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A LOW-WASTE PROCESS FOR THE PRODUCTION OF BIODIESEL

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ABSTRACT

The acceptance of methylesters (biodiesel) as an alternative fuel has rapidly increased in recent years. This development has been followed by increasing research activities in the field of methylester processes. After listing reasons that supporte arguments for biodiesel and a survey of production methods, a low-waste process for biodiesel is introduced.

INTRODUCTION

The interest in renewable raw materials as an energy source has grown rapidly during the last years. Considerable attention has been directed to oil seeds and the possibility of using vegetable oil as a fuel. There are four main advantages in the use of vegetable oils as alternative fuel:

- Alternative, renewable energy
- Alternative agricultural product
- Biodegradable, nontoxic fuel
- CO_2 cycle, no SO_2 emissions

Due to the decreasing reserves of crude oil, it is very important to look for new energy sources. However, in this area vegetable oils can only satisfy a small part of the energy demand. In this field various activities have to be initiated to solve the growing problem.

Looking at agricultural production, a change to oil seeds could help to avoid excess production. Especially in Europe, a partial change from food-production to energy-production is a way to overcome the problems of the farming industry.

Another advantage of the plant-bound energy is the recycling of CO_2 in very short periods. As an example, the overall CO_2 production caused by 1 L of biodiesel is only 25% of the overall CO_2 production of 1 L of diesel from mineral oils (1). This figure considers all CO_2 equivalents produced during the production and burning of the respective fuel.

Several authors report that the most important advantage of vegetable oils as a source of energy is their biodegradability. Due to the fact that only a small part of diesel can be substituted by biodiesel, consideration must be given as regarding to the areas in which vegetable oils and derivatives should be used as fuel substitute. It is a fact that 1 L of diesel from mineral oil can contaminate large amounts of water. Vegetable oils and their products can also contaminate water, but they are degraded biologically within several days (2). Therefore, fuel from vegetable oils should preferably be used in areas where accidents with diesel engines can cause enormous damage to the environment by contaminating water, especially groundwater.

There are two principle ways of using vegetable oils for fueling. First, they can be used directly in burners for heavy oil or in modified diesel engines (Elsbett engine) (3). Experiments, using vegetable oils directly in normal diesel engines, failed. Secondly, for fueling diesel engines, vegetable oil had to be modified. The best results were obtained by transferring vegetable oils into methylesters.

Tests with methylesters were started in the early seventies. The results showed that it is possible to use either a mixture of biodiesel and normal diesel or pure biodiesel. Several engine tests have been carried out, leading to a broad acceptance of biodiesel by motor constructors.

Subsequently, many processes for the production of biodiesel were developed. Some of those processes were derived from well-known production processes of the fatty alcohol industry. Others were new processes, developed especially for biodiesel production

STATE OF THE ART

In the production of biodiesel the triglycerides of vegetable oils are contacted with methanol and a catalyst producing methylester and glycerine according to the following overall reaction.

The reaction can be carried out under different conditions and by using different catalysts. In Table 1, the representative processes are summarized.

The production of the methylesters is based on different processes used in the chemical industry. Production of biodegradable detergents starts with the splitting of triglycerides by transesterification to methylesters. The methylesters are then further converted to fatty alcohols and to detergents. The high-pressure and high-temperature transesterification process is the main technology used. Acidic catalysts can be used (4,5). When using acidic catalysts, it is possible to convert an

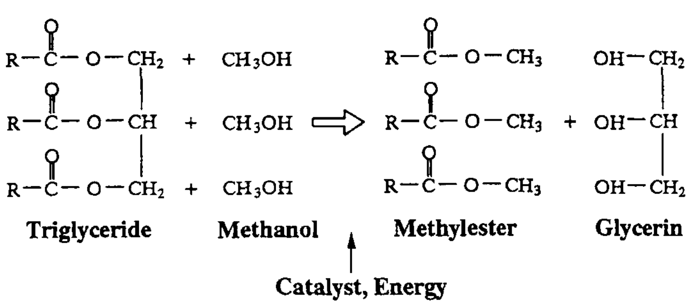

FIGURE 1. Transesterification reaction.

