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Fatty Acid Methyl Esters (FAME) Synthesis Using Continuous Vortex Fluidic Device: Influence of Different Process Variables

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ABSTRACT

Currently, biodiesel synthesis is undergoing rapid technological reforms in both industry and academic institutions. At present, the major challenge of biodiesel synthesis is the cost of production compared to conventional biodiesel. Thus, numerous studies on the use of technologies and different methods to evaluate optimal conditions of biodiesel synthesis technically and economically have been carried out. The dynamic thin film (changes of height and length due to free movement of material as a result of fluid exposure to air and vapour) in VFD is generated by the continuous addition of fluid to a rapidly rotating glass sample tube surface. In this work, virgin sunflower oil was subjected to the transesterification process and the maximum crude biodiesel (impure) of 89.4% concentration was obtained. This work comprehensively studied parameters for biodiesel synthesis using VFD to make give a better understanding. This work is probably the first attempt to comprehensively study parameters for biodiesel production using the VFD platform. The optimum operational condition is 0.9 M KOH, 5250 rpm; 0.5 mlmin-1 for both oil and methanol and at an inclination of 45º relative to a horizontal position. From the results obtained VFD is effective in biodiesel synthesis from first-generation feedstock (1G) at room temperature under continuous mode. This process is effective in converting fatty acid from sunflower oil to methyl esters at room temperature without the use of co-solvent, with no soap formation and down-streaming process.

Keywords: Sunflower oil; Transesterification; Methanol, biodiesel; Vortex Fluidic Device; Fatty Acid Methyl Ester, Potassium hydroxide

INTRODUCTION

Because of the current trend in the challenge of climate change [1], rise in the price of fossil fuels, over-dependence on conventional fuel, environmental degradation, declining of global oil reserves [2], energy conservation and management, and CO2 reduction to accomplished COP26 Glasgow 2020, [3], there is an urgent need for alternative renewable and sustainable sources of energy. Biodiesel is needed in the transport, agriculture, manufacturing industry, commercial and domestic sectors [4][5][6][7].

Biodiesel has the potential for providing us with energy that is sustainable and renewable [7]. The major prospects for biodiesel are manufacturing and transportation industries, which mostly rely on liquid oils for power generations [3]. However, the rise in biodiesel production has caused concerns about the choice of feedstock. It is because of the alarming competition between foods and fuel. Development in research, policies, and technology can make biodiesel compete with fossil diesel [8].

Over the years biodiesel was produced using a traditional method of a batch process, which has been challenges faced with which include: long reaction time, high catalyst consumption, higher volumetric ratio, higher temperature, and high stirring time. Attempts have been made by researchers to address these problems. Rashid et al [9] 1wt% NaOH, 6: 1 methanol to sunflower oil) molar ratio, the temperature of 60 °Ca and yield of 97.1%. In addition,1wt% KOH with methanol to oil molar ratio of 8: 1, 60 C°, mixing rate of 600 rpm for 90 minutes which gave a yield of 96% [10]. Furthermore, solvents such as Diethyl ether, Dimethyl ether, Tetrahydrofuran, and Tert-butyl methyl ether were used to enhanced mass transfer of transesterification reaction of sunflower with methanol (molar ratio of 1: 8). The catalyst loading of 1 wt%, a reaction time of 20 minutes, stirring frequency of 2.8Hz yielded only 78% at room temperature [11].

Some of the solutions practice today to address the challenges facing batch processes are continuous technologies to efficient heat and mass transfer in the transesterification reaction. These technologies include static mixers, microchannel, continuous oscillatory flow, cavitational, microwaves, spinning discs, and ultrasonic reactors.

On a larger scale, a static mixer was used to convert palm fatty acid distillate in a three steps continuous process. Biodiesel yield of 98.65 wt% at 60 °C for 60 minutes [12]. In another similar approach, crude biodiesel of 129 wt% was later purified to obtained 86.4 wt% for approximately 15 minutes reaction time [13]. In 2018, Nguyen et al., [14] converted waste cooking oil using a static mixer under the optimum conditions 6: 1 methanol to oil molar ratio, 60 °C reaction temperature, catalyst loading of 1.0 wt% NaOH. The FAME yield 97.8% within 2 seconds of residence time.

Using microchannel biodiesel was synthesis from rapeseed at catalyst (CaO/MgO) loading of 7.9 wt%, methanol to oil molar ratio of 1.75: 3, reaction temperature of 70 °C, co-solvent in a ratio of 0.575: 1 was added to favour the reaction forward [15]**.** While Yasmud et al. [16] investigated the effects of operational parameters and reported using the same reactor conversion of pork fat to FAME (yield 95.4%) at 65 °C, methanol to oil ratio of 6: 1 optimum, catalyst (KOH) loading of 1.3 wt% and the reaction time was 5 – 20 seconds.

A continuous flow oscillatory reactor with a length of 1.5 meters and 25 mm internal diameter was reported with rapeseed oil and methanol as the major reactants. NaOH was used as a catalyst with a molar ratio of 1.5 to 1 methanol to oil. However, this process requires heating of 60 °C to attained optimum yield conditions [17].

The cavitational reactor is another technique employed to enhance mixing and mass transfer in the transesterification reaction. Laosuttiwong et al. [18] employ palm oil using NaOH for biodiesel production. The parameters used were 1 wt%, 60 °C, 6: 1, and 3 hours for catalyst loading, reaction temperature, methanol to oil molar ratio, and reaction time respectively which has a yield efficiency of 80%. Mohod et al., [19] investigated the efficacy of biodiesel production under the following parameters; maximum FAME yield 92.3% for fresh cooking oil under the optimum conditions of the reaction time of 120 minutes, the molar ratio of methanol to oil as 12: 1, 3 wt% loadings of KOH as the catalyst and temperature of 50 °C.

The microwave platform also accelerates a transesterification reaction by reducing the viscosity of triglycerides. Barnard et al., [20] reported 94.60% conversion of Virgin Soybean at optimum operational conditions are 1 wt% catalyst loading, 50 °C reaction temperature, methanol to oil molar ratio of 6: 1, the reaction completed in 1 minute. In another work, Azcan et al., [21] reported 99.4% and 93.7% conversions rapeseed with (1 wt% each) KOH and NaOH respectively. Other conditions of the reaction are reaction temperatures of 50 °C and 40 °C and 5- and 3- minutes reaction times respectively. Also, using the same microwave method, FAME was achieved at 1 wt% (NaOH), methanol to oil molar ratio of 10: 1 from *Carthamus tinctorus L*. 98.4% FAME was achieved when the reactants were heated for 2 hours at 60 C [22]. Furthermore, when *Ceiba pentandra* was converted to biodiesel it requires 2.15 wt% KOH, 57.09 °C reaction temperature, methanol to oil molar ratio of 9.85: 1, the reaction reached it peak at 3.29 minutes [23]. In a similar approach Dhingra et al., [24] reported a KOH (0.99 wt%) catalytic conversion of waste cooking sunflower oil at methanol to oil molar ratio of 9.05: 1 at 57.31 °C reaction temperature. 96.33% of FAME was achieved after the mixture at 494.94 rpm for 77.12 minutes.

Chen, [25] reported the conversion of soybean with KOH (1.5 wt%) to produced biodiesel FAME 96.9% and other operational conditions include 6: 1 methanol to oil molar ratio, 60 °C, a flow rate of 773ml/min, and rotational speed of 2400 rpm. The ultrasonic reactor was able to synthesize 93.8% FAME yield from waste cooking oil under the optimum operational conditions: 1.5 wt% KOH, 4: 1 methanol to oil molar ratio, and the reaction completed within 0.93 minutes at room temperature [26]. There is a need to improve on these technologies to address the challenges of cost of biodiesel production, high temperature, long reaction time, high ratio of methanol to oil, and high catalyst loading. Novel vortex fluidic technology has the capability of intensifying (high mixing, high heat/mass transfer as well maximum surface area for the interphase of methanol and oil) the production of biodiesel through transesterification reaction [27, 28] as well as general chemical reactions [29, 30, 31, 32].

In 2014 Raston and Britton reported the application of VFD in converting sunflower oil to biodiesel at a moderate condition compared to other biodiesel production technologies. Some of the parameters explored were catalyst concentrations and resident time. The optimum operating parameters are 1.0 moldm-3 KOH, methanol to oil volumetric ratio which is equivalent to 23.5 to 1 molar ratio, the rotational speed of 5250 rpm, and the only feature which the VFD has is the inclination angle of 45°, the process took place at room temperature [27]. In addition, VFD does not require down streaming process like centrifugation to separate the output into excess methanol, biodiesel, and glycerol. However, to shift the reaction forward, more methanol is required compared to some of the continuous flow processes such as static mixer [12, 13, 14], oscillatory [17], or cavitational which operate at 6: 1 methanol to oil molar ratios or less [18, 19].

In a different work, Britton and Raston [28] reported the conversion of high free fatty acid oleic acid to biodiesel by esterification reaction with rotational speed being studied comprehensively. Application of biomass (fungal and wet microalgae) was reported for biodiesel synthesis with the focus of assessing the effect of the VFD in converting high moisture content feedstocks. The wet microalgae were converted to 96 % biodiesel at 6000 rpm, biomass to methanol molar ratio of 1: 24, 45 inclination angles relative to a horizontal position. The catalyst concentration was 3 w/v% and the reaction was completed within 2 minutes at a flow rate 0.5 ml/min [33].

