Design of Biodiesel Production Process from Rapeseed Oil

ELENA VLAD, COSTIN SORIN BILDEA, VALENTIN PLESU, GEORGE MARTON, GRIGORE BOZGA
University Politehnica of Bucharest, Department of Chemical Engineering,, Centre for Technology Transfer for the Process Industries, 1-7 Gh. Polizu Str., 011061, Bucharest, Romania

An integrated design for biodiesel production process from rapeseed vegetable oil was developed. The process simulation software ASPEN PLUS was used as a 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. Moreover, the detailed composition of the rapeseed oil was taken into account. This was determined experimentally by transesterification combined with gas chromatography and IR spectroscopy. Considerations regarding the importance of the physical properties during the process simulation activity are also presented.

Keywords: biodiesel, integrated process, design and simulation, transesterification reaction, gas chromatography, IR spectroscopy

Nowadays, the major part of the used energy is provided by fossil fuels (coal, oil, natural gas) [1]. Energy obtained from fossil fuels, hydroelectric and nuclear power is called conventional. During the last years, concerns were raised regarding the depletion of fossil fuels and the environmental impact of the conventional energy use. These concerns were justifiable considering that the fossil fuels are formed over a period of millions of years, but are consumed much faster. Consequently, efforts were made to discover new ways to produce energy using as much as possible what nature can offer and to reduce emissions of both air pollutants and greenhouse gases. This solution is called renewable energy and adds to hydroelectric power a diverse collection of energy sources such as solar, wind, tidal, wave, geothermal, and bio energy. Renewable energy is therefore energy from sources that are replaced as fast as they are used. There is a lot of interest in developing new renewable biofuels 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. In this context, two products appear as promising sources energy: bioethanol and biodiesel. In Europe the attention focuses on biodiesel due to the larger proportion of diesel engines. In the Unites States, bioethanol is the principal attraction because of the higher potential for corn production.

In the last years, biodiesel has gained some advantage considering that the production technology is rapidly evolving, the production equipment becomes more sophisticated and refined and more European countries with a high agricultural potential are interested in biodiesel production [2]. On the other hand biodiesel has a considerable market potential. Biodiesel is known as a fuel composed by mono alkyl esters of the fatty acids. 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 sulfuric 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 has been the subject of a small number of studies. The researchers [3] 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 [4]. When vegetable oil is used as raw material, the alkali-catalyzed process involves smallest process equipment units compared to the acid-catalyzed process. The use of waste cooking oil reduces the raw material cost, but the alkali-catalyzed process is unfeasible because the free fatty acids from the raw materials are transformed in soaps which lead to foaming and very difficult separation. Therefore, the acid-catalyzed process becomes a competitive alternative. The authors suggested the option of a two-step process, where an acid-catalyzed pre-treatment step is followed by an alkali-catalyzed step. It should be remarked that the design presented in the above-cited work uses two different units to perform the same operation (for example FAME purification), one for each step of the process. In this respect design presented in the above-cited works is not an integrated one.

In this work, we present an integrated design of biodiesel production process. 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.

In general, the composition of the oil used as raw material depends on its source. In most simulation, the

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* *email: e_vlad@chim.upb.ro; Tel.: +40 21 4023916*

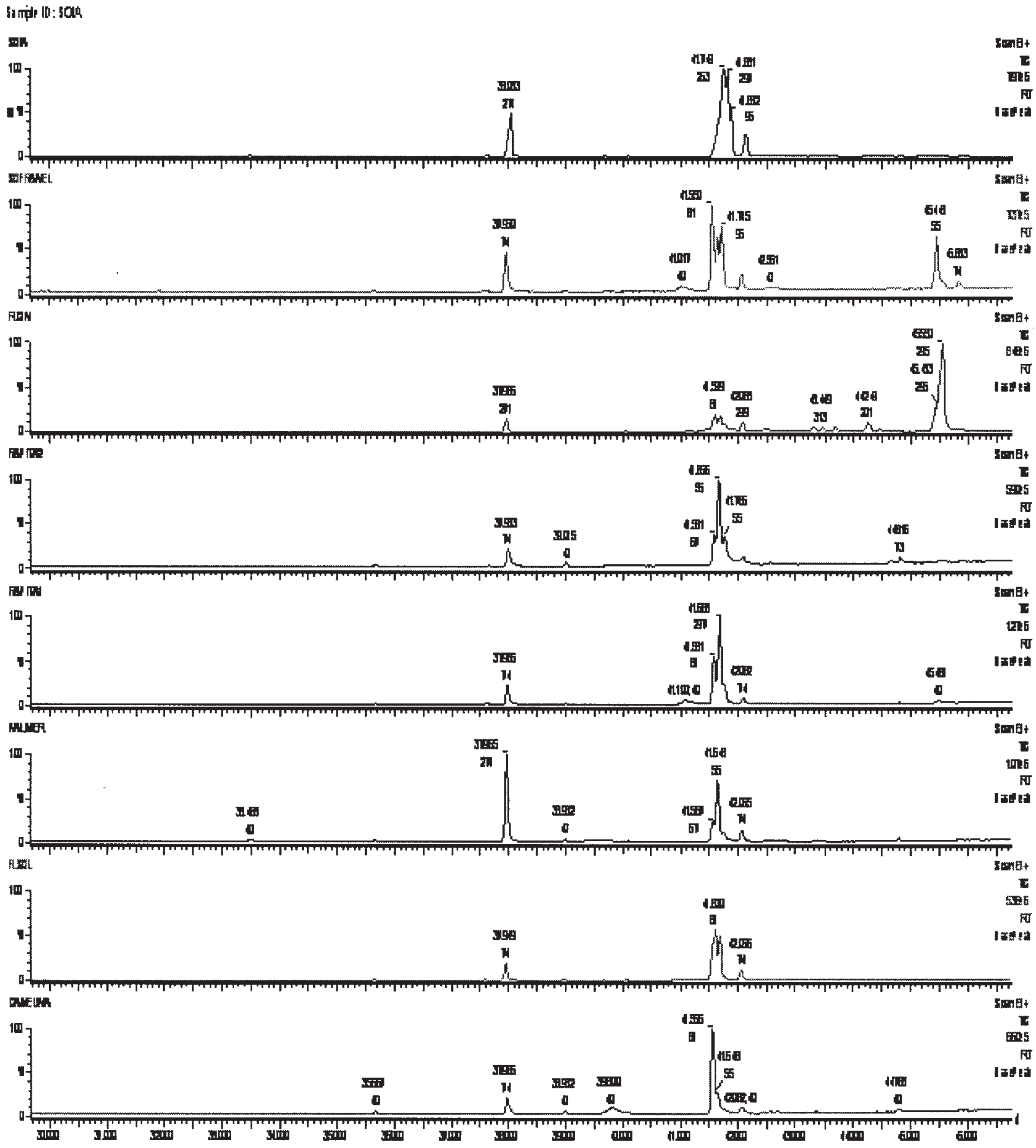

Fig. 1. