

# New trends in Oleochemistry for fuels

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## Abstract

High petroleum cost and environmental concerns stimulated in the last years a living attention to renewable energy sources. One of the more interesting chances is given by vegetable oils and their derivatives. Fatty acid methyl esters (FAME) for car fuel and energy generation are reaching the same annual volume as the sum of all the other oleochemical productions. Several biodiesel plants, 100.000 tons/year capacity, are going on stream mainly in EU and US.

Despite the old tradition and the established technical knowledge of FAME production, the economic and quality requirements of the new use force to a deep revision of the existing technologies, and to the development of new, more efficient processes. An impressive number of patents documents these technical efforts in the last 10 years.

This lecture presents the economic and legal constraints which influence the characteristics of the new processes and discusses, on the basis of physical and chemical principles, the technical aspects of existing and new processes.

In a more long perspective, performances of the current products and technologies in front of the desired characteristics are discussed. The need of more suitable vegetable raw materials is underlined.

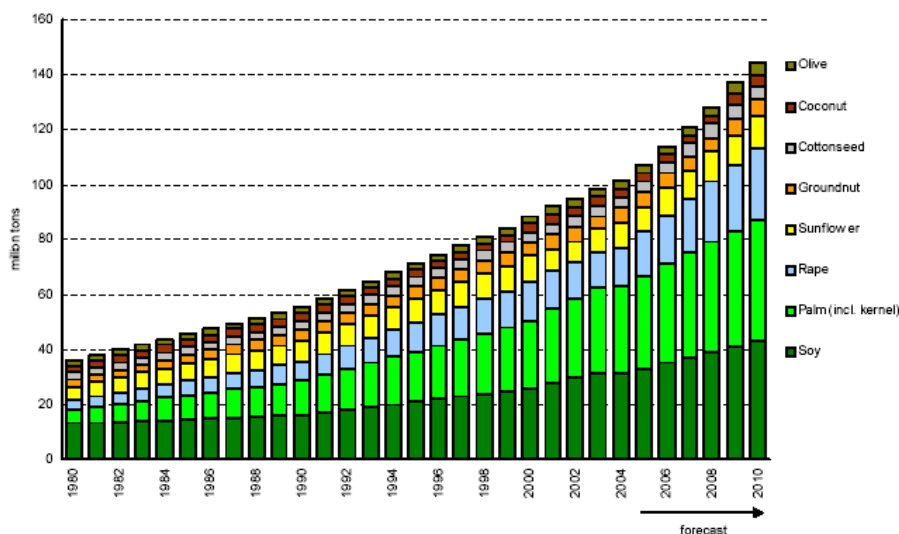
The different roles of Agronomists, Chemists and Chemical Engineers for the new technologies development are depicted.

## The reference frame

Oleochemistry is a very old and well established matter, which originated a consolidated industry. It is, by size, the second chemical industry after that petroleum derived, and, from an historical point of view, it is more ancient than petrolchemistry.

Today world oil production amounts to more than 100 million tons per year, and it is rapidly growing.

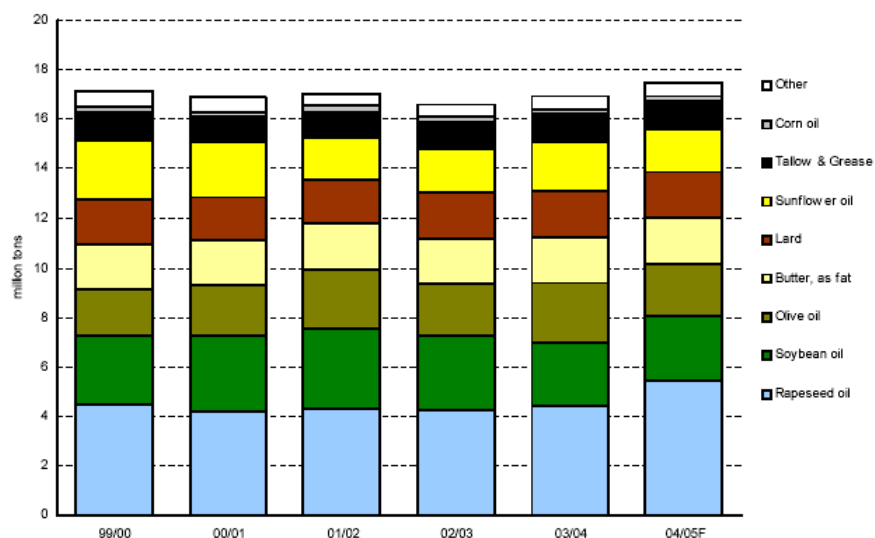
**Figure 1: Worldwide production of selected vegetable oils**



Source: Rabobank, Oil World, Meyeroil

European production of fats and oils amounts about to 20 million tons per year, but, as a difference, it is quite stable during the time.

**Figure 2: European production of oils and fats**



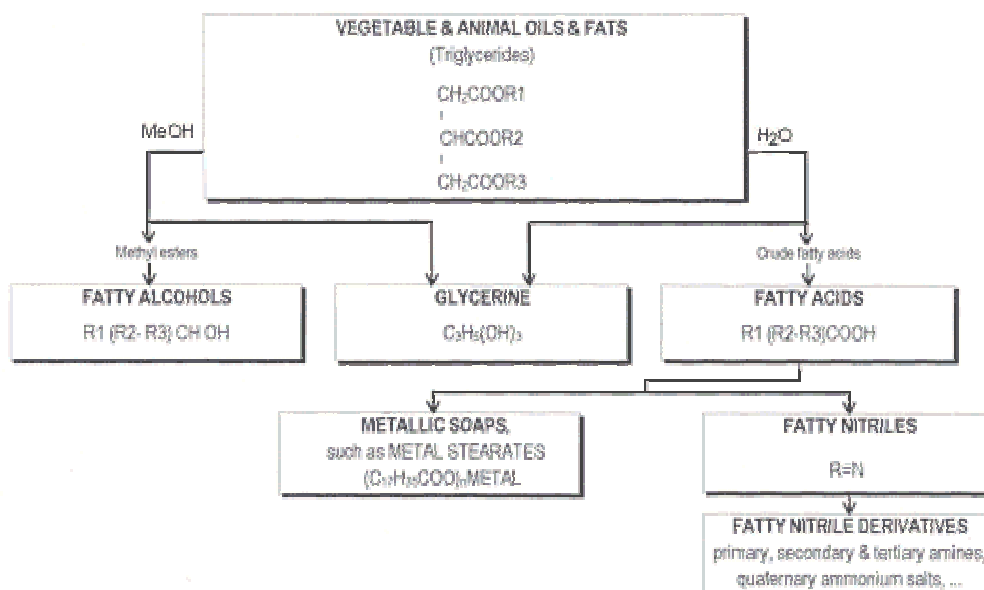
Source: Oil World

The main use of vegetable and animal fats is in the food sector, both for human and animal nutrition. While the global statistics on the oil production are quite defined, figures relative to the quantities used for industrial uses are less available. The reasons are that the fraction of the global

production used in non food industry is comparatively low, about 10 – 15 %, the single uses are various and sketchy, and it is difficult to divide the food industrial uses from the non food uses. Our interest, today, is to analyse the non food uses, in the field that is known as “oleochemical product”, as a parallel to the “petrochemical products”.

APAG (The European Oleochemicals and Allied Products Group) identifies the “Oleochemical family” as the group of products included in the following scheme:

**Figure 3: The oleochemical family**



Source: APAG Internet site.

If we look for a more detailed list of products, and for their end uses, we can consider Table 1, which lists the main product families, giving the final utilisation and the percent of the total capacity of oleochemical products.

**Table 1: Main industrial uses of vegetable oils**

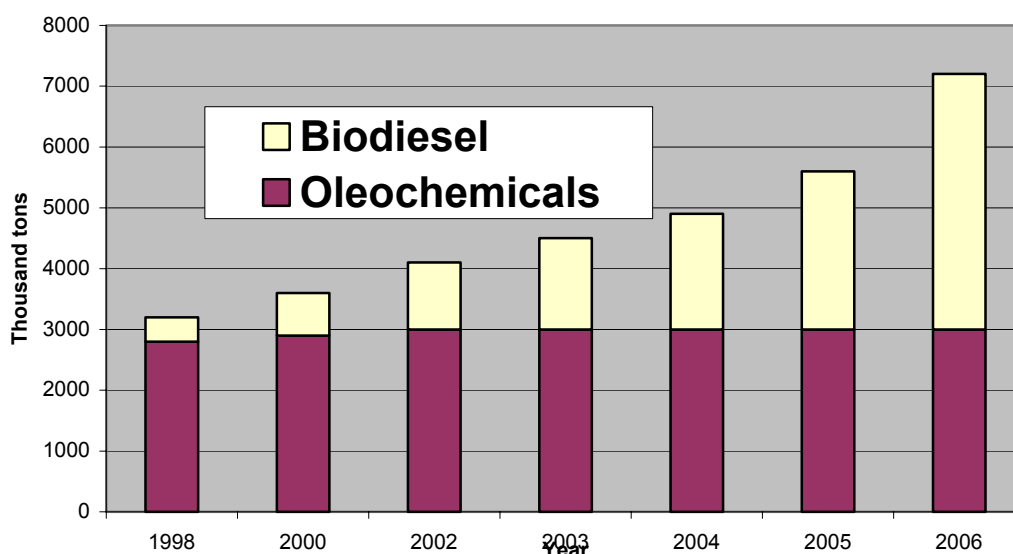
| Product  | % of total | Main uses   |
|--|------------|---|
| Amines   | 4.0%       |   |
| Quats  | 2.0%       | Fabric softeners, lubricants, dyes, textiles  |
| Ethoxilated amines                             | 2.0%       | Emulsifiers, lubricants, crop protection  |
| Esters   | 6.9%       | Lubricants, plastics, food, personal care, textiles, fabric softeners, paper.                                 |
| Heavy metal salts                              | 4.7%       | Plastics, paper   |
| Acid oligomers (monomers, dimers and trimers)  | 4.1%       | Non nylon polyamide resins, stearic acid  |
| Ester quats                                    | 2.8%       | Fabric softeners, lubricants, dyes, textiles  |
| Fatty acids - polyamines condensates and quats | 2.2%       | Corrosion inhibitors, emulsifiers, mining, fabric softeners   |
| Anionic specialty surfactants                  | 1.7%       | Soap  |
| Fatty acid amides                              | 1.7%       | Lubricants  |
| Amphoteric surfactants                         | 1.0%       | Shampoos, soaps, industrial cleaners  |
| Shorter chain fatty acids                      | 0.9%       | Azelaic and pelargonic acids, for plasticizers and synthetic lubricants                                       |
| Alkyl ketene dimers                            | 0.6%       | paper   |
| Fatty acids and salts                          | 18.9%      | Cosmetics, soaps, polishes, household and industrial cleaners, emulsifiers, rubber compoundings, animal feed. |
| Alkyd resins                                   | 1.7%       | Drying oils   |
| Fatty alcohols and derivatives                 | 44.5%      | Detergents  |

Source: NREL/TP-510-34796

That total capacity has been recently indicated for the European industry as amounting to 3 million tons/year. The growing rate is, however, very low. The oleochemical derivatives demand is related to the GPR of nations, and it suffered the economy stagnation period passed in the last years.

That is true if we consider the traditional oleochemical products. However the situation changes if we consider also the biodiesel production. In this case Figure 4 the increase of capacity is exponential, following the increase of the oil price and the politics of the national States and of the European Union.

**Figure 4: European overall capacity of industrial oleochemicals**



Source: ECN, 17-23 October 2005, page 21

So, if we have to comment what it is changing in the oleochemical industry in the first 2000's we have to take into consideration biodiesel. In few years biodiesel capacity equated the overall capacity for oleochemical products required by all the other end uses.

Biodiesel is intended today as a mixture of fatty acid methyl esters (FAME) derived from triglycerides. From the chemical point of view FAMES are not new products. Transesterification with methanol of a vegetable oil was conducted as early as 1853, by scientists E. Duffy and J. Patrick, many years before the first diesel engine became functional.

FAMES are used in the oleochemical industry, since the beginnings of the last century, as such, or as raw materials to be reduced to fatty alcohols.

Nevertheless when FAMES have to be used as biodiesel we have to consider them as a new product, or, better, as a family of new products.

We have to distinguish between two possible and actual applications of FAMES:

- Fuel to produce energy (mainly electric energy) in power generation plants;
- Fuel for automotive, as a substitute or as an extender of petroleum diesel.

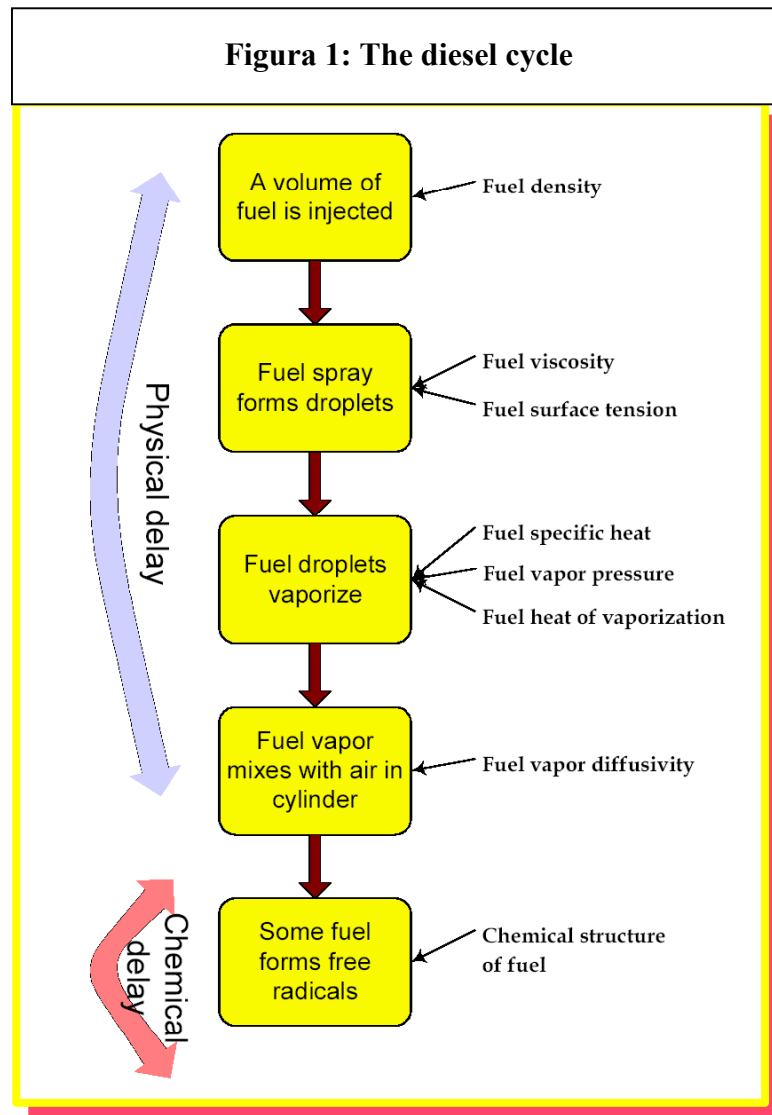
Obviously requirements and specifications should be different for the two uses, and not related with that of traditional industry. The following table collects the main characteristics required for the automotive usage in the US and in the European community:

**Table 2: Biodiesel specification for automotive**

| Property   | Units              | US specs<br>ASTM 6751 | EU specs<br>EN 14214      | Diesel specs<br>EN 590     |
|--|--------------------|-----------------------|---------------------------|----------------------------|
| Flash Point  | °C                 | >130.0                | >100                      | >55                        |
| Kinematic<br>Viscosity, 40°C                             | mm <sup>2</sup> /s | 1.9 - 6.0             | <5                        | 2 – 4.5                    |
| Sulfated Ash   | % mass             | <0.020                | 0.01                      | <0.01                      |
| Sulfur   | % mass             | <0.05                 | 0.01                      | <0.005                     |
| Cetane Number  |                    | >47                   | >49                       | >46                        |
| CFPP   | °C                 |                       | 0, -10, -20 <sup>1)</sup> | 00, -10, -20 <sup>1)</sup> |
| Cloud Point  | °C                 | Report to<br>Customer |                           |                            |
| Carbon Residue   | % mass             | <0.050                | <0.03                     | <0.03                      |
| Acid value   | MgKOH/g            | 0.8                   | 0.5                       |                            |
| Total Glycerin   | % mass             | 0.240 max.            | 0.25                      |                            |
| Phosphorus Content                                       | % max              | 0.001 max..           | 0.001                     |                            |
| Distillation<br>Temperature, 90%.<br>Recovered (T90) *** | °C                 | 360 max               |                           |                            |
| FAME content   | % volume           | >96.5                 |                           | <5 <sup>2)</sup>           |

- 1) According to the season and the country.
- 2) FAME shall meet the requirements of EN 14214.

Why this kind of properties has to be fulfilled? Because biodiesel has to behave in the existing car engines like the usual petrodiesel. As an example consider the property Cetane number. The diesel engine has to support the working cycle of the engine which is depicted in the following slide. All of us know that basically the fuel is injected into the combustion chamber, where it is sprayed in very small droplets. The droplets vaporize and vapours, mixed with air, compressed so that the temperature goes up over the autoignition point of the fuel. Ignition is a quite complicated chemical process, during which oxidation starts forming free radicals which induce the chain combustion reaction.



Source: NREL/SR-540-36805

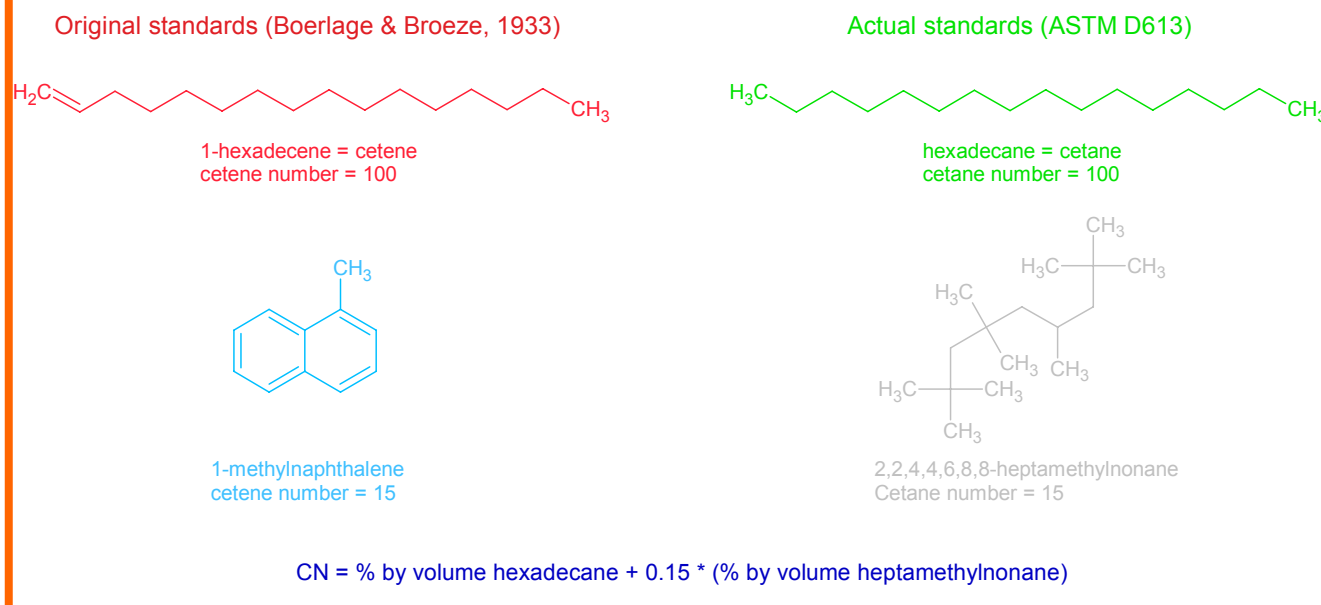
Each step in the process requires some time: their sum represents the delay time between the instant of injection and that of oxidation. This time is measured by the “cetane number”. The current engines are optimised for fuels which have cetane numbers higher than 50.

Really cetane number is not a direct measure of the delay time. It is related to composition. The method was developed in the Netherlands in 1933, measuring the combustion delay times of mixture formed by Hexadecene (cetene) an methyl naphthalene in a standard diesel engine. To pure cetene, which burns very easy, was assigned a cetene number of 100, to methyl naphthalene of 15. Due to the difficulty of have pure cetene it was substituted by cetane as reference standard with cetane number of 100. Cetane has a cetene number of 0.88.

Methyl esters of fatty acids show quite high cetane numbers. More saturations they have, lower the cetane numbers.



**Figure 5: Cetane number standards**



Source: NREL/SR-540-36805

An other relevant property is the CFPP (Cold Filter Plug Point), which is the temperature at which the fuel filter plugs. It is related to the Cloud Point and to the pour point of the fuel and, basically, to the crystallization temperatures of the constituent esters. Methyl esters of fatty acids generally show quite high CFPP. Unsaturated fatty acids give esters with lower CFPP.

The requirement on CFPP is strictly related to the use of the biodiesel. It is clear that when we use biodiesel as a 100% fuel (the so called B100) the required properties are more stringent than in the case we add the biofuel to a petrofuel (the so called B2 or B5). The European legislation admits a maximum of 5% of biodiesel in the standard diesel (EN 590), and the properties are related to the final mixture.

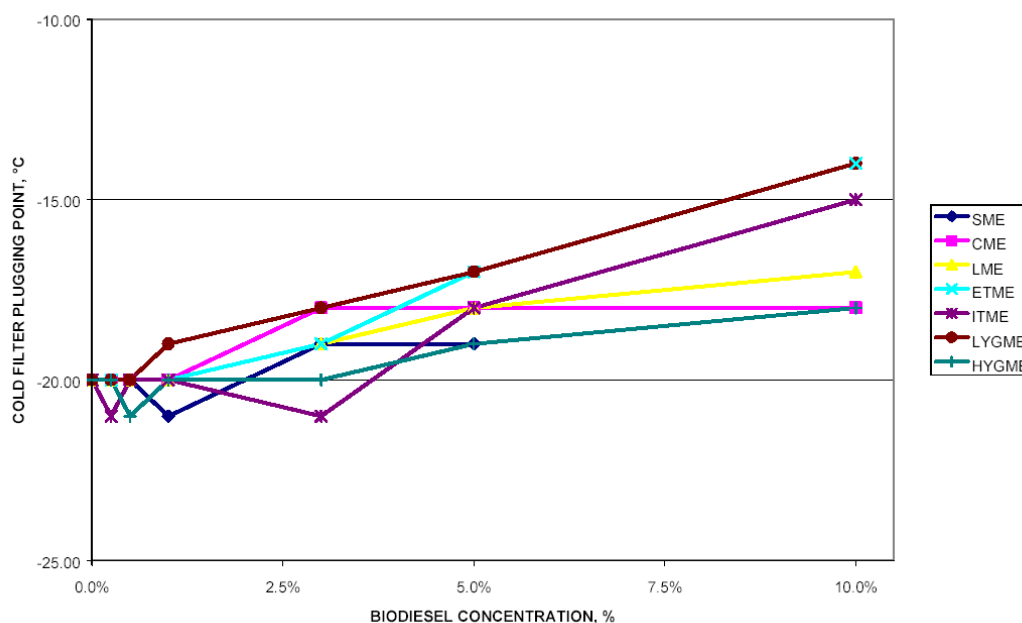
**Figura 2: Reference norms for diesel fuels**

| Final fuel | Norm for the fuel | Norm for FAME |
|------------|-------------------|---------------|
| B0 to B5   | EN 590            | Nothing       |
| B6 to B99  | n.a.              | n.a.          |
| B100       | EN 14214          | EN 14214      |

Source: Dieter Bockey, Union zur Förderung von Oel- und Proteinpflanzen e.V. (UFOP)

In this case the relevant properties have to be measured directly on the final mixture. In this sense is important to know how, for each FAME mixture, the CFPP (or the related properties of cloud and pour point) varies. The following graph gives some results:

**Figura 3: Diesel/biodiesel blends cold filter plugging points**



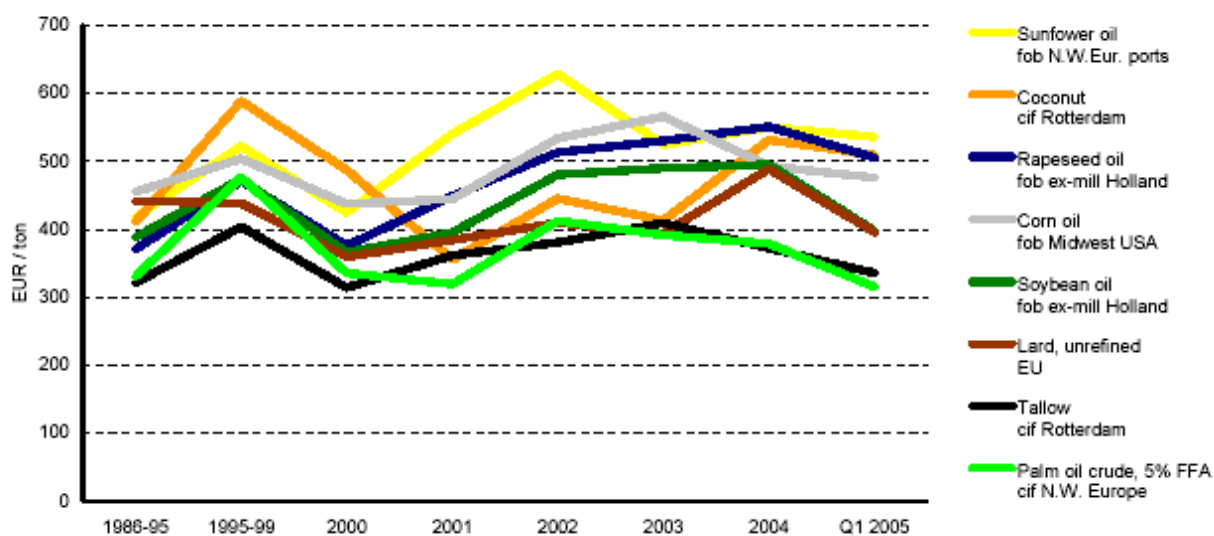
See footnote for acronym explanations<sup>1</sup>

Source: *Biodiesel Handling and Use Guidelines*. Available electronically at <http://www.osti.gov/bridge>

We can appreciate that blending petrodiesel with limited quantities of FAME does not change in a significant extent the properties of the final diesel. This fact makes possible the use of raw materials of low quality and low cost, like animal fats, as feedstock for FAME synthesis. This consideration is of the paramount importance, in view of the fact that the FAME production cost has to be comparable with that of petrodiesel. When oil cost is at the current level, 70 \$/barrel, the petrodiesel production cost is about 600 \$/ton. Historical series of prices of different oil show that the vegetable oil prices are quite high, in front of the admitted FAME cost, and that, unfortunately, sunflower oil shows the highest prices:

<sup>1</sup> SME= soy methyl ester, CME=canola methyl ester, LME=lard methyl ester, ETME=edible tallow methyl ester, ITME=inedible tallow methyl ester, LYGME=low free fatty acid yellow grease, HYGME=high free fatty acid yellow grease. As a note, since these tests, we have found that the free fatty acid content of the starting feedstock, whether it is yellow grease or some type of animal fats, does not have any effect on fuel properties. So LYGME and HYGME can be viewed as two different samples of yellow grease methyl esters.

