterification reactions are found to be enhanced by optimizing the ABS filament printed rotor–stator hydrocavitation reactor. The hydrodynamic cavitation reactor provides lower energy consumption and a higher possibility to scale up for commercial-scale FAME production process from high FFA content of crude palm oil.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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