

Synthesis of Biodiesel in Microstructured Reactors under Supercritical Reaction Conditions

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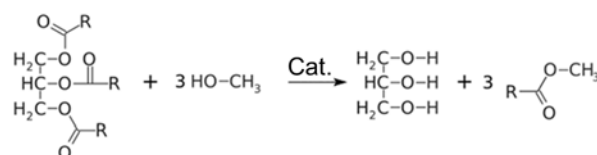
At IMM the advantages of an alternative synthesis route for biodiesel under supercritical conditions in micro-structured reactors applying heterogeneous catalysts are currently under investigation. Target of the development work is to build a pilot plant with an annual production capacity of 40 t which covers all process engineering steps and verifies their functionality in laboratory and field trials. The supercritical process applying catalysts has not been investigated in a continuous plant to date.

The development work covers so far the optimization of the supercritical process conditions in absence of catalyst, which revealed full conversion in less than 5 min residence time. The preliminary screening of heterogeneous catalysts applying a model feed (Tricaprin) revealed full conversion in less than 30 s residence time over alumina catalysts. Based upon an ASPEN model of the process, a flow scheme of the future plant was set up.

1. Introduction

Biodiesel, a mixture of mono alkyl esters of long chain fatty acids, is currently added in a quantity of 7 % to regular diesel fuel and up to 20 % to heating oil. Through its lubricating properties it replaces lubricating sulphur compounds formerly present in diesel fuel. It reduces the CO₂ emissions compared to conventional diesel by almost 70%. The admixture limit of the vegetable oil is increased through the transesterification, because the viscosity of the esters is much lower compared to the oils. The combustion properties of heating oil are improved by the addition of biodiesel.

The transesterification of biodiesel from vegetable oils produces the Alkyl esters and the by-product glycerol:



(1)

The conventional, homogeneously catalysed method has a number of drawbacks such as the large reactor volume required, the sensibility against free fatty acids and water, the poor quality of the glycerol by-product and the complex waste water treatment. These drawbacks get increasingly relevant, when decentralized production in mobile plants is considered, which has advantages concerning the transportation cost when compared to centralized plants of larger scale. The conversion of alternative feedstock such as animal grease or waste cooking oil further complicates the process (Maddikeri et al., 2012). In the current work the catalyst-free and heterogeneously catalysed biodiesel production under supercritical conditions, which was reported first time by Saka et al. (Saka and Kusdiana, 2001) was subject of the investigations. Eco-balances and economic analysis of the process revealed advantages of this process compared to conventional technology, when waste oils are used as feedstock (Morais et al., 2010, Lee et al., 2011). The supercritical process is neither affected by water present in the feedstock up to concentrations of 10-20 % and more (Kusdiana and Saka, 2004) nor by free fatty acids, while the glycerol by-product has a much higher purity compared to the conventional process, which creates economic advantages. The

process has the potential of replacing methanol by less toxic ethanol, which further reduces the environmental impact (Nascimento et al., 2013).

2. Experimental

The catalysts were coated onto stainless steel microchannels by applying a washcoating process. The microstructured plates were cleaned with isopropanol in an ultrasonic bath and then annealed at 800°C for two hours in order to induce the formation of oxide layers on the steel surface leading to improved adhesion of the coatings. The α - and γ -Al₂O₃ powders were used as received from ALFA AESAR (α -Al₂O₃) and SASOL (Puralox SBa-200). For the preparation of the acid treated powders, γ -Al₂O₃ and α -Al₂O₃ were impregnated with 1.5 molar phosphoric acid similar to the method described by McNeff et al. (McNeff et al., 2008). The impregnated powder was boiled under reflux for 4 hours, then evacuated and calcined at 350°C. An aqueous suspension containing PVA (polyvinyl alcohol) as a binder, acetic acid (except for the acid treated catalysts) and the alumina powder was applied for the coating process. Initially, PVA was dissolved in water under constant stirring at 65°C for 3 hours. Then the alumina powder was added together with acetic acid (except for the acid treated catalysts) and the mixture was stirred for 3 hours at 65°C, again. Afterwards, stirring at room temperature was continued for 2 to 3 days until a homogeneous suspension was achieved. With the as-prepared suspension, the microchannels were filled completely and excess suspension was wiped off with a sharp tool, e.g. a blade. Finally, the coated plates were dried at room temperature and calcined at 600°C for two hours. Table 1 shows characterization data as determined for the catalysts.