TABLE 1. TRANSESTERIFICATION PROCESSES

	High-Pressure Transesterification	Low-Pressure Transesterification
Pressure	up to 90 bar	up to 10 bar
Temperature	up to 250 °C	up to 100 °C
Catalysts	alkaline homogeneous catalysts acidic homogeneous catalysts oxidic heterogeneous catalysts	

oil feed stock with a high content of free fatty acids. However, these processes are very expensive and only applicable for products of high benefit.

In the production of biodiesel low-temperature / low-pressure processes have been preferred. Alkaline catalysts, mainly sodium methylate, have been used. These processes are carried out at temperatures of 60 to 80°C and within a pressure range between ambient pressure and 10 bar (5,6,8).

By carrying out the transesterification in two steps, a maximum yield of methylester is obtained. Fresh methanol and catalyst are added to each step. The glycerine phase is separated after each step. At a lower temperature, the methylester and the glycerine form two phases with a very low mutual solubility. The yield of transesterification is approximately 99%.

BOUNDARY CONDITIONS FOR THE DEVELOPMENT OF A LOW-WASTE PROCESS

As biodiesel had to compete with normal diesel on the market, the price for biodiesel was a given boundary. Keeping in mind the production costs, the boundary conditions for the development of a biodiesel process were set by the following figures:

1. low-pressure process, if possible at ambient temperature;
2. low quality requirements for the vegetable oil;
3. high degree of transesterification with high yield;
4. constant and guaranteed quality of the biodiesel; and
5. saleable by-products, if possible, for agricultural application.

These requirements are in good agreement with the operating conditions of low-pressure processes. But the use of sodium-containing catalysts causes the formation of several by-products which have to be treated as wastes (mainly sodium salts). These processes require a high-quality feed.

Due to the fact that biodiesel is an agricultural product, the use of potassium hydroxide as a catalyst shows some interesting aspects. The idea of using the catalyst potassium hydroxide has been mentioned in the literature before. Experience in the practical application of this catalyst is not reported. Therefore, the catalyst potassium hydroxide was investigated.

RESULTS OF THIS INVESTIGATION

- With the catalyst potassium hydroxide, the transesterification can be carried out at ambient pressure and ambient temperature. Conversion of 80 to 90% can be achieved within 5 minutes, even when using stoichiometric amounts of methanol.

- Carrying out the reaction in two steps results in a conversion rate of 99%.

- Even a content of free fatty acids in the feed up to 3% does not affect the process negatively. Phosphatides up to an amount equivalent to 300 ppm of phosphorus can be accepted.

- The process is applicable for processing waste frying oil.

- The product, methylester, meets the quality requirements of Austrian and European standards for biodiesel without further treatment (e.g. distillation).

The results obtained within the basic experiments were very promising and encouraged the construction of a pilot plant in the college for agricultural education in Silberberg, Austria. After several months of operation, a full-scale process was offered on the market by the Austrian company Vogel & Noot Industrieanlagenbau GmbH. The first industrial plants, running with the low-waste VN-process (8,9) using the catalyst potassium hydroxide, were small plants with a capacity of 500 tons of methylester per year. They are operated by farmer associations in which the farmers use ~15% of their land to grow rape seed. The biodiesel, produced from this rape seed, covers the whole consumption of diesel fuel of the farmers in the association. Figure 2 shows a block diagram of the process.

DESCRIPTION OF THE VN-PROCESS

First, methanol is mixed with KOH in a separate vessel. The solution is mixed with the oil. When the reaction is finished, the glycerine phase is separated by gravity. In a second step, further methanol-KOH solution is added to the methylester phase of the first reaction step. A conversion of 99 % is then achieved. Again, the glycerine is separated. After the recovery of methanol, the methylester has the quality required by the Austrian standard for biodiesel.

The amount of glycerine formed during transesterification is about 20% of the total amount. Therefore, it is very important to provide markets for the utilization of this product. Table 2 compares the composition of the glycerine phase of the sodium process and the potassium process and gives a survey of proposed utilizations. It is possible to use the glycerine phase from the potassium process for direct application in the agricultural industry.

