Method and System for the Esterification of Fatty Acids

The invention relates to a method for the esterification of fatty acids and/or fatty acids contained in fats and oils with low monovalent alcohols, especially methanol, whereby the fatty acids with strong mineral acids, such as sulphuric acid, dissolved in lower alcohols, especially in methanol and/or exclusively in lower alcohols, especially in methanol, are compounded with acid ion exchanger resins. Furthermore, the invention relates to a system for the implementation of said method.

From the textbooks for organic-preparatory chemistry, such as „Organikum", 13th ed.,1974 page 441 et seq. or Weygand/Hilgetag, „Organisch- Chemische Experimentierkunst, 4th ed., 1970, page 377 et seq., it is known that carboxylic acid esters or fatty acid esters may be esterified by esterification of the free acids with lower alcohols, preferably at the temperature of ebullition of the alcohols in presence of strong acids, such as hydrogen chloride, sulphuric acid or sulphonic acids.

A method for the esterification of a fatty acid/fatty acid ester mixture, isolated from the "glycerine phase", is described in EP 708 813 A, whereby the free fatty acids obtained from the neutralisation of the "glycerine phase" are heated to a temperature of 85 °C for two hours, with methanol and concentrated sulphuric acid acting as a catalyst, whereby the content of free fatty acids decreases from about 50 % to 12.5 % and whereby the entire mixture is supplied without any further treatment to an alkali-catalysed transesterification and the catalyst acid is exported through the transesterification process.

Further methods for the esterification of free fatty acids are described in EP 127 104 A, EP 184 740 A and US 4 164 506 A, whereby the free fatty acids are present in a mixture with fatty acid triglycerides and the esterification is carried out by means of heating with methanol at 65 °C, whereby sulphuric acid or a sulphonic acid act as a catalyst.

The serious disadvantage of all these known methods lies in the fact, however, that the esterification step requires an enormous amount of time. Thus, as a rule said kind of esterification requires stirring over a period of two to three hours.

Disclosed herein is a method of the above-mentioned type which allows a rational production in an economically acceptable system, preferably in an industrial-sized system, but is also economic in small systems.

In a first aspect of the present invention, there is provided a method for the esterification of fatty acids and/or fatty acids contained in fats and oils with low monovalent alcohols, especially methanol, whereby the fatty acids with strong mineral acids, such as sulphuric acid, dissolved in lower alcohols, especially in methanol and/or exclusively in lower alcohols, especially in methanol, are compounded with acid ion exchanger resins, characterised in that in a reaction section the interphases of the mixture are enlarged by high or powerful dynamic shear forces and/or turbulence, whereby the esterification starts under high pressure and the pressure is reduced during the esterification, whereby

the pressure loss maintains a high interphase, and in that said reaction is carried out in the reaction section at a high temperature.

In a second aspect of the present invention, there is provided a system for the implementation of the method as defined in the first aspect, characterised in that the reaction section is a pipe filled with balls of the same size or different sizes and/or possibly has devices such as baffles, propellers or the like.

The method disclosed is characterised in that in a reaction section the interphases and boundary surfaces respectively of the mixture are increased by means of high or powerful dynamic shearing forces and/or turbulence, whereby the esterification starts under a high pressure and the pressure is reduced during esterification, whereby the pressure loss maintains a high interphase, and in that said reaction is carried out in the reaction section at a high temperature.

Disclosed herein allows for the first time a pre-product for the production of bio-diesel by means of base-catalysed transesterification. Thus, the possibility is provided to produce diesel fuel, so-called eco-diesel or bio-

diesel, in ecologically optimal conditions of production while maintaining all the advantages thereof. Positive economic and ecological arguments can be provided which will stimulate a more intensive discourse on the role of renewable energy and resources.

Another surprising results is disclosed , namely in the field of waste management or hazardous waste disposal. It is also possible to recycle and reuse used table oil ecologically, even if said oil has a high content of fatty acids. The use of used table oil in the method disclosed is possible without reservations due to the high purity of the end products.

It is possible to accelerate the reaction through the enlargement of the interphases and through dynamic processes during the transesterification. Due to the high and powerful dynamic turbulence respectively, the size of the drops in the liquid phases is effectively reduced, so that much smaller drops are produced, resulting in a much larger surface, which means that the chemical balance state is reached faster. Reaching the chemical balance state may take less than a minute. This means an enormous shortening of the reaction time. However, said method is not suited for the so-called sedimentation method, since the sedimentation times would be too long due to the fine distribution of the drops.

According to a special feature disclosed herein, the pressure at the beginning of the reaction section lies at 2 to 500 bar, in particular at 50 to 200 bar and most preferably between 70 and 150 bar. Due to the high pressure, the methanol remains liquid.

In accordance with a further particular feature disclosed, the reaction is carried out in the reaction section at a temperature of 50 to 300 °C, in particular at 80 to 150 °C. Due to the high temperature, the high reaction rate is reached.

According to an embodiment of the invention, the high shear forces and powerful dynamic turbulence respectively are produced by mechanical devices. Said type of devices is easy to install and therefore does not require much maintenance during operation. The turbulence is created primarily by the rapid flow of the mixture around said devices. Moreover, such a reactor is inexpensive and extremely compact.

According to another embodiment of the invention the large interphases are created by ultrasound. Integrating an ultrasound device has proven to be advantageous, since the transesterification can therewith be specifically accelerated through large interphases. According to another special feature disclosed, the reaction section is followed by a non-turbulent post-reaction section. By means of the residence time of the reaction mixture in the post-reaction section, an increase of the esterification degree is obtained.

According to one embodiment of the invention, in the post-reaction section a pressure, preferably the initial pressure of the reaction section, is maintained or possibly further reduced. Maintaining the pressure also contributes to the improvement of the esterification degree. According to specific parameters in the esterification process, however, a further reduction of pressure may also be of advantage.

According to a special further development, the post-reaction section is filled with strong-acid ion

exchangers. In a process implementation with ion exchangers, the compounding of the fats with acids is omitted in a known manner. Also with such a process an optimal esterification process is achieved.

One embodiment also provides a system for the implementation of said method.

The system disclosed is characterised in that the reaction section is a pipe filled with balls of the same size or different sizes and/or possibly has devices such as baffles, propellers or the like. The turbulence can be created primarily by the rapid flow of the mixture around the balls or devices.

In accordance with another embodiment of the invention, an ultrasound device is provided in the reaction section. With the integration of an ultrasound device the transesterification can be specifically accelerated through large interphases.

According to a further embodiment of the invention, the reaction section is preceded by a heater, and a cooler possibly follows the reaction section or the post-reaction section. By means of the heater, the reaction mixture can be brought to the desired high temperature and can be cooled down with the cooler according to the parameters for the process.

According to a further development, a pump, in particular a high-pressure pump, can be provided to introduce the liquid into the reaction section. With the integration of a high-pressure pump, the turbulence can achieve high dynamics and thus *a* large interphase for the transesterification.

The invention will now be explained in more detail based on an embodiment which is illustrated in the drawing.

The Fig. schematically shows a system for the implementation of the method for the esterification of fatty acids.

According to the Fig., the raw material, such as higher, saturated and/or unsaturated fats of vegetable and/or animal origin, containing free fatty acids, flows into a supply line 2 leading to a reaction section 3. The method is particularly suitable for fats having a higher or high content, preferably more than 5 %, of free fatty acids. Said method may, for example, be used with the production of fatty acid methyl ester, whereby a high profitability can be guaranteed.

Naturally, the method may also be used with pure fatty acids.

The lower alcohol, in particular methanol, is pumped into the supply line 2 leading to the reaction section 3 together with the acid, in particular sulphuric acid.

Said reaction mixture 3 is brought to the corresponding temperature by a heater 5 which is arranged before the reaction section 3. The reaction in the reaction section 3 is carried out at a temperature of 50 to 300 °C, in particular at a temperature of 80 to 150 °C.