**Figura 4: Hystorical series for oil costs**



Source: Oil World

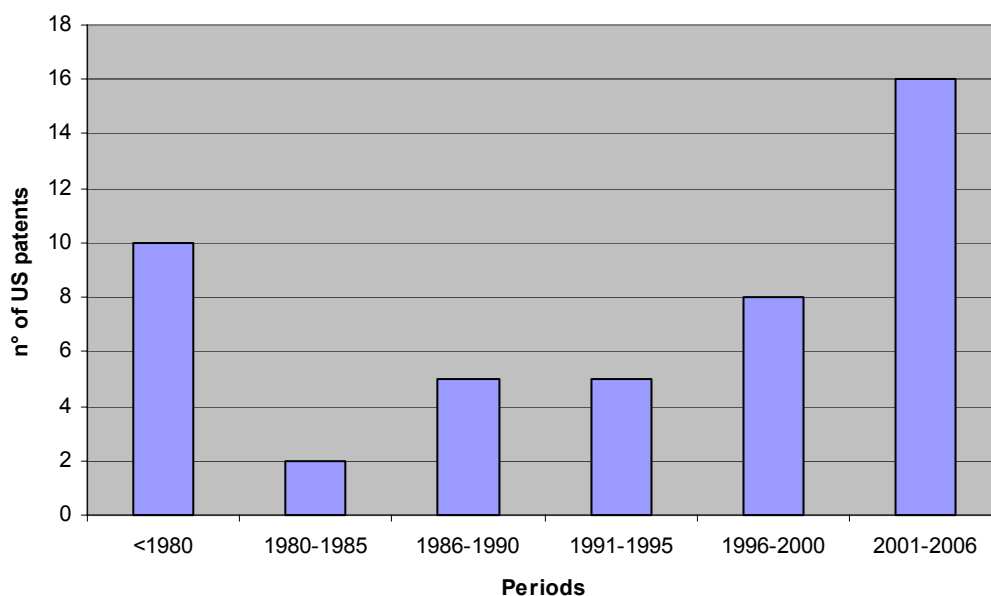
Due to this economic reason the traditional technologies for methyl esters production have to be revised, with two principal aims:

- Contain costs at the best;
- Meet specifications for B100 starting from any type of oil feedstock.

## Transesterification technologies overview.

It is quite astonishing that a so old technology, operated since a century, necessitated a so big research effort when the new use of FAME as fuel was focused. About 50 US patents were found on the triglycerides transesterification processes. Interestingly, a lively interest is shown after the beginning of the new century:

**Figure 6: Patent issues on FAME technologies**



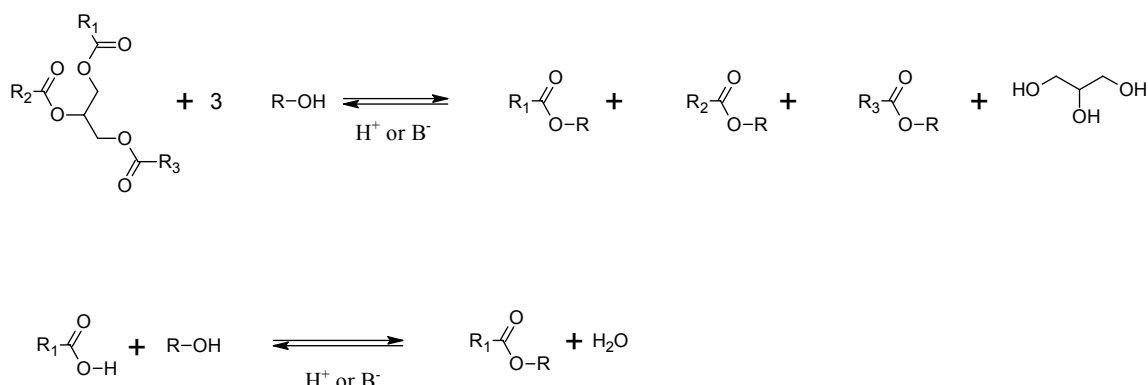
Source: Serichim

The reason of such a high number of new inventions resides in the thermodynamic and physical constraints of the reactions.

### Conversion.

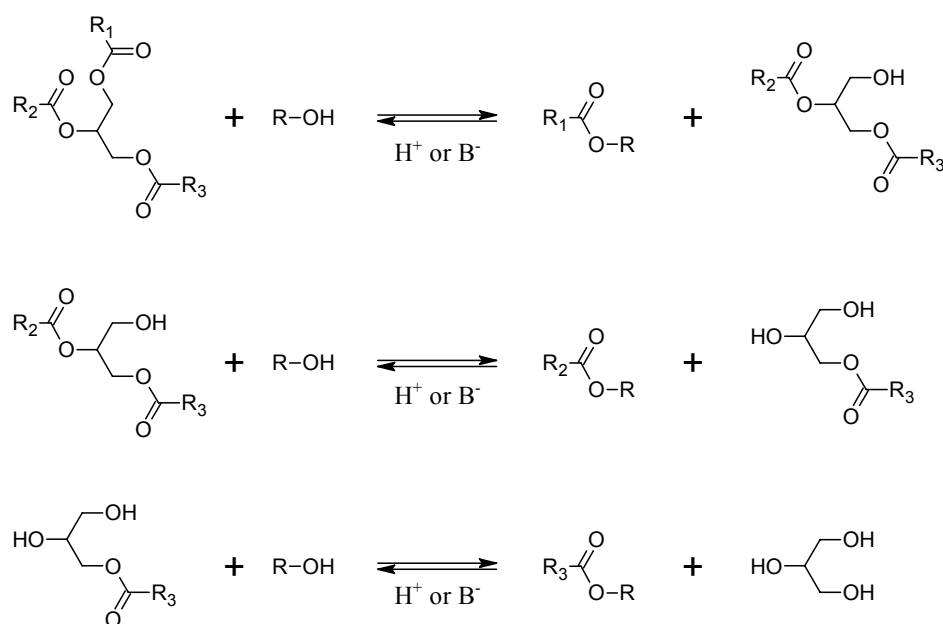
Fat transesterification processes include two different reactions: the transesterification of glycerides and the esterification reaction of the free fatty acids always present in natural feedstocks.

### Scheme 1: Reaction scheme for Triglycerides methanolysis



The heart of the problem is that both the reactions are equilibrium reactions. The transesterification reaction collects three consecutive steps, each of them being an equilibrium step:

### Scheme 2: Detailed reaction sequence of glycerides methanolysis



Specifications require that the content of the so called bondend glycerol (mono and diglycerides content) be low, so that the reaction has to be as complete as possible. In order to select reaction conditions suitable to reach complete conversion to FAME a knowledge of equilibrium constants for the three reactions should be of invaluable value. Unfortunately we were not able to find complete and reliable values for those reactions. In a recent thesis<sup>2</sup> values for the equilibrium constant for the last reaction are reported. The mean value is about 5-10. With this constant values it is very difficult to reach high conversion, also with relevant excess o a reactant.

