ESTERFIP, A TRANSESTERIFICATION PROCESS TO PRODUCE BIO-DIESEL FROM RENEWABLE ENERGY SOURCES

A. Hennico, J. A. Chodorge and A. Forestière

INSTITUT FRANCAIS DU PETROLE
RUEIL-MALMAISON (92500), FRANCE

Keywords : Transesterification, Vegetable Oils, Bio-Diesel.

1 - INTRODUCTION

Vegetables oils and products synthesized from natural raw materials (either of vegetable or animal origin) are having a strong "come back" in the recent decades. One of the major reasons for the increased utilization of fatty chemicals for industrial use has been the ability to tailor the products to specific needs. This trends is clearly indicated in Table 1 that gives an estimate of the world fat production in millions tons and in the case of vegetable oils, the yields per unit area (hectare) per year.
End uses of upgraded products or derivative compounds are extremely numerous but usually highly specialized. Major areas of applications are :
Food industry, soap and detergents, cosmetics, pharmaceuticals, textile and paper industry, oild field chemicals, fat based emulsifiers, synthetic lubricants, metal working fluids and last but not least introduction into the automative fuel sector. This last application will be the subject of this presentation.
In the early days of diesel engines, vegetable oils were tested (their original compositions unchanged) as a possible motor fuel but the idea never took hold owing to incompatibility problems such as deterioration of the oil with time, high viscosity, and fouling of the engine.
Recently the bio-diesel route has been reactivated for a number of reasons as outlined hereafter :

- It has been found that vegetable oil can be transformed via esterification into a product which is much more adequate as a diesel fuel than the original oil itself.
- A wide variety of vegetable oils can be used as raw material for transesterification; this has led to the idea that bio-diesel production could be a way to extend the role of agriculture (more jobs created and reduced financial burden for petroleum imports in developing countries, slow-down in the current reduction of cultivated surfaces for developed countries like those of the European community).

2 - THE ESTERFIP PROCESS DEVELOPED BY IFP* FOR THE TRANSESTERIFICATION OF VEGETABLE OILS

Transesterification of natural glycerides with methanol to methylesters is a technically important reaction that has been used extensively in the soap and detergent manufacturing industry. IFP has done extension R and D work in the transesterification field with the aim of creating a product that would be suitable as an excellent substitute for diesel fuel.
As a result, a new process called ESTERFIP was developed that allows the elimination of certain impurities from the product that otherwise would be detrimental to classical diesel engines.
The ESTERFIP process was developed by IFP first on a laboratory scale, then tested in a pilot plant (1987) and demonstrated in a commercial plant that is operating satisfactorily since 1992 (capacity 20 000 t/yr). Originally the design was developed for batch operation which is very suitable for small capacities and then further upgraded to continuous operation, an economically dictated choice for intermediate and large capacities.

2 - 1 Chemistry Involved

The reaction of transesterification involves the reaction of methanol with the triglycerides of the rapeseed oil to form the corresponding methylesters and glycerine as indicated on the following reaction scheme :

* Jointly with Sofiproteol (France)

Vegetable Oil + Methanol → Esters + Glycerine
(Triglyceride)

This global stoichiometry is of course an oversimplification as we are in presence of a three-step reversible reaction with di - and monogycerides as intermediate products. The reaction takes place in presence of a catalyst that is most commonly sodium hydroxide, potassium hydroxide or sodium methylate. In the case of bio-diesel manufacturing, the main objective is to achieve the maximum possible conversion towards methylester (in excess of 97 %). This aim puts certain specific constraints on the reaction scheme, such as long hold-up time or eventually unreacted feed components recycling, involving a difficult separation between reactants and product.

Furthermore to avoid operating problems in the ESTERFIP process the vegetable oil used as feedstock should be partially refined to eliminate phospolipides, gummy substances, free acid and water.

Typical feed specifications are :

- Phosphorous content : 10 ppm wt maximum
- Water content : 0,1 wt % maximum
- Acidity index : 1 maximum

The situation is also complicated by solubility problems. For example in the present case neither methanol is soluble in the starting material triglyceride nor the end products glycerine and fatty acid methyl esters are miscible, whereas methanol is soluble in fatty acid methyl esters. We can therefore expect different time dependent situations - at the beginning a two-phase system, followed by an almost complete solution. Then as soon as a considerable amount of glycerine is formed, a new two phase system will again prevail.

2 - 2 Composition of Fatty Acids in three common Vegetable Oils

Whereas in Europe methylesters from rapeseed oil and sunflower oil are the most common feedstocks for bio-diesel the US leans heavily upon soybean oil as raw feedstock.

The Table 2 gives the composition of three of the most common renewable vegetable sources that are used in the preparation of bio-diesel.

Although the feed composition is quite different, a careful selection of operating conditions (t, p) and amount of catalyst used permits the production of a bio-diesel that satisfies the most stringent specifications required by the automobile industry.

It is however important here to stress the importance of experimental data checking and unit modeling based upon practical experience, before undertaking the conceptual design of a large size industrial unit.