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Catalyst	Specific surface area [m ² /g]	P content (measured by XRF)	Acid strength [adsorbed amount of NH ₃ in μ mol/g]
α -Al ₂ O ₃	8	-	82.15
phosphated α -Al ₂ O ₃	7	P: 0,064±0,004	65.13
γ -Al ₂ O ₃	198	-	383.12
phosphated γ -Al ₂ O ₃	110	P: 14,2±0,7	154.76

Tricaprin (C₃₃H₆₂O₆) was chosen as a model feedstock to allow the identification of feedstock and products by the available GC-MS system through off-line analysis and to simplify the analysis procedure. The substance was dissolved in an excess of heptane, while octane served as internal standard. Hexane has been used as co-solvent for supercritical biodiesel production to reduce the critical parameters by other authors (Muppaneni et al., 2012). The GC-MS analysis of transesterification products was carried out with an Agilent Model 6890.GC coupled to a 5973N Mass Selective Detector, with linear scanning (10-560 Da, 2.74 scans/sec), using a 28 m x 0.25 mm i.d. fused capillary column HP-5MS (Agilent 19091S-433., 0.25 μ m film thickness), which was temperature programmed from 40 °C (hold 3 min) to (20 °C/min) 310 °C (hold 6.5 min). The run time per analysis was 23 min. Mass spectrometric data were acquired and processed using the GC-MS data System (G1701 DA MSD ChemStation) and the identification and quantification of the peaks was made by comparison with the NIST-mass spectra-library and authentic standards. The run and the analysis methods were optimised after a) three mixtures of each component Standards (decane acid methyl ester, Mono-, di- and triglyceride of tricaprins) were injected and the peaks of the TIC (total ion chromatogram) identified and b) each of the components of different concentrations were calibrated.

Figure 1 shows a scheme of the test rig applied for the measurements in absence and presence of catalyst. The alcohol (methanol in most cases) and the heptane/tricaprin/octane mixture are dosed into the reactor by HPLC pumps and mixed through a micro mixer, which improves the feed homogeneity. The feed then entered the reactor which was a tubular reactor (see Figure 2a) when the homogeneous catalyst-free reaction was investigated. Tube diameters of 1/8 " and 3/8 " were used at 0.5 m and 1 m length to achieve the desired residence times between 15 min and 2.5 min. Stacks of microstructured stainless steel plates forming monolithic reactors were used for the investigations in presence of catalyst. The catalysts were introduced as coatings into the microchannels (see Figure 2b) according to a method described elsewhere (Zapf et al., 2003). For each catalyst sample a new reactor was prepared by wet chemical etching of the plates, catalyst coating and sealed by laser welding.

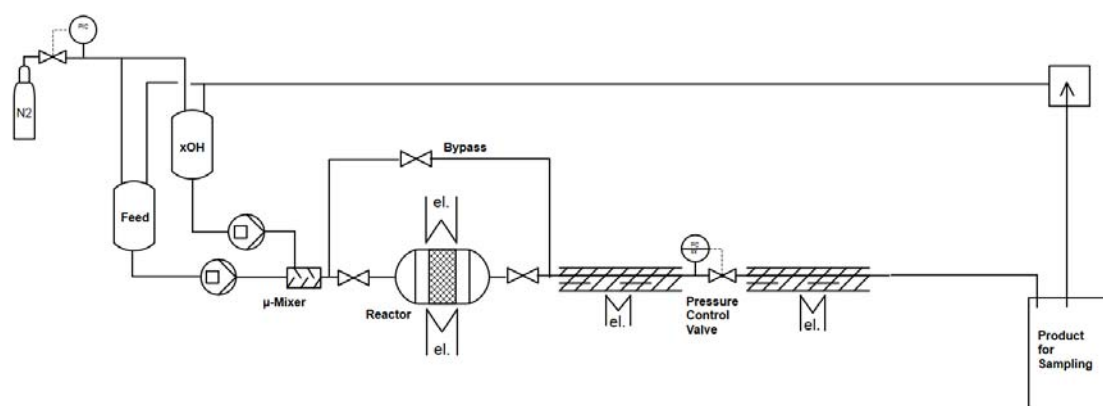


Figure 1: Flow scheme of the laboratory test rig for continuous production of biodiesel under supercritical conditions

The measurements were performed at reaction temperatures between 300 °C and 375 °C at residence times between 2.5 min and 15 min applying pressures between 100 bar and 200 bar, alternatively methanol, ethanol and methyl acetate as reactant and in case of methanol between 5 and 40-fold molar excess. A reaction pressure of 100 bar was determined as sufficient to reach supercritical conditions from calculations applying Triolein as feedstock.

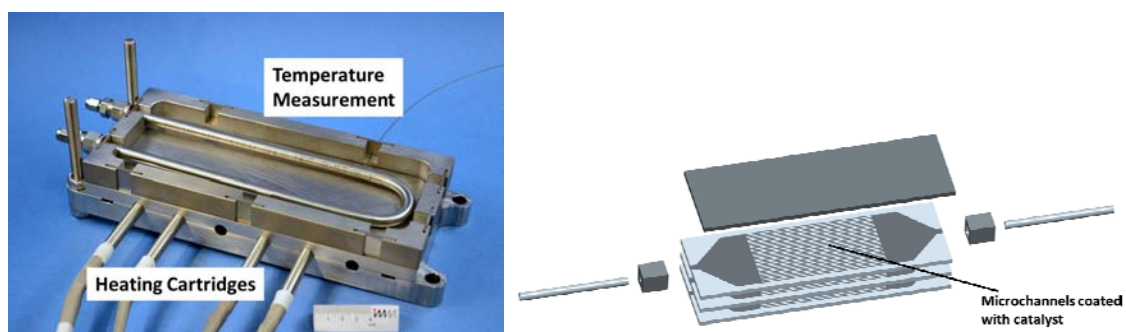


Figure 2: Testing reactors; (a), left: tubular reactor (3/8 ") for homogeneous reaction without catalyst; (b), right: CAD model of the plate stack carrying microchannels, which were coated with heterogeneous catalysts

3. Results

Figure 3a shows the Tricaprin conversion as determined for different methanol excess for different reactants, which is significantly lower for ethanol and methyl acetate. As shown in Figure 3b, higher system pressure did not improve this situation. This was also the case for higher residence times as shown in Figure 3c. It is obvious that the conversion gained with methanol is by far highest under all experimental conditions chosen. Other authors found also lower activity of ethanol (Santana et al., 2012) and higher residence times required (Velez et al., 2012) when compared to methanol in the supercritical process. Similar results were recently found for methyl acetate (Niza et al., 2011). Therefore all further experiments were performed applying methanol. It gets obvious from Figure 4a that at a pressure of 100 bar, 15 min residence time and a reaction temperature of 375 °C is required to achieve full conversion of the feed. However, lower reaction temperatures are not necessarily preferred, because even largest Fatty Methyl Ester (FAME) molecules are stable in supercritical methanol up to a temperature of at least 325°C (Shin et al., 2011) and the decomposition of unsaturated FAMEs even improves the quality of the biodiesel fuel (Anitescu and Bruno, 2012). Figure 4b shows that a pressure of 200 bar is required to achieve full conversion of the Tricaprin at 5 min residence time.

The better mass transfer in the plate reactors compared to the tubular reactors lead to increased conversion of the Tricaprin as shown in Fig. 5a, which was also observed for reactors of different design

by other authors (Xiang et al., 2011). When switching to the plate reactors containing the catalyst coatings, much higher conversion was achieved immediately. As shown in Figure 5a, full conversion of the Tricaprin could already be achieved at 5 min residence time and a lower pressure of 100 bar over α -alumina catalyst. Through the introduction of γ -alumina and treatment of the catalysts with phosphoric acid the residence time required to achieve full conversion of the feed could be reduced to less than 15 s.

An ASPEN model was set up of the complete process applying triolein (Gomez-Castro et al., 2010) as model feedstock. The mixture of triolein and methanol is introduced by high pressure pumps through a micro-mixer into the process and then pre-heated through a heat-exchanger to the reaction temperature and supercritical conditions. The product is then cooled down by the heat-exchanger mentioned above and a pressure relief valve reduces the pressure of the product. Gaseous methanol is fed to a condenser, while a vacuum rectification column with 5 theoretical plates separates the remaining methanol from the biodiesel/ glycerol mixture. The vacuum rectification reduces the critical energy consumption of the process compared to conventional rectification (Kiwjaroun et al., 2009). The vacuum for the rectification process is provided by the condenser, In a decanter downstream of the rectification column the biodiesel product is separated from the glycerol. Continuous centrifuges are not yet suited for the plant size envisaged. The methanol is then fed back to the process. Figure 6 shows a CAD model of the entire plant with a production quantity of 40 t/y, which could be already a practical size for certain applications (Kelloway et al., 2013). Owing to the low residence time required for the heterogeneously catalyzed process, the reactor volume amounts to only 0.25 L.

