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Process intensification of catalytic liquid-liquid solid processes: Continuous biodiesel production using an immobilized lipase in a centrifugal contactor separator

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HIGHLIGHTS

- Centrifugal separator contactors have been used for L-L-S reactions.
- The concept was demonstrated for continuous biodiesel synthesis using an immobilized enzyme.
- Further improvements were possible in a cascade of a CSTR and CCCS.
- Average biodiesel yield at steady state conditions was 86%-mol for a 9 h run.

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ABSTRACT

Biodiesel or fatty acid methyl ester (FAME) synthesis from sunflower oil and methanol using an immobilized lipase, an example of a liquid-liquid solid reaction, was studied in batch and various continuous reactor set-ups including the use of a centrifugal contactor separator (CCCS). The latter is an example of a highly intensified device, integrating liquid-liquid reactions and subsequent phase separations. An exploratory study in batch was performed to optimize enzyme and buffer concentrations. Close to quantitative biodiesel yields were obtained at 30 °C when using 20% (w/w) of enzyme after a batch time of about 250 min. Subsequent continuous biodiesel synthesis was performed in a stirred tank reactor (CSTR) and a CCCS device. In the latter case, the immobilized enzyme was present in the annular, outer zone of the device. Average biodiesel yields in the CSTR and CCCS were similar (72%-mol respectively) when using a weight hourly space velocity (WHSV) of 3.3 and 3.03 h^{-1} respectively, at 30 °C. Cascade experiments were performed in a CSTR followed by a CCCS with the immobilized enzyme present in both reactors. The cascade was run for 9 h without any operation issues and an average FAME yield of 85%-mol was obtained. The advantage of the use of the cascade compared to a single CSTR is an improved yield combined with an efficient separation of the biodiesel layer and the glycerol. The biodiesel yield was about constant during the run, indicating that enzyme deactivation was negligible. The performance of the various reactor configurations were modelled successfully using standard balances for continuous reactors in combination with a kinetic model derived from the batch experiments.

1. Introduction

Biodiesel has increased in popularity the last decade and is an attractive alternative for diesel fuel due to its renewable character and its ability to be used in existing engines without substantial modifications [1,2]. The worldwide production of biodiesel has grown from 2.4 billion litres per year in 2004 to 29.7 billion litres per year in 2014 [3]. Production volumes are expected to further increase in the future, giving biodiesel a bright future.

The main technology to produce biodiesel is the transesterification of triglycerides with alcohols (in most cases methanol) catalyzed by either chemo- or bio catalysts (Fig. 1). Chemo catalysts like inorganic bases are commonly used due to their low cost and high reaction rates [4]. Biocatalysts have recently attracted a lot of attention as they have shown to perform better than base

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Nomenclature

[*Acyl*]	concentration of acyl groups, mol m^{-3}
CCCS	continuous contactor centrifugal separator
CSTR	continuous stirred tank reactor
[*FAME*]	concentration of FAME, mol m^{-3}
K_M	the Michaelis Menten constant, kinetic parameter in Eq. (11), mol m^{-3}
k_r	reaction rate constant in the enzyme kinetic rate Eq. (11), mol kg^{-1} s^{-1}
MW	molecular weight, kg.mol^{-1}
[*MeOH*]	concentration of methanol, mol m^{-3}
r_{enz}	rate of the enzyme catalyzed reaction, mol m^{-3} s^{-1}
t	time, s
V	volume, m^3
w^0	initial mass, kg
w_{enz}	mass concentration of enzyme, kg m^{-3}
Y	FAME yield, %-mol

Greek symbols

ρ	density, kg m^{-3}
τ	average residence time ($=V/\phi_v$), s
φ_v	volumetric flow rate m^3 s^{-1}

Subscripts

0	initial
aq	aqueous phase
cccs	continuous contactor centrifugal separator
cstr	continuous stirred tank reactor
enz	enzyme
FAME	fatty acid methyl ester
liq	liquid
MeOH	methanol
oil	sunflower oil
tot	total

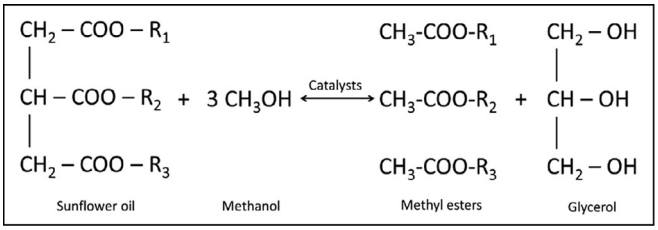

Fig. 1. Sunflower oil transesterification with methanol.

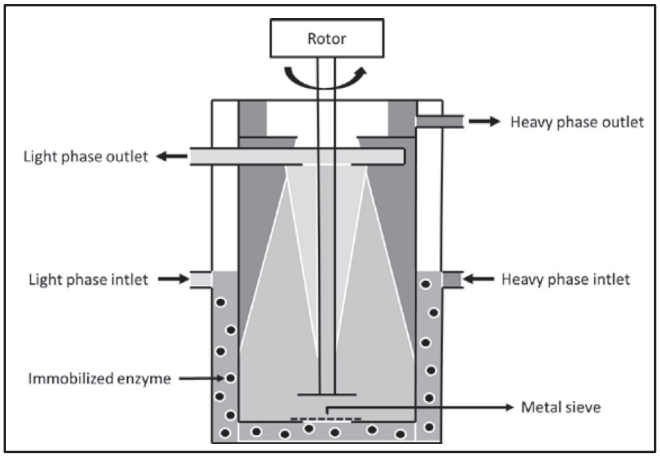

Fig. 2. Schematic representation of the continuous centrifugal contactor separator (CCCS) used in this study. Reproduced from [20].

catalysts like i) a better compatibility with oils and fats contaminated with free fatty acids (like used cooking oils), ii) soap formation is avoided, iii) a less complicated biodiesel work-up, and iv) a lower energy input [1,4].

Current commercial biodiesel processes are still typically performed in batch or fed-batch reactors. However, there is an incentive to use continuous production configurations as they allow for better product consistency and reduced downtimes [1,5–7]. Possible reactors for biodiesel production using immobilized catalysts are stirred tank and packed bed reactors [5,6,8–10]. Easy of operation and less complications regarding product-catalyst separation favour the use of packed-bed reactors [10–12]. With the use of immobilized enzymes, the recovery of the lipase is not an issue. On the other hand, the recovery of the lipase when using the free enzymes is difficult and costly while at the same time running the biodiesel synthesis with free enzymes and without recovery of the lipase would be excessively expensive. Biodiesel synthesis is an example of a biphasic liquid-liquid reaction. At the start of the reaction, the oil/fat and methanol are not fully miscible and form a liquid-liquid system. At the end of the reaction, biodiesel and glycerol again form two separate liquid phases. During reaction, intense mixing is required between the two phases to eliminate possible mass transfer limitations that will reduce the overall rate of the reactions. In addition, the product layers need to be separated after reaction by using a settler. Recently, we have shown that biodiesel synthesis may be carried out very efficiently in a continuous mode when using a continuous centrifugal contactor separator (CCCS). It is a device that integrates both intense mixing of two immiscible liquids and subsequent separation (Fig. 2) [13,14]. Originally, the CCCS-type of devices was used for cleaning-up of nuclear waste [15]. Subsequently, the CCCS was also applied in oil-water separation with oil spillages, liquid-liquid extraction [13] and reactive extraction [16–18].

The CCCS device basically consists of a hollow rotor positioned in a larger vessel. The two immiscible liquid phases are introduced in the annular zone between the outside of the rotor and the inside of the outer housing. Here, an efficient and fast mixing between the two phases occurs, which is suitable for a two-phase liquid-liquid catalytic reaction. The mixture is then transferred inside the centrifuge through a hole in the bottom of the rotor, where the two phases are separated by centrifugal forces whilst moving upwards, after which they leave the device through separate exits making use of an ingenious weir system [19]. As such, the device is an interesting example of process-intensification, acting both as a mixer-settler for biphasic liquid-liquid systems.

Recently, we have reported [19,20] the successful application of such a CCCS device for biphasic liquid-liquid reactions including the transesterification of sunflower oil with methanol using an alkaline catalyst and the esterification of oleic acid with 1-butanol using a liquid lipase formulation as the catalyst. In subsequent studies, the use was expanded to ethyl ester synthesis from