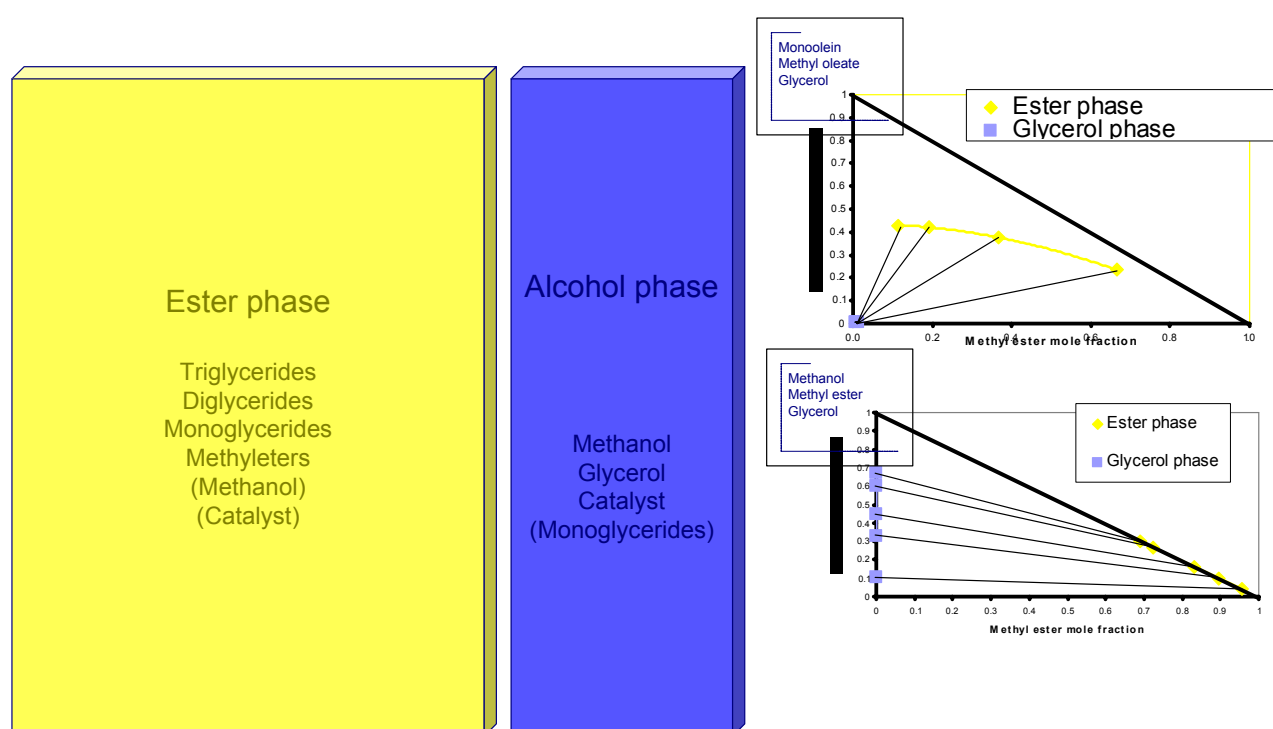
There is a reason why thermodynamic data are not so available:

<sup>2</sup> Kimmel, "Kinetic Investigation of the Base-Catalyzed Glycerolysis of Fatty Acid Methyl Esters", Technischen Universität Berlin, Berlin, 2004

- first, in order to calculate equilibrium constant we need the complete description of composition of the equilibrium mixtures, but the analytical methods for mono, di and triglycerides are quite complex;
- second, the reaction system is also very complex, and the right thermodynamic analysis of the equilibrium conditions is not so simple.

At this time we can only state that the reaction is an equilibrium reaction, and that some tricks have to be adopted in order to achieve high conversions. The tricks usually consist in the use of an excess of methanol or in the selective removal of the produced glycerol from the reactor. Both methods have been used in the current transesterification technologies. Selective removal of glycerol is facilitated by the fact that the reaction medium is biphasic.

**Figure 7: Distribution of products in the triglycerides transesterification**

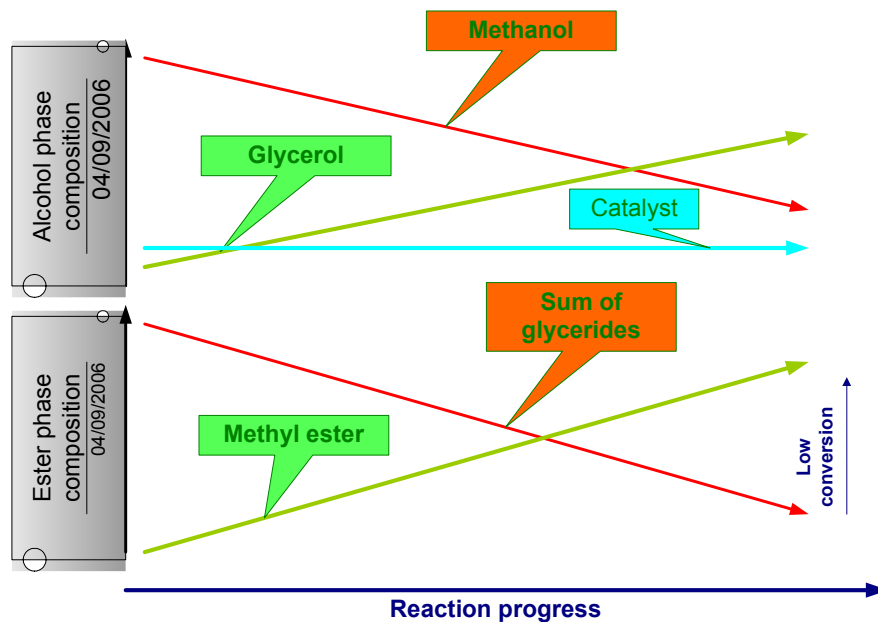


A recent paper reports the phase behaviour for the systems glycerol, methanol and methyl oleate and glycerol, monoolein and methyl oleate<sup>3</sup>. It shows that both methanol and glycerol are immiscible with the methyl ester and with monoolein. It confirms the current experience of who is familiar with triglycerides transesterification.

The reaction occurs between the alcoholic phase, which is the reservoir of the reactant methanol and the sink of the produced glycerol, and the ester phase, which change composition but carry over all the fatty compounds:

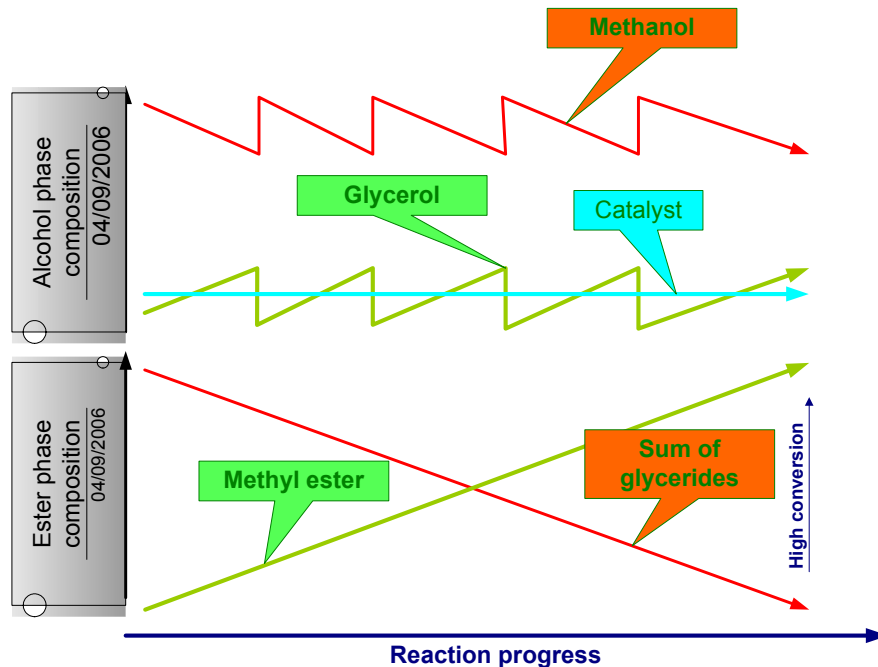
<sup>3</sup> Ind. Eng. Chem. Res., 2006, 45, 3693-3696.

