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Development of an environmentally benign process for the production of fatty acid methyl esters

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Abstract

The production of fatty acid methyl esters (FAME) is an important intermediate step in oleochemistry. The oleochemical production route starts with the renewable raw materials fat and oil and ends at fatty alcohols and different special products. Fatty acid methyl esters can be formed at mild reaction temperatures by transesterification of natural triglycerides (fats and oils). This contribution will show the development of a continuous process which is considering the main principles of production integrated environmental protection. The main advantages of this process are low energy consumption and minimal waste production. The process alternatives are shown and a scope on future problems which have to be solved to reach a real additional improvement of the fatty acid methyl esters production is given. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Oleochemistry; Transesterification; Reactor design; Catalysis; Process design

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1. Introduction

1.1. Survey on the production processes of fatty acid methyl esters

Fatty acid methyl esters (FAME) are important intermediate products in oleochemistry (Fig. 1). They can be produced by esterification of fatty acids formed by hydrolysis of fats and oils or directly by transesterification of the natural triglycerides with methanol (Jeromin, 1994; Breucker et al., 1995; Gutsche, 1997; Dieckelmann and Heinz, 1989).

In any case the by-product is glycerol. Since the fat splitting gives a strongly with water diluted glycerol (only 10% of the mass is glycerol) and the energy consumption of the glycerol processing has to be taken into account the transesterification route on the way to fatty alcohols is preferable. Nevertheless fat splitting is an important step in oleochemistry because fatty acids are interesting intermediates for the production of different special products in many applications such as esters for cosmetics.

The transesterification at temperatures below 100°C catalysed by alkaline catalysts has great advantages compared to the alternative process at high temperatures of 200–240°C and corresponding pressures of more than 50 bar. The low temperature process shows lower energy consumption and lower investment costs but the raw materials must have a higher quality (Gutsche, 1997). The oils and fats for low temperature transesterification must have a very small content of free fatty acids because the catalyst reacts with the fatty acids under formation of soaps which do not have any catalytic performance at the chosen reaction conditions. A more detailed summary of transesterification technology is given by Jeromin (1994) and Gutsche (1997).

1.2. Transesterification of triglycerides

Fats and oils are natural triglycerides, i.e. fatty acid esters of glycerol. Transesterification of triglycerides is a

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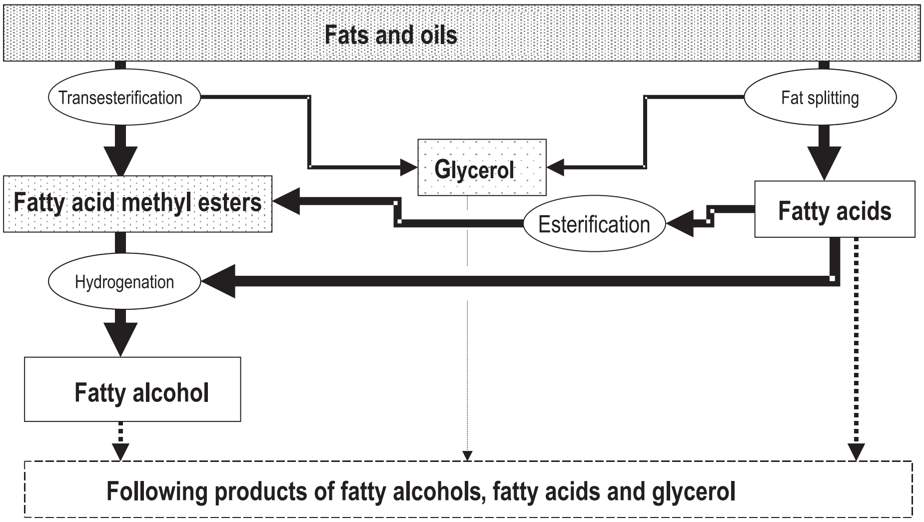

Fig. 1. Oleochemical production routes.

three-step reaction system with the intermediate products diglyceride and monoglyceride (see reaction Eqs. (1a)–(1c):

$$\text{Triglyceride} + \text{Methanol} \rightleftarrows \text{FAME} + \text{Diglyceride} \tag{1a}$$

$$\text{Diglyceride} + \text{Methanol} \rightleftarrows \text{FAME} + \text{Monoglyceride} \tag{1b}$$

$$\text{Monoglyceride} + \text{Methanol} \rightleftarrows \text{FAME} + \text{Glycerol} \tag{1c}$$

Fig. 2 illustrates the reaction progress using a concentration–time diagram for the reaction components triglyceride (TRI), diglyceride (DI), monoglyceride (MONO), glycerol (GLY) and FAME. This diagram shows own results of the transesterification of the pure triglyceride trilaurate measured at 60°C in an ideally stirred laboratory vessel. This experiment was done to clear the kinetics of the reaction: By postulating the order of each reaction of the system it is possible to determine activation energies and preexponential factors and to calculate the temperature dependent rate constants of the three forward and three back reactions. The concentrations shown in Fig. 2 were determined by gas chromatography after quenching the samples with acidified cold ethanol to interrupt the reaction immediately. As Noureddini and Zhu (1997) have shown the reaction progress can be simulated very well by postulating three equilibrium reactions each of second order if it is a homogeneous system.

Typical of oleochemistry used reaction systems show a very special mixing behaviour. The educts triglyceride and methanol are not completely soluble. The starting mixture consists of two liquid phases. With the production of the emulsifying intermediates di- and monoglyceride the reaction system becomes quasi-homogeneous and at higher conversions when the monoglyceride maximum is passed the mixture splits into an ester- and a glycerol phase. The glycerol phase contains the solved alkaline catalyst. The mixing behaviour can explain the acceleration of the reaction after a starting phase of 1 min (Fig. 2).

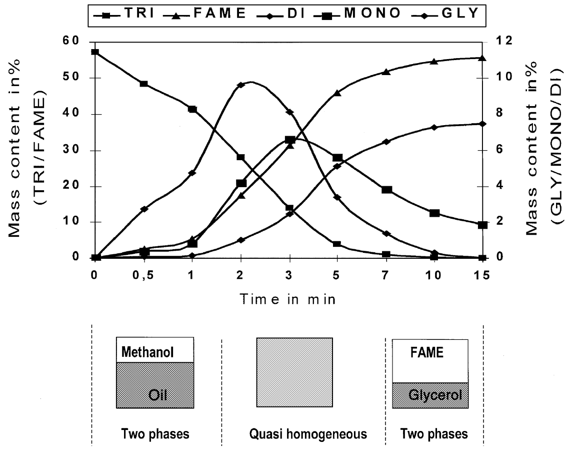

Fig. 2. Kinetic and mixing behaviour – transesterification of trilaurate at 60°C.

The reaction can be catalysed by sodium- or potassium hydroxide dissolved in methanol. In the methanolic solution the corresponding alkoxide is formed which is the active form of the catalyst. The reaction Eq. (2) shows this reaction for sodium hydroxide. Beside Eq. (2) also shows that the more effective catalyst should be the alkoxide in methanolic solution.

$$NaOH + CH_3OH \rightleftarrows NaOCH_3 + H_2O \qquad (2)$$

2. Pretreatment of oils and fats – deacidification

Natural fats and oils are not pure triglycerides. They contain some other components like free fatty acids, phospholipids, tocopherol, carotene and sterols. The content of free fatty acids can reach some weight percents. This is important to know because the base-catalysed transesterification at temperatures below 100°C can only use deacidified and water-free raw materials.

Free fatty acids (FFA) in the raw materials of the transesterification will neutralize the alkaline catalyst and the formed soaps are inactive, i.e. with higher content of FFA the catalyst consumption increases and the result is a higher environmental load because catalyst and soaps leave the process with the by-product glycerol. With increasing water content the activity of the catalyst is reduced, too: Free fatty acids are formed and furthermore the alkoxide equilibrium is unfavourably influenced.

The classical pretreatment of oils and fats is a process normally used in oil mills for deacidification and degumming of the raw materials (Fig. 3). It is an alkaline deacidification, i.e. the FFA are neutralized with sodium hydroxide and the soaps and phospholipids are separated on centrifuges. The oil has to be washed to separate the soaps completely. The soapstock and the used washing water together are treated with sulphuric acid in a soap splitting. The fatty acid produced in the soap splitting is a by-product of the oil refining process with quite low quality. Finally the oil has to be dried and bleached. The described process is able to produce a high quality oil which is absolutely necessary for the use in food applications.

