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Catalyst-free microwave-assisted conversion of free fatty acids in triglyceride feedstocks with high acid content

Jeroen Geuens [a,b], Sergey Sergeyev [a], Bert U.W. Maes [a], Serge M.F. Tavernier [b,*]

[a] University of Antwerp, Department of Chemistry, Groenenborgerlaan 171, B-2020 Antwerp, Belgium
[b] Karel de Grote University College, Department of Applied Engineering, Salesianenlaan 30, B-2660 Hoboken, Belgium

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ABSTRACT

The catalyst-free microwave-assisted conversion of free fatty acids (FFA) to alkyl esters in triglyceride feedstocks with a high acid content was studied. To this end, esterification of FFA with higher alcohols was investigated using the response surface modelling approach (RSM). A model was constructed using stearic acid and 1-butanol. The influence of reaction temperature and the FFA content in the triglyceride feedstock were studied by varying both parameters on 5 levels between 175 °C and 275 °C, and 30 mass% and 100 mass% FFA respectively. Afterwards, the general applicability of the model was verified using other FFA, fatty acid distillates (FAD) from industry and other alcohols. When using other FFA, FAD or primary alcohols other than 1-butanol, the model is able to accurately predict the actual conversion with a typical deviation between actual and predicted data of 2%. After 1 h of reaction at temperatures above 250 °C, conversions over 90% were reached.

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1. Introduction

Currently, most fatty acid alkyl esters are produced by means of alkali-catalysed transesterification of triglycerides of food quality or a quality close to that. Low-grade triglyceride streams such as used cooking oils and lipid fractions from municipal sewage sludges contain too much free fatty acids (FFA) to be converted by means of said process and therefore they are often treated as waste [1]. However, these FFA-rich triglyceride streams could be given a second life by converting the FFA into fatty acid alkyl esters using homogeneous or heterogeneous acidic catalysis [2–4]. When a homogeneous catalyst is used, washing steps are required to remove the catalyst after reaction. The use of heterogeneous catalysts could be beneficial because said steps can be omitted, thus avoiding the production of large quantities of waste water. Literature reports several heterogeneous catalysts which can be used for the production of methyl esters from FFA [5,6]. However, most of these catalysts are either very expensive, cannot be reused due to leaching or require high temperatures to carry out the esterification. As an alternative, catalyst-free esterification could also be considered. It requires higher temperatures but does not suffer from high catalyst costs or the need for washing steps to remove the catalyst.

Earlier publications indicate that the catalyst-free esterification of FFA is possible when using a high temperature (270–300 °C) and a high alcohol to FFA molar ratio (42:1) [7–10]. A recent publication by Pinnarat et al. showed that, for the esterification of oleic acid with ethanol, 90% conversion can be obtained when performing the reaction at 200 °C with a molar ratio of 7:1 (ethanol:oleic acid) [11]. However, 300 min of reaction time are needed to obtain this conversion. Moreover, the reaction between oleic acid and ethanol was only studied as such, while in 'real life' situations, FFA will mostly be present in feedstocks containing also triglycerides (and to a lesser extent also mono- and diglycerides).

At the moment, most esterification reactions on FFA are conducted using methanol, however, methanol is a petroleum-based chemical and therefore this process is not renewable. Other alcohols such as for example ethanol and butanol can be produced in a renewable way using fermentation processes [12]. Moreover, fatty acid alkyl esters of higher alcohols have a wider application range (lubricants [13,14], plasticizers [15,16], phase change materials [17,18], cosmetics [19–21], …) while the use of fatty acid methyl esters is more or less limited to biofuel or biofuel-related applications.

The reaction mixture was heated by means of microwave irradiation because this heating method has several advantages over conventional heating [22]:

1. if at least one of the components in the reaction mixture couples with microwaves, much higher heating rates can be achieved;

* Corresponding author. Tel.: +32 3 613 19 24.
E-mail addresses: jeroen.geuens@kdg.be (J. Geuens), serge.tavernier@uantwerpen.be (S.M.F. Tavernier).

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2. microwave energy is remotely introduced, there is no contact between the energy source and the reaction mixture;
3. since some chemical compounds couple more efficiently with microwaves, selective heating can theoretically be achieved. If the containment material is microwave transparent, only the reaction mixture will be heated.

The advantages mentioned above make microwave heating an ideal method for performing chemical reactions in closed vessel conditions under increased pressure which means higher temperatures can be used, leading to increased reaction rates.

In this publication, the response surface modelling approach was used to study the influence of reaction temperature and concentration of FFA in the triglyceride feedstock on the catalyst-free microwave-assisted esterification of FFA with higher alcohols. The model was constructed using stearic acid and 1-butanol. To vary the amount of acid, stearic acid was diluted with rapeseed oil. After construction of the model, its general applicability was tested using other FFA, 'real life' industrial waste streams with a high FFA content and other alcohols.