**Figure 8: Phase composition during straight transesterification reaction**



If we withdraw some glycerol product and restore the methanol content, we obtain higher yields:

**Figure 9: Phase compositions during optimised transesterification reaction**



The specific methods and politics of the excess methanol generation and product glycerol withdrawal constitute the object of several patents.

### Free fatty acids.

The second problem we have to face using vegetable oils is the presence of free fatty acids.

It is well known that transesterification reactions are catalysed both by acids and by bases: basic catalysts are preferred because the reaction rate is very higher. Basic catalysts are incompatible with the presence of free fatty acids, so that we have to remove them before the transesterification reaction. We have a lot of possibilities:

1. Neutralisation of acids and separation of the resulting salts before the TE reaction;
2. Neutralisation and separation after the TE reaction;
3. Esterification in a first stage with methanol, under acidic catalysis, and after switching to the basic conditions;
4. Esterification with glycerol.

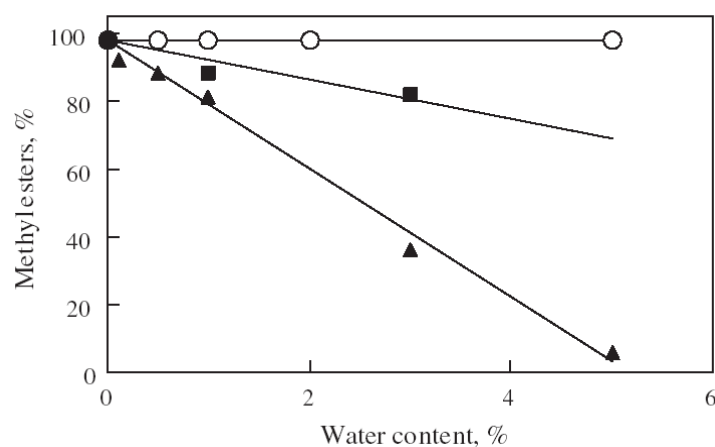
Each choice has its operating limits, its advantages and its problems. The combination of the different possibilities for the acid removal and the different politics can be adopted in order to obtain complete conversion generates an high number of arrangements, each one eventually object of a patent.

## Catalysis

While in the past acid catalysed processes were practically ignored, in the last years they are gaining more consideration. The reason is that acid catalysis admits the use of feedstocks containing free fatty acids without the need of a previous acid removal step.

Esterification reaction is an acid catalysed reaction, and also transesterification can be acid catalysed, also if the catalyst efficiency is lower and reaction times are longer. The more logic choice should be to perform the two reactions at the same time. Nevertheless transesterification in the presence of fatty acids does not occur at any significant extension. Chemical reasons of this behaviour are not well defined, but it seems that water produced by the esterification reaction deactivates the catalyst. In effect the mechanism of acid catalysis passes through a carbocation formed by the addition of a proton to the CO of the carboxylic group, and the formation of this complex can compete with solvation of the proton by water. A recent paper was devoted to the systematic study of the effect of water on acid catalysed transesterification, unfortunately only in supercritical methanol (350°C). It shows that the methyl ester yield lowers increasing the water content.

**Figure 10: Water effect on the triglycerides transesterification with methanol**



(○) supercritical methanol;

(■) alkaline-catalyzed

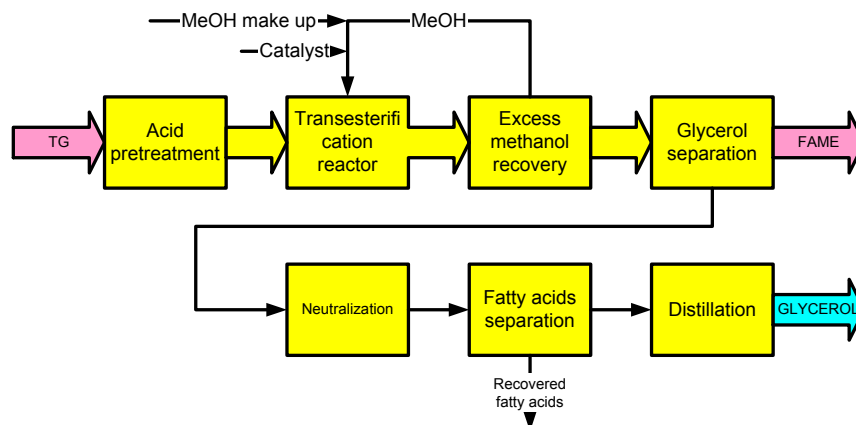
(▲) acid-catalyzed

Source: Bioresourc. Technol. 2004, 91, 289-295.



As a consequence of the incompatibility between the esterification and transesterification reactions they have to be performed in two steps: that results in the general scheme for the biodiesel production process shown in Figure 11.

**Figure 11: General scheme of triglycerides transesterification process**



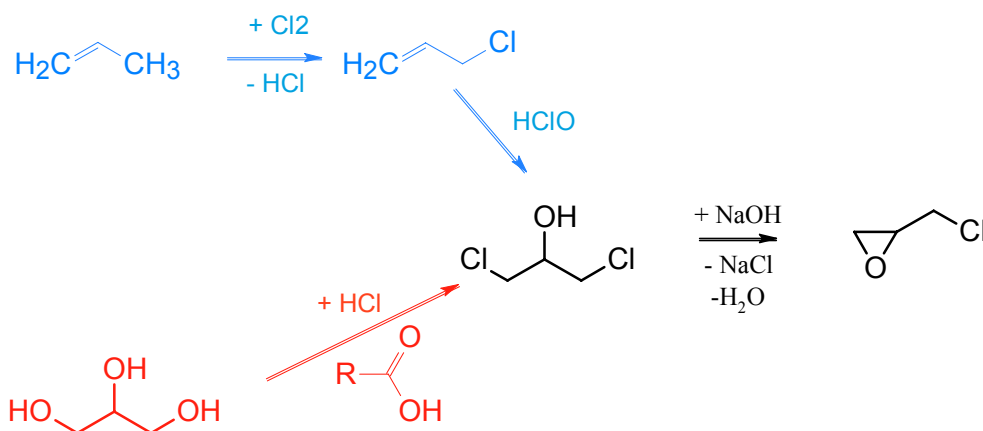
There is only one technology able to carry out esterification and transesterification at the same time: it is the reaction at very high temperature, 350°C, under the autogen methanol pressure, in practice in supercritical conditions for methanol. While results look very interesting, the technique requires high pressure vessel, high temperature facilities and complicated heat recovery systems. Extreme economies in the transesterification process and the need to use all kind of vegetable oils necessarily bring to complex plants and technologies. The “green statements” are generally found in Internet, like “Do yourself your biodiesel!” do not seem anymore realistic.

### The glycerol problem.

It is well known that for 100 tons of FAME about 10 tons of glycerol are co produced. At the beginning of the biodiesel history that was considered an opportunity, because the quite high value of glycerol; today it is the major unresolved problem. Direct uses of glycerol in cosmetic, lubricants, pharmaceutical and food industry do not seem able to absorb the expected 2-3 million tons/year of glycerol. It is a job for chemists to find new uses of glycerol as a raw material for chemical production.

The C3 skeleton of glycerol qualify it as a substitute for propylene derivatives. The first steps in this directions have been announced by the new plants of Solvay and Dow for epichlorohydrin.

### Scheme 3: Epichlorohydrin synthesis from propylene and from glycerol

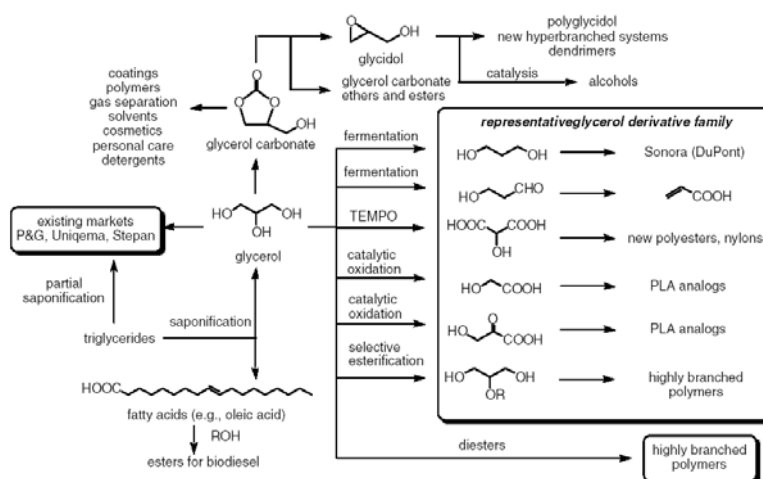


We can expect that glycerol can replace propylene in this application. with a global consumption of about 1 million tons.

As the price of propylene is related to that of petroleum, and the main consumption of propylene, that is for polypropylene, amounts to more than 20 million tons/year, glycerol should be a raw material cheaper than propylene in the long range. So all kind of studies of new processes for existing C3 chemicals are justified.

Several other products can be derived from glycerol. A nice scheme of the different possibilities has been proposed by NREL:

### Scheme 4: Tentative glycerol three



Source: NREL/TP-510-34796

## Beyond FAMEs.

Also if recent and future improvements of FAME technologies will resolve existing problems, at the end FAME will remain a fuel for automotive less efficient than petrodiesel.

That is due to the cold flow properties of FAME derived from all kind of oils, also the more expensive ones:

**Figure 12: Biodiesel performances**

|                                | Units                | EN 14214 standard requirements | Rapeseed biodiesel | Soybean biodiesel | Animal fat biodiesel | Coconut biodiesel | Jatropha biodiesel | Petroleum diesel |
|--------------------------------|----------------------|--------------------------------|--------------------|-------------------|----------------------|-------------------|--------------------|------------------|
| <b>Laboratory test results</b> |                      |                                |                    |                   |                      |                   |                    |                  |
| Freezing point (CFPP)          | ° C                  | depends on season              | - 10               | - 5               | + 7                  | - 9               | - 3                | - 19             |
| Viscosity (at 40° C)           | mm <sup>2</sup> /sec | 3.5 - 5.0                      | 4.8                | 4.3               | 4.5                  | 2.8               | 4.3                | 3.1              |
| Stability (iodine value)       |                      | ≤ 120                          | 118                | 125               | 57                   | 12                | 98                 | -                |
| Carbon residue                 | %m/m                 | ≤ 0.3                          | 0.22               | 0.12              | 0.03                 | 0.02              | 0.15               | 0.04             |
| Cetane number                  |                      | ≥ 51                           | 59.4               | 57.0              | 62.7                 | 58.8              | 59.9               | 57               |
| <b>Engine test results</b>     |                      |                                |                    |                   |                      |                   |                    |                  |
| Fuel consumption               | g/kWh                |                                | 447                | 434               | 434                  | 482               | 416                | 346              |
| injector nozzle clogging*      |                      |                                | 29 %               | 4 %               | 20 %                 | 17 %              | 1 %                | 0 %              |
| NOx emissions                  | g/kWh                |                                | 12.3               | 12.8              | 11.0                 | 10.1              | 12.8               | 11.8             |

In order to have the same performances of a petrochemical derived diesel we have to imagine derivatives of vegetable oils different from FAME. Which kind of derivatives?

In order to answer to this question we have to examine the composition of a petrodiesel, and correlate properties to chemical nature of constituents. Petroleum derived diesel are essentially 50/50 mixtures of normal and isoparaffins with minor quantities of naphthenic compounds, with chain length centred on C16-C18 chains. The major chemical differences with a biodiesel are:

- the absence of the carboxymethyl group;
- the ramified nature of paraffinic compounds.

In order to chemically transform vegetable oils to petrodiesel compounds carboxylic group has to be reduced to paraffin. That is possible forcing the ester reduction conditions that are normally operated in order to produce fatty alcohols from fatty esters: at higher temperature than 250-300°C hydrogenation converts alcohols to hydrocarbons.

Paraffinic chains of vegetable oils are linear chains. In order to meet the required ratio of isoparaffin to normal paraffin isomerisation processes have to be developed. Once again it is chemically possible. The question is if it is economically compatible.

It is well known that the major cost of biodiesel production is the cost of oil. Short margins exist for the transformation costs. Chemists ask for a cheaper raw material, in order to have room for paying the transformation costs of the chemical processes able to afford better products.

## Conclusions

FAME as renewable biodiesel components will have a big role in the automotive fuels in the next year. However several improvements are needed in order to make vegetable oil derivatives competitive with petroleum derivatives both from the economical and technical point of view. There is room for several different multidisciplinary contributions.

**Chemists** have to resolve several problems. In the short time they have to

- Find new uses for glycerol;
- Find new catalytic systems which allow esterification of fatty acids and transesterification of triglycerides at the same time.

In the long time they have to find chemistries able to convert fatty acid esters (or, better, triglycerides) in mixtures with a composition similar to that of the petrodiesel.

**Chemical engineers** have to find optimal processes to produce FAME.

What the role of **agronomists**? My opinion is that they have to improve as much as possible the field productivity of oil rich crops, selecting the types which give the lowest harvesting and extraction cost and the highest yield in oil; quality requirements are at the moment less stringent.