

## Process Design of Biodiesel Production from Rapeseed Oil

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An integrated design for biodiesel production process from rapeseed vegetable oil is developed. The process simulation software ASPEN Plus version V7.0 is used as a computer aided process engineering (CAPE) tool. The process consists of two steps. The acid-catalyzed pre-treatment achieves total conversion of free fatty acids and partial conversion of triglycerides. This is followed by an alkali-catalyzed step where high conversion of triglycerides is achieved. Compared to other designs reported in the literature, each operation which is common to both steps is performed in one unit, leading to smaller investment cost. Different types of vegetable oil are studied. Among them the rapeseed oil is chosen as raw material for biodiesel production because the rapeseed oil oleic acid content is high and because it is the most common oil in Romania. Moreover, the detailed composition of the rapeseed oil is taken into account. This is determined experimentally by transesterification combined with gas chromatography coupled with mass spectroscopy (GC-MS) and Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy.

### 1. Introduction

During the last years, efforts were made to develop new renewable bio fuels, with the goal of reducing the dependence on imported oil which is associated with political and economic vulnerability, of diminishing pollutants and of revitalizing the economy by increasing demand and prices of agricultural products. Two products appear as promising energy sources: bio ethanol and biodiesel. In Europe the attention focuses on biodiesel due to the larger proportion of diesel engines.

Biodiesel is a fuel composed by mono alkyl esters of the fatty acids, especially methyl esters (FAME). The fatty acids sources used for biodiesel production are vegetable oils and animal fats. The manufacturing process consists of a transesterification reaction that involves triglycerides, alcohols and various catalysts. In this way highly viscous triglycerides are converted to long chain monoesters with much lower viscosity and better combustion properties. Homogenous or heterogeneous catalysis can be used to enhance the reaction rate. The homogeneous catalysis involves substances with a basic or an acidic character, sodium hydroxide or sulphuric acid, respectively, being widely used. The heterogeneous catalysis uses solids with an acid character, such zeolites, clays and ion exchange resins.

Despite the interest in biodiesel, design and simulation of production facilities have been the subject of a small number of studies. Zhang et al. (2003a) considered four different continuous commercial scale processes for biodiesel production from virgin vegetable oil or waste cooking oil under alkaline or acidic conditions. Detailed operating conditions and equipment designs for each process were obtained. A technological assessment of these four processes was carried out to evaluate their technical benefits and limitations. The economics of these processes was analyzed in Zhang et al. (2003b).

In this work, an integrated design of biodiesel production process is presented (Vlad et al., 2010). The acid-catalyzed pre-treatment achieves the total conversion of free fatty acids and partial conversion of triglycerides. The alkali-catalyzed step completes conversion of triglycerides. The separation operations that are common to the acid- and alkali-catalyzed step are performed in the same unit. Experimental results concerning the amount of various triglycerides in several vegetable oils are reported. Among them, the rapeseed oil (most common in Romania) is chosen as raw material and the experimentally-determined composition of the rapeseed oil is used for process simulation. Process simulation is performed in Plus version V7.0 (Aspen Technology Inc., 2008), using NIST database, for a more accurate representation of the physical properties and interaction parameters.

## 2. Experimental

The composition of different oils (Soybean, Ricin, Saffron, Rapeseed, Sunflower and Camelina) was experimentally determined. Methyl esters of fatty acids (FAME) are obtained by the transesterification reaction of oils and methanol. In each experiment, a total of 0.6 mL of oil was weighed into a 100 mL balloon and 10 mL solution of potassium hydroxide/methanol 0.5 N was added. The mixture was stirred and heated to reflux temperature (65 °C) for an h. Then, 2 mL of perchloric acid was added and the mixture was heated to reflux for five minutes. Finally, 20 mL of heptane was added and the mixture was heated again to reflux for two minutes. The mixture was cooled and the organic phase was separated and dried over sodium sulfate.

The methyl esters obtained by transesterification reaction were characterized using GC-MS using a Saturn IV chromatograph equipped with HP5-MS 30 m column. The initial temperature was 60 °C. This temperature was maintained for two minutes and then increased with 5 °C/min until the temperature reached 280 °C. The final temperature of 280 °C was maintained for another minute.

Table 1 presents the fraction of methyl esters obtained after transesterification of the different vegetable oils. It can be observed that the oleic acid is present in significant amounts in all oil types. Rapeseed oils contain the largest quantities of oleic acid, while Ricin oil contains the smallest quantities. Linoleic acid is an important component of Soya, Sunflower and Camelina oils, while palmitic acid is present in large quantities in Palm oil. Ricinoleic acid can be found only in Ricin oil. The amount of stearic acid is relatively small for all oil types.

Table 1 Mass fraction of triglycerides in different oil types.

Oil	Palmitic [% wt.]	Stearic [% wt.]	Oleic [% wt.]	Linoleic [% wt.]	RicinOleic [% wt]
Soybean	12.65	6.92	35.03	44.58	
Saffron	7.21	3.79	42.25	18.90	
Ricin	2.68	3.5	12.67	7.88	57.52
Rapeseed 1	7.32	3.28	62.23	19.37	
Rapeseed 2	6.79	2.30	68.88	13.98	
Palm	35.28	7.32	44.38	10.75	
Sunflower	7.79	5.23	39.6	46.51	
Camelina	9.05	4.10	23.65	62.86	

FTIR-ATR spectroscopy performed in the range 7000 - 400  $\text{cm}^{-1}$  confirms GC-MS results. The spectra of different oil probes appear similar (Figure 1, left). However, the Principal Component Analysis (PCA, Figure 1, right), used in a range 7000-400  $\text{cm}^{-1}$ , show that the two Rapeseed oil probes are similar. The same conclusion applies for camelina and sunflower oil. Ricin and soybean oil probes appear to be quite different compared to the other types.

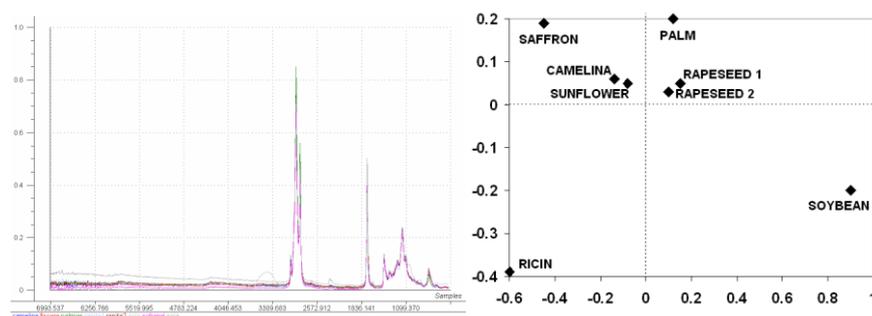


Figure 1: Results of FTIR-ATR spectroscopy (left) and PCA (right).

### 3. Process Design

Today, the high production cost caused by the raw materials is the major obstacle for a large biodiesel market. Research work is focused on finding cheaper feedstock and best catalysts. In basic catalysis (Martinho et al., 2008), the reaction rate is high, 95 % conversion can be reached in one hour. The reaction conditions are accessible and the ratio alcohol / vegetable oil is reasonable. However, the vegetable oil must be of high purity. Especially, the free fatty acids (FFA) should be avoided because they undergo saponification reactions which make the separation very difficult due to foaming.