If oil and fats are used as raw materials in alkaline catalysed transesterification processes the requirements are not as high as in food industry, it should be sufficient to use deacidified raw materials with low water content. So a pretreatment was developed which is able to convert the free fatty acids to fatty acid methyl esters by esterification of the fatty acids with methanol (Jordan and Gutsche, 1999; Breucker et al., 1995). This preesterification can be carried out very advantageously at 60–80°C in a fixed bed reactor with a heterogeneous catalyst. Catalyst is a strongly acidic macroporous ion-exchange resin. The preesterification process consists of one reaction step and one distillation step to separate the water formed by reaction. The distillation can be done on falling film evaporators.

In relation to the FFA-content in the treated oils and fats the methanol excess must be very high because the catalyst has a high water affinity. Due to the high water concentration at the reactive centres the esterification equilibrium is influenced unfavourably and the methanol excess must be very high. If low quality oils and fats with high acid values of more than 15 are used the methanol excess gets so high that it is interesting to think

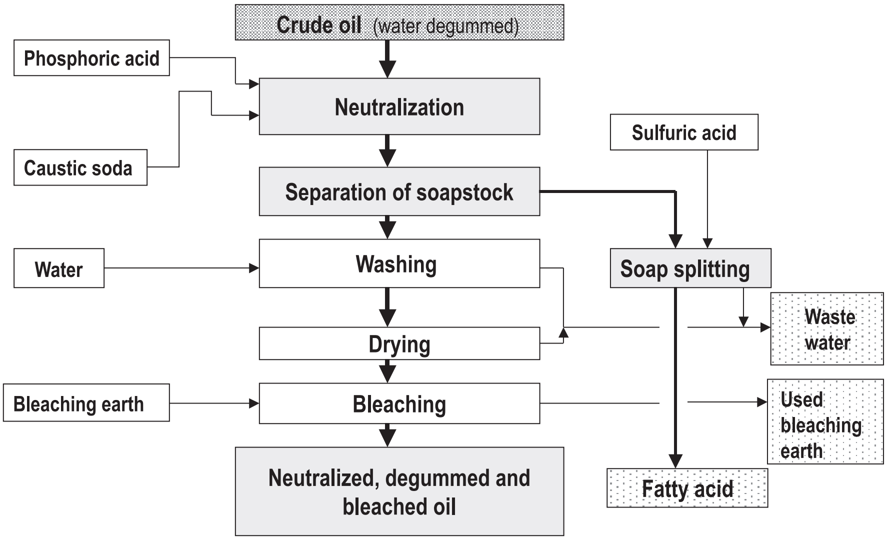

Fig. 3. Chemical oil refining by neutralization.

about a more sophisticated reaction technology such as counter current esterification. Counter current processes are for example used in oleochemistry to produce fatty acid methyl esters by esterification of fatty acids with methanol (Jeromin, 1994).

The main advantage of the preesterification compared to the classical refining is that there are no waste streams and the free fatty acid is not lost but also converted to a high quality product (FAME). To guarantee a longterm activity for the catalyst the oils have to be degummed to remove the phospholipids. This can be done by different processes (Buchhold, 1993; Alfa Laval, 1995).

3. Development of a continuous and environmentally benign transesterification process

The transesterification of deacidified and waterfree oils and fats needs only some minutes to reach the equilibrium conversion (Fig. 2), i.e. a batch process in an ideally stirred vessel should have complete conversion in some minutes, too.

A batch process is easily realized (Jordan and Gutsche, 1999). In those simple batch processes a methanolic sodium hydroxide solution is normally used to catalyse the reaction. The catalyst solution, methanol and oil can be premixed in a tube with static mixers and pumped into a stirred reaction vessel. The reaction is carried out under methanol reflux. After completed conversion the mixture is pumped into a settling tank and the ester-and glycerol phase can be separated.

The one-step batch transesterification has the following main disadvantages (Jordan and Gutsche, 1999):
- If conversions of more than 99.5% have to be realized a high methanol excess will be necessary.
- If methanolic sodium hydroxide solutions are used the catalyst consumption will be high.
- Due to high catalyst dosing the salt content of the by-product glycerol is very high, too.
- The discontinuous operation mode does not allow economical energy recovery.

If a high production output is to be realized a continuous process will be more favourable. This continuous operation mode also gives the possibility to realize energy recovery.

