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Biodiesel synthesis using integrated acid and base catalysis in continuous flow

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ABSTRACT

The use of biodiesel derived from oils and fats is making an increased contribution as a renewable energy source. The synthesis of biodiesel involves transesterification of triglycerides to the monoalkyl esters, a process often made challenging by the presence of free fatty acids (FFA). Herein an integrated flow system for the synthesis of biodiesel, employing a solid supported acid catalyst for esterification of FFAs, followed by transesterification using polymer supported *N*-heterocycle carbene (NHC) catalyst is reported. This system delivers biodiesel in high yields from a variety of fat and oils, using robust and recyclable catalysts.

1. Introduction

As energy consumption shifts from fossil fuels, the use of biofuels is making an increased contribution to energy production. The EU has targeted the use of 10% biofuels in the transportation sector by 2020,[1] while US production of biodiesel is expected to exceed 6.4 million tonnes in 2016. Biodiesel is a fuel consisting of long chain monoalkyl esters derived from vegetable oils or animal fats. Biodiesel is an attractive replacement for petroleum based diesel, as the two fuels can be blended in any proportion and biodiesel can be used in existing diesel engines without modification. The use of biodiesel reduces emissions of particulate matter,[2] carbon monoxide and hydrocarbons by a significant amount (45–70%), although NO_x emissions are introduced slightly.[3,4] The lifecycle CO_2 emissions of biodiesel are dependent on the feedstock material and land usage.[5,6] However, the use of third generation feedstock oils derived from algae have shown a 68% reduction in CO_2 emissions compared to traditional diesel fuel.[7]

Although the first diesel engines demonstrated by Rudolf Diesel were powered by peanut oil the high viscosity of triglycerides means that they not ideal fuels, and are more commonly converted to the monoalkyl esters before combustion. This is typically achieved by transesterification to the methyl ester in the presence of a catalyst.[6] The most common method for transesterification employs a homogeneous Brønstead base catalyst, such as alkali metal alkoxides or hydroxides. Heterogeneous base catalysts such as metal oxides, zeolites, and hydrotalcites have also been extensively used, which can improve separation and recycling of catalyst from reaction mixtures.[8] Li and co-workers recently reported the synthesis of biodiesel from soybean oil, using an *N*-heterocyclic carbene (NHC) catalyst generated in situ by thermolysis of a NHC–CO_2 adduct.[9] This method employs low reaction temperatures and provides high yields of biodiesel when using oils and fats with low water, and free fatty acid (FFA), content (<1%). Unfortunately, many inexpensive feedstocks have significantly higher levels of FFAs, which neutralise the catalyst and lead to soap formation that can inhibit separation of the biodiesel from glycerol. In addition to base catalysts, homo- and heterogeneous acid catalysts have been used for the production of biodiesel.[6] These catalysts, while less sensitive to FFA, are typically less efficient, requiring higher temperatures and corrosion-resistant reaction vessels. In practice, many processes employ a two-stage procedure, where the fat or oil is first treated with an alcohol under acidic conditions to esterify the FFAs. This mixture of monoalkyl esters and triglycerides is then treated with a basic transesterification catalyst, producing a separable mixture of glycerol and biodiesel.

Continuous flow processes potentially offer a number of advantages in the production of biodiesel, allowing integration of multiple steps and ease of scale-up.[10] A number of continuous flow approaches to biodiesel production have been reported employing microwave heating,[11,12] ultrasonic reactors[13] or recirculating membrane reactors.[14] Herein, a new integrated continuous flow

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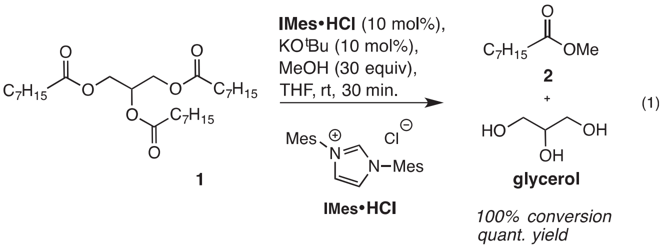
process for biodiesel production using fixed-bed catalytic reactors is reported. This process integrates esterification of FFAs over a solid acid catalyst with transesterification of triglycerides over a polymer-supported NHC catalyst.

2. Results and discussion

2.1. Transesterification of triglyceride 1

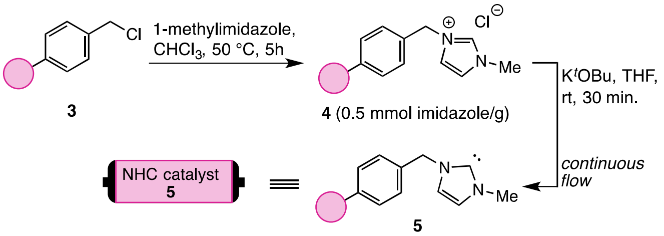
Studies began by demonstrating the NHC catalysed transesterification of triglyceride **1** with methanol. While the intention was to exploit an immobilised NHC catalyst studies commenced by examining batch transesterification of triglycerides. Concurrent reports by Hedrick/Waymouth[15] and Nolan[16] demonstrated that IMes is a highly efficient transesterification catalyst. Although subsequent studies were unlikely to exploit immobilised IMes (vide infra) it was decided to proceed with this catalyst as a model due to its use in the studies mentioned. Furthermore, these studies found that alkyl imidazole derived NHCs behaved similarly in the transesterification reaction. Pleasingly, with moderate modification to the reported conditions it was possible to convert triglyceride **1** to methyl ester **2** at room temperature in quantitative yield in less than an hour (Scheme 1).



100% conversion
quant. yield

Scheme 1. IMes catalysed transesterification of **1**.

The solid-supported NHC catalyst **5** was prepared in two steps. Thus, commercially available Merrifield resin **3** was treated with 1-methylimidazole in $CHCl_3$ to yield polymer supported imidazolium chloride **4**[17] with around 0.5 mmol/g of imidazolium as determined by elemental analysis. Activation of **4** was achieved by passing a solution of KO^{t}Bu across the catalyst under continuous flow, followed by washing with THF (Scheme 2). To allow good solvent flow the catalyst was diluted with ground 3 Å molecular sieves in glass Omnifit columns. All experiments were performed using a Vapourtec E-series equipped with temperature control and pressure monitoring.

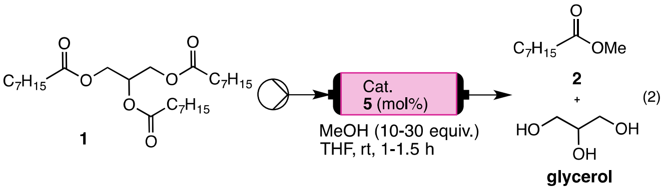


Scheme 2. Preparation of polymer supported NHC **5**.

Optimisation of the continuous flow transesterification began by examining the impact of catalyst loading on the reaction (Table 1). Increasing the catalyst loading from 5 mol % (Table 1, entry 1) to 10 mol % increased the yield while 20 mol % resulted in only marginal additional increase (Table 1, entries 2 and 3). Similarly increasing residence time from 30 min to 60 min gave a small increase in yield (Table 1, entry 4), while a further increase to 90 min showed no further improvement (Table 1, entry 5). Finally, increasing methanol content from 10 to 20 or 30 equiv with 10 mol % catalyst led to quantitative conversion, and a 98% isolated yield of monoalkyl ester **2** (Table 1, entry 6 and 7).

Having established conditions for the continuous flow transesterification of triglyceride **1**, the stability of the polymer-supported NHC catalyst was examined. A column of catalyst **5** was subjected to five consecutive runs for the conversion of **1** to the monoalkyl ester **2** (Scheme 3, runs 1–5). Over five runs, a drop of 5–6% was observed in the conversion and yield, indicating that the solid catalyst **5** was largely stable to the reaction conditions. It was speculated that formation of channels through the catalyst bed might reduce the effective contact of the solution with the catalyst, and cause the small reduction in yield. To test this hypothesis, the NHC catalyst was removed under a nitrogen atmosphere then repacked into the reactor column. This reloaded catalyst was subjected to the same reaction conditions and the reaction repeated (Scheme 3, run 6), unfortunately its performance was not improved. Next the possibility the NHC catalyst was being deactivated by protonation was examined. Thus, the catalyst was reactivated with KO^{t}Bu (1.5 equiv) followed by washing with THF. These washings were performed until no spectroscopic evidence for KO^{t}Bu was observed. This is necessary as in control experiments it has been demonstrated that homogeneous transesterification can be achieved using KO^{t}Bu. After this treatment the transesterification was carried out 3 more times, displaying improved reactivity similar to the initial activity of the catalyst (Scheme 3, runs 7–9).

Table 1
Optimisation of NHC catalysed transesterification



Entry	Cat. **5** (mol %)	Residence time (min)	Methanol (equiv)	Conversion (%)[a]	Yield (%)[b]
1	5	30	10	84	80
2	10	”	”	90	87
3	20	”	”	91	88
4	10	60	”	92	87
5	”	90	”	92	88
6	**”**	**60**	**20**	**100**	**98**
7	”	”	30	100	98

[a] Determined by GC analysis.
[b] Isolated yield of **2** following column chromatography.