Scale-up studies for intensified production of biodiesel from used cooking oil

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In this paper the effect of channel size on the transesterification of used cooking oil (UCO) with methanol using KOH as catalyst to produce biodiesel was investigated for capillaries with internal diameter ranging from 1 to 3 mm. A T-junction was used as the mixing zone of the two liquid phases. The effects of different parameters such as, internal diameter, methanol-to-oil molar ratio, reaction time, temperature, and catalyst concentration were investigated. Results showed that the conversion efficiency to biodiesel is increased by decreasing the channel size, whilst the interactions of the other variables are also discussed.

INTRODUCTION

Biofuels are considered as promising alternatives to fossil fuels, because of the need to reduce emitted CO_2, and the problems associated with the security of supply and geopolitical issues. The last decade their annual growth rate was at 10% and is expected to grow even more, while other renewable alternatives are still under development [1]. Biodiesel is one of the biofuel products that has received considerable attention and is already used in the transportation sector since it is compatible to current engine designs and performs very well in most conditions [2]. Biodiesel is a fatty acid methyl ester, mainly produced from vegetable oils of palm, soybean, coconut, and rapeseed. During the esterification process, the vegetable oil reacts with an alcohol, mostly methanol or ethanol, in the presence of a catalyst at 60 ºC [3]. Biodiesel biodegrades rapidly and is 100% non – toxic, which means that any spillages will be of far less risk compared to spillages of fossil diesel. Despite the many benefits associated with biodiesel, research is needed on its production, for a clean, effective, and environment-friendly technology to make it cost effective and increase its competency against conventional fossil fuels [4]. Another major concern is the use of edible oils for the majority of the biodiesel worldwide from crops that compete with arable land. To overcome this problem, an alternative, less expensive feedstock can be used. Options of feedstocks that are cheaper include non–edible oils and used cooking oils. The main issue with low cost oils is that they hold high levels of unwanted components including water and free fatty acids, which means that pre-processing steps should be considered in the production process. The production of biodiesel is usually carried out in liquid-liquid contactors where currently used technologies are old. Substantial process intensification can be achieved with the use of small-scale contactors where the reduced length scales result in thin fluidic films which enhance mass transfer rates, while increased surface to volume ratios improve the control of the flow patterns [5]. To increase throughput in the small scale contactors, large channel sizes should be considered that still however, preserve the benefits of small scale operations. There is a trade-off, therefore, between mass transfer performance and throughput and energy requirements, which need to be carefully considered when designing the whole process. Many works have been conducted on biodiesel production in micro-channels, the majority of which have investigated the conversion of vegetable oils. A recent review summarizes most of these works [6]. Regarding the use of waste cooking oil in the production of biodiesel, very few investigations have been conducted in the last decade. Mohadesi *et al.* [7] designed a bundle of 50 micro-reactors of 0.8 mm ID, and obtained conversion efficiency ~99% at 2 min, for methanol-to-oil ratio of 9.4:1 using KOH as catalyst. In another work, Tanawannapong *et al.* [8] investigated the production of biodiesel from waste cooking oil in a two-step reaction and found that the methyl ester content of the biodiesel was ~91%.

In this work, a one-step reaction is proposed for the transesterification of used cooking oil using KOH as a catalyst. The studies are carried out in channel sizes from 1 to 3 mm and the interaction of different variables, such as methanol-to-oil molar ratio, reaction time, temperature, and catalyst concentration are investigated.

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MATERIALS AND METHODS

Materials

Used cooking oil (UCO), with low acid value (0.02 mg KOH/g) and saponification value of 184 mg KOH/g was used. High-purity methanol, potassium hydroxide, heptane and internal standard methyl heptadecanoate were obtained from Sigma-Aldrich.

Experimental setup

A schematic of the experimental setup used for the continuous production of biodiesel is shown in Fig. 1. The experiments were carried out at atmospheric pressure. Two high-precision pumps were used to feed the two phases into the main reaction channel via a T-junction mixer. The mixer was made of FEP with all branches having the same internal diameter as that of the main reaction channel. Both the reaction channel and the mixing zone were immersed in a water bath with temperature control to maintain the desired reaction temperature. At the end of the reaction channel, the two phases were collected in an iced bath to terminate the reaction and separated using a gravity funnel. The post-processing of the samples included washing (5 times with warm water) to remove any remaining residuals, and drying to remove the remaining water. The flow was visualised with a high-speed camera (Photron APX) with a maximum resolution of 1024 × 1024 at 2000 fps.
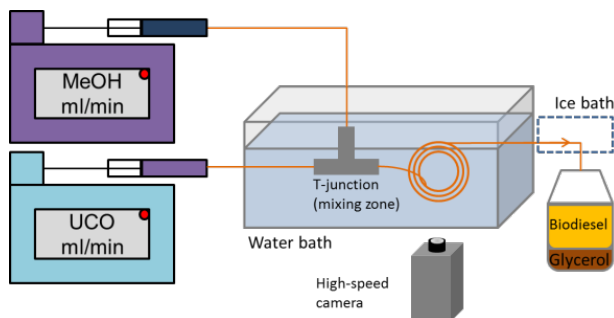
Fig. 1. Schematic of the experimental setup for biodiesel production

Analytical method.

The free fatty methyl ester (FAME) content of the biodiesel samples was measured with gas chromatography (Agilent 6890 Series GC), using a fused silica capillary column (Stabilwax 30 m × 0.25 mm × 0.25 μm) and a flame ionization detector. The analysis was performed following standard procedures (EN 14103) and methyl heptadecanoate was used as the internal standard.

Experimental design

The effect of the different variables, i.e. internal channel diameter, oil-to-methanol molar ratio, temperature, catalyst concentration, and reaction time in the conversion efficiency of the biodiesel was investigated. The table with the minimum and maximum values of the different parameters is shown in Table 1. The total length of the reaction channels was kept constant at 1.3 m, and the flow rates of the two phases were adjusted to give the appropriate reaction time and molar ratios.

Table 1. Experimental conditions for the production of biodiesel.

| Variables	Range
Methanol-to-oil molar ratio	6-18
Catalyst concentration (% w/w)	1-3
Temperature (ºC)	50-70
Reaction time (min)	1-8
Internal diameter	1-3

RESULTS AND DISCUSSIONS

The molar ratio is one of the most significant variables in the production of biodiesel. The transesterification reaction is reversible and thus an excess of methanol is required to move the reaction forward. Theoretically, 3 mol of methanol is required for the transesterification of 1 mol of oil to yield 3 mol of methyl ester and 1 mol of glycerol. The molar ratio, however, also affects the two-phase flow pattern in small channels. Using a T-junction to introduce the two liquid phases in the test section (Fig. 1) plug flow is established as shown in Fig. 2. When the molar ratio increased from 6 to 18 more segments were obtained, and higher interfacial area was available for mass transfer.
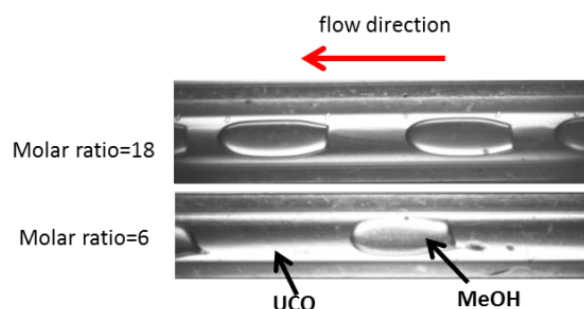
**Fig. 2.** Flow patterns in the 1 mm channel at two different molar ratios at 60 °C

Hydrodynamic and mass transfer performances are highly interdependent, so changes in the flow pattern are expected to affect the biodiesel conversion as well. In Fig. 3 the effect of molar ratio for two different channel sizes is shown. In the smaller channel (1 mm) the temperature was 60 °C, while in the bigger one it was at 70 °C. For both cases the conversion efficiency is higher at the

higher molar ratio i.e. 18, even though both molar ratios are larger than the stoichiometric one. Conversion efficiency in general is higher in the smaller channel, although the temperature is not the same to allow direct comparison.
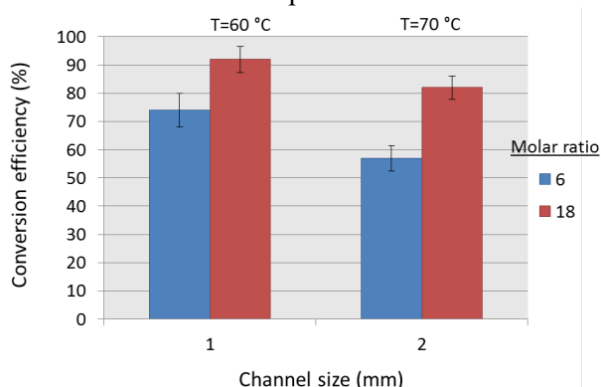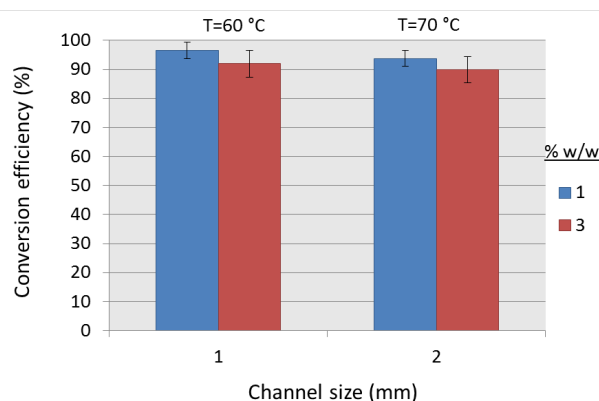

Fig. 3. Conversion efficiency as function of molar ratio for channel sizes 1 and 2 mm (Reaction time=4.5 min; KOH=2% w/w).

The effect of temperature is shown is Fig. 4. The transesterification reaction is an endothermic reaction, which means that the reaction rate increases with increasing temperature. However, at 50 °C the conversion efficiency reaches >95%, while it drops to 80% at 70 °C. This phenomenon is attributed to the fact that an increase in the temperature can also accelerate the saponification of the triglycerides (oil) by the alkaline catalyst before the completion of the alcoholysis.
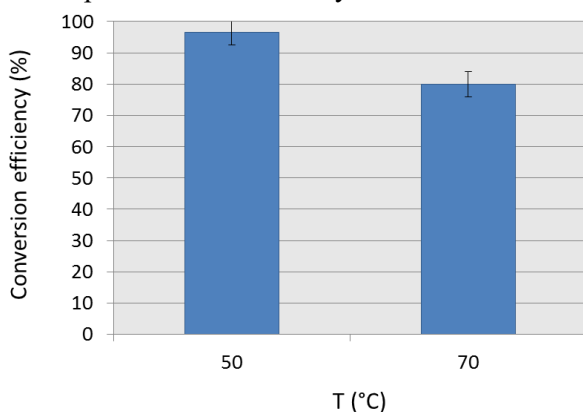
Fig. 4. Conversion efficiency as a function of temperature for the 1 mm channel (Molar ratio=12; Reaction time=4.5 min; KOH=2 %w/w)

The effect of catalyst concentration is shown in Fig. 5. It can be seen that for both channel sizes and temperatures, the conversion efficiency decreases by increasing the catalyst concentration.

Fig. 5. Conversion efficiency as a function of the catalyst concentration for two channel sizes i.e.1 and 2 mm (Reaction time=4.5 min; Molar ratio=12).

However, the difference in biodiesel conversion efficiency between concentrations of 1 and 3 % w/w is very small. Increased catalyst concentration can enhance the saponification of biodiesel, but it can also affect the properties of the glycerol formed.

The reaction time also plays a crucial role in the conversion of used oil to biodiesel. By increasing the reaction time, with all the other variables constant, the conversion efficiency increases by 15% in the 2 mm channel (Fig. 6).
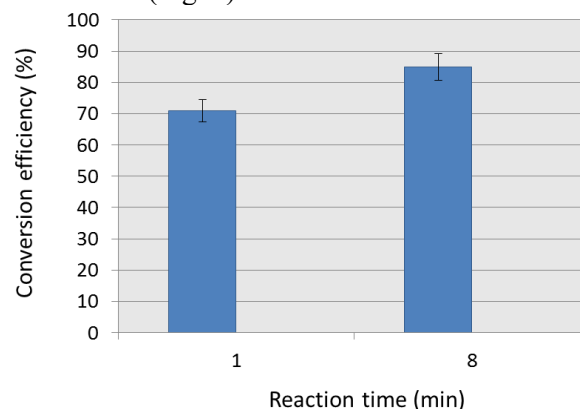
Fig. 6. Conversion efficiency as a function of reaction time for the 2 mm channel (Molar ratio=12; T=70 °C; KOH=2 %w/w)

To allow high throughputs, a larger channel size of 3 mm internal diameter was investigated. The conversion efficiency was compared to that of the 1 mm ID channel for a reaction time of 4.5 min, keeping all the other conditions constant. As it can be seen in Fig. 7, the conversion efficiency drops by 25% when the channel diameter increases from 1 to 3 mm.
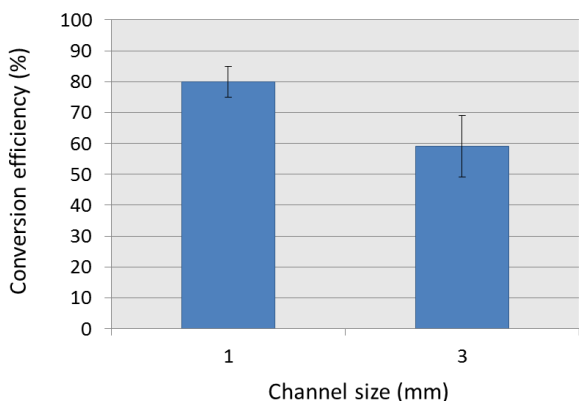
Fig. 7. Conversion efficiency as a function of channel size (Molar ratio=12; Reaction time=4.5 min; KOH=2 %w/w, Temperature=70 °C)

CONCLUSIONS

In this work the effect of channel size on the production of biodiesel was investigated under different operating parameters. A one-step transesterification reaction of used cooking oil with MeOH/KOH to produce biodiesel was studied for channel sizes ranging between 1 and 3 mm internal diameter. It was found that the biodiesel conversion efficiency increased with decreasing channel size. The molar ratio affected the conversion significantly since it has a direct impact on the flow patterns that form in the small channels. An increase in the molar ratio led to an increase in the biodiesel conversion efficiency. Longer reaction times also increased the conversion.

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