Said heated reaction mixture is introduced into the reaction section 3 via a high-pressure pump 6. In the reaction section 3 the reaction mixture is exposed to high shear forces, whereby powerful dynamic turbulence is produced. This results in the interphases of the reaction mixture becoming immensely enlarged. The high shearing forces or the powerful dynamic

turbulence are created by mechanical devices in the reaction section 3.

The mechanical devices in the reaction section 3 may be balls 7 of the same size or different sizes. However, it is also possible to provide, possibly in addition, devices such as baffles, propellers or the like.

The enlargement of the interphases of the reaction mixture may also be achieved by an ultrasound device. Of course, said device may also be provided in addition to the mechanical devices.

Due to the high and powerful dynamic turbulence respectively, the size of the drops in the liquid phases is effectively reduced, so that much smaller drops are produced, resulting in a much larger surface, which means that the chemical balance state is reached faster. Reaching the chemical balance state may take less than a minute. This means an enormous shortening of the reaction time.

In the reaction section 3 part of the pressure that is present at the beginning of the reaction section 3 is reduced.

In order to increase the esterification degree, the reaction section 3 may be followed by a non-turbulent post-reaction section 8 which, possibly under the initial pressure of the reaction section 3, calms down the reaction mixture. For this purpose, the post-reaction section 8 is provided with a pressure keeping valve at its end. If this should prove to be more advantageous for the procedure of the process, pressure may also be reduced in the post-reaction section 8.

According to an alternative procedure of the process without the addition of acid, in particular sulphuric acid, at the beginning of the reaction section, there may be provided a strong-acid ion exchanger, in particular an ion exchanger resin, in the post-reaction section .

The post-reaction section can be followed by a cooler, which can cool down the reaction mixture correspondingly, before it is collected in a container for further processing.

In conclusion, it must be pointed out that for better legibility the individual components and assemblies in the drawing are not shown proportionally or to scale.

PATENT CLAIMS

1.A method for the esterification of fatty acids and/or fatty acids contained in fats and oils with low monovalent alcohols, especially methanol, whereby the fatty acids with strong mineral acids, such as sulphuric acid, dissolved in lower alcohols, especially in methanol and/or exclusively in lower alcohols, especially in methanol, are compounded with acid ion exchanger resins, characterised in that in a reaction section the interphases of the mixture are enlarged by high or powerful dynamic shear forces and/or turbulence, whereby the esterification starts under high pressure and the pressure is reduced during the esterification, whereby the pressure loss maintains a high interphase, and in that said reaction is carried out in the reaction section at a high temperature.

2.A method according to claim 1, characterised in that at the beginning of the reaction section the pressure lies at 2 to 500 bar, in particular at 50 to 200 bar and most preferably between 70 and 150 bar.

3.A method according to claim 1 or 2, characterised in that the reaction in the reaction section is carried out at a temperature of 50 to 300 °C, in particular at 80 to 150°C.

4.A method according to claim 1 or 2, characterised in that the high shearing forces and the powerful dynamic turbulence respectively are produced by mechanical devices in the reaction section.

5.A method according to at least one of the claims 1 to 3, characterised in that the large interphases are created by ultrasound.

6.A method according to at least one of the claims 1 to 5, characterised in that the reaction section is followed by a non-turbulent post-reaction section.

7.A method according to at least one of the claims 1 to 6, characterised in that in the post-reaction section a pressure, preferably the initial pressure of the reaction section , is maintained or possibly further reduced.

8.A method according to at least one of the claims 1 to 7, characterised in that the post-reaction section is filled with strong-acid ion exchangers.

9.A system for the implementation of the method according to at least one of the claims 1 to 8, characterised in that the reaction section is a pipe filled with balls of the same size or different sixes and/or possibly has devices such as baffles, propellers or the like.

10. A system according to claim 9, characterised in that an ultrasound device is provided in the reaction section.

11. A system according to claim 9 or 10, characterised in that the reaction section is preceded by a heater and in that the reaction section or the post-reaction section is followed by a cooler.

12. A system according to at least one of the claims 9 to 11, characterised in that a pump, in particular a high-pressure pump , is provided for the introduction of liquid into the reaction section.