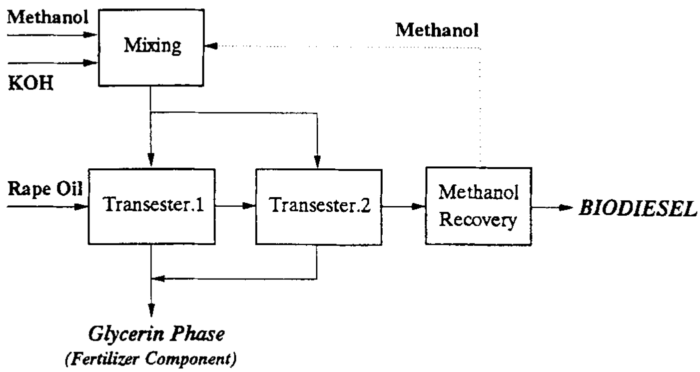

FIGURE 2. VN-process for the production of biodiesel without utilization of the glycerine phase.

TABLE 2. COMPOSITION AND UTILIZATION OF THE GLYCERINE PHASE

Common Processes	VN-Process
Glycerine	Glycerine
Water	Water
Methylester	Methylester
Sodium Soap	Potassium Soap
Sodium Hydroxide	Potassium Hydroxide
Utilization	
Preparation of Crude Glycerine by Separation of the Soaps	
Crude Glycerine	Crude Glycerine
Fatty Acids	Fatty Acids
Solid Waste	Fertilizer Component
Direct Utilization	
Fuel	Fuel
Biogas	Biogas
---	Fertilizer Component
---	Compost

The glycerine phase from the small plants is used directly in fertilizer by mixing it with liquid manure. Practical experience with this mixture shows an increased fertilizing quality of the manure.

The first industrial-scale application of the VN-process was realized in Bruck/Leitha in Austria. Constructed in 1992, the plant has a production capacity of 15,000 tons of methylester per year. Economic considerations led to a subsequent treatment of the glycerine by producing glycerine of pharmaceutical quality. A block diagram of the process is shown in Figure 3.

The principle of the transesterification process is the same as that in the small plants. For the treatment of the glycerine phase several steps have been added. First, the glycerine phase is neutralized with phosphoric acid (10) to obtain a three-phase mixture of potassium phosphate, a fatty acid phase, and crude glycerine. Phosphoric acid is used, as it is a fertilizer component. The phases are separated, and the crude glycerine is purified to obtain pharmazeutical glycerine.

The fatty acid phase is used for energy production, with the excess sold as heating oil. The potassium phosphate is dried and sold as a fertilizer.

At present, another plant with a capacity of 30,000 tons of methylester per year is being erected in Olomouc in The Czech Republic. In this plant the methylester is produced in the same way as described above. The difference from the Bruck/Leitha production is that in Olomouc the by-products had to be only crude glycerine and a fatty acid phase. There was no use for the solid phase, and therefore hydrochloric acid was used for the neutralization of the glycerine phase. The obtained potassium chloride is soluble in the crude glycerine, and the crude glycerine itself can be sold to a producer of pharmaceutical glycerine.

Recent developments of the process have dealt with the treatment of the fatty acid phase. Experience shows that the fatty acid phase can hardly be sold for fueling purposes. On the other hand, the fatty acid phase could be changed into methylester, thereby increasing the economic output of a methylester plant. Therefore, an esterification process, considering the esterification of the fatty acids to methylesters again (11), was developed. The esterification is carried out with

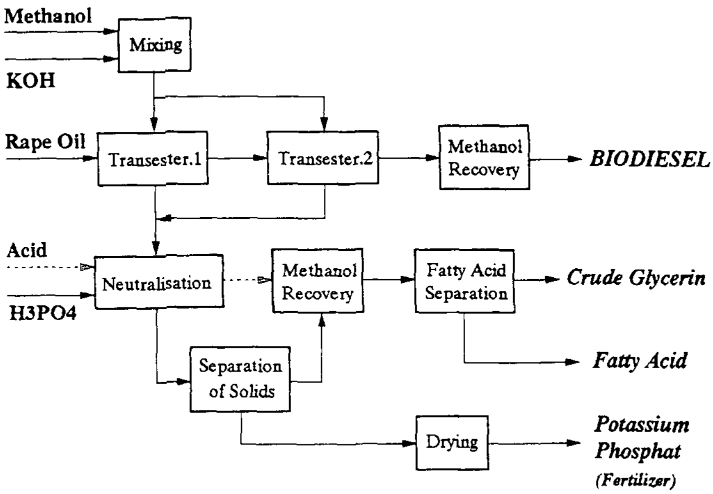

FIGURE 3. Transesterification process with production of crude glycerine, potassium phosphate, and fatty acid.

very small amounts of acidic catalyst, and the product is added to the transesterification mixture without any further treatment. The development, with a very small extension of the process equipment, resulted in a significant effect on the economic results. A block diagram of this process is given in Figure 4.

