BIODIESEL REACTION SCREENING USING OSCILLATORY FLOW MESO REACTORS

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Abstract: This paper is concerned with performing laboratory scale alkali-catalyst transesterification for biodiesel reaction and ranking conversion and performance between a stirred tank reactor, and oscillatory flow meso reactors in both batch and continuous mode. The results show that a comparative conversion can be achieved for the same reaction conditions, thereby demonstrating that batch and continuous meso reactor configurations can be used for a high throughput screening biodiesel reactions.

Keywords: biodiesel; oscillatory flow; meso reactor; screening.

INTRODUCTION

Biodiesel is promoted as a sustainable alternative to petroleum diesel and is characterized as the methyl or ethyl esters of long chain of fatty acids derived from vegetable oils or animal fats. Transesterification is currently the predominant chemical process to produce biodiesel, often referred to as fatty acid methyl ester (FAME), by reacting vegetable oil with methanol in presence of an alkaline catalyst. Advantages of using biodiesel or blended biodiesel with petroleum diesel as a fuel include lower overall life cycle CO₂ emissions, and reduced air pollution (Choi and Oh, 2006; Fernando *et al.*, 2006; Peng *et al.*, 2006; Tan *et al.*, 2004).

Biodiesel Production

The transesterification reaction in which the triglyceride molecule reacts with alcohol, e.g., methanol to form three FAME molecules and one glycerol molecule includes three consecutive steps of reversible reactions (Freedman *et al.*, 1986; Schwab *et al.*, 1987).

The overall reaction can be written as

In practice, since all three reactions are reversible, a significant excess of methanol with catalyst is necessary to obtain a high conversion. A molar ratio of 6 : 1 of methanol to vegetable oil gives maximum conversion using 1% sodium hydroxide (Freedman *et al.*, 1984, 1986; Ma and Hanna, 1999). Either acid or alkali, such as sodium hydroxide, sodium methoxide, and potassium hydroxide can be used as catalysts. Sodium methoxide has an advantage that it does not produce water and thus prevents saponification side reactions, although it is more expensive and requires greater care in handling (Freedman *et al.*, 1984; Vicente *et al.*, 2004). A catalyst concentration of 0.5 mol% sodium methoxide and up to 2 mol% sodium hydroxide was suggested by Schuchardt *et al.* (1998). Studies have also been carried out to investigate alternative heterogeneous catalysts (Kim *et al.*, 2004) and enzymes (Jackson and King, 1996) for biodiesel production.

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The production of biodiesel can either be conducted in a batch process or continuous operation (Ma and Hanna, 1999). Continuous processes can be more efficient, in terms of overall reaction cycle times, cost and product quality control.

Biodiesel is produced at various scales from what amounts to back yard operations using agitated vessels or pump round mixing followed by settling and purification in the same vessel to large scale continuous plant. Some medium scale operations also use batch processing usually with a separate purification train. Most continuous plants use a combination of static in line mixers followed by long tubular reactors and complex purification trains, often involving distillation. The Cambridge OFM reactor is designed for medium scale continuous operations and can be skid mounted for ease of transport. It combines many of the advantages of the batch and tubular reactor and is very compact.

With few exceptions the process takes place at about 60°C and just above ambient pressure to ensure that the methanol stays in the liquid phase. In the continuous plants the reactants are normally pre-heated but in the batch process heating is usually carried out in the reaction vessel. The most important factor in biodiesel production tends to be mass transfer rather than heat transfer as it is vital to get the reactants, which have widely differing viscosities mixed as rapidly as possible. Once the first step in the reaction is initiated the methanol will dissolve in the products hence facilitating the subsequent steps.

The usual way of trialling biodiesel reactions and reactors is currently to conduct small scale batch reactions in stirred tank followed by larger scale pilot and continuous production reactors. In this paper a 'meso scale' 5 ml batch and a continuous reactor were used with an initial object to show performance comparison with stirred laboratory scale batch reactor performance and also demonstrate proof of concept for the continuous meso reactor. The use of the batch meso reactor will allow screening of potential feedstocks and catalysts for a small scale than even stirred batch laboratory reactor. The continuous meso reactor has the potential to screen many continuous processing reaction conditions; establish optimal conditions and in principle the reactor configuration could be scaled up without further trials for a large scale biodiesel production.