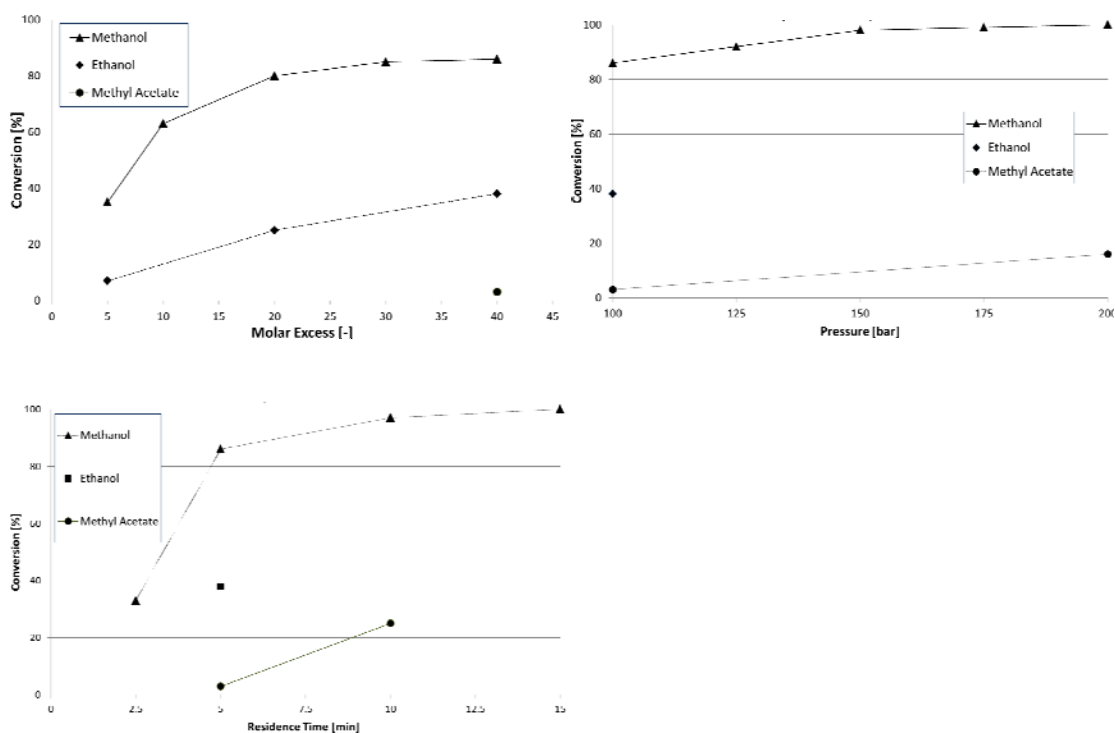


Figure 3; (a),top left: Tricaprin conversion for different reactants and molar excess thereof as determined at 375 °C reaction temperature, 100 bar pressure and 5 min residence time; (b),top right: Tricaprin conversion for different reactants and reaction pressure as determined at 375 °C reaction temperature, 40 fold excess of methanol and 5 min residence time; (c),bottom left: Tricaprin conversion for different reactants and residence time as determined at 375 °C reaction temperature, 40 fold excess of methanol and 100 bar reaction pressure

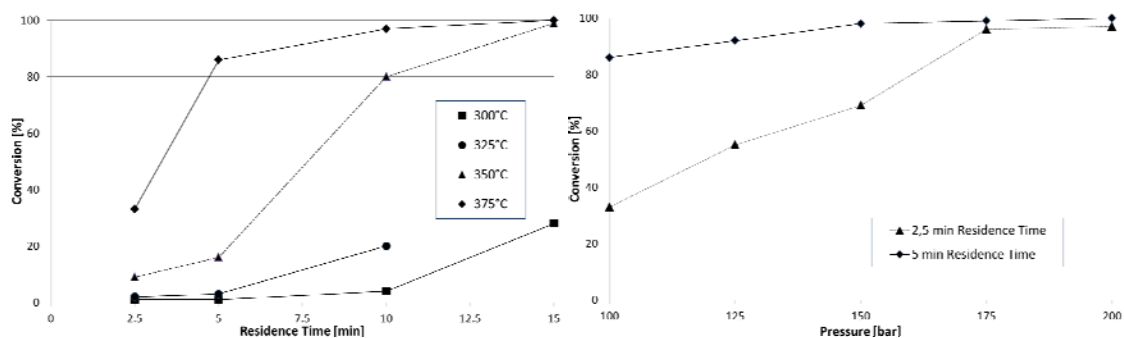


Figure 4; (a), left: Tricaprin conversion at different residence times and temperatures as determined at 100 bar reaction pressure and 40 fold methanol excess (b), right: Tricaprin conversion at different reaction pressure and residence time as determined at 375 °C reaction temperature and 40 fold molar excess of methanol