3.1. Reduction of methanol excess

The transesterification consists of three equilibrium reactions running in series. The mass-action expression of the total reaction

$$\text{Triglyceride} + 3\text{Methanol} \rightleftarrows 3\text{FAME} + \text{Glycerol} \tag{3}$$

look as follows:

$$K = \frac{[\text{FAME}]^3[\text{GLY}]}{[\text{CH}_3\text{OH}]^3[\text{TRI}]} \tag{4}$$

(K is the equilibrium constant and the expressions in brackets are the concentrations of the components triglyceride (TRI), methanol (CH_3OH), glycerol (GLY) and FAME. Eq. (4) contains the simplification that the activities are replaced by concentrations.)

Eq. (4) shows the possibility to reduce the methanol excess if the concentration of the by-product glycerol is kept low. The ideal solution of this problem is a reaction with simultaneous separation of the glycerol formed by reaction, e.g. by a glycerol selective membrane (Fig. 4).

The actual knowledge of membrane, distillation or extraction processes do not offer any process with the ability to separate glycerol selectively from the reaction mixture of the described system. But the mixing behaviour gives the possibility to separate the glycerol if the conversion is so high that enough glycerol is arised to form a glycerol phase. By using intermediate settling and separation of the glycerol phase it is possible to get near the ideality of a continuous and selective separation of the by-product. Freedman et al. (1984) have pointed out this possibility and compared one-step to multi-step reactions.

Own investigations with coconut oil and other important raw materials have shown that a two step process can reduce the methanol excess to 60% of the excess of the single step process. This gives a big reduction of energy consumption in the methanol processing.

Fig. 5 shows the two-step reaction process (Aßmann et al., 1989a). The feed materials and the catalyst solution are mixed in a tubular reactor with the help of static mixers and after a reaction time of some minutes the mixture reaches the phase separator where the first reaction step is completed and a glycerol phase is separated. Since the glycerol solves methanol and catalyst it is necessary to feed new methanol and catalyst to the second reaction step. The second step looks like the first. The feed materials are mixed in a tubular reactor and in a second vessel the formed glycerol phase is separated. Due to the kinetics of the reaction in a well-mixed system the use of tubular reactors has great advantages:
- the reactors can be realized with low investment costs; and

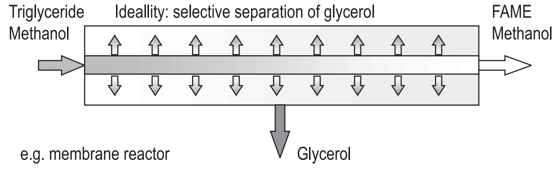

Fig. 4. Reduction of excess in equilibrium reactions by removal of by-product.

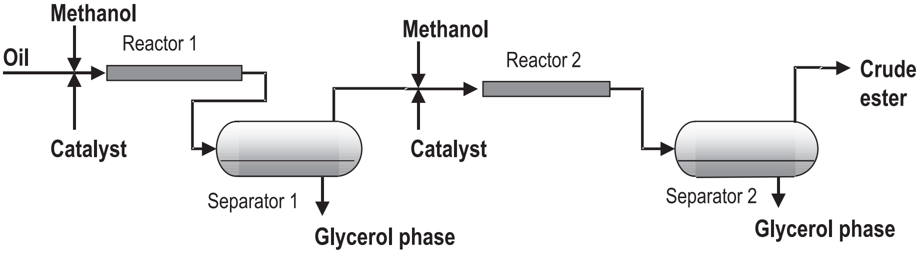

Fig. 5. Transesterification in two stages.

- because of the very good mixing the catalyst dosing can be minimized to the ratios estimated in laboratory experiments.

However it is necessary to guarantee a minimum flow rate. At low flow rates methanol and triglyceride run in two separated layers through the reactor and the mass transfer resistances between the two phases are so high that the reaction becomes very slow and the planned conversions will not be reached. The influence of mixing on the reaction progress was shown by Noureddini and Zhu (1997) for stirred vessels and by own measurements in pilot scale tubular reactors.

Therefore, plants with large loading range use continuous stirred tank reactors or loop reactors (Gutsche, 1997).

3.2. Optimization of catalyst dosing

The first measure to use as low catalyst dosings as possible is the reactor design. By the use of tubular reactors (Aßmann et al., 1989a) with excellent mixing caused by the turbulent flow and by static mixers it is possible to work with the lowest dosing rates.

Furthermore by the pretreatment of the raw material it has to be guaranteed that the FFA-content is as low as possible. The acid value of the feeded oils and fats should be below 0.15. This is a value which is normally guaranteed by an alkaline refining process and the preesterification must be able to reach these oil qualities, too. This step guarantees that only a neglectable portion of the catalyst reacts directly with fatty acids (see reaction Eqs. (5a) and (5b)) and becomes inactive at the chosen reaction temperatures below 100°C.

$$\text{Sodium Hydroxide} + \text{Fatty acid} \rightarrow \text{Sodium Soap} + \text{Water} \tag{5a}$$

$$\text{Sodium Methylate} + \text{Fatty acid} \rightarrow \text{Sodium Soap} + \text{Methanol} \tag{5b}$$

Another aspect which has to be considered is the water content in the reaction mixture. The oils and fats and the methanol should be nearly free of water. Own laboratory tests showed that a water content above 0.3% in the reaction mixture is not tolerable. In technical applications water contents below 0.1% are surely guaranteed. With increasing water content the catalyst is converted from the active alkoxide to the hydroxide form. Besides in small scale fatty acids are formed and these neutralize the catalyst. Therefore an increasing water content results in a decreasing reaction rate.

Zellner (1989) has done a comparison of different catalysts and shown that the use of alkoxides is more efficient than the use of hydroxides. From this if follows that it is necessary to use a methanolic sodium alkoxide solution instead of the cheaper hydroxides if a maximum in environmental protection has to be guaranteed. By the described measures the average salt content of the by-product glycerol can be reduced to 60% of the values of a simple process with low quality raw materials.

4. Process design

Fig. 6 shows the complete transesterification process. The deacidified and dried oil or fat is converted in two steps to the products FAME and glycerol. In the two-step reaction with phase separation a light phase with high ester content and a heavy phase with high glycerol content are produced. The excess methanol is in both phases and has to be separated by distillation.

The separation can be done in multistage falling film evaporator units (Jordan and Gutsche, 1999). Due to the use of such a multistage evaporation energy recovery is possible. The hot products are used to preheat the first evaporating steps and the energy consumption of the evaporator units can be minimized. The separated methanol vapours are not condensed, they are fed directly into the methanol recovery column where water and fatty materials are separated. (Jordan and Gutsche, 1999). By this measure a great part of the heat of the evaporation units can be recovered and used to provide the methanol recovery with energy.

The methanol-free glycerol phase is treated with acid to split the formed soaps. By this splitting reaction fatty

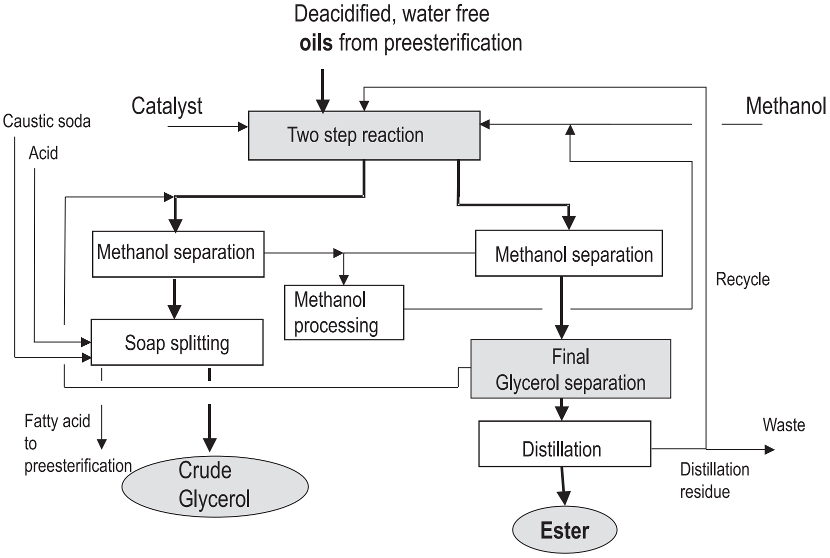

Fig. 6. Transesterification process.

acid is produced and continuously separated as a light phase from the glycerol. The acidic glycerol has to be neutralized by caustic-soda solution. This process must be controlled by an applicable pH-control to minimize the dosage of acid in caustic-soda solution and to minimize the salt content of the produced crude glycerol, too. The fatty acid is washed with water to separate traces of acid and can be recycled completely to the process by feeding into the preesterification.

