Process intensification of biodiesel production using a continuous oscillatory flow reactor[†]

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Abstract: Oscillatory flow reactors (OFRs) are a novel type of continuous reactor, consisting of tubes containing equally spaced orifice plate baffles. An oscillatory motion is superimposed upon the net flow of the process fluid, creating flow patterns conducive to efficient heat and mass transfer, whilst maintaining plug flow. Unlike conventional plug flow reactors, where a minimum Reynolds number must be maintained, the degree of mixing is independent of the net flow, allowing long residence times to be achieved in a reactor of greatly reduced length-to-diameter ratio. Many long residence time processes are currently performed in batch, as conventional designs of plug flow reactor prove to be impractical due to their high length-to-diameter ratios, which lead to problems such as high capital cost, large 'footprint', high pumping costs and, also control is difficult. The OFR allows these processes to be converted to continuous, thereby intensifying the process. The transesterification of various natural oils to form 'biodiesel' is a 'long' reaction, usually performed in batch. Conversion to continuous processing should improve the economics of the process, as the improved mixing should generate a better product (rendering the downstream separation processes easier), at lower residence time (reduction in reactor volume). These improvements can decrease the price of 'biodiesel', making it a more realistic competitor to 'petrodiesel'. This paper shows that it is feasible to perform this reaction in an OFR at a lower residence time. The reaction was performed in a pilot-scale plant, using rapeseed oil and methanol as the feedstocks, and NaOH as the catalyst.
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Keywords: oscillatory flow; biodiesel; process intensification

NOTATION

D	Diameter (m)
f	Frequency (Hz)
m	Viscosity ($kg\,m^2\,s^{-1}$)
r	Density ($kg\,m^{-3}$)
Re_n	Net flow Reynolds number
Re_o	Oscillatory Reynolds number
Str	Strouhal number
v	Velocity ($m\,s^{-1}$)
x_o	Centre-to-peak amplitude
y	Velocity ratio

INTRODUCTION

It was observed[1] that oscillatory flows through geometries in which a surface was presented transversely to the flow could produce uniform and efficient mixing patterns. The optimal geometry for uniform mixing of fluid within a tube was found to be equally spaced orifice plates 1.5 tube diameters apart of 0.25 fractional open cross-sectional area.

In the resultant 'oscillatory flow reactor', each baffle essentially behaves as a stirred tank, hence, if there are
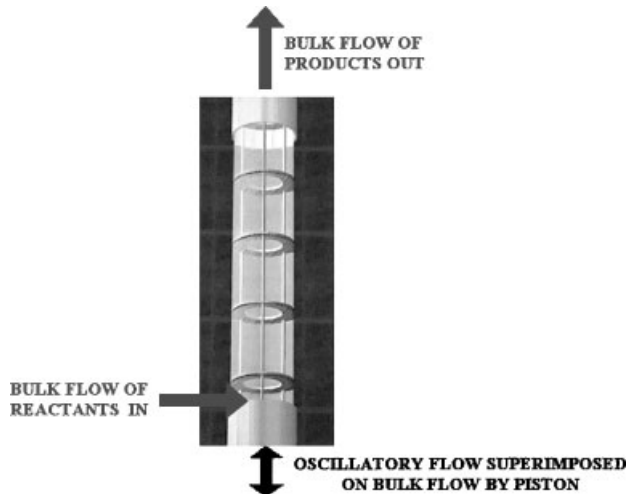
Figure 1. The oscillatory flow reactor.

enough baffles in series, a good approximation to plug flow can be achieved. It has been shown[2] that the residence time distribution depends upon the interaction of the net and imposed oscillatory flows. The dimensionless groups used to characterise the reactor's