A biodiesel production process that uses an acid catalyst accepts raw materials with more than 4 % FFA (Goff et al., 2004). This happens because the esterification of free fatty acids and the transesterification of triglycerides occur simultaneously. Therefore, residual oil can be used resulting in a decrease of the production cost. At the same time

the saponification reaction is excluded. However, the reaction is much slower, a 97% conversion being achieved after four hours. Moreover, in order to obtain a high efficiency in a reasonable time, the process needs large catalyst concentration and large molar ratio alcohol/vegetable oil and is sensitive to the water in the system. The strong acids that are used as catalyst are corrosive and have a negative environmental impact. Considering the advantages and disadvantages of the two processes, integrated alternative appears attractive (Chang and Liu, 2010). An integrated process consists in a pre-esterification step that uses an acid catalyst (sulphuric acid) to convert the FFA and a part of the triglycerides, followed by a transesterification step that uses a basic catalyst (sodium hydroxide) to achieve high triglycerides conversion.

The next part of this section presents the design and the simulation of an integrated process for biodiesel production. The process simulation software ASPEN Plus version V7.0 is used with a biodiesel production of 10 tons/h. The procedures for process simulation mainly involve defining chemical components, selecting a thermodynamic model, checking up properties required, choosing proper operating units and setting up input condition. Information on most components, such as methanol, glycerol, sulphuric acid, sodium hydroxide and water is available in the component library.

The rapeseed oil (Table 1, probe 2) is considered as raw material because of its oleic acid content and because is the major vegetable oil used in Romania for biodiesel production. Tri-olein, tri-linolein, tri-palmitin, tri-stearin and oleic acid define the raw material. Methyl-oleate, methyl-linoleate, methyl-palmitate and methyl-stearate are the biodiesel components.

Due to the presence of the highly polar components, UNIQUAC activity model is used. The unavailable interaction parameters coefficients such as methanol/methyl-linoleate, glycerol/methyl-linoleate, etc., are estimated using UNIFAC method. Other pure component properties that are not available in the ASPEN Plus version V7.0 database are estimated by adequate methods (Poling et al., 2004), for example critical volume is estimated by Joback method, vapour pressure is estimated by Riedel method or ideal gas heat capacity is estimated by Benson method.

The main processing units include reactors, distillation columns, heat exchangers, filters, mixers and separators. Because detailed information on the kinetic is not available, a stoichiometric reactor model with 50 % oil conversion is used for the esterification reaction catalysed by sulphuric acid. Similarly, the oil conversion in the transesterification reaction catalysed by sodium hydroxide is taken as 95 %.

Distillation is used for methanol recovery as well as for purification of both the FAME and glycerol products. Although two steps can be distinguished in the integrated process, some processing units are common for the both steps (the column used to purify FAME, the glycerol column). The flowsheet of the process is presented in Figure 2 and is described in the rest of this section.

The esterification reactor *R1* purifies the raw material by eliminating the free fatty acids. A partial conversion of triglycerides is also achieved. Methanol is mixed first with sulphuric acid and the mixture is fed into reactor. The oil is heated first and then is fed into reactor. The esterification reaction is carried out at 80°C and 4 bar, with a 30:1 methanol to oil molar ratio, a 1.3 : 1 sulphuric acid to oil molar ratio. For this reactor, 50% oil conversion and 100% free fatty acid conversion are assumed.

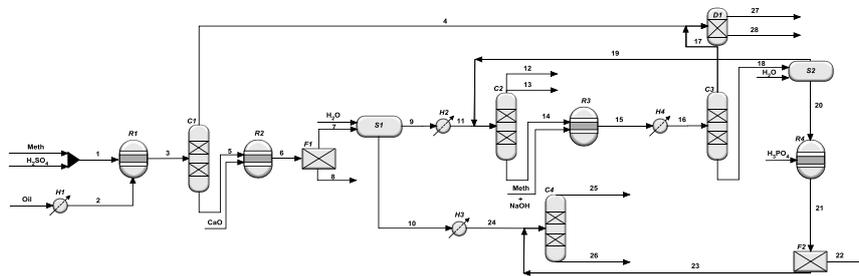


Figure 2: Flowsheet of the integrated biodiesel production plant.

The methanol recovery column *C1* separates the methanol from the reaction mixture. It has seven theoretical stages and the reflux ratio is set to 2. Stream *4* recovers 99% of the methanol. The recovered methanol is dried in a dryer *D1*. The bottom product of the column is directed to the acid removal unit. For this column the condenser duty is  $17 \times 10^3$  kW and the reboiler duty is  $18 \times 10^3$  kW.