2. Materials and methods

2.1. Materials

FFA and alcohols were purchased from Merck or Acros, 1-butanol was purchased from Brenntag NV and rapeseed oil was obtained from A.K. Gistel. Two fatty acid distillates (FAD) were kindly provided by De Smet Ballestra, i.e. palm FAD and animal FAD. In order to obtain different concentrations of FFA, the FAD were mixed with the oil/fat they originated from, i.e. palm oil or animal fat. The latter were also provided by De Smet Ballestra. The concentration of FFA in rapeseed oil, palm oil, palm FAD, animal fat and animal FAD were determined by means of an acid titration using a Mettler Toledo DL53 Titrator equipped with a DG113-SC electrode. Next to that, the water content of the different oils/fats was determined by means of a Karl-Fischer titration using a Mettler Toledo V20 Volumetric KF Titrator and the amount of mono-, di- and triglycerides was determined by means of size exclusion chromatography on an Agilent 1100 series system using isocratic elution with THF and refractive index detection. The results of these measurements can be found in Table 1.

The fatty acid profiles of all 4 industrial FFA streams, as well as the fatty acid profile of the rapeseed oil were measured by means of gas chromatography (GC) using a 15% (vol/vol) solution of sulphuric acid in methanol to convert the FFA and the triglycerides to fatty acid methyl esters, followed by an extraction with heptane. For information about the GC method and the results of the analyses we refer to the Supplementary Data.

2.2. Esterification reactions

All esterification reactions were performed in a Synthos 3000 multimode microwave reactor (Anton Paar GmbH). Since organic solvents such as 1-butanol become microwave transparent at higher temperatures, SiC passive heating elements were used in order to reach the set temperatures. All reactions were performed using a molar ratio of 8.5:1 alcohol:FFA, whereas either pure FFA or a mixture of FFA and triglycerides was used. For example, stearic acid (9.15 g) was mixed with 1-butanol (25 mL). After reaction, a sample from the reaction mixture was analysed by means of an acid titration in order to determine the degree of conversion of the acid into the corresponding alkyl ester. More detailed information on the experimental procedure can be found in the Supplementary Data.

Table 1
Acid content of the oils and fats used in the experiments.

Oil/fat	FFA (mass%)	Water content (ppm)	TG (%)	DG (%)	MG (%)
Rapeseed oil	0.7	580	96	3	1
Palm oil	6.2	640	87	3	1
Palm FAD	91.3	1540	1	3	1
Animal fat	25.6	720	44	16	3
Animal FAD	83.6	2200	3	5	8

3. Results and discussion

3.1. Theoretical model

A circumscribed central composite design (CCC) was set up for the 2 parameters (reaction temperature and % of FFA) using the Design-Expert 8.0 software from Stat-Ease. It was decided to measure 6 center points. Together with 4 axial points and 4 factorial points, this leads to a total of 14 design points. Since all the design points were measured twice, a total of 28 experiments was performed. Recent research by our group showed that triglyceride streams containing up to 30% FFA can be converted to fatty acid alkyl esters with a yield of 80% and higher at temperatures starting from 245 °C [23]. Since lower reaction temperatures are beneficial for the process (less energy consumed), the temperature was set to vary on 5 levels between 175 °C (−1.4) and 275 °C (+1.4). The FFA content was varied between 30% (−1.4) and 100% (+1.43), also on 5 levels. Variations in the FFA content were obtained by adding rapeseed oil to the stearic acid. The reaction time was kept constant at 2 h. A graphical presentation of the design is given in Fig. 1.

Because of the use of SiC passive heating elements, it was not possible to use a direct contact temperature probe. Thus, temperature was monitored by means of an infrared (IR) temperature measurement on the outside of the vessel (at the bottom). Comparative measurements using the direct contact temperature probe confirmed that the IR measurements were always ca. 30 °C lower than the actual temperature inside the vessel [24]. All temperatures mentioned in this manuscript refer to temperatures inside the reaction vessel, measured by means of the IR sensor and corrected using a 30 °C correction factor.

During the experiments, it was noticed that not all vessels reached the set temperature, therefore, the average measured temperature during the total reaction time was used to construct the model, rather than the set temperature.

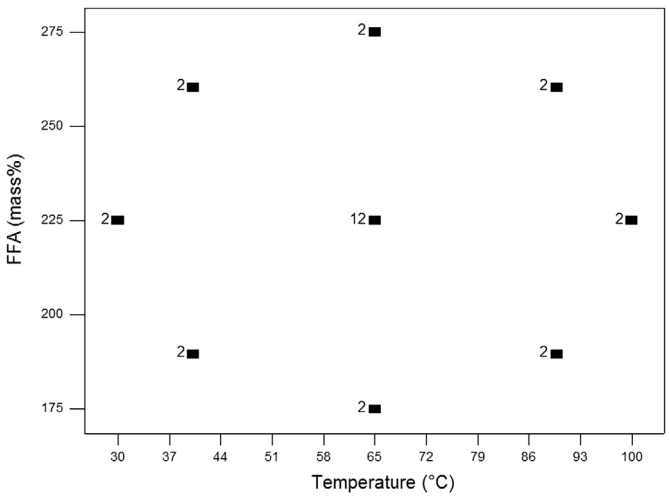

Fig. 1. Graphical presentation of the used CCC design.

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