2 - 3 ESTERFIP Process Description (continuous scheme)

A complete block flow scheme is given on Figure 1. The sequence of processing steps is as follows:

- Transesterification of the vegetable oil by dry methanol in presence of a basic catalyst.
- Decantation to completely separate methyl esters from glycerine.
- The ester phase is water-washed and purified in a continuous operation in order to eliminate the last traces of catalyst particles. This step is very critical to avoid harmful deposits during the combustion in the diesel engine.
- Vacuum evaporation of the methyl ester product to recover traces of methanol and water.
- The raw glycerine recovered in the settler is evaporated (the main methanol removal step), neutralised, decanted to separate fatty acids, and finally completely freed from methanol.

2 - 4 Overall Material Balance (Rapeseed Oil Case)

Refer to Figure 2.

2 - 5 Product Properties

Bio - Diesel (Methyl esters)		Glycerine (by - product)	
Specific gravity	0.88	Glycerine content, wt %	> 80
Flash point, °C	55 mini	Ash content, wt %	< 10
Cetane number	49	Other organic compounds, wt %	< 2.5
CFPP, °C	- 12	Methanol content, wt %	< 0.2
Viscosity (cSt 20°C)	7.52	Water content	< 10

2 - 6 Bio-Diesel based Commercial Fuels in France

In the diesel fuel application two main blends of methyl esters are currently commercialised in France, namely :

- A 5 % mixture of bio-diesel in conventional diesel which is for sale to the public in service stations (without distinctive labelling obligation)
- 30 to 50 % mixtures of bio-diesel for use in bus fleets run by municipalities.

The estimated tonnage of bio-diesel commercialised in France for the total year 1994 is 150,000 Tons.

2 - 7 Environmental Advantages of Bio-Diesel

The main distinctive features of bio-diesel versus conventional diesel fuel are :

- No sulphur
- No aromatics
- Presence of oxygen in the molecular composition
- Renewable energy.

The engine emissions are sulphur free and the other exhaust components are given (on a comparative basis with conventional diesel) in Figure 3.

3 - CONCLUSIONS

Bio-diesel is at present the most attractive market among the non-food applications of vegetable oils. The different stages in the production of rapeseed methyl ester generate by-products which offer further outlets. Oil cake, the protein rich fraction obtained after the oil has been extracted from the seed is used for animal feed.
Glycerol, the other important by-product has numerous applications in the oil and chemical industries such as the cosmetic, pharmaceutical, food and painting industries. New applications are under investigations.
The bio-diesel market in the European Union has a very strong potential growth position due to special fiscal measures that are already applied in several countries and under serious considerations in others.

TABLE 1 - ESTIMATED WORLD VEGETABLE OIL + FAT PRODUCTION

	Production (10^6 T) (1)			Yield, metric t/ha per year
	1980	1990	2000	
Soybean	14.4	16.9	23.2	0.2 - 0.6
Rapeseed (canola, colza)	3.4	8.1	10.7	1.5 - 2
Palm	4.7	10.6	17.4	5 - 8
Sunflower	5.6	8.0	9.9	1 - 1.5
Coconut	3.0	3.0	3.3	3 - 4
Sesame	0.7	1.3	2.1	0.2
Others	11.4	12.7	15.3	
Total	43.2	60.6	81.9	
Animal fat	16.1	18.6	21.5	

TABLE 2 - COMPOSITION OF FATTY ACIDS AND METHYL ESTERS

	* C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C22:1
FATTY ACIDS metyl ester oil	Palmitic %	Stearic %	Oleic %	Linoleic %	Linolenic %	Arachidic %	Gadoleic %	Behenic %	Erucic %
methyl ester Rapeseed oil	5	2	59	21	9	< 0,5	1	< 0,5	< 1
methyl ester Soybean oil	10	4	23	53	8	< 0,5	< 0,5	< 0,5	—
methyl ester Sunflower	7	4	22	65	< 0,5	< 0,5	< 0,5	< 0,5	—

*Cx : y : hydrocarbon chain with X = a number of carbon atoms and Y the number of double bonds.

(1) : A.J. Kaufman + R.J. Ruebusch, J. Amer. Oil Chemist's Soc. - Inform 1, 1034 (1990)

Figure 1
Esterfip Process-Block Diagram

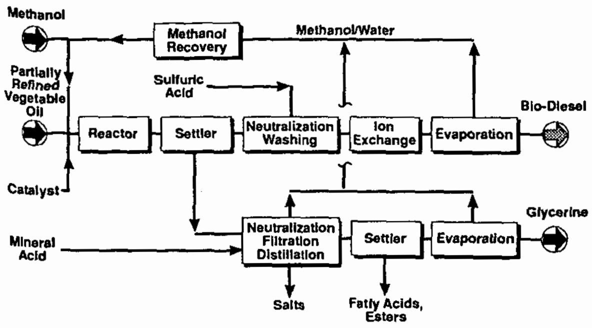

Figure 2
Overall Material Balance (Rapeseed Oil Case)

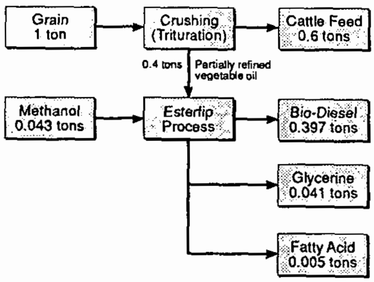

Figure 3
Exhaust Emissions Compared: Bio-Diesel vs Diesel