The Oscillatory Flow Reactor

The oscillatory flow mixing (OFM) is a process intensification technology to improve mixing as well as other process properties, such as heat transfer (Mackley and Stonestreet, 1995; Stephens and Mackley, 2002), mass transfer (Mackley *et al.*, 1998; Ni *et al.*, 1995), plug flow residence time distribution (RTD) (Howes *et al.*, 1991; Mackley and Ni, 1993; Mackley *et al.*, 1996), and multiphase suspensions (Mackley *et al.*, 1993; Ni *et al.*, 2003). The oscillatory flow reactor (OFR) is a tubular reactor containing periodically spaced low orifice constrictions where the fluid oscillations are applied in an axial direction within the tube as shown in Figure 1. A macro-scale OFR containing sharp periodic baffles (SPB-OFR, or baffled OFR) was developed for a wide variety of reactions (Chew *et al.*, 2004; Fabiyi and Skelton, 2000; Harvey *et al.*, 2001; Lee *et al.*, 2002; Ni *et al.*, 2001) including the biodiesel production reaction (Harvey *et al.*, 2003).

In the OFR with sharp periodic baffles, the interaction of the orifice baffles with the oscillating fluid causes periodic toroidal vortices between each baffle (Howes *et al.*, 1991; Ni *et al.*, 2002). Applying net flow in this OFR, the residence time distribution can be close to that of plug flow (Stonestreet and Van der Veecken, 1999). Unlike conventional plug flow reactors in which the plug flow is caused by turbulent net flow, the plug flow achieved in an SPB-OFR is obtained by the oscillation conditions. This offers the SPB-OFR an important process intensification feature that it allows 'long' (e.g., greater than 15 min) reactions to be performed in a plug flow reactor of relatively small length-to-diameter ratio (Harvey *et al.*, 2001).

Recently, a meso-scale OFR containing smooth periodic constrictions (SPC-OFR, or meso reactor) as shown in Figure 1(b) was developed at Cambridge for the scale-down pharmaceutical and biological screenings and production. Similar periodic vortex shedding flow patterns (Reis *et al.*, 2005) and a near plug flow RTD (Reis *et al.*, 2004) were observed within the meso reactor as in SPB-OFR. A continuous meso reactor was developed to carry out multiphase reactions (Reis *et al.*, 2006) such as biodiesel reaction in lab scale.

The oscillatory Reynolds number, Re_o , and Strouhal number, St , characterize the hydrodynamics within an OFR to describe the oscillatory flow as well as the geometrical configuration of the baffles. The Re_o and the St , are defined

Figure 1. The configuration of oscillatory flow reactors (OFR).

as follows:

$$Re_o = \frac{2\pi f x_o \rho D}{\mu} \quad (5)$$

$$St = \frac{D}{4\pi x_o} \quad (6)$$

where x_o is the centre to peak amplitude of oscillation; f is oscillatory frequency (Hz); D is the tube diameter (m); ρ is fluid density (kg m^{-3}) and μ is fluid viscosity (Pa s). The oscillatory Reynolds number describes the intensity of mixing applied to the tube, where $2\pi f x_o$ represents the maximum oscillatory velocity (m s^{-1}); the Strouhal number is the ratio of the tube diameter to the oscillatory amplitude. A net flow Reynolds number, Re_n , becomes relevant for the case where there is an additional net flow along the tube, described as follows:

$$Re_n = \frac{\rho u D}{\mu} \quad (7)$$

where u is the superficial net flow velocity through the tube (m s^{-1}).

In this paper, a biodiesel reaction was carried out in a batch and continuous meso reactor, and the reaction kinetics was compared with a standard laboratory stirred vessel reactor. Effective oscillation conditions were established in the batch meso reactor and reaction conversions were studied in all three types of reactors.

EXPERIMENTAL

Experimental Materials

Refined vegetable oil (Holland UK Ltd) with a density of 0.894 g ml^{-1} was used as the source of triglyceride. The viscosity was 0.06 Pa s at 20°C and 0.02 Pa s at 60°C measured by a controlled strain rheometer (Rheometric Scientific, Ares). The methanol/catalyst phase was 4.2% (wt/wt) sodium methoxide (Sigma-Aldrich) in methanol (Fluka, Germany) solution.

The volume ratio of oil and alcohol solution was 4 : 1, which corresponded to 1 : 6 in molar ratio. The reaction was carried out at 60°C for all three types of reactors.

Experimental Methods and Reactor Configurations

Batch stirred reactor

A 42 mm internal diameter and 57 mm depth glass vessel with a circulation outer jacket was used as the batch stirred reactor. The solution held inside the reactor was stirred using a 25 mm $\times$ 7 mm magnetic stirrer at the bottom of the vessel. The rotation speed of the stirrer was maintained at 200 rpm, Reynolds number $Re_i = 444$, using a hot plate with a digital rotation control. The impeller Reynolds number was estimated by (Oldshue, 1983)

$$Re_i = \frac{\rho N D_i^2}{\mu} \quad (8)$$

where N is the stirring speed (rps), D_i is impeller diameter (m). A schematic diagram of the batch stirred reactor is shown in Figure 1 below.

Eight millilitres of methanol/catalyst solution was added into 32 ml preheated vegetable oil in a glass stirred reactor as shown in Figure 2. The temperature was controlled at 60°C by circulating hot water via a stirred thermostatic pump (Grant, Cambridge, UK) fitted in a water bath.

Reactions were carried out for 40 min. Samples of 0.25 ml were obtained at 5 min intervals from the beginning of reaction and transferred into a 2 ml centrifuge tube. The samples were quenched by adding 0.25 ml of 0.1 N hydrochloric acid to stop reaction and then centrifuged (Beckman, USA, TJ-6). About 0.15 ml clear top phase were removed into a clean centrifuge tube for analysis in GC. The experiments were carried out three times to obtain repeat samples for each time point.

Batch oscillatory flow meso reactor

The batch oscillatory meso reactor consists of a Smooth Periodic Constriction (SPC) tube, an oscillator and a metal

Figure 2. The schematic diagram of batch stirred reactor.

Figure 3. A schematic diagram of batch meso reactor.

fitting frame (as shown in Figure 3). A vertically mounted SPC (meso-) tube (20 cm long, 5 mm maximum inner diameter glass tube with a heating/cooling jacket) was shown in Figure 4.

The inner glass wall was periodically 'pinched' to produce smooth periodic constrictions. The spacing, λ , between any two constrictions was 15.2 mm (approximately three times the tube diameter) and the length, δ , of each constriction was 6.4 mm. The minimum diameter, h , of the constricted zone was 1.6 mm, representing 10% of the maximum cross-sectional area. The total volume of the meso-tube is 4.8 ml.

Figure 4. The geometry of a meso tube ($d = 5.0$ mm, $\lambda = 15.2$ mm, $h = 1.6$ mm, $\delta = 6.4$ mm, $\beta \approx 45^\circ$).

A vertical jacketed meso-tube and an electromagnetic oscillator (LDS, UK, V406) were connected using a PTFE fitting fixed to a metal frame, as shown in Figure 4. A signal generator (LDS, UK, PO100) and amplifier (LDS, UK, PA25E) controlled the amplitude and frequency of oscillation. Typical oscillation frequencies and amplitudes used were between 0 and 20 Hz and 0 and 3 mm (centre-to-peak) respectively.

The reaction was carried out at 60°C by circulating hot water via a stirred thermostatic pump (Grant, Cambridge, UK) fitted in a water bath. 3.8 ml vegetable oil was injected into the pre-heated meso tube from the bottom inlet, and started oscillation for 2 min to obtain a uniform temperature. 0.95 ml methanol/catalyst solution was added into the meso tube via a 1 ml syringe with a 10 cm needle when the oil was oscillating.

Different oscillation conditions and reaction time were carried out to screen for optimal oscillation conditions in the batch meso reactor. The detail of experimental conditions was listed in Table 1.

Samples were collected at the end of the reaction after 30 or 40 min by a 10 ml syringe via a 20 cm needle, and transferred into a 50 mm $\times$ 19 mm glass vial. The sample was quenched immediately and centrifuged. One millilitre of top clear phase was removed into a 3 ml vial for GC analysis.

The optimal oscillation condition was investigated by comparing the final Triglyceride conversions at different oscillation frequency and amplitude. The reaction was then carried out under this condition to study the concentration change with time. Samples were collected from each batch with the reaction time of 5, 10, 20, 30 and 40 min. Three experiments were carried out for each time interval. The samples were centrifuged and analysed by GC (see later for details).

Continuous oscillatory flow meso reactor

Continuous flow experiments were carried out using an apparatus shown in Figure 5. The apparatus consisted of a product vessel, a mixing unit, syringe pumps, feed tanks, and 8 meso tubes (with a tube length of 730 cm) with U-bends, providing a total volume of 103 ml. The experimental oscillation conditions were selected as oscillation frequency 10 Hz and amplitude 2 mm (centre to peak).

Vegetable oil was filled into a 1 l glass feed tank and the methanol/catalyst solution was added from a 500 ml glass feed tank, which were both equipped with a magnetic stirrer and a feedback temperature controlled hot plate. A controllable feed from the tanks was produced using two double acting syringe pumps (Pharmacia, P500) which feed both components to the reactor mixing head that was immediately above the oscillator. The flowrate of vegetable oil was 101 ml h^{-1} , and that of methanol solution was 25 ml h^{-1} ,

Table 1. Oscillation conditions for maximum conversion screening.

Oscillation frequency (Hz)	Oscillation amplitude (mm)	Re_o	St	Reaction time (min)
10	1	67	0.4	30/40
8	2	107	0.2	30/40
10	2	134	0.2	30/40
12	2	161	0.2	40
6	3	120	0.13	30/40
15	3	301	0.13	40

Figure 5. A schematic diagram of continuous meso reactor.

which provided a mean residence time of 49 min. The temperature of meso tubes and product vessel was controlled at 60°C. After 100 min of operation, about 0.25 ml samples were taken from each of the seven sample ports (as shown in Figure 5) and the final sample was collected from the product vessel. Three sets of samples were taken after further 30 min intervals for each sample position. Samples were quenched with 0.1 N HCl and centrifuged immediately and the top layer was separated for GC analysis.

Analytical Methods

An automatic 'cool on column' injection Gas Chromatograph (GC, Agilent Technologies, USA, 6890) was used for analysis of concentration of product samples from the reaction in accordance with British Standard EN14205. A capillary GC column (Agilent Technologies, USA, DB-1HT) with 0.32 mm i.d. was used in the apparatus. The temperature of flame ionization detector was 380°C, and carrier gas pressure was 80 kPa. The analysis of biodiesel for each sample was carried out by silylating then dissolving 100 mg of biodiesel sample in 8 ml of heptane and injecting 1 μ L of this solution in GC. Two internal standards are used, one for glycerol and one for the glycerides. The monoglyceride (MG), diglyceride (DG), triglyceride (TG) contents were expressed as weight percent (w/w%). The instrument was calibrated using glycerol, monoolein, diolein and triolein in n-heptane solutions in accordance with BS EN 14105. The viscosity of FAME was measured by the Ares rheometer (Rheometric Scientific) at 20°C and 60°C.

RESULTS AND DISCUSSION

Batch Stirred Reactor

The concentration change of monoglyceride (MG), diglyceride (DG), triglyceride (TG) contents with the reaction time is shown in Figure 6. The data shows that 98% of the

Figure 6. Concentration of Mono-, di-, triglyceride contents (wt/wt%) in batch stirred reactor at impeller speed = 200 rpm and temperature = 60°C.

reaction occurs within 10 min, however, in order to reach adequately low DG and TG concentration (allowed by the EU standard EN14214), a total reaction time of order 35 minutes is required. Figure 6 shows that after 15 min reaction, the concentration of MG remains at 0.5% until the end of reaction. The concentrations of DG and TG continue to decrease as the reaction proceeds. This results show that each of the three step reaction [equations (1)–(3)] moves forward; after about 10 min the overall reaction rate of reaction (2) is faster than that of reaction (1), and almost equivalent to that of reaction (3). Figure 6 also shows after 40 min the amount of MG, DG and TG are all acceptable by the EU standard EN14214.

Oscillatory Flow Meso Reactor

Mixing conditions

In order to establish satisfactory mixing conditions within an oscillatory flow meso reactor, a series of experiments were carried out (see Table 1) and it was found that a minimum of 40 min reaction time and an effective mixing condition were necessary to achieve a high conversion of triglyceride allowed by EU Standard EN14214. The final concentrations of TG after 30/40 min reaction time are shown in Figure 7.

The data shows that in order to achieve the conversion allowed by the EU standard, a combination of oscillation

Figure 7. Effect of oscillation conditions on triglyceride conversion after 30 and 40 min.

frequency 8 Hz and amplitude 2 mm was required, which corresponds to $Re_o > 107$, and $St < 0.2$. At this oscillatory Reynolds number, the flow separation occurs after each constriction within the meso tube (Reis *et al.*, 2005). It shows that the fluid oscillation conditions control the vortex mixing intensity, and therefore influence the droplet break-up and emulsion formation in the initial two phase system. The results show that the mass transfer between the oil phase and methanol phase was enhanced at higher oscillation frequency and amplitude during the reaction. In order to achieve the required conversion with minimum energy input, 10 Hz and 2 mm was selected as the oscillation condition for the biodiesel reaction in both batch and continuous meso reactor.

Batch meso reactor

The concentration changes of monoglyceride (MG), diglyceride (DG), triglyceride (TG) contents with the reaction time within the batch oscillatory flow meso reactor are shown in Figure 8. The concentration responses and the overall conversion of TG obtained in batch meso reactor were similar to those in the batch stirred reactor. However the consumption of TG, and generation of DG and MG were slower in the batch meso reactor than batch stirred reactor in the first 5 min, and there was a stepper change of TG concentration curve between 10–30 min while it was linear in batch stirred reactor. In general, there is little difference between the conversion kinetics in the batch stirred reactor and batch meso reactor.

Continuous meso reactor

In the experiments carried out in the continuous meso reactor, the oscillatory frequency was 10 Hz, and amplitude was 2 mm, corresponding to the oscillatory Reynolds number $Re_o = 134$ and Strouhal number $St = 0.2$. At the experimental condition, a net flow Reynolds number $Re_n = 1.9$ was achieved, giving a ratio of $\psi = Re_o/Re_n = 70$. Previous studies showed that the oscillatory flow dominated the system at this operating condition, so that the net flow did not affect the fluid oscillations and mixing (Harvey *et al.*, 2001; Stonestreet and Van der Veeke, 1999). The results showed that the net flow was decoupled with mixing, and the reaction could be carried out within the reactor using the

Figure 8. Concentration of Mono-, di-, triglyceride contents (wt/wt%) in batch meso reactor at oscillation frequency = 10 Hz, amplitude = 2 mm and temperature = 60°C.

Figure 9. Concentration of Mono-, di-, triglyceride contents (wt/wt%) in continuous meso reactor at oscillation frequency = 10 Hz, amplitude = 2 mm, total net flowrate = 126 ml h⁻¹ and temperature = 60°C.

oscillation for mixing and thereby enabling the net flow to provide an independent control of residence time.

For the continuous biodiesel reaction in the meso reactor, samples were taken at different positions along the tube, thereby obtaining the conversions as a function of different residence times. The concentration changes of each component with mean residence time are shown in Figure 9. The trend of conversion versus time in the continuous flow meso reactor was found to be similar to the conversion kinetics observed in the batch meso reactor (Figure 8) and stirred reactor (Figure 6). This demonstrated that the continuous meso reactor conversion kinetics matched that of batch reactor and that axial dispersion in the flow reactor did not appear to have a significant effect on conversion. For the continuous meso reaction, after 40 min reaction time, both TG and DG concentration were below EU standard upper limits, and the DG and TG concentration was lower than the concentration at equivalent reaction time in the batch meso reactor.

It would have been useful to evaluate power densities for both the stirred vessel and Smooth Periodic Constriction meso tube reactor. Correlations exist for both impeller stirring reactors (den Hollander *et al.*, 2002; Oldshue, 1983) and also Sharp Edge Baffles OFM units (Ni *et al.*, 1995, 2003); however in one case a magnetic bar stirrer was used for the batch reactor and in another case the meso tube contains smooth periodic constrictions, at present power density correlations do not exist for both cases.

CONCLUSIONS

This paper has shown that at a laboratory scale a transition from (1) batch stirred to (2) batch meso to (3) continuous meso reactor can be made where for the same reactants, reaction time and temperature the results show an equivalent conversion.

The conversion kinetics of the reaction described in Figures 6, 8 and 9 all show that the bulk of the reaction occurs within 10 min, however in order to obtain an EU standard of DG and TG concentration, it is necessary to continue the reaction for a further 30 min. From optical observation of

the reactor showed that the initial early stages of conversion appeared to be two phases, whereas at the later stages, e.g., mean residence time $t > 2.5$ min, the reaction fluid was optically homogeneous. This indicates that the reactor design could be divided into two stages. Initial intense mixing is required for the first stage of reaction where the fluid is a two phase system, however as the reaction continues less intense mixing is necessary in order to obtain a homogeneous reactant.

The fact that a similar conversion was achieved between the batch meso reactor and continuous meso reactor suggests that adverse dispersion along the reactor tube does not occur, because if significant dispersion was present the conversion kinetics would be different (Busto *et al.*, 2006). The results demonstrate that the meso reactor can be used for continuous reaction on a laboratory scale. Previous studies (Smith and Mackley, 2006) have demonstrated scaling in an oscillatory flow sharp edge baffled tube can be easily scaled up. The fluid mechanics within a meso reactor is similar to that within a baffled tube, therefore successful reaction conditions established in a meso reactor should be able to be translated to larger scale oscillatory flow baffled reactor.

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Queries

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