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behaviour are as follows:
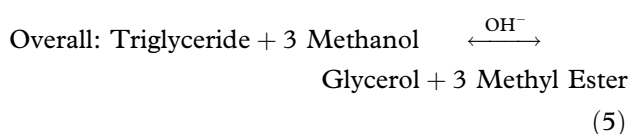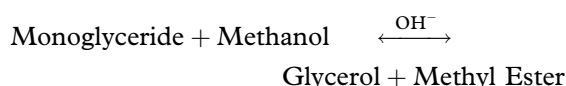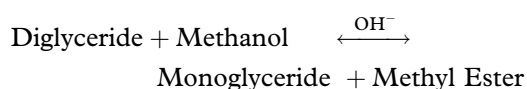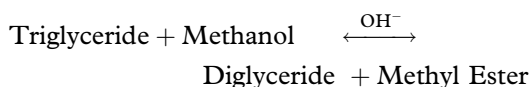
Net flow Reynolds number:
$$Re_n = \frac{\rho v D}{\mu} \qquad (1)$$

Oscillatory Reynolds number:
$$Re_o = \frac{\rho 2\pi f x_o D}{\mu} \qquad (2)$$

Velocity ratio:
$$\psi = \frac{Re_o}{Re_n} \qquad (3)$$

Strouhal number:
$$Str = \frac{D}{4\pi x_o} \qquad (4)$$

where ρ is the fluid density, v, the net flow velocity, D, the tube diameter, μ, the viscosity, f, the oscillation frequency and x_o, the centre-to-peak amplitude. It was shown that, if a velocity ratio of between approximately 4 and 10 were maintained, then a good approximation to plug flow would be achieved. This can be achieved along with heat transfer[3] and mass transfer enhancement.[4,5]

The OFR potentially has a number of niche applications, but we are most interested in its ability to perform 'long' reactions in reactors of greatly reduced length-to-diameter ratio. This is possible because, unlike conventional PFRs, the mixing is no longer directly dependent upon the Reynolds number of the net flow through the reactor, but is instead principally dependent upon the oscillation conditions. The requirement for high velocities in conventional PFRs to achieve Reynolds numbers which are high enough for turbulence inescapably leads to designs of reactor which are long and thin and are often impractical. Hence, the OFR allows many 'long' batch processes to be converted to more efficient continuous processes, where this was not previously considered feasible or practical. A number of these processes have been studied in the OFR already[6,7] and shown to be viable, but this paper is concerned with a new process for the OFR: the production of 'biodiesel'. 'Biodiesel' refers to methyl or ethyl esters produced by trans-esterifying the triglycerides that constitute most natural oils and fats. Equation (5) shows the conversion of triglycerides to methyl esters (biodiesel).

$$\text{Triglyceride} + \text{Methanol} \xleftarrow{\text{OH}^-}$$
$$\text{Diglyceride} + \text{Methyl Ester}$$

$$\text{Diglyceride} + \text{Methanol} \xleftarrow{\text{OH}^-}$$
$$\text{Monoglyceride} + \text{Methyl Ester}$$

$$\text{Monoglyceride} + \text{Methanol} \xleftarrow{\text{OH}^-}$$
$$\text{Glycerol} + \text{Methyl Ester}$$

$$\text{Overall: Triglyceride} + 3\text{ Methanol} \xleftarrow{\text{OH}^-}$$
$$\text{Glycerol} + 3\text{ Methyl Ester}$$
$$(5)$$

The molecules produced are typically of chain length 16–22, and are thus suitable for use in modern diesel engines The raw oils and fats themselves cannot be used in a modern diesel engine, as their viscosity is too high, but biodiesel can be used directly as a replacement for diesel, as its viscosity is a factor of at least 6 lower than the feed vegetable oil. The same distribution infrastructure can be used for both fuels and they can be blended together in any ratio.

As biodiesel comes from renewable sources, it is considered to be CO_2-neutral. Hence it does not add to global warming. Using biodiesel rather than crude oil-derived diesel is not only good for the environment in terms of its effect on CO_2, but also directly on air quality, as biodiesel is a 'cleaner' fuel than fossil fuel-derived diesel, generating lower emissions of hydrocarbons, particulates and carbon monoxide.[8] Another positive effect of biodiesel use, is that the wear on engines is reduced, due to the greater lubricity of biodiesel.[9] Indeed many countries are introducing 2% biodiesel blends, precisely for the improved lubricity,[10] often to replace the lubricating effect of sulfur compounds in low-sulfur diesel fuels.