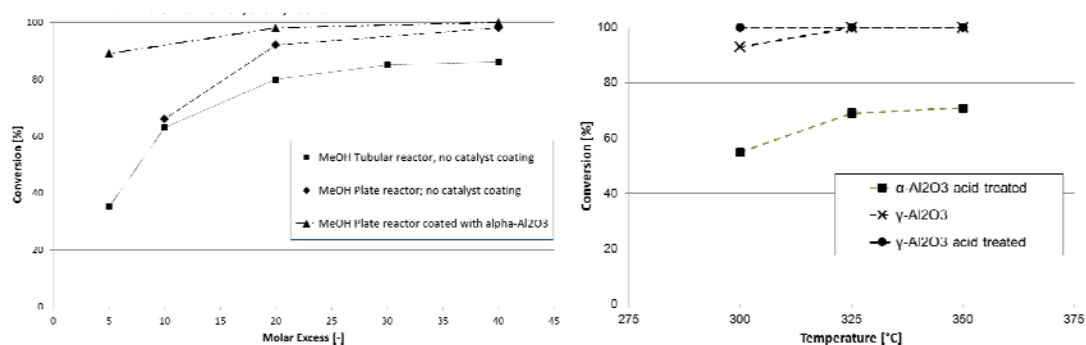


Figure 5; (a), left: tricaprin conversion at 40 fold molar methanol excess as determined without catalyst (tubular reactor) and with α -Al₂O₃ catalyst (plate reactor) at 100 bar reaction pressure, 5 min residence time and 375 °C reaction temperatures; (b), right: tricaprin conversion as determined in plate reactors at different reaction temperature and catalysts at 11 s residence time, 100 bar reaction pressure and 40 fold molar excess of methanol

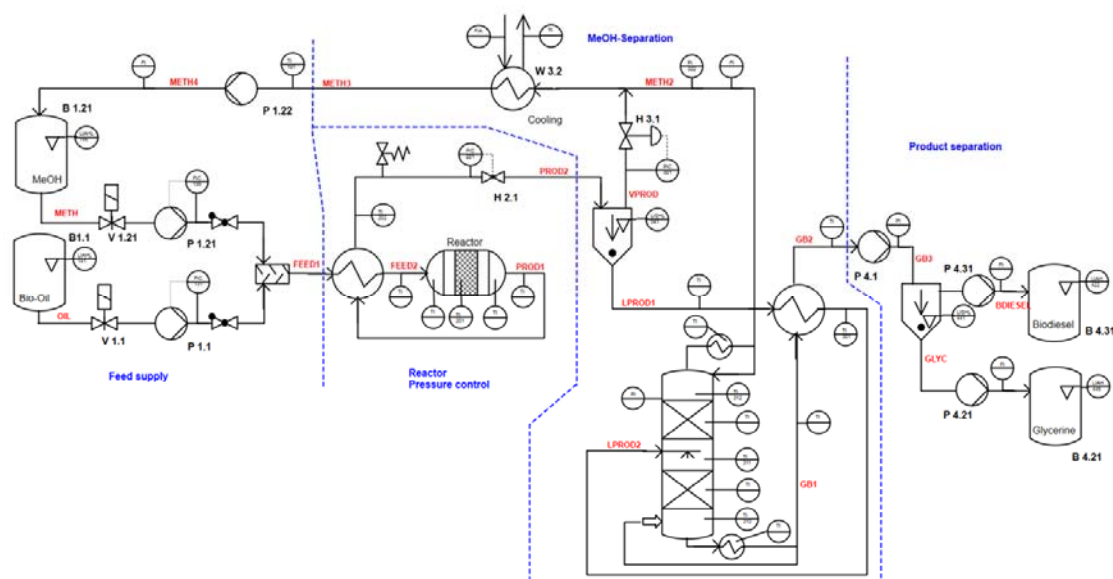


Figure 6: CAD model of the a complete demonstration plant for the continuous production of biodiesel under supercritical conditions with a capacity of 40 t/y

4. Conclusions

The current work revealed complete conversion of the model feed tricaprin under supercritical conditions in absence of catalyst at 200 bar reaction pressure, 5 min residence time and 40 fold methanol excess. Alternative feedstock such as ethanol and methyl acetate showed much lower activity compared to the methanol. By the introduction of heterogeneous catalysts the required pressure could be reduced to 100 bar and the residence time to less than 15 s.

Future work will cover the investigation of alternative catalyst formulations, the verification of the long term stability of the catalysts developed and the verification of their suitability and durability for the conversion of alternative feedstock such as waste cooking oil and the set-up and operation of the pilot plant followed by an economic analysis of the process compared to conventional biodiesel plants.

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