After methanol separation of the ester phase the crude ester still shows a content of glycerol dispersed in very small droplets. Due to the small size of the droplets a phase separation in a simple settling tank takes much time. In some plants this separation is realized by a treatment with water to wash out the glycerol (Gutsche, 1997), but a washing step has the main disadvantage that a strongly diluted glycerol is produced. A better possibility seems to be a separation of the undissolved glycerol by coalescence separators (Aßmann et al., 1989b) (Fig. 7). The coalescence separation produces a concentrated glycerol which can be fed into the described glycerol treatment. The crude glycerol can be refined to highly pure glycerol which is normally done by distillation. If the produced esters are used in the production of fatty alcohols it is necessary to separate the non-reacted materials. A residue is produced which contains partial glycerides and inert substances like unsaponifiables. Due to the presence of inert substances

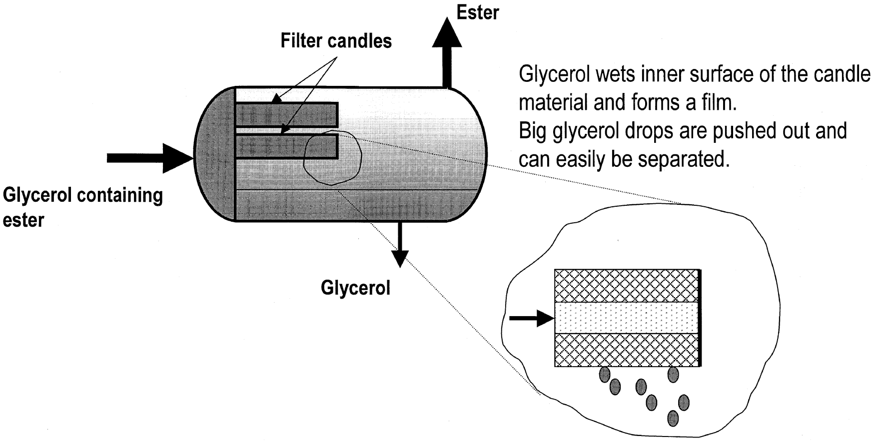

Fig. 7. Final glycerol separation by coalescence separators.

this residue cannot be recycled completely. A part has to be taken out of the cycle. The ratio between recycle and waste production is dependent on the used raw materials and their content of inert substances.

5. Potentials for future improvements

In the following some ideas are discussed which will give an additional improvement of the described transesterification of fats and oils regarding environmental protection.

Up to now only homogeneously catalysed transesterifications are known. The by-product glycerol has always a salt load which gives a waste stream in the following glycerol refining process. It has been shown that it is possible to keep the catalyst consumption as low as possible but a heterogeneously catalysed reaction would be preferable because only by this measure waste streams are avoided.

The preesterification is designed as a one-step fixed bed process. Due to the adsorption of water on the catalyst the methanol excess must be extremely high. A reaction with simultaneous separation of the formed water will be an important step to realize an additional energy saving. Therefore heterogeneously catalysed counter current processes have to be developed.

The residue produced by ester distillation cannot be recycled completely. An utilization must be found. The residue contains partial glycerides and inert substances which are natural fat accompanying substances. These substances could be used to produce active substances for pharmaceutical or food applications, i.e. the produced residue could be used in an economically interesting way.

6. Conclusions

Low temperature transesterification is an environmentally friendly process in the oleochemical production route to fatty alcohols. The shown process concept has the following main advantages:

- Semi-refined (degummed) oils and fats with high acid value can be used because the free fatty acid of the raw materials reacts in a first step to fatty acid methyl esters.
- The reaction of free fatty acids to fatty acid methyl esters is catalysed heterogeneously.
- The transesterification is carried out in two steps with intermediate removal of the by-product glycerol to keep the methanol excess as low as possible.
- The dosing rate of the transesterification catalyst is optimized to have a low catalyst consumption and a low salt content in the by-product stream.
- The continuous process allows energy recovery and a decrease of energy consumption compared to batch processes.

Nevertheless there are some potentials for future improvements. The most important innovation would be a process with a heterogenously catalysed transesterification. By such a new reaction technology it is possible to produce a salt-free glycerol which will lead to a glycerol processing with minimal waste production.

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