From the literature, the VFD platform has a new potential in converting a variety of feedstocks [27] despite the challenges of high free fatty acids [28], moisture contents, and does not require heat input [33]. Within a short time the VFD has proven to be a potential platform for chemistry transformation in addition to biodiesel production, as follows: (1) Enhance mass transfer due to formation of the dynamic thin film shears and in essence, increase biodiesel yield [27] (2) Superior mass transfer due to rotational tube reactors that enhanced the shearing of the liquids time created by the gravitational force from the inclination of the tube also optimized the biodiesel products [29]. (3) Enhances the mixing even at a micro-level characterized by fluidic pressure waves as a result of the oil and alcohol being fed separately and therefore the reaction reaches completion. This minimizes the amounts of intermediates such as monoglycerides and diglycerides and maximizes the contents of triglycerides [27]. (4) VFD accelerates and increases the efficiencies of transesterification reaction by optimizing rapid heat and mass transfer (5) VFD operates at room temperature and avoids the use of other solvents such as acetone and thereby reducing energy costs [27, 28].

Here we reported a comprehensive parametric study of biodiesel synthesis using the VFD platform, these include Inclination angle, rotational speed, and flow rates, which are significant for the understanding of biodiesel production using the VFD platform. Most importantly, we were able to synthesise 89.40% raw biodiesel at mild 0.9 KOH concentration with flow rates of methanol to oil kept at 1: 1 volumetric ratio, 45° inclination angle, 5250 rpm rotational speed. This is due to frequent collusion between reactants and the KOH originated by the VFD.

2.0 EXPERIMENTAL METHODOLOGY

2.1 Materials

Virgin sunflower oil was purchased from KTC, United Kingdom. KOH (99% purity) and methanol (99.9% purity) are obtained from Sigma Aldrich. For FAME analysis, heptane (analytical grade: 99.5%)

was obtained from Fisher Scientific while Methyl Nonadecanoate, C19 (Analytical grade) was obtained from Sigma Aldrich.

2.2 Production of the BIODIESEL

The transesterification of sunflower oil was performed using the VFD as illustrated in figure 1. The VFD was equipped with a 20 mm external diameter glass tube. The sunflower oil and methanol mixed with KOH catalyst were injected via automated pumps at a different flow rate. Products were collected in a graduating cylinder and transferred into a separatory funnel. The product collected is separated into two, sometimes three layers of biodiesel. The lower layer (glycerol) was removed first, followed by the middle layer (biodiesel) then the top layer. In a situation where the output separates into two layers, the bottom layer was removed as glycerol and the top layer was analyzed as biodiesel. The biodiesel collected is always stored in refrigeration until (approximately 2.5 ºC) it is used for off-line GC analysis. The biodiesel samples were analyzed using Perkin Elmer Clarus gas chromatography (580S, GC) equipped with mass spectroscopy to quantify their FAME content.

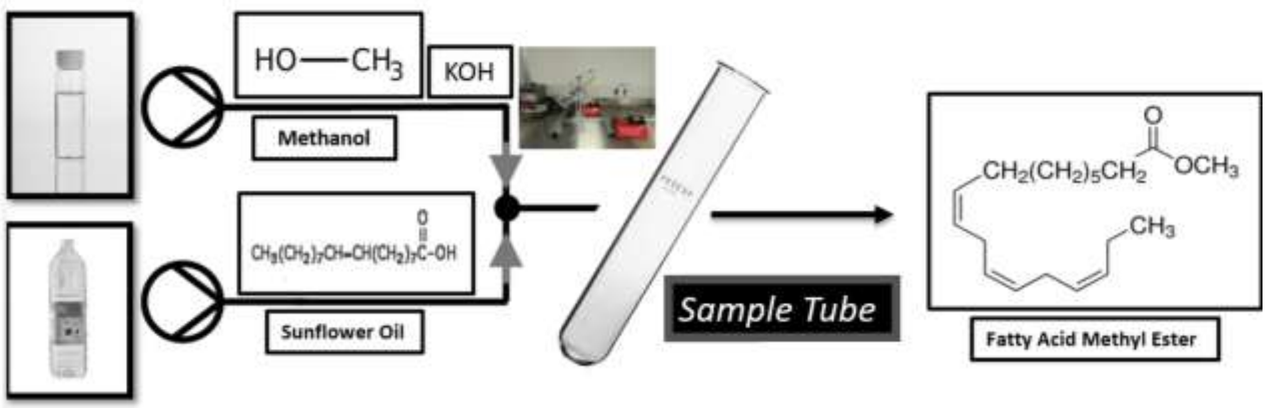

Figure 1. Schematic diagram for biodiesel production

To achieve an optimum condition, all the process parameters were fixed except for one, in turn, is changed to obtain the maximum biodiesel yield. The test variables were catalyst concentration (M), flow rate (mL/min), rotational speed (rpm), and inclination angle (θ) while the response factor variable was FAME yield (%).

Each experiment was carried out three times for validation and the average biodiesel yield was calculated using the British Standard method (EN ISO 14103) for calculating the percentage of total FAME (equation 1) and linolenic acid methyl ester (LAME. Equation 2) [34].

FAME yield. The optimum catalyst concentration for biodiesel production using sunflower oil and KOH was determined by varying the catalyst concentration at 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, and 1.2 M while keeping other parameters fixed at 5250 rpm rotational speed, 0.5 mL/min flow rates for both methanol and sunflower oil, 45º inclination angle relative to a horizontal position. To study flow rate, 0.5 ml/min, 0.6 ml/min, 1.0 ml/min 2.0 ml/min, and 3.0 ml/min were studied and parameters such as catalyst concentration, inclination angle, and rotational speed were kept constant at 0.9 M, 45° and 5250 rpm respectively. Another important parameter study was sample tube inclination relative to a horizontal position. The parameters include 25°, 35°, 45°, 55°, 65°, 70° and 80°, other parameters such as catalyst concentration, flow rates, and rotational speed was kept constant at 0.9 M, 0.5 ml/min for both methanol and sunflower volumetric ratio respectively. Finally, rotational speed was studied, the variables include 1000 rpm. 2000 rpm, 3000 rpm, 4000 rpm, 5000 rpm, 5250 rpm, 6000 rpm, 7000 rpm, and 7500 rpm. Other parameters were kept constant, these parameters include catalyst concentration of 0.9 M, 0.5 ml/min for both methanol and sunflower volumetric ratio, and 45° inclination angle respectively.

This process was repeated for each of the other process parameters to achieve the optimum condition for biodiesel production from sunflower oil.

2.3 FAME GC - MS Analysis

The FAME content of the prepared biodiesel sample was quantified by a Perkin Elmer Clarus Gas Chromatography (580S, GC) equipped with a mass spectroscopy (560S, MS) instrument [Figure 2]. The operational conditions for Perkin Elmer Clarus 560S GC-MS are summarised in Table 1. The chromatographic separation was achieved on an Elite 5MS capillary column (30.0 m 250 m) and helium was used as a carrier gas at a constant flow rate of 1ml per minute. The initial oven temperature in the column was programmed at 60 ºC for 0 min then ramped to 200 ºC then increased to 270 ºC at 10 ºC finally, the temperature was held for 5 minutes to remove any remaining traces of sample residue. Biodiesel samples were injected in splitless mode with a split ratio of 2:1. The transfer line temperature and the injection temperature were kept at 250 ºC. GC MS was operated in the 70 Ev electron ionization mode with a collected scanning mass range of 50 – 600 Da [30]. The GC instrument was calibrated using a reference FAME mixture and the biodiesel sample was prepared by dissolving (100 ±5) mg in 5ml of the solution of internal standard (C19) with n-Heptane using an ultrasonic machine. 1.0 ml of the prepared solution of the sample was transferred into 2.0 ml of GC automated sampler vial for injection, followed by the instrument injecting automatically 0.5 l of this solution into the GC instrument. Turbo MassTM software was used for data processing and reporting. The method to calculate the percentage of total FAMEs has been reported elsewhere [35] and the FAME composition result for obtained biodiesel is presented in Table 1.

$$\text{Total FAME (\%)} = \frac{(\sum A) - AIS}{AIS} \times \frac{CIS \times VIS}{W} \times 100 \qquad \text{Equation 1}$$

$$\text{Linolenic acid methyl ester} = \frac{AL}{(\sum A) - AEI} \times 100 \qquad \text{Equation 2}$$

Where $\sum A$ = Total peak area of methyl esters

A_{EI} = Peak area of methyl ester Nonadecadecanoate

C_{IS} = Methyl ester Nonadecadecanoate concentration in mg/mL used as internal standard.