Currently, the price of biodiesel derived from fresh rapeseed oil in the UK is significantly higher than the price of crude oil-derived diesel, but there are other economic factors to be taken into account, including the use of waste oil as a feedstock, greater independence and flexibility of fuel supply, particularly for nations which do not have large enough fossil fuel resources, and the long term increase in the price of oil as stocks diminish.

MATERIALS AND METHODS

The reactor consisted of two vertically positioned jacketed QVF tubes of 1.5 m length and 25 mm internal diameter, connected at the top by an inverted QVF U-tube, fitted with a manually operated purge valve. The overall internal volume of the reactor was 1.56 dm³. Reactor temperature was maintained by a Haake F6/B5 heater/circulator unit. The feeds were pumped from the feed vessels using a twin-headed positive-displacement metering pump. Temperatures were maintained in the feed vessels and supply lines by Eurotherm temperature controllers, regulating the outputs to the hotplates beneath the feed vessels, and the heating tapes around the supply lines respectively. The fluid oscillation was provided a 'nutating cam' arrangement. This unit is well suited for use in the laboratory, as it allows full, instant control of both the amplitude (0–17 mm), controlled by the translational motor, and the frequency (0.2–12 Hz), controlled by the rotational speed of the camshaft. The flowsheet is shown in Fig 2.

The molar ratio of methanol to rapeseed oil used was maintained at 1.5 (a volumetric ratio of 0.2, due to the higher molar density of methanol). It was necessary to use an excess of methanol to move the equilibrium of the reaction to the product side. Solid 98.62% pure NaOH (32.4 g) was dissolved in each dm³ of the 99.99% pure methanol feed. It was important to
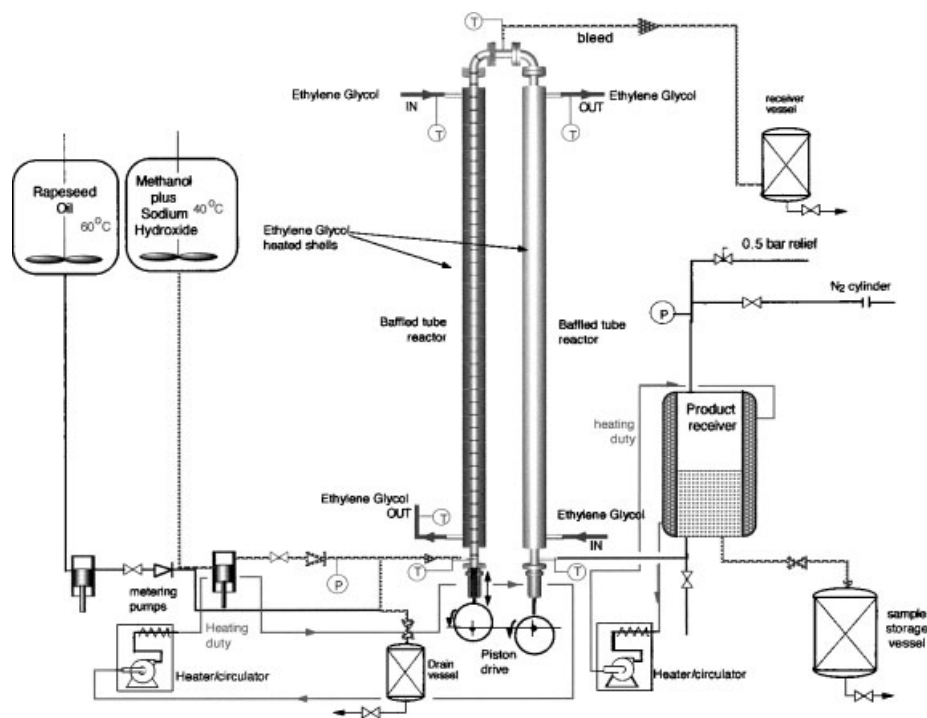
Figure 2. Biodiesel production in the OFR: flow diagram.

minimise the amount of water present as it would effectively be a poison to the reaction, by opening up other reaction pathways, particularly saponification reactions. The NaOH was mixed with the methanol before each experiment for at least 1 h at 40 °C in the feed vessel. The feed vessel temperature would ideally be reaction temperature (usually 50 or 60 °C) to reduce the heating duty required between the feed vessel and the reactor, thereby guaranteeing that the system was isothermal, but this would lead to too great an evaporative loss of methanol, which would change the NaOH/methanol ratio, as well as being unsafe. The rapeseed oil, as it was far less volatile, was kept at 60 °C in its feed vessel. The main feedstock was pure rapeseed oil, but a waste oil feedstock was also investigated.

