

CONTINUOUS BIODIESEL PRODUCTION WITH CONTINUOUS LIQUID-LIQUID EXTRACTION AND ONLINE MS ANALYSIS

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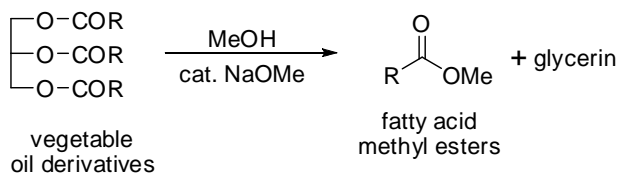
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Introduction

Biodiesel is an alternative fuel for diesel engines that is gaining attention in the US. Its advantages are that: it is a renewable fuel; it is non-toxic and is biodegradable and can be used in diesel engines without requiring extensive engine modification.¹⁻³

Biodiesel production involves the conversion of triglycerides into fatty acid esters, typically under Zemplén conditions. The rate limiting step in these reactors is not chemical kinetics, but mass transfer due to the immiscibility of the vegetable oil and the alcohol. The shear forces in the stirred tank reactors are not sufficient to effectively mix the two phases.



Scheme 1. Transesterification of vegetable oil into biodiesel

The petrochemical industry has purposely adopted continuous flow processes over batch processing to maximize both yield and efficiency. The use of microreactors in biodiesel production offers many advantages when compared with traditional batch processing. Mixing is achieved in very short time frames, even for immiscible phases. The continuous flow allows for rapid process optimization, as stoichiometry and reaction conditions are more easily manipulated^{4,5}. Finally, both scale-up and scale-out are supported in continuous flow processes, allowing for rapid commercialization. Herein we report the application of a commercially available continuous flow microreactor system to the efficient production of biodiesel.

Continuous flow production readily lends itself to Process Analytical Technology (PAT) by facilitating the precise control and measurement of process-critical parameters in real time. To apply this to our method for biodiesel production, a commercially available autosampler and mass spectrometer were used in-line to continuously analyze the product stream. The use of in-line sampling and analysis eliminated the need for tedious sample preparation steps and allowed for real time analysis of the crude biodiesel product stream.

To further streamline the process, in-line aqueous extraction⁶ allowed for continuous removal of the glycerol byproduct from the biodiesel stream. This was achieved via introduction of water to the reaction stream, with the glycerol/aqueous immiscible phase being separated via a microfluidic channel fitted with a polytetrafluoroethylene (PTFE) membrane.⁶ The hydrophobic

biodiesel was able to traverse the membrane, whilst the hydrophilic aqueous/glycerol phase did not.

Experimental

Transesterification. The oil used in this study contained circa 80 % triolein² by mass, where R = (CH₂)₇CH=CH(CH₂)₇CH₃., it was diluted with 2 parts dichloromethane (DCM). Methanolic sodium methoxide (0.1 M) was used for the transesterification. The microfluidic apparatus consisted of two dual piston Syrris reagent pumps, a Syrris two input 250 μL microreactor (Fig. 1), and the Syrris Flow Liquid-Liquid Extraction (FLLEX) module (Fig. 2).

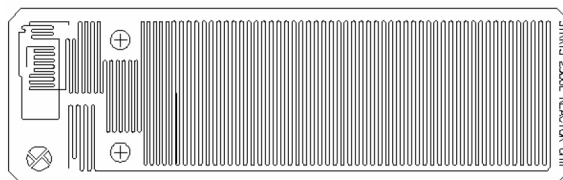


Figure 1. Commercial 250 μL continuous flow microreactor channel width 300 μm; the microreactor had two inputs channels combining at a T-piece and one output channel

The triolein solution (50 μL/m) was combined with the methanolic solution (50 μL/m) in the microreactor. The two immiscible flow streams formed an alternating slug/plug flow of microdroplets of oil-aqueous-oil-aqueous; this 'slug/plug-flow' is a common phenomenon in the microfluidic region.⁷ The admixture exiting the chip was diluted with water (100 μL/m) in the FLLEX module. Liquid-liquid extraction of the admixture in flow affords biodiesel in DCM, while the aqueous layer contains the methanol and glycerol byproducts.

