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Rapid high conversion of high free fatty acid feedstock into biodiesel using continuous flow vortex fluidics

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Conversion of high free fatty acid (FFA) feedstock (94.4 %) to biodiesel with undetectable FFA content is effective using room temperature vortex fluidic flow chemistry, with the conversion taking < 1 minute residence time, using dramatically less methanol and acid catalyst compared to other processes. Optimum conditions are 1:6 volumetric ratio of oil feedstock to methanol and 0.2 molar equivalents of H_2SO_4 catalyst loading, for a combined flow rate of 3.50 mL/min in a 17.7 mm internal diameter tube rotating at 7500 rpm. This work furthers the viability of using high FFA content feedstocks for biodiesel production.

With the global population exceeding seven billion and a 22.6 fold increase in energy usage over the last century, the pressure on planetary resources is rising.[1, 2] Current and continuing increasing energy usage while reducing the impact of this requires access to renewable fuel sources. This is compounded by crude oil estimated to run out by 2044.[3] The transport sector uses the largest proportion of crude oil as the feedstock for hydrocarbon based fuels, and it is therefore important to target a renewable feedstock that can provide suitable replacement liquid fuel to the same extent.[4] Biodiesel has been put forward as an alternative fuel source due to its ability to be used in diesel engines with little or no modification.[5] Biodiesel is synthesised using acid or base catalysed transesterification of triglycerides that are found within lipid oil.[6, 7] Such oil can be sourced from four main areas, namely edible and non-edible fats and oils,[8] animal fats,[9, 10] and algal oils.[11, 12] Algae derived lipid oil is particularly promising given the rapid rate of lipid synthesis, the higher turn over frequency, year round cultivation and the ability for the organism to be grown in non-competing, lower quality environments.[13]

Currently, biodiesel may be viewed as an energy source that is not economically attractive, given the cost of virgin oil feedstocks, which accounts for 60-75 % of the overall cost of biodiesel production.[2, 14] Virgin oils, such as sunflower oil, are expensive and using arable land for fuel crops instead for food has sparked much debate.[15-17] Nevertheless, virgin oils are readily converted into biodiesel under mild conditions, including under continuous flow processing using a vortex fluidic device (VFD).[18] For biodiesel to become a more viable solution it is important to utalise different feedstocks, whilst incorporating sustainability metrics, but this is challenging. Algal oil, palm fatty acid distillate, waste cooking oil and tall oil, as possible feedstocks for biodiesel, often contain high levels of FFA, and are regarded as unsuitable for effective transesterification of the remaining triglycerides in the lipid oil.[2] Pre-treatment of the lipid oil involves catalysed esterification of the carboxylates in the presence of an alcohol, to lower the level of FFA which is necessary to avoid saponification in subsequent processing.[19] Saponification is the conversion of free carboxylates to the corresponding salts, usually a potassium or sodium salt, and their presence is undesirable. It lowers the yield of biodiesel, makes the separation from glycerol more energy and time intensive, and requires a higher catalyst loading.[19] Overall, the presence of residual FFA can be detrimental in the subsequent transesterification process. Successful transesterifications are possible in the presence of ≤ 0.5- 3 % FFA, depending on the nature of the catalyst and processing regime.[20] The acid content of biodiesel is related to the amount of potassium hydroxide required to neutralise the FFA in one gram of oil (mg KOH). For ASTM International and European standards, the acid content of usable biodiesel must be ≤ 0.50 mg, which equates to ~ 0.25 % FFA.[21]

Most pre-treatments of lipid oils use acidic methanol, which is highly effective in reducing FFA to acceptable levels.

Sulphuric acid is the most common choice of catalyst, although much effort has focused on using less corrosive catalysts such as ferric sulphate, calcium oxide and potassium carbonate.[22] While these pre-treatments are effective, they have environmental consequences arising from the large ratios of methanol (up to 201:1) [19] and acid catalyst (up to 90 % weight)[22] relative to the molar ratio of FFA in the feedstock (Table 1). All previous catalytic reactions require heating, up to 460 °C with zeolites, or the use of microwave energy. This overcomes the low reactivity of the carboxylate compared to the triglyceride, and the low mass transport of the biphasic system.[22] Reaction times are inherently long, averaging ~ 17.4 hours,[22] and there are a limited number of systems available for rapidly and efficiently converting high FFA content feedstocks to biodiesel with acceptable levels of residual FFA. Most processes converting lipid oils with high FFA content employ a separate pre-treatment stage. This involves the use of acidic catalysts, super critical methanol or removing the FFA before transesterification with a soap separation and neutralisation step, thereby avoiding saponification and energy intensive separations.[23] Continuous flow transesterifcation reactors have been developed,[23-33] but progress on continuous flow pre-treatment systems utilising high FFA (>40 %) lipid oil is limited. It often involves the use of high pressure and temperature, super critical solvents and long(er) residency times, and there are environmental impact concerns.[2, 34-37]