V_{IS} = Used volume of Nonadecadecanoate concentration in mL

W = Mass of the sample in mg

Figure 2. Gas Chromatography-Mass Spectroscopy Instrument

Table 1.: Operational conditions for the Perkin Elmer 580S GC equipped with Mass Spectroscopy 560S

Perkin Elmer Clarus 560S MS Parameters

Column	Elite 5ms with dimension 30.0 m × 250µm
Injection temperature	250
Carrier gas	Helium
Carrier gas flow	1.0 mL
Split ratio	2: 1
Oven programmed	Initial temp 60 °C for 0 min, ramp 10 °C/min to 200 °C, hold 10 min, ramp 10 °C/min to 270 °C hold 5 min.
Total run time	36 min
Dilution	n-Heptane
Solvent delay	4.0 min
Injection volume	0.5 µL
Ionization source	EI + TIC
Electron energy	70 EV
Source temperature	180 °C
Transfer line temperature	250 °C
Scan range	50 to 600 Da

3. RESULTS AND DISCUSSION

The fatty acid methyl esters concentration was investigated under different conditions including rotational speed, inclination angle, and various flow rates. To establish optimum conditions for the transesterification process of sunflower oil to Fatty Acid Methyl Esters. The transesterification of sunflower oil with methanol using KOH as a catalyst is a liquid-liquid reaction (two-phase system) at which the mass transfer rate of reactant molecules between the sunflower-methanol-KOH is very slow [10]. The yield rate is normally found to increase with an increase in rotational speed due to an increase in the miscibility of the sunflower oil into methanol [22]. The major parameters affecting the conversion of vegetable oil to FAME are catalyst concentration, flow rate, inclination angle, and rotational speeds [27][28][33].

3.1 Catalyst concentration

In this work, we first investigated the catalyst concentration of homogeneous catalyst, KOH, and a sigmoidal relationship was observed with 0.1 M KOH giving a noticeable FAME yield, which different from zero conversion reported by Britton and Raston [27].

From figure 3. significantly increased conversion was observed at catalyst concentration 0.75 M KOH, but less than 97% conversion reported [27], and then there was dropped of FAME yield at 0.80 M and 0.90 M but FAME yield reached its peak at 0.90 M. Steady conversion of sunflower oil to biodiesel instead was reported from catalyst concentration 0.75 M, 0.80 M, 0.9 M and 1.00 M where optimum catalyst performance was observed. This is attributed to the reactive selectivity and dynamic nature of the VFD platform [36]. At 0.9 M (Figure 3) the optimum catalytic activity was observed and a FAME yield of 89.40 was recorded and the activity reduces to 68. 64% FAME yield. Catalyst concentration has a significant influence on biodiesel synthesis. This is because increasing the catalyst concentration in the system leads to an increased in the activity of the catalyst which results in a faster reaction rate to reached reaction equilibrium. In the continuous flow process, the catalyst has a short residence time to recycle to other parts of the reaction tube [37][38], this affects the whole process not as in batch process where catalyst depends on diffusion control [39]. As such increase in catalyst concentration detrimentally affects conversion rate [35][40][41][42]. The degree of conversion increases with increases in catalyst concentration indicating a correlation between the rate of conversion/FAME yield with the parameter catalyst concentration.

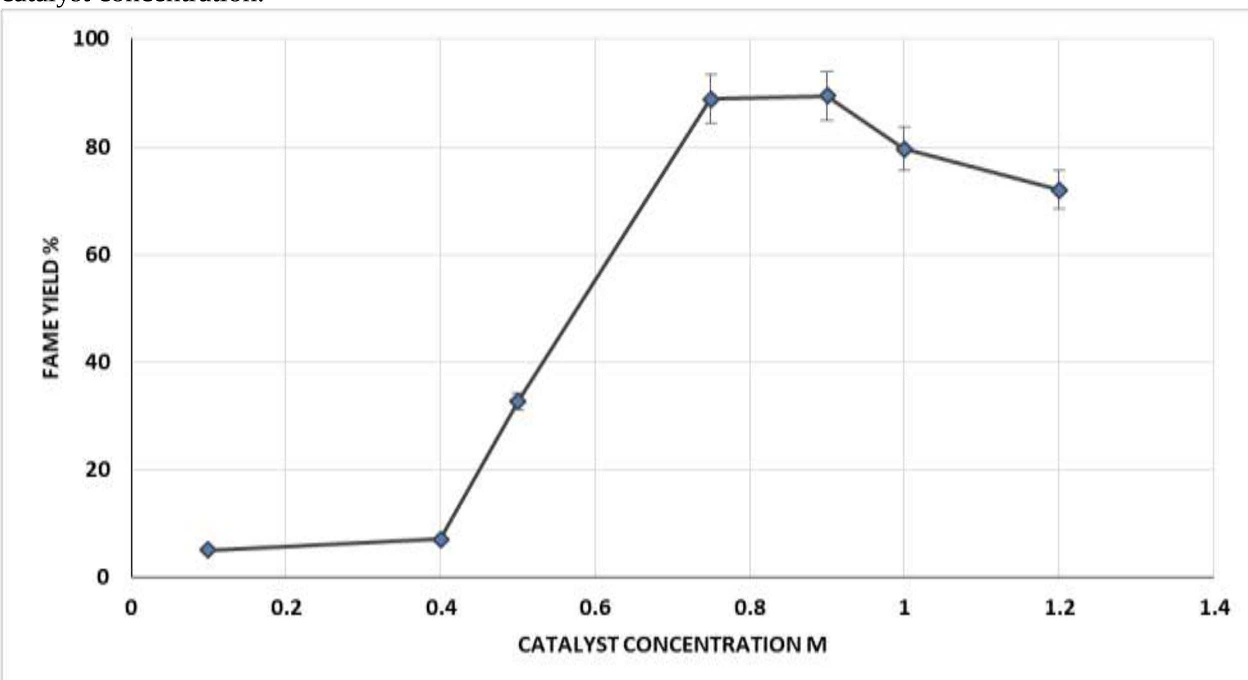

Figure 3. Variation in the concentration of KOH and FAME yield from 1: 1 methanol to sunflower oil volumetric ratio, for a rotational speed of 5250 rpm, and 45° relative to the horizontal position.

3.2 Flow rate

In addition to what was reported in the literature, we experimentally investigated the effect of flow rate in the conversion of sunflower oil to FAME using KOH as a catalyst [Figure 4]. In the same context, 0.5ml/min, 1.0 ml/min, 2.0 ml/min and 5.0 ml/min were reported with steady decreased in the conversion of sunflower oil to FAME to 99.9%, 95.0%, 92.0 respectively, and a significant drop in conversion to 72.0 % conversion yield [22]. Here we reported gap bridge of this parameter, flow rate, with 0.5 ml/min, 0.6ml/min, 1.0 ml/min, 2.0 ml/min, 3.0 ml/min and 5.0 ml/min giving 89.4%, 73.56%, 57.94%, 53.49% and 27.52% respectively.

In addition, we studied total flow rate: 1.0 ml/min, 2.0 ml/min, 4.0ml/min, 5.0 ml/min and 7.0 ml/min which gave equivalent of 89.40%, 65.9%, 53.7%, 36.8% and 33.6% FAME yields respectively. At a catalyst concentration of 0.9 M, a rotational speed of approximately 5250 rpm and an inclination angle of 45° yielded lower FAME at the total flow rate of 7.0 ml/min as shown in Figure 5. This result is inconsistent with what was reported in the literature the higher the flow rates the thicker the film and vice versa. When the flow rate is reduced the film becomes thinner and that increases the surface area of the reactants thereby increasing the FAME yield. On the other hand, when the flow rates are increasing as we can see with 3.0 ml/min and 5.0 ml/min [22] the products yield increases, not a conversion of sunflower oil to FAME.

Fluid dynamics are highly dependent on flow rate and rotational speed when the VFD is operated in a continuous mode [31]. Higher flow rate hindered high shear stress which drives transesterification reaction. This also results to product evaporation and eventually lower the FAME contents [36][37][43][44][45][46]. Lower flow rates make catalyst-reactants contacts which aid the rate of the reaction by increasing mixing, heat/mass transfer of the molecules involved. This parameter is important to determine the reaction's residence time to other parameters such as catalyst concentration, rotational speed, and inclination to determine the outcome of a reaction.

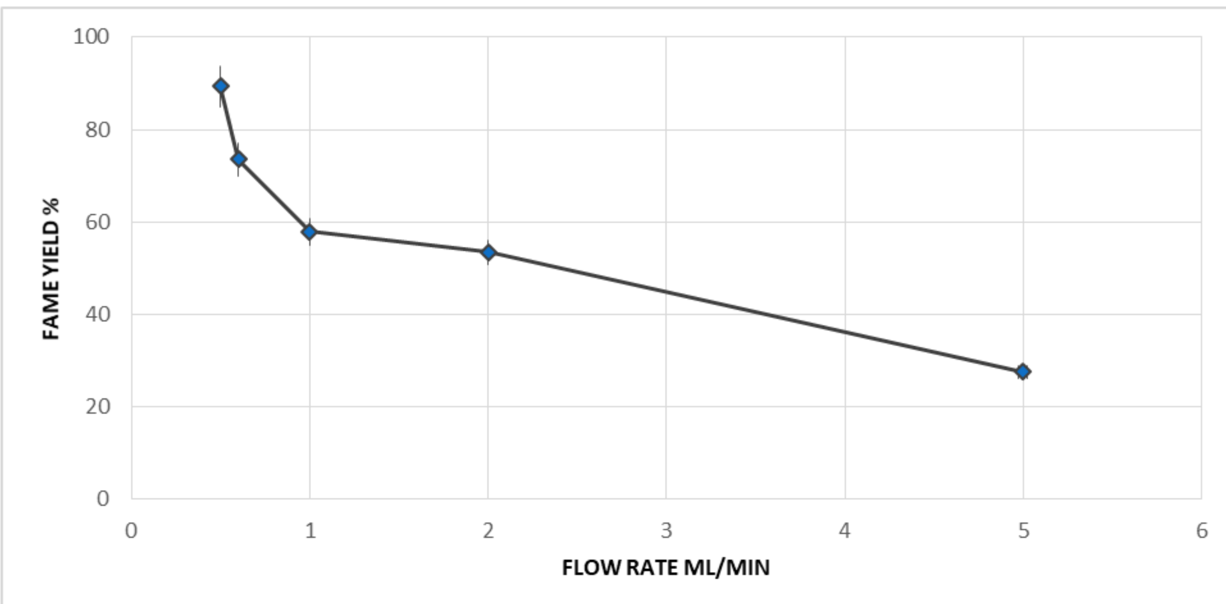

Figure 4. Variation in the flow rates (ml/min) and FAME yield from 0.9 M KOH, for a rotational speed of 5250 rpm, and 45° relative to the horizontal position.

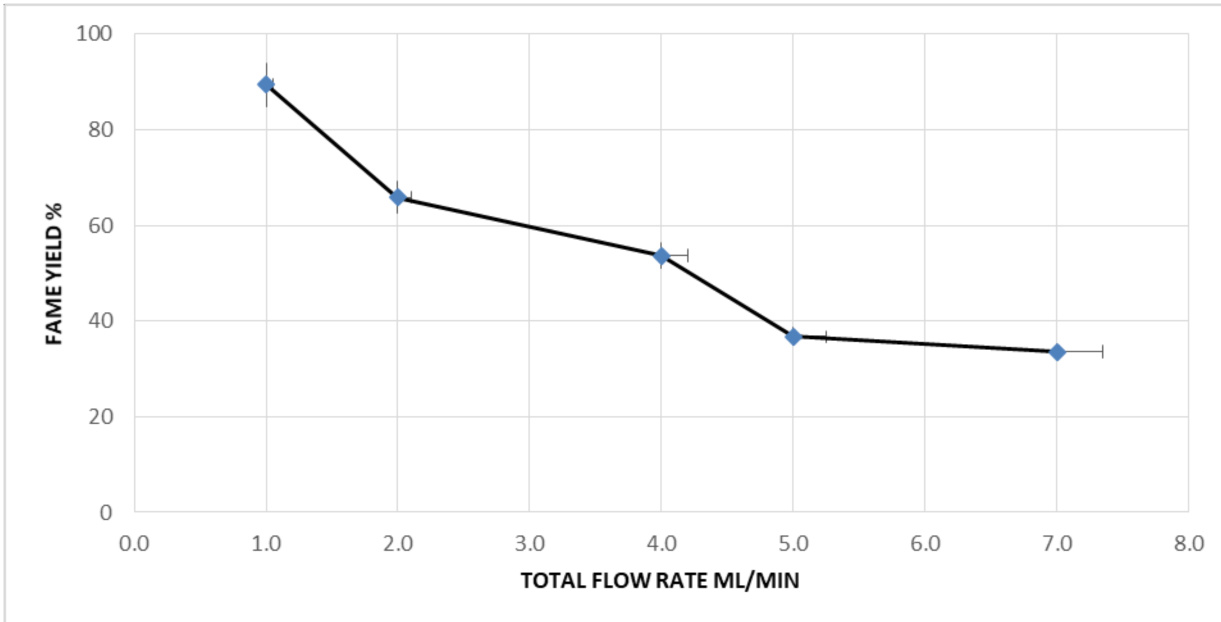

Figure 5. Variation in the flow rates (ml/min) and FAME yield from 0.9 M KOH, for a rotational speed of 5250 rpm, and 45° relative to the horizontal position.

3.3 Inclination angle

The inclination angle is another important parameter we studied hitherto (Figure 6). It was reported in almost all the related work that 45° inclination relative to a horizontal position is the angle that provides high shear as a result of viscous drag within the rotation tube [27][28]. However, Yasmin et al [36] conducted research on Aldol and Michael's addition reaction and go beyond 45° inclination angles. 15°, 30°, 45°, 60°, 75°, and 90° was reported using a sample tube with an internal diameter of 10 mm. From their result, it shows that 15° inclination having the lowest conversion with 90° inclination having the highest conversion rate. There was a tumble between 60° to 75° inclination [36]. Here, we reported 15°, 35°, 45°, 55°, 65°, 70°, and 80° for the transesterification reaction of sunflower oil with methanol to synthesized fatty acid methyl esters. We found out that even at 0 inclination significant FAME yield of 85.65% was synthesized. The trend of FAME yield increases from 15° (FAME yield 85.89%) to its peak of 89.40% at 45° inclination. However, we observed a significant fall in FAME yield at 65°, FAME yield 71.08%, and further decline at 80°, FAME yield 68.16% and we could not go beyond 80° due to evaporating loss of the product. The trend was reported by Yasmin et al., [36] in their work Aldol condensation and Michael addition reaction. In an organic aldol and Michael addition, you may need more energy to break its nucleophilic bonds than in a transesterification reaction involving ester bonds. As such there are differences in the selectivity of the angles where the reactivity and selectivity took place. In addition, this shows how important and unique the VFD platform is for its inclination flexibility compared to other methods such as spinning disc and rotating tube processors. The rotating tube forms dynamic thin films at high rotational speed for volumes of liquid [41]. The shear regimes within the films depend on both the rotational speed and the tube inclination position [29][36][46]. This work has further confirmed that 45° inclination is the best orientation for shear formation within the thin layers for the transesterification reaction of sunflower oil with methanol to synthesized fatty acid methyl esters.

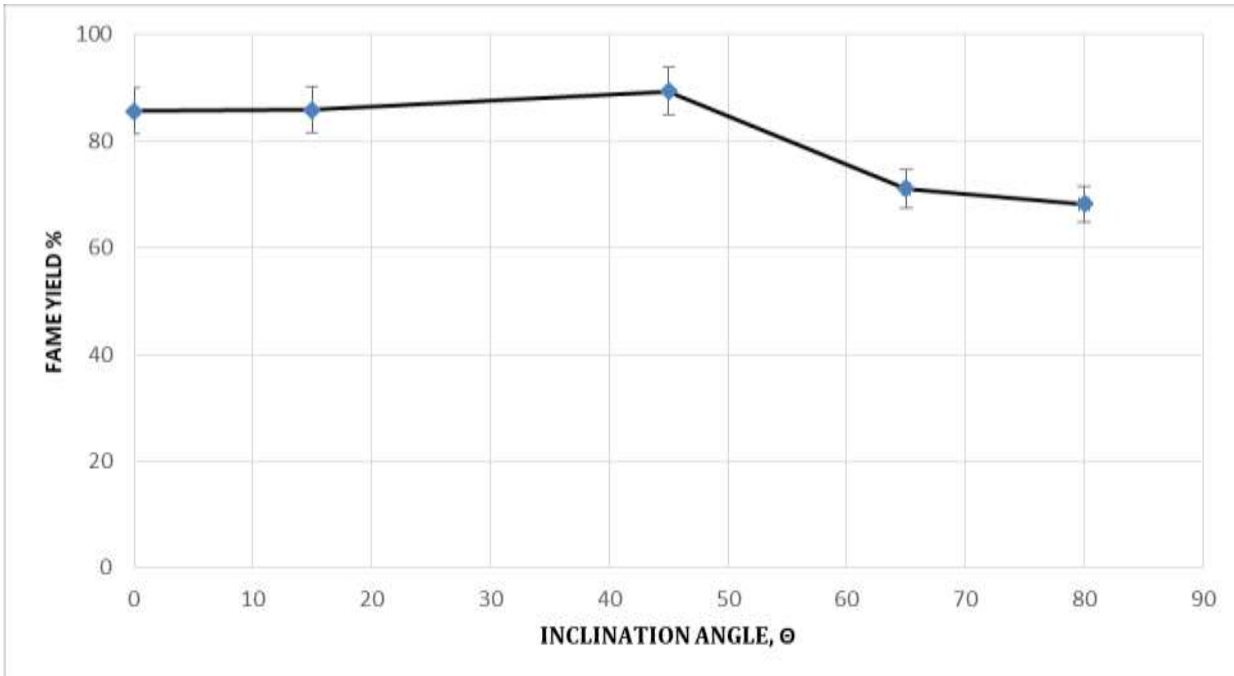

Figure 6. Variation in inclination angle and FAME yield from 0.9 M KOH, for a rotational speed of 5250 rpm, 1: 1 methanol to sunflower oil volumetric ratio.

3.4 Rotational speed

To understand the effect of the VFD platform on the transesterification reaction of sunflower oil and methanol we investigated different rotational speeds at room temperature with inclination angle, methanol to sunflower oil volumetric ratios kept constant for 45° and 1: 1 respectively (Figure 7). The rotational speed is 1000 rpm, 2000 rpm, 3000 rpm, 5 000 rpm, 5250 rpm, 6000 rpm, 7000, 7500 rpm with corresponding FAME yields of 3.3%, 1.69%, 1.48%, 47.34%, 89.40%, 59.49%, 67.40% and 51.48%, respectively. The optimum rotational speed for the conversion of sunflower oil to fatty acid methyl esters was found to be 5250 rpm, the same result was reported in the literature [27]. This since at high rotational speed intense shear is generated in the resulting thin films depending on the speed and the orientation together with other operational variables [30][36].

The was no significant yield FAME at lower rotational speed, 1000 rpm, 2000 rpm, 3000 rpm but the yield picked up from 4000 rpm until it reaches 5250 rpm where it declined at 6 000 rpm. The FAME yield became steady between 6 000 rpm and 7000 rpm but declined further at 7000 rpm. At 5250 rpm the equilibrium was attained with FAME yield found to be 89.40% as a result of enough force applied by the VFD to breakdown surface tension resulting in mass transfer [47][48][49]50[]. Rotational speed 5250 rpm was reported to converted sunflower oil to pure biodiesel at 99.9% [27] which did not agree with 89.40% we got from the same rotational speed. This could be as a result of post-reaction processing from the former which did not happen with the later products. According to the literature rotational speed above 5750 generates Stewartson/Ekman layers and subsequently, the interface between the reacting molecules begins to evaporate and mixed [37][44].

In addition, because the VFD operates in a continuous flow mode there was additional shear generated in the thin films from the viscous drag as the fluid whirls along the sample tube [36]. The rotational speed is very significant working with the VFD platform due to the waves and ripples generated on the surface of the sample tube, the centrifugal forces come with high-speed rotational speed accelerate the transesterification reaction [51][52].

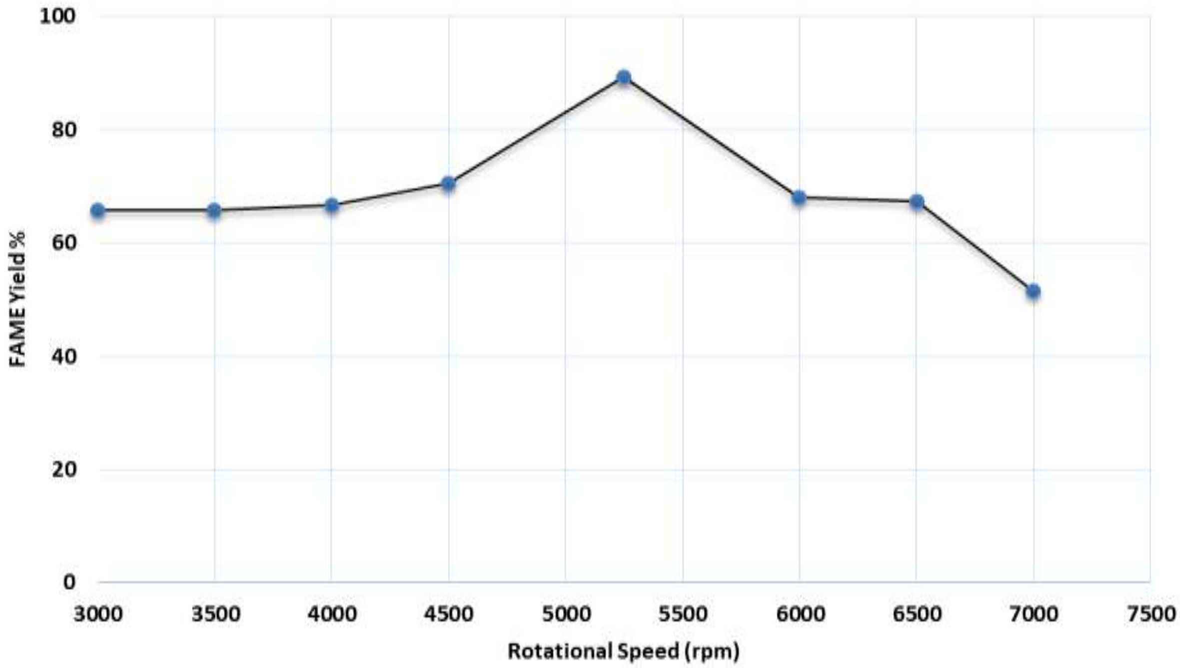

Figure 7. Figure 6. Variation in rotational speed, rpm and FAME yield from 0.9 M KOH, for a 1: 1 methanol to sunflower oil volumetric ratio and 45° relative to the horizontal position.

Figure 8. Photographs of the two-phases separated and the colour change from bottom to middle layer.

From the samples GC-MS data we can give a qualitative assessment of the FAME based on their composition of methyl esters. As shown in the above diagram (Figure 8), the output instantaneously separated into two most of the time and sometimes three layers. The clear top layer when two clear layers were obtained is a good indicator of the purity of the biodiesel [53]. The middle and the lower layers have 0.51 and 1.51 g/cm3, with glycerol having the highest density, ~1.5 g/cm3, and can be readily removed, for use in a wide range of industrial applications. The middle layer is the biodiesel, while the upper layer was contained methanol. In the case where two layers were obtained, the top layer is the biodiesel while the bottom contained glycerol.

The oxidative stability of biodiesel is determined by the composition of the fatty acid methyl esters in the biodiesel, the more you have polyunsaturated fatty acid they undergo oxidation to form peroxides and they polymerized to form larger molecules. These larger molecules increase the biodiesel viscosity in addition to increasing acid value and colour change (yellow to brown) [54]. From the samples collected, the GC MS analysis indicates the presence of Linoleic acid (C18: 2), Oleic acid (C18: 1), and Stearic acid methyl esters (C18: 0) (Table 2) compared to other methyl esters. Figure 10 compared the concentration of the Stearic, Oleic, Linoleic with Linoleic acid methyl ester having the highest concentration while Stearic acid with the lowest.

A higher cetane number is required for a diesel engine to function well with biodiesel. Same on the composition of the biodiesel, cetane number can determine our biodiesel having FAME components: Linoleic, Oleic, and Stearic mainly proving the quality of the biodiesel. According to Ali [55], higher cetane number fatty acid methyl esters such as saturated FAME (Lauric and Stearic) and unsaturated FAME (Oleic, Linolenic, and Linoleic) has been observed.

Table 2: Fatty acids methyl ester composition obtained from VFD direct transesterification of sunflower oil operated in continuous mode. The conversion of sunflower was conducted at KOH concentration of 1.0 M, 45º inclination relative to horizontal position, and 5250 rpm but different flow rates.

Fatty Acid Methyl Esters	***Formula***	***Retention time***	***Wt.% Content***
Myristic acid methyl ester	C14:0	14.13	0.08
Palmitoleic acid methyl ester	C16:1	16.65	0.07
Palmitic acid methyl ester	C16:0	17.05	6.02
Linoleic acid methyl ester	C18:2	21.32	52.93
Oleic acid methyl ester	C18:1	21.54	34.56
Elaidic acid methyl ester	C19:1	21.65	1.15
Stearic acid methyl ester	C18:0	22.36	3.82
Gadoleic acid methyl ester	C20:1	27.41	0.14
Arachidic acid methyl ester	C20:0	27.91	0.26
Behenic acid methyl ester	C22:0	30.63	0.74
Lignoceric acid methyl ester	C24:0	32.97	0.24

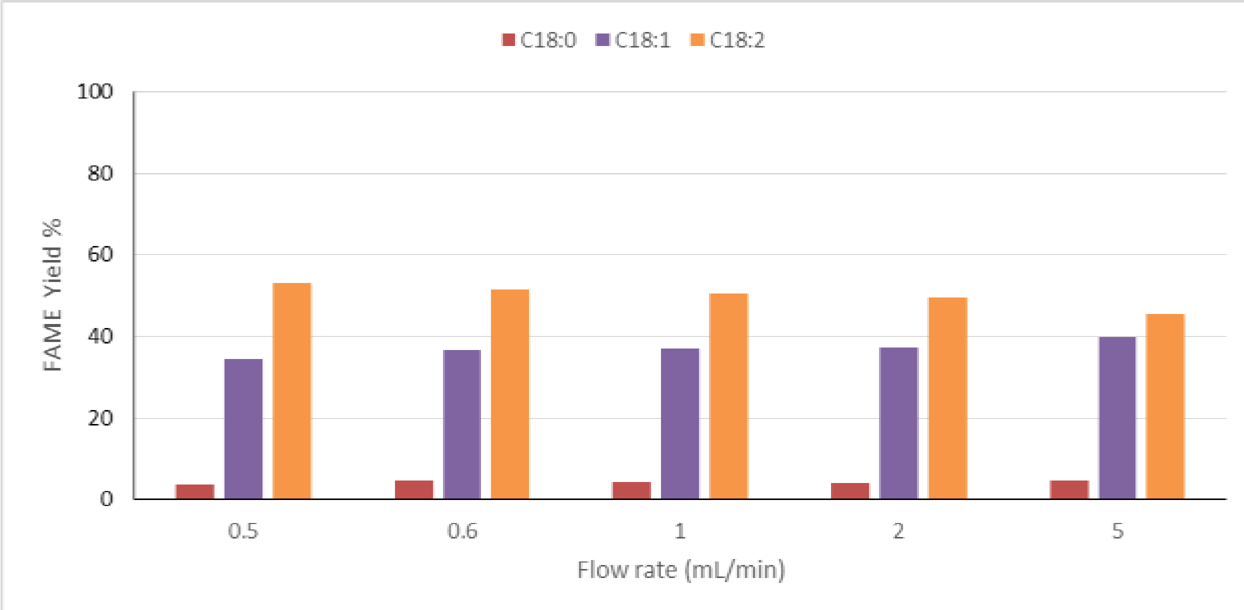

Figure 9. FAME composition obtained from the VFD direct transesterification reaction of sunflower oil and methanol at various flow rate with KOH concentration kept at 0.9 M, 5250 rpm and 45° inclination angle relative to horizontal position.

In the following table, we made a comparison of our VFD with other continuous flow process technologies. The VFD platform has proven to be efficient in terms of facilitating research on a micro-scale, minimize waste, energy management, and above all has operational safety.

Table 3: Comparison of VFD processing of biodiesel with related continuous flow processes

Reactor type	***Residence time***	***Temperature***	***Methanol to oil ratio***	***Yield %***	***Reference***
Microwave	77.12 minutes	57.31 °C	9.05: 1	96.33	[20 - 24]
Oscillatory flow	25 minutes	60 °C	1.5: 1	92.70	[17]
Microchannel	5 – 20 seconds	65 °C	6: 1	95.40	[15 - 16]
Static mixer	60 minutes	60 °C	6: 1	97.80	[12 -14, 57, 58]
Spinning disk	2 – 3 seconds	60 °C	6: 1	96.90	[25, 56]
Ultrasonic	0.93 minute	20 – 25 °C	4: 1	93.80	[26, 59]
VFD	<65 seconds	20 – 25 °C	1:1	89.40	

4. Conclusions

In conclusion, the VFD platform is effective in producing biodiesel through direct transesterification of sunflower oil. The maximum crude fame yield of 89.40% was obtained at room temperature. Here, we have developed the use of a continuous flow vortex fluidic device for generating high purity biodiesel from sunflower oil at room temperature. This requires a simple set of conditions using cheap, caustic bases in methanol. Another highlight of the work is that the glycerol layer can be easily removed, based on density differentials, which also avoids the need for additional down streaming processing, in generating a usable by-product. When the new process is applied, it can bring a significant contribution to the sustainable development of the economy to meet the ever-increasing demand for energy and protect the environment in the meantime. Comparison of VFD processing with related continuous flow processing, Table 3, highlights some advantages in using the VFD. These include the much lower operating temperature and ratio of methanol to oil, without compromising on the yield, which relates to the nature of the shear within the VFD during the processing. In addition, given the low capital outlay of the VFD relative to other conventional processing, coupled with the improved green chemistry metrics of the processing, we foreshadow that the VFD has significant potential in biodiesel production.

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REFERENCES

1. AL-MULALI, U. & CHE SAB, C. N. B. 2018. The Impact of Coal Consumption and CO2 Emission on Economic Growth. Energy Sources, Part B: Economics, Planning, and Policy, 13, 218-223.
2. BP STATISTICAL REVIEW OF WORLD ENERGY JUNE, 2018 67th Editionhttps://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review/bp-stats-review-2018-full-report.pdf. [Accessed 24 August 2018].
3. SHAARI, A. 2020. The Effects of Energy Consumption and National Output on CO2 Emissions: New Evidence from OIC Countries Using a Panel ARDL Analysis. *Sustainability (Basel, Switzerland)*, *12*(8), 3312–. https://doi.org/10.3390/su12083312
4. BARNWAL, S. 2005. Prospects of biodiesel production from vegetable oils in India. *Renewable & Sustainable Energy Reviews*, *9*(4), 363–378. https://doi.org/10.1016/j.rser.2004.05.007
5. TAO J, DAI C, JIANG B. 2009. The Current Status and Prospect of Biodiesel. *Energy & Environment*. 20-21(8-1):1397-1405. doi:10.1260/0958-305X.20/21.8/1.1397
6. RAJENDRAN, M. 2017. How does technology pathway choice influence economic viability and environmental impacts of lignocellulosic biorefineries? *Biotechnology for Biofuels*, *10*(1), 268–268. https://doi.org/10.1186/s13068-017-0959-x
7. DEMIRBAS, A. 2008. Biofuels sources, biofuel policy, biofuel economy and global biofuel projections. *Energy Conversion and Management*, *49*(8), 2106–2116. https://doi.org/10.1016/j.enconman.2008.02.020
8. CHEN, K. 2013. Food vs. Fuel: The Effect of Biofuel Policies. *American Journal of Agricultural Economics*, *95*(2), 289–295. https://doi.org/10.1093/ajae/aas039
9. RASHID, A. 2008. Production of sunflower oil methyl esters by optimized alkali-catalyzed methanolysis. *Biomass & Bioenergy*, *32*(12), 1202–1205. https://doi.org/10.1016/j.biombioe.2008.03.001
10. SOLEIMANI, U, AZARI, A. P., SHARFI, R., ATYABI, S. M. AND NOROUZIAN, D. 2013. Optimization of Biodiesel Production by Chemical Transesterification of Sunflower Oil. Journal of Applied Chemical Research, 7, 1, 50 – 56.
11. GUAN, S. 2009. Synthesis of biodiesel from sunflower oil at room temperature in the presence of various cosolvents. *Chemical Engineering Journal (Lausanne, Switzerland : 1996)*, *146*(2), 302–306. https://doi.org/10.1016/j.cej.2008.10.009.
12. NGUYEN, V. P., NGUYEN, H. H. M., NGUYEN, D. T., NGUYEN, H. L. & HUYNH, T. M. 2018. Optimization of biodiesel production from waste cooking oil using static mixer technology in Vietnam. Biofuels, 9, 567-574.
13. SOMNUK, K., SOYSUWAN, N. & PRATEEPCHAIKUL, G. 2019. Continuous process for biodiesel production from palm fatty acid distillate (PFAD) using helical static mixers as reactors. Renewable Energy, 131, 100-110.
14. NGUYEN, N. 2018. Optimization of biodiesel production from waste cooking oil using static mixer technology in Vietnam. *Biofuels (London)*, *9*(5), 567–574. https://doi.org/10.1080/17597269.2018.1426165

15. MOHADESI, M., AGHEL, B., KHADEMI, M. H. & SAHRAEI, S. 2017. Optimization of biodiesel production process in a continuous microchannel using response surface methodology. (Report). Korean Journal of Chemical Engineering, 34, 1013.
16. YAMSUB, A., KAEWCHADA, A. AND JAREE, A., 2014. Pork lard conversion to biodiesel using a microchannel reactor. *Korean Journal of Chemical Engineering*, *31*(12), pp.2170-2176.
17. HARVEY, A. P., MACKLEY, M. R. & SELIGER, T. 2003. Process Intensification of Biodiesel Production Using a Continuous Oscillatory Flow Reactor. *Journal of Chemical Technology and Biotechnology*, **78**,338-341.
18. LAOSUTTIWONG, T., NGAOSUWAN, K., KIATKITTIPONG, W., WONGSAWAENG, D., KIM-LOHSOONTORN, P. & ASSABUMRUNGRAT, S. 2018. Performance comparison of different cavitation reactors for biodiesel production via transesterification of palm oil. Journal of Cleaner Production, 205, 1094-1101.
19. MOHOD, A. V., GOGATE, P. R., VIEL, G., FIRMINO, P. & GIUDICI, R. 2017. Intensification of Biodiesel Production Using Hydrodynamic Cavitation Based on High Speed Homogenizer. *Chemical Engineering Journal*, **316**, 751-757.
20. BARNARD, T.M., LEADBEATER, N.E., BOUCHER, M.B., STENCEL, L.M. AND WILHITE, B.A., 2007. Continuous-flow preparation of biodiesel using microwave heating. *Energy & Fuels*, *21*(3), pp.1777-1781.
21. AZCAN, N. AND DANISMAN, A., 2008. Microwave assisted transesterification of rapeseed oil. *Fuel*, *87*(10-11), pp.1781-1788.
22. DUZ, M.Z., SAYDUT, A. AND OZTURK, G., 2011. Alkali catalyzed transesterification of safflower seed oil assisted by microwave irradiation. *Fuel Processing Technology*, *92*(3), pp.308-313.
23. BOKHARI, A., CHUAH, L.F., YUSUP, S., AHMAD, J., SHAMSUDDIN, M.R. AND TENG, M.K., 2015. Microwave-assisted methyl esters synthesis of Kapok (Ceiba pentandra) seed oil: parametric and optimization study. *Biofuel Research Journal*, *2*(3), pp.281-287.
24. DHINGRA, S., BHUSHAN, G. AND DUBEY, K.K., 2016. Validation and enhancement of waste cooking sunflower oil-based biodiesel production by the trans-esterification process. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, *38*(10), pp.1448-1454.
25. CHEN, C. 2014. Intensified production of biodiesel using a spinning disk reactor. *Chemical Engineering and Processing*, *78*, 67–72. https://doi.org/10.1016/j.cep.2014.02.009
26. THANH, O. 2010. A two-step continuous ultrasound assisted production of biodiesel fuel from waste cooking oils: A practical and economical approach to produce high quality biodiesel fuel. *Bioresource Technology*, *101*(14), 5394–5401. https://doi.org/10.1016/j.biortech.2010.02.060.
27. BRITTON, J. & RASTON, C. 2014. Continuous flow vortex fluidic production of biodiesel. RSC Advances, 4, 49850-49854.
28. BRITTON, J. & RASTON, C. L. 2015. Rapid High Conversion of High Free Fatty Acid Feedstock into Biodiesel Using Continuous Flow Vortex Fluidics. *Royal Chemical Society Advances*, **5**, 2276–2280.
29. BRITTON, J., MENEGHINI, L. M., RASTON, C. L. & WEISS, G. A. 2016. Accelerating Enzymatic Catalysis Using Vortex Fluidics. *Angewandte Chemie International Edition*, **55**, 11387-11391.
30. BRITTON, J., STUBBS, K. A., WEISS, G. A. & RASTON, C. L. 2017. Vortex Fluidic Chemical Transformations. *European Journal*, **23**, 13270- 13278.
31. BRITTON, J., STUBBS, K. A., WEISS, G. A. & RASTON, C. L. 2017. Vortex Fluidic Chemical Transformations. *European Journal*, **23**, 13270- 13278.
32. YASMIN, L., CHEN, X. J., STUBBS, K. A. & RASTON, C. L. 2013. Optimising a Vortex Fluidic Device for Controlling Chemical Reactivity and Selectivity. *Scientific Reports*, **3**, 2282.

33. SITEPU, E. K., CORBIN, K., LUO, X., PYE, S. J., TANG, Y., LETERME, S. C., HEIMANN, K., RASTON, C. L. & ZHANG, W. 2018. Vortex Fluidic Mediated Direct Transesterification of Wet Microalgae Biomass to Biodiesel. Bioresource Technology, 266, 488-497.
34. EN ISO 14103, Fat and Oil Derivatives – Fatty Acid Methyl Esters (Fame) – Determination of Esters and Linolenic Acid Methyl Ester Contents (ISO 14103: 2011).
35. GARDY, J., OSATIASHTIANI, A., CESPEDES, O., HASSANPOUR, A., LAI, X., LEE, A. F., WILSON, K. & REHAN, M 2018. A Magnetically Separable SO_4/Fe-Al-TiO_2 Solid Acid Catalyst for Biodiesel Production from Waste Cooking Oil. Applied Catalyst B: Environmental, 234, 268-278.
36. YASMIN, L., CHEN, X. J., STUBBS, K. A. & RASTON, C. L. 2013. Optimising a Vortex Fluidic Device for Controlling Chemical Reactivity and Selectivity. *Scientific Reports*, **3**, 2282.
37. RASTON, C. 2016. Vortex Fluidic Technology: A Paradigm Shift in Chemistry. Available online at http://www.vortexfluidictechnologies.com/news [Accessed 4 November 2019].
38. BRITTON, J., DALZIEL, S. B., & RASTON, C. L. 2016. The Synthesis of Di-Carboxylate Esters Using Continuous Flow Vortex Fluidics. Green Chemistry, 18, 2193–2200.
39. GARDY, J., NOURAFKAN, E., OSATIASHTIANI, A., LEE, A. F., WILSON, K., HASSANPOUR, A. & LAI, X. 2019. A core-shell SO4/Mg-Al-Fe3O4 catalyst for biodiesel production. Applied Catalysis B: Environmental, 259, 118093.
40. GARDY, J., HASSANPOUR, A., LAI, X., AHMED, M. H. & REHAN, M 2017. Biodiesel Production from Cooking Oil Using a Novel Surface Functionalised TiO2 Nano-Catalyst. Applied Catalyst B: Environmental, 207, 297-310.
41. GARDY, J., HASSANPOUR, A., LAI, X. & AHMED, M. H. 2016. Synthesis of Ti(SO4)O solid acid nano-catalyst and its application for biodiesel production from used cooking oil. Applied Catalysis A: General, 527, 81-95.
42. ANTOLIN, G., TINAUT, F., BRICENO, Y., CASTANO, V., PEREZ, C. & RAMIREZ, A. J. B. T. 2002. Optimisation of biodiesel production by sunflower oil transesterification. 83, 111-114.
43. BRITTON, J., DALZIEL, S. B. & RASTON, C. L. 2015. Continuous Flow Fischer Esterification Harnessing Vibrational-Coupled Thin Film Fluidics. Royal Chemical Society Advances, 5, 1655-1660.
44. BRITTON, J., CHALKER, J. M. & RASTON, C. L. 2015. Rapid Vortex Fluidics: Continuous Flow Synthesis of Amides and Local Anesthetic Lidocaine. Chemistry - A European Journal, 21, 10660-10665.
45. BRITTON, J., CASTLE, J. W., WEISS, G. A. & RASTON, C. L. 2016a. Harnessing Thin-Film Continuous-Flow Assembly Lines. Chemistry - A European Journal, 22, 10773-10776.
46. GANDY, M. N., RASTON, C. L. & STUBBS, K. A. 2015. Photoredox Catalysis under Shear Using Thin Film Vortex Microfluidics. Chemical Communications, 51, 11041-11044.
47. BRITTON, J., MENEGHINI, L. M., RASTON, C. L. & WEISS, G. A. 2016b. Accelerating Enzymatic Catalysis Using Vortex Fluidics. Angewandte Chemie International Edition, 55, 11387-11391.
48. BRITTON, J. RASTON, J. C. & GREGORY A. 2016. Weiss Rapid Protein Immobilization for Thin Film Continuous Flow Biocatalysis. A Chemical Communication, 52, 10159—10162.
49. SWAMINATHAN IYER, N. 2008. Loading Molecular Hydrogen Cargo within Viruslike Nanocontainers. *Angewandte Chemie*, *120*(34), 6462–6466. https://doi.org/10.1002/ange.200802441 (14)
50. GHIASY, B. 2012. Thermographic analysis of thin liquid films on a rotating disc: Approach and challenges. *Applied Thermal Engineering*, *44*, 39–49. https://doi.org/10.1016/j.applthermaleng.2012.04.006
51. LODHA, H., JACHUCK, R. & SUPPIAH SINGARAM, S. 2012. Intensified Biodiesel Production Using a Rotating Tube Reactor. *Energy & Fuels*, **26**, 7037-7040.

52. LODHA, J. (2012). Intensified Biodiesel Production Using a Rotating Tube Reactor. *Energy & Fuels*, *26*(NOVDEC), 7037–7040.
53. HARVEY, A. P., MACKLEY, M. R. & SELIGER, T. 2003. Process Intensification of Biodiesel Production Using a Continuous Oscillatory Flow Reactor. *Journal of Chemical Technology and Biotechnology*, **78**,338-341.
54. BARBARAS, I. & TODOMI, I. A. 2011. ‘’Biodiesel Quality Standard and Properties.’’ In Biodiesel – Quality, Emissions and By-Products. Rijeka, Croatia: InTech..
55. ALI, M. 2016. Effects of different chemical additives on biodiesel fuel properties and engine performance. A comparison reviews. *MATEC Web of Conferences*, *38*, 3002–. https://doi.org/10.1051/matecconf/20163803002
56. MOHADESI, M., AGHEL, B., KHADEMI, M. H. & SAHRAEI, S. 2017. Optimization of the biodiesel production process in a continuous microchannel using response surface methodology. (Report). Korean Journal of Chemical Engineering, 34, 1013.
57. CHEN, K. J. & CHEN, Y. S. 2014. Intensified Production of Biodiesel Using A Spinning Disk Reactor. *Chemical Engineering and Processing: Process Intensification*, **78**, 67-72.
58. SOMNUK, K., SOYSUWAN, N. & PRATEEPCHAIKUL, G. 2019. Continuous process for biodiesel production from palm fatty acid distillate (PFAD) using helical static mixers as reactors. Renewable Energy, 131, 100-110.
59. NGUYEN, V. P., NGUYEN, H. H. M., NGUYEN, D. T., NGUYEN, H. L. & HUYNH, T. M. 2018. Optimization of biodiesel production from waste cooking oil using static mixer technology in Vietnam. Biofuels, 9, 567-574.
60. CHEN, G., SHAN, R., SHI, J. & YAN, B. 2014. Ultrasonic-assisted production of biodiesel from transesterification of palm oil over ostrich eggshell-derived CaO catalysts. Bioresource Technology, 171, 428-432.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at

Supplementary Material for:

Fatty Acid Methyl Esters (FAME) Synthesis Using Continuous Vortex Fluidic Device: Influence of different Process Variables

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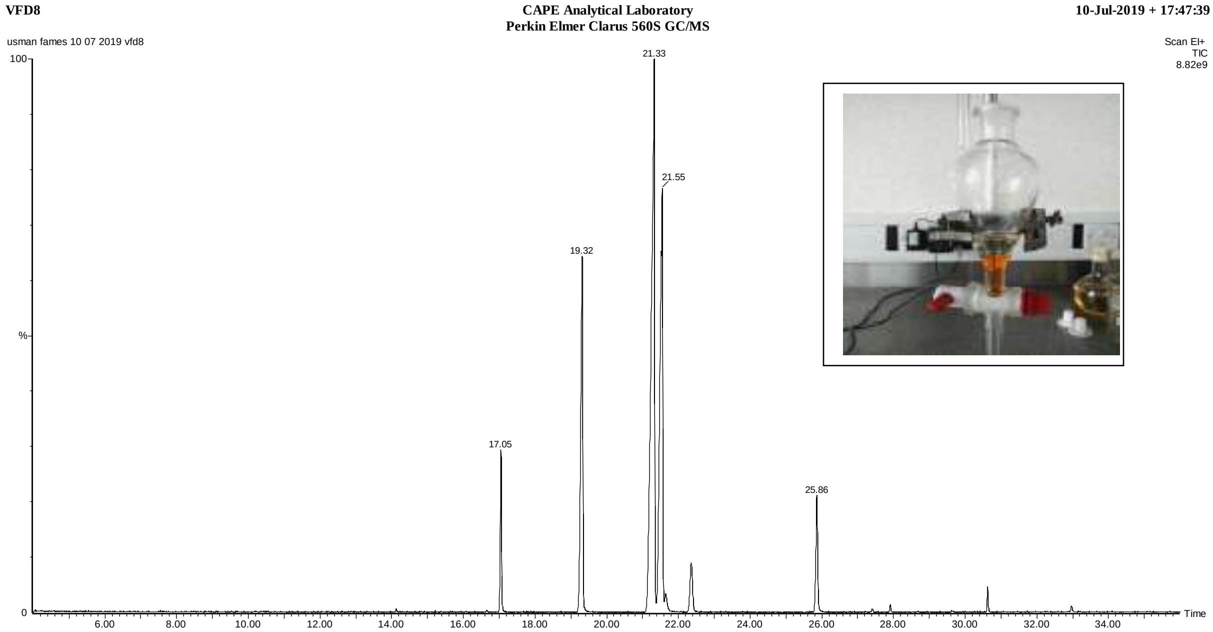

Fig. 1. Chromatogram of the reference material

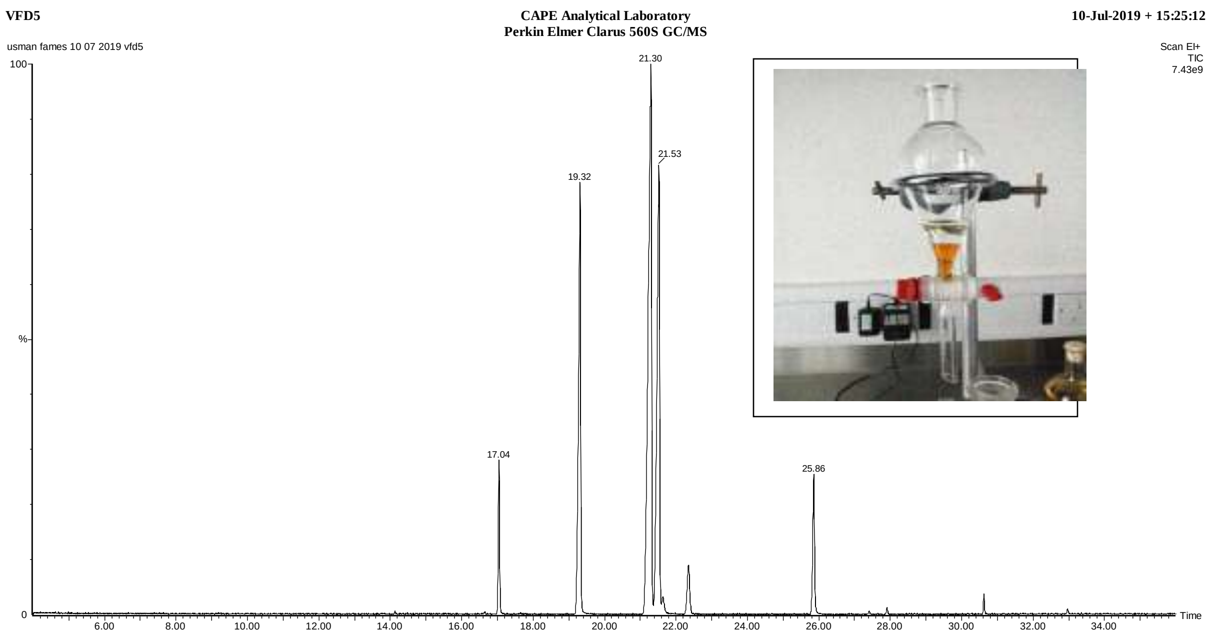

Fig. 2. Chromatogram of the reference material

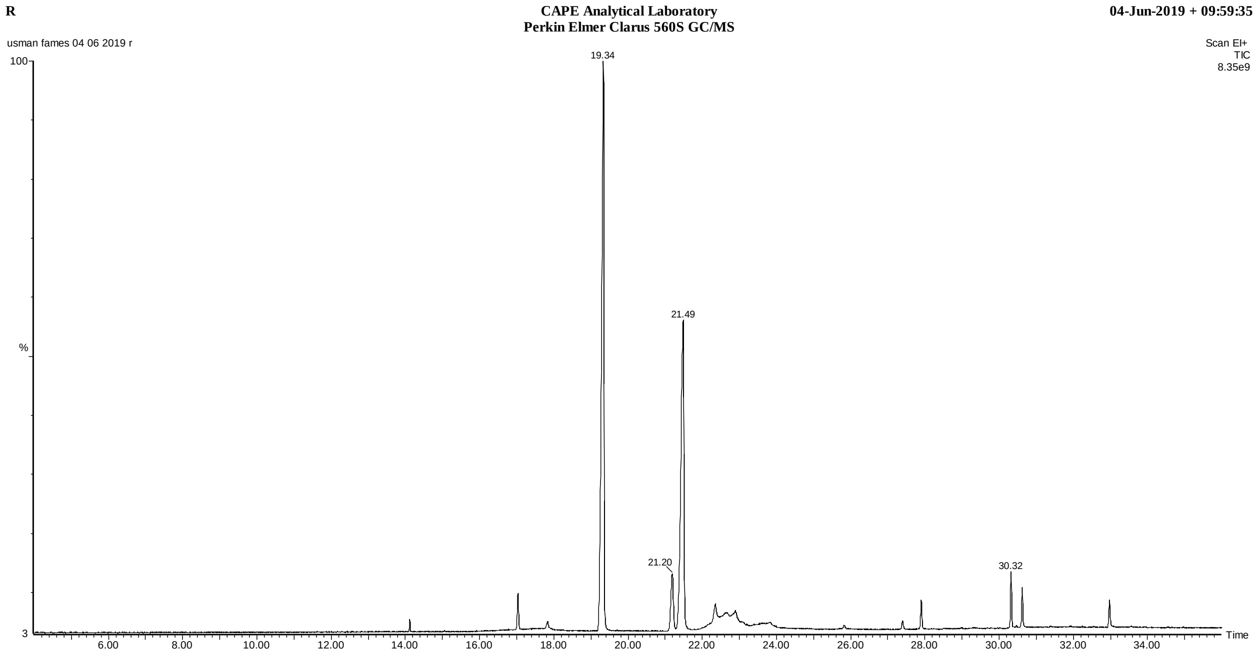

Fig. 3. Chromatogram of the reference material

Table 1: Fatty acid methyl ester composition for biodiesel Reference material

Fatty Acid Names	*RT (min)*	*Area (Uv*Sec)*	*Area (%)*
Octanoic acid, methyl ester	6.39	65244	0.00%
Decanoic acid, methyl ester	9.34	23589	0.00%
Dodecanoic acid, methyl ester	11.77	0	0.00%
Myristic acid, methyl ester	14.12	4212793	0.70%
Palmitoleic acid, methyl ester	16.6	5806	0.00%
Palmitic acid, methyl ester	17.03	20917920	3.40%
Heptadecanoic acid, ME (IS)	19.33	595764544	
Linoleic acid, methyl ester	21.19	61761748	10.10%
Oleic & linolenic acid, ME	21.49	419737056	68.40%
Elaidic acid, methyl ester	21.7	0	0.00%
Stearic acid, methyl ester	22.35	18250428	3.00%
Eicosadienoic acid, ME	26.61	0	0.00%
Gadoleic acid, methyl ester	27.4	5700213	0.90%
Arachidic acid, methyl ester	27.9	15956234	2.60%
Erucic acid, methyl ester	30.32	28718684	4.70%
Behenic acid, methyl ester	30.63	20939436	3.40%
Nervonic acid, methyl ester	32.58	336108	0.10%
Lignoceric acid, methyl ester	32.97	17038464	2.80%
Total			100.1