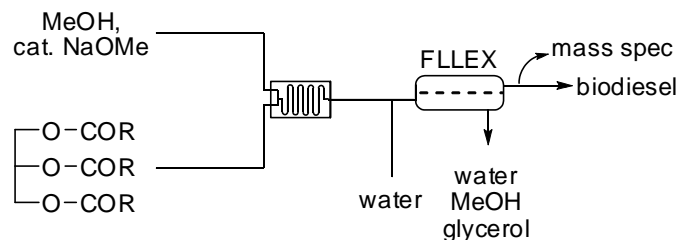


Figure 2. Continuous flow production of biodiesel

Optimization of the transesterification reaction was undertaken by modulation of the residence time in the microreactor at ambient temperature. A residence time of 2.5 minutes at room temperature was sufficient for complete conversion of triolein to methyl oleate (Fig. 3,4). This method is significantly faster than reported microwave flow methods while proceeding at ambient temperature.^{4,8}

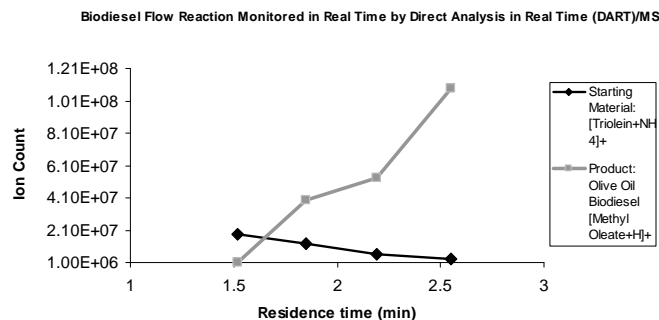


Figure 3. Depletion of starting material and production of biodiesel.

Analysis. An aliquot of the total flow stream was continuously fed into a mass spectrum system comprising a Ionsphere DART (Direct Analysis in Real Time) Atmospheric Pressure Ionization Source and a Finnigan LCQ Deca (Ion Trap) mass spectrometer. The in-line mass spectrum system was quickly used to quantify the reaction progression (Fig. 4)

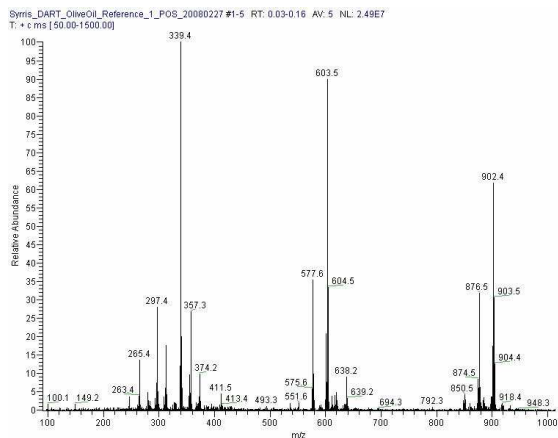


Figure 4A. Triolein DART Reference Spectrum

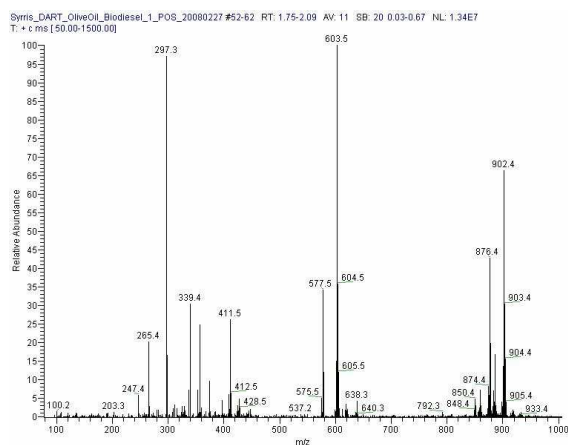


Figure 4B. Biodiesel DART Spectrum: Triolein with a 3 molar equivalents of methanol, partial conversion triolein to methyl oleate. Residence time on microreactor 1.5 minutes.

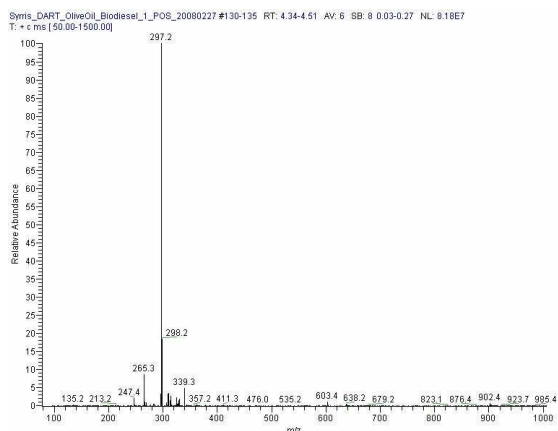


Figure 4C. Biodiesel DART Spectrum: Triolein with a 3 molar equivalents of methanol, 100 % conversion triolein to methyl oleate. Residence time on microreactor 2.6 minutes.

Conclusion

This proof of principle experiment demonstrates the utility of microfluidics in the production of biodiesel. The use of continuous flow liquid-liquid separation facilitates rapid and efficient isolation of the fatty acid methyl esters, while in-line analysis allows for real time monitoring and optimization of the process conditions.

Acknowledgment

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