The quality of the biodiesel, produced in the plants described above, is listed in Table 3. This table also contains the values given in an Austrian Standard and the values suggested for the European Standard.

The cost of production of the methylester, excluding the costs for the feed, lies between 70 and 90 U.S.dollars per ton of methylester and varies with the plant size and with the different ways of the utilization of the by-products. As the by-products of the VN-Process are saleable products, the cost of production of this process is in the lower part of the given range of costs.

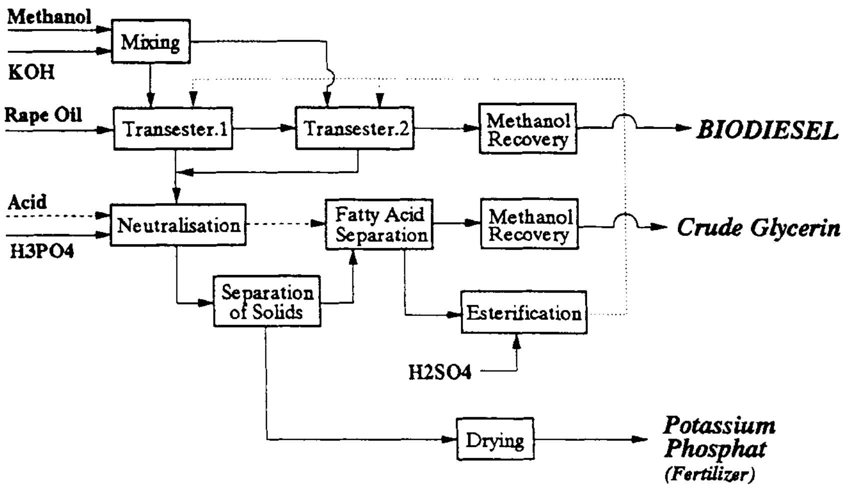

FIGURE 4. Transesterification process with production of crude glycerine and potassium hydroxide, esterification of fatty acids.

Keeping in mind that the VN-Process is also suitable for low-quality oils and for waste cooking and frying oils, it is obvious that the methylester produced by this process is an economic substitute for normal diesel.

Due to tax regulations for biodiesel in some states of Europe, it is possible to compete with normal diesel on the market.

FUTURE DEVELOPMENTS

Although the by-products of the process are saleable products, we still need to develop a catalyst that can be recycled and used for a longer time. Such a process would have several advantages over the present, with the major advantages being:

- very low consumption of catalyst, and
- catalyst-free glycerine phase.

TABLE 3. QUALITY OF BIODIESEL FROM VN-PROCESS COMPARISON WITH STANDARDS

Parameter	Unit	VN-Process	Austrian Standard	European Standard, Proposal
Density	g/cm^3	0.880	0.87 - 0.89	0.86 - 0.90
Viscosity at 20°C	mm^2/s	7.06	6.5 - 8.0	3.5 - 5.0 (40°C)
Flashpoint	°C	150	min 100	min 100
Conradson	wt%	0.025	max 0.10	max 0.03
Sulfate Ash	wt%	0.01	0.02	max 0.01 (Oxide Ash)
Neutralization Number	mg KOH/g	0.25	0.8	0.5
Methanol	wt%	0.1	0.2	0.3
Free Glycerine	wt%	0.02	0.2	0.03
Total Glycerine	wt%	0.15	0.24	0.25

A catalyst, corresponding with these boundaries, has been found at the Institut für Organische Chemie, Universität Graz. Present work at the Institut für Thermische Verfahrenstechnik und Umwelttechnik, Technische Universität Graz, concentrates on investigating and testing this catalyst in bench-scale experiments and in a small pilot plant.

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