We have developed a continuous flow acid catalysed esterification of high FFA lipid oil, as a pre-treatment process to remove FFA. This uses the recently developed VFD microfluidic-processing platform that is effective in controlling organic reactions, which includes an environmentally benign transesterification conversion of lipid oil, catalysed by methanolic KOH or NaOH.[18, 38-42] The VFD can operate under the so called continuous flow mode where jet feeds deliver liquid to the base of a rapidly rotating tube where there is intense micromixing and shearing. The thickness of the resulting thin film is primarily controlled by the rotational speed, with the flow rate and tilt angle, θ, setting the fluid dynamical properties within the device. Controlling the delivery of a drop of liquid into the hemispherical bottom of the VFD tube sets the level of shearing and when the liquid exits the hemisphere, a helical wave is formed, which is likely to provide additional shearing due to the viscous drag of the liquid against the rotating tube. Schematics and device workings are summarised in Figure 1, having been previously elaborated. [38]
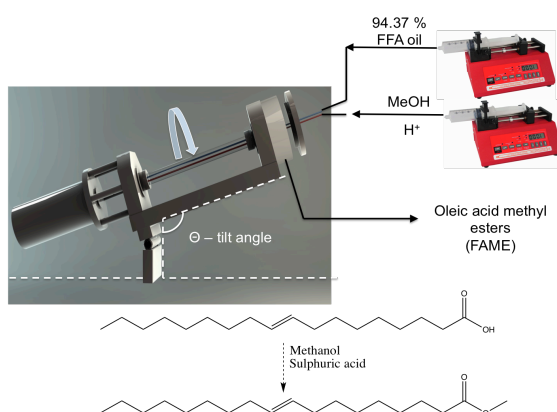

Figure 1 Schematics of a VFD operating at a specific tilt angle, θ, with two separate feed jets injecting oil and acidic methanol. The resulting FAME is collected through an exit channel.

Experimental

General: The VFD was set at a tilt angle, θ, of 45 degrees relative to the horizontal position. A commercially available, pristine boro-silicate glass NMR tube (internal diameter of 17.7 mm) was inserted. Two jet feeds were used in this procedure, having previously been shown that this leads to an increase in mixing and chemical reactivity between oil and alcohol.[18] In the first instance the glass tube was rotated at 6950 rpm and the reagents added through jet feeds *via* the use of an automated syringe pump. This speed has been established as maximising for shear intensity in contemporary esterification studies.[43] For the volumetric ratios of acidic methanol to oil described herein, for example 6:1, one drop of oil (0.500 mL/min) was released to six drops of acidic methanol (3.00 mL/min) using pre-mixed solution of H_2SO_4 in methanol. The oil was collected through a teflon exit and immediately quenched in an ice bath at ~ 2 °C. This quenching method was trailed and after three hours there was no significant change in yield, and thus this was deemed an effective quench. The sample was then centrifuged at 7180 g, due to laboratory convenience, for 20 mins at 10 °C. The methanol layer was discarded and the oil washed with Milli-Q water (3 x 25 mL). The oil was again centrifuged at a reduced temperature to allow the water to separate. The oil was then removed, dried under vacuum and then weighed. A sample of 10 mL of oil was used each time, and the results were carried out in triplicate. The oil used was purchased from Sigma (~ 90 % technical grade Oleic acid) and was used as received for modelling a high FFA system.

Calculation of FFA content: To calculate the acid value the EU standard EN14104 was used as guidance, but modified as described below. A solution of approximately 0.1 M KOH in propan-2-ol was prepared. The resulting solution was standardised against benzoic acid (50.0 mg) in 50 mL propan-2-ol with phenolphthalein as an indicator, and this was carried out five times in deriving an average concentration. The solution of KOH was standardised at the start of each day, and was titrated against ~ 4.0 g of oil each time. The oil to be tested was dispersed in 50 mL of propan-2-ol and swirled for 30 seconds whereupon three drops of phenolphthalein indicator was added and the solution titrated until it held a faint pink colour for ten seconds. In accordance with EN14104, the molarity of the solution, the acid content, and the percentage conversion were calculated using equations 1 - 3, respectively:

$$Concentration\ of\ KOH: \frac{1000 \times M_{Ba}}{122.1 \times V_o} \quad (1)$$

$$: Acid\ Value\ (AV): \frac{56.1 \times (V_t - V_n) \times C}{M_{Oil}} \quad (2)$$

$$\% \ FFA\ conversion: \left(\frac{AV_i - AV_f}{AV_i}\right) \times 100 \quad (3)$$

M_{ba} = mass of benzoic acid (g), V_0 – Volume of KOH titrant used (mL), V_t – Volume of titrant used (mL), V_n – Volume of titrant required to naturalise 50 mL propan-2-ol (mL), C – Concentration of titrant (moles L^{-1}), M_{oil} – mass of oil sample (g), AV_i – Initial acid value (mg KOH g^{-1}), AV_f - Final acid value (mg KOH g^{-1}).

Results and Discussion

The volumetric ratio of methanol to oil (feedstock) was optimised first, noting this ratio is important in traditional bath processing of lipid oil (Figure 2). Larger volumes of methanol shift the equilibrium towards the methyl ester as well as

increasing the solubility of the resulting biodiesel. We have used a volumetric ratio rather than a molar ratio, being more practically convenient in dealing with volumetric flow rates through the jet feeds in delivering two liquids to the base of the rapidly rotating tube.

Initially ratios of five and six parts of methanol to oil were established as being optimum for a number of different flow rates (Figure 2). Further optimisation followed with finer control of the lipid oil flow rate for these two ratios (Figure 3), establishing a dramatic reduction in residual FFA to 1.41 % for a six to one volumetric ratio of methanol to oil, for an oil flow rate of 0.450 mL/min. A slightly faster flow rate of 0.50 mL/min resulted in 1.82 % residual FFA, and this flow rate was chosen for further optimisation. The combined methanol to oil ratio corresponds to a system with a total flow rate of 3.50 mL/min, which corresponds to a 47 second residence time for the tube rotating at 6950 rpm, as established for passing methanol through the VFD (Figure 4). As expected there is an exponential reduction in residency time for increasing flow rate, and these conditions were then further optimised. Also noteworthy is that the liquid mixture appears visually mono phasic when passing through the VFD, demonstrating high mass transfer under shear.
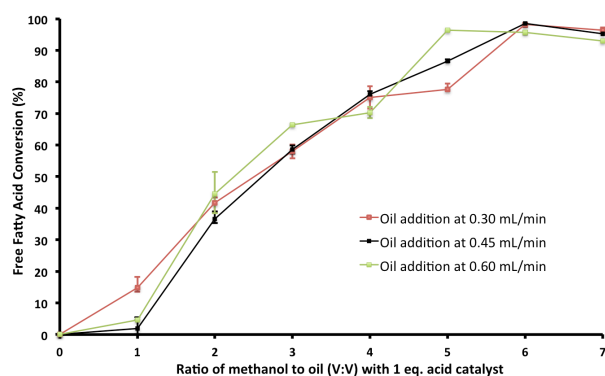

Figure 2 – Effect of volumetric ratio of methanol to oil on the conversion of FFA to the corresponding methyl ester using the VFD, for different flow rates of the lipid oil. Results are in triplicate and the average taken.
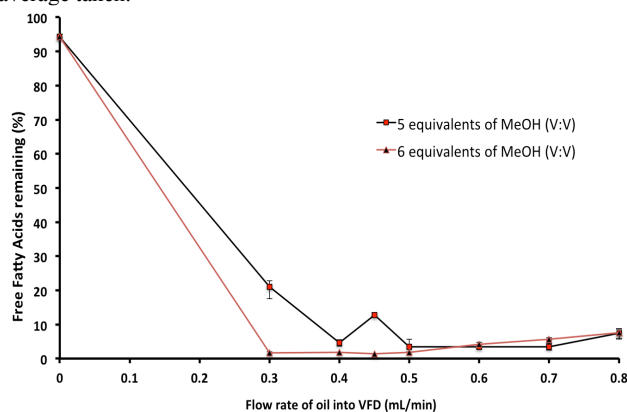

Figure 3 – Flow rate of oil into the VFD for both five and six volumetric ratios of methanol to oil. Results are in triplicate and the average is taken.

In general, the catalyst loading significantly influences biodiesel processing, and this is even more important in flow chemistry systems, as in using the VFD. The VFD operates under plug flow conditions, and thus the catalyst has limited time (47 seconds) to recycle to other parts of the tube, with the

effectiveness of the VDF relating to a system not governed by diffusion control. The catalyst loading of the system is a direct molar ratio between the FFA present and the moles of sulphuric acid used. Surprisingly the molar equivalents of sulphuric acid could be reduced to 0.2 equivalents with a consistent conversion of 98.1 % (Figure 5). Although this seems surprising, the shape of the graph (Figure 5) has been reported before, where an increase in catalyst loading detrimentally effects conversion rates.[19]

The rotational speed of the tube in the VFD controls the thickness of the dynamic thin film, and the faster the rotational speed the greater is the shear stress, and the thinner the film. In this study 6950 rpm was chosen as a starting rotational speed given that it results in the greatest reactivity in chemical synthesis.[43] However, given that rotational speed is an important processing parameter of the VFD, it was further varied at 250 rpm increments, in mapping out any rotational speed variation dependence (Figure 6). This established the most efficient rotational speed for the production of biodiesel form the high FFA content feedstock was 7500 rpm, where remarkably there was no evidence for the presence of any residual FFA, as established using colorimetric titrations, NMR and GCMS. A comparison of the utility of the VFD to convert high FFA feedstock into usable feedstock is given in Table 1. This clearly establishes that the VFD results in greater reactivity, cost effectiveness and green chemistry metrics than using other synthetic strategies.[19]
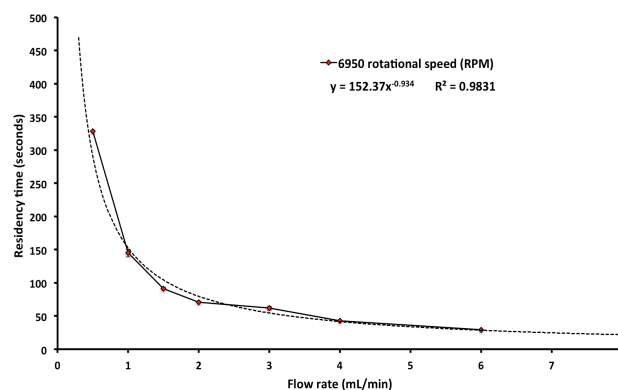

Figure 4 – Residence time of methanol in the rotating tube at 6950 rpm, tilted 45 degree relative to the horizontal position. Results are in triplicate and the average taken.
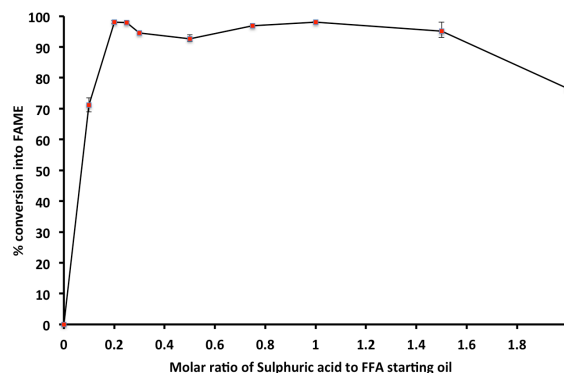

Figure 5 – The molar ratio of sulphuric acid to FFA in the lipid oil feedstock. Results are in triplicate and the average take.

Oil type	FFA level (%)	MeOH: FFA molar ratio	Sulphuric acid - % weight of FFA	Temperature (°C)	Ending FFA (% FFA)	Total reaction time (mins)
Sunflower[44]	2.99	60: 1	5	60	< 0.5	120
Rubber seed[45]	16.88	13: 1	6	45 ± 5	< 2	30
Mahua (two step)[46]	19.00	16 – 103: 1	10.76 – 90.06	60	< 0.5	120
Jatropha[47, 48]	14.9	24 - 36: 1	5.7 - 20.88	50-60	< 1 - 2	60 - 80
Palm Fatty Acid Distillate[49]	93.0	8: 1	1.83	70	< 2	60
Crude palm[50]	7.5	44: 1	4	Microwave	< 2	60
Waste cooking[51]	37.96	18: 1	10.54	95	~ 1	240
Tobacco[52]	35.00	18: 1	5.71	60	< 1	25
VFD	94.37	0.45: 1	0.074	Room temp	Undetectable	0.78

Table 1 – Comparison of VFD processing with other FFA pre-treatment processes for a range of feedstocks (adapted from Mingming Lu. *et al.*[19]). The level of FFA was taken into consideration when comparing the ratios of alcohol and weight of acid catalyst, for a meaningful comparison. Equations used for comparison:[19]

$$Methanol\ to\ FFA\ molar\ ratio : \frac{\left(\frac{Methanol:oil_{Molar\ ratio}}{MW\ of\ oil}\right)}{\left(\frac{FFA\ \%}{MW\ FFA}\right)}$$

$$Acid\ to\ FFA\ \%\ weight : \left(\frac{Acid\ to\ oil\ \%\ weight}{FFA\ \%}\right)$$
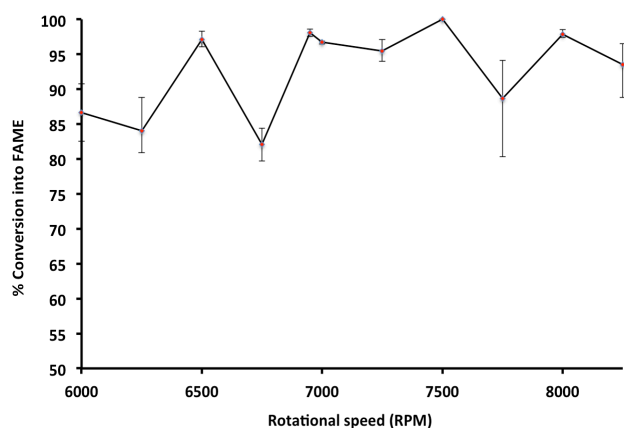

Figure 6 – Effect of rotational speed of the tube on the conversion of FFA into FAME. Results are triplicate and the average taken.

Conclusions

We have developed a continuous flow process for esterifying FFA in lipid oil. This relies on the generation of dynamic thin films in a vortex fluidic device which are effective in overcoming otherwise mass transport and mixing limitations in a biphasic systes. The optimised conditions allow a modelled feedstock with an unusually high FFA content of ca 94% to be converted to biodiesel with no traces of FFA, in less than a minute residence time, at room temperature, with a significantly reduced catalyst and methanol loading. We believe that this process sets the scene for the ability to process feedstocks that have been previously viewed as problematic, to become commercially viable for biodiesel production.
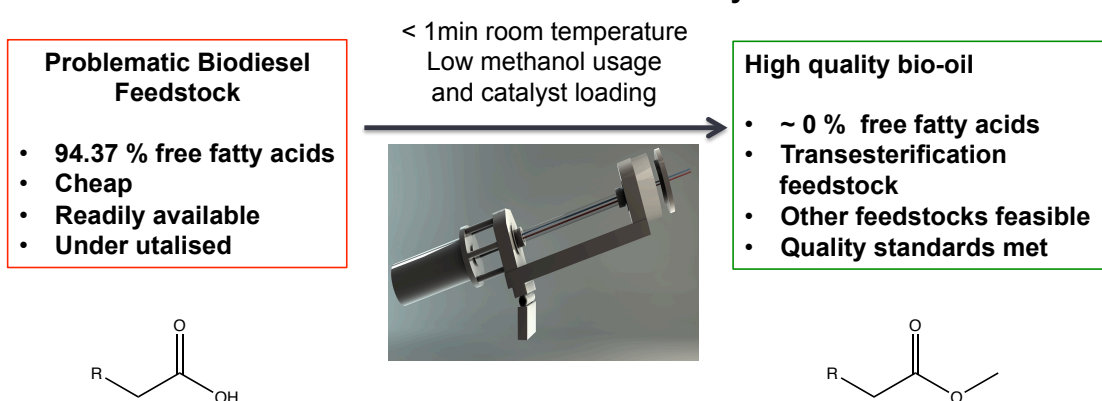
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Vortex Fluidic Flow Chemistry

Problematic Biodiesel
Feedstock

- **94.37 % free fatty acids**
- **Cheap**
- **Readily available**
- **Under utalised**

< 1min room temperature
Low methanol usage
and catalyst loading

High quality bio-oil

- **~ 0 % free fatty acids**
- **Transesterification feedstock**
- **Other feedstocks feasible**
- **Quality standards met**

Rapid reduction of free fatty acids in biodiesel feedstock: The rapid conversion of problematic free fatty acids in bio-oils has been achieved using room temperature, environmentally benign vortex fluidic flow chemistry.