All product samples were immediately quenched by being placed in an ice-bath to prevent further reaction as the product settled. Before all analyses the product was allowed to settle overnight.

The main parameters of interest in this initial series of experimental runs were the temperature and residence time. These were varied within the ranges 20–70 °C and 10–30 min respectively. All other variables such as molar ratio and amount of catalyst were kept constant.

The product qualities that could be quantified 'in-house' were viscosity, density, pH and the volume fraction of glycerol, but these measurements were not sufficient to determine the quality of the biodiesel. Hence, the samples were sent to a commercial laboratory for cetane number, glyceride and cold filter pour point (CFPP) analysis.

RESULTS AND DISCUSSION

The viscosities of all samples, from both fresh and waste oil, were found to be in the range 3.5–5.0 mm^2 s^{-1}, which satisfies DIN 51606, the German standard for biodiesel, and all other standards. The densities were also satisfactory (range: 0.875–0.900 g cm^{-3}). The volume fractions (at ~0.80) of glycerol were all consistent with the desired high degree of conversion (although the degree of error, at ±5%, was relatively large). pH readings were also consistent with those expected.[11] The top fraction of the product, the biodiesel itself, was extremely clear after settling, which is also a good indicator of the purity of the product.

Although the viscosity measurements are as desired, viscosity itself does not give insight into the composition of the biodiesel. Viscosity itself is not proof that the biodiesel is a suitable fuel, therefore further tests were performed. A subset of samples was analysed externally by ITS laboratories for cetane number and glycerides to investigate the effects of temperature and residence time on the conversion (see Table 1).
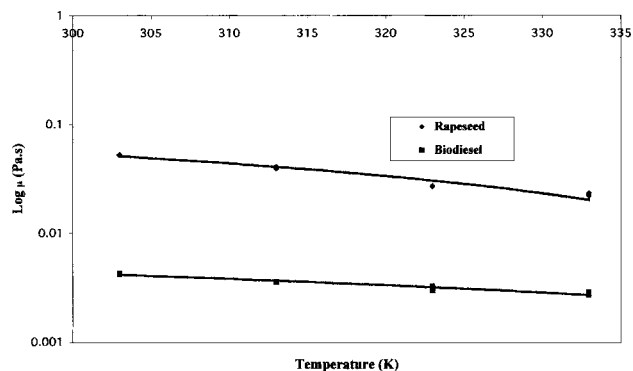

Figure 3. Viscosity of a typical rapeseed oil and biodiesel products *versus* temperature.

Temp (°C)	Residence time (min)	Cetane number	Triglyceride (%)	Diglyceride (%)	Monoglyceride (%)	Glycerol (%)
50	10	42.0	0.34	0.15	0.42	0.16
50	15	43.4	0.00	0.02	0.37	0.25
50	30	45.3	0.00	0.01	0.40	0.46
60	10	43.3	0.00	0.02	0.37	0.28
60	15	44.6	0.00	0.02	0.39	0.37
DIN	51606	49.0	0.40	0.40	0.80	0.02

Table 1. Analysis of biodiesel samples

Cetane numbers can be seen to increase with increasing residence time and temperature, indicating that the degree of conversion increases with these parameters. The value of 45 achieved at 50 °C and 30 min residence time would render the sample acceptable by the ASTM standard, although not by the DIN (requires a cetane number of 49). All samples would pass the current UK 'fiscal standard', but this will be superseded by a European standard in the next few years, which will probably be similar to DIN 51606.