In reactor *R2*, sulphuric acid is completely neutralized with calcium oxide (1620 kg/h) to produce  $\text{CaSO}_4$  and  $\text{H}_2\text{O}$ . Calcium oxide is used primarily due its low-cost relative to other alkali substances. Gravity separator *F1* removes solid  $\text{CaSO}_4$ .

The water washing step *S1* separates the FAME and unconverted oil from glycerol and water. After adding 1.8 kg/h water (20°C), the two product streams contain 63% glycerol and 34% water (*10*), respectively 45% unconverted oil and 54% FAME (*9*).

In order to obtain a final biodiesel product with high purity, the FAME purification column *C2*, with eight theoretical stages, partial condenser and a reflux ratio of 2, is used. *C2* is operated under vacuum to keep the temperature low enough to prevent degradation of the biodiesel product. Water and methanol are removed in stream *12* as vent gases. FAME product (99% purity) is obtained in stream *13* as liquid distillate. Unconverted oil remains at the bottom and is directed to the transesterification reactor *R3*. It is important to mention that this column processes FAME mixture resulting from both steps of the process (acid and basic catalysis). The condenser duty is  $5.7 \times 10^3$  kW and the reboiler duty is  $6.4 \times 10^3$  kW.

The stream *14* from the FAME distillation column containing 66% tri-olein and 20% tri-linolein is fed into the transesterification reactor *R3* which is modeled as a stoichiometric reactor. The reaction is carried out with a 6:1 molar ratio of methanol to oil. The concentration of NaOH catalyst is 1%. The reaction takes place at 60 °C and 4 bar. For this reactor a 95% oil conversion is suggested.

The methanol recovery column *C3* separates the methanol which was not converted in the acid-catalyzed step. Seven theoretical stages and a ratio reflux of 2 are necessary to obtain a good separation. 99% of the methanol is found in the distillate stream *17*. The column is operated under vacuum to keep temperature low enough to prevent degradation of the biodiesel product. The condenser duty is  $0.49 \times 10^3$  kW and the reboiler duty is  $0.93 \times 10^3$  kW.

The water washing step *S2* separates the FAME from glycerol and water. 500 kg/h water (20 °C) is added. After processing the stream *20* contains 50 % glycerol, 39 % water and catalyst. The stream *19* contains 94% FAME.

In the reactor *R4*, sodium hydroxide is completely neutralised with phosphoric acid (20.6 kg/h) to produce  $\text{Na}_3\text{PO}_4$  and  $\text{H}_2\text{O}$ .  $\text{Na}_3\text{PO}_4$  is removed in a gravity separator.

Glycerol purification column has eleven theoretical stages and a reflux ratio of 2. The column is operated under vacuum to keep temperature low enough to prevent degradation of the glycerol product. Glycerol product (99.5 %) is obtained in stream 26 as residue liquid. The distillate liquid contains 97% water. As for FAME purification, the glycerol purification column is fed with the streams containing glycerol and water from both the esterification reaction and from the transesterification reaction. The condenser duty is  $2.4 \times 10^3$  kW and the reboiler duty is  $2.1 \times 10^3$  kW.

#### 4. Conclusions

- (i) The detailed composition of seven oil types was experimentally determined (Table 1) with the goal of using this information for the design and simulation of biodiesel production process.
- (ii) An integrated biodiesel production process, using rapeseed oil as raw material, is designed and an ASPEN Plus simulation is built. The process uses a pre-treatment step with the acid-catalysis and a transesterification step with basic-catalysis. The separation operations that are common to the acid-catalysed and alkali-catalysed step are preformed in the same unit.
- (iii) Future work will consider design and simulation of biodiesel production using kinetic models of the esterification and transesterification reaction, with information from literature and experiments performed in the laboratory as source of data.

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