It is clear that a residence time of 10 min at 50 °C does not produce the conversion required, as un-reacted triglyceride remains in the product, and the level of diglyceride is high. Even so, this sample, as all others, meets the German standard DIN 51606 for all glycerides. All other samples contain negligible amounts of triglyceride and diglyceride. That the monoglyceride is relatively high in all these samples is to be expected from transesterification kinetic studies.[12]

In these data, as the settling period was similar for all samples the free glycerol content is indicative of the degree of conversion, and can be seen to follow the same trends as the cetane number (increases with temperature and residence time). The free glycerol reading can be lowered to an acceptable value by allowing the product to settle for a longer period, but in a fully continuous plant a faster method would be required. This part of the process is currently being investigated.

The samples were also analysed for Cold Filter Plugging Point (CFPP), and were all found to be in the range −10 to −11 °C, which is usually acceptable in the UK (seasonal and geographical dependence). The value of ψ, at around 18, although meaning that the reactor was equivalent to ∼eight tanks-in-series, was strictly too high, but was limited by the size restrictions of the reactor itself. Hence, the lowest practicable value of ψ was used. A Re_o of typically 700 was required for good mixing to be achieved. Further experiments will use a reactor of greater L/D ratio to allow ψ to be in the desired range, thereby possibly lowering the required residence times further.

Overall it has been demonstrated that the OFR is suitable for the transesterification of vegetable oil to 'biodiesel'. A suitable conversion can be achieved in a residence time substantially lower than that of batch processes. The optimisation of the reaction conditions is on going.

Further advantages of producing biodiesel in the OFR should be realised when a heterogeneous catalyst is used, as the OFR has been shown[13] to be ideal for suspending particles of solid catalyst or polymer supported catalyst.

ACKNOWLEDGEMENTS

REFERENCES
1 Brunold CR, Hunns JCB, Mackley MR and Thompson JW, Experimental observations on flow patterns and energy losses for oscillatory flow in ducts containing sharp edges. *Chem Eng Sci* **44**:1227–1244 (1989).
2 Stonestreet P and van der Veeken PMJ, The effects of oscillatory flow and bulk flow components on residence time distribution in baffled tube reactors. *Chem Eng Res Des* **77**:671–684 (1999).
3 Mackley MR and Stonestreet P, Heat transfer enhancement and energy dissipation for oscillatory flow in baffled tubes. *Chem Eng Sci* **50**:2211–2224 (1995).
4 Hewgill MR, Mackley MR, Pandit AB and Pannu SS, Enhancement of gas–liquid mass transfer using oscillatory flow in baffled tubes. *Chem Eng Sci* **48**:799–803 (1993).
5 Ni X, Gao S and Pritchard DW, A study of mass transfer in yeast in a pulsed baffled bioreactor. *J Biotech and Bioengng* **45**(2):165–175 (1995).
6 Harvey AP and Stonestreet P, A case study of the process intensification of a batch saponification plant, in *Proceedings of the 6th World Congress of Chemical Engineers*, *paper no 432, Melbourne, Australia*, 24th–29th September (2001).
7 Ni X, Johnstone JC, Symes KC, Grey BD and Bennett DC, Suspension polymerisation of acrylamide in an oscillatory baffled reactor: from drops to particles. *AIChE J* **47**(8):1746–1757 (2001).
8 Wang WG, Lyons DW, Clark NN, Gautam M and Norton PM, Emissions from nine heavy trucks fueled by diesel and biodiesel blend without engine modification. *Env Sci and Tech* **34**(6):933–939 (2000).
9 Graboski MS and McCormick RL, Combustion of fat and vegetable oil derived fuels in diesel engines. *Prog Energy and Comb Sci* **24**(2):125–164 (1998).
10 Anastopoulos G, Lois E, Serdari A, Zanikos F, Stournas S and Kalligeros S, Lubrication properties of low-sulfur diesel fuels in the presence of specific types of fatty acid derivatives. *Energy and Fuels* **15**(1):106–112 (2001).
11 Tickell J, From the fryer to the fuel tank, Tickell Energy Consulting (2000).
12 Noureddini H and Zhu D, Kinetics of transesterification of soybean oil. *J Am Oil Chem Soc* **74**(11):1457–1463 (1997).
13 Fabiyi ME and Skelton RL, Photocatalytic mineralisation of methylene blue using buoyant TiO_2-coated polystyrene beads. *J Photochem and Photobiol A—Chem* **132**(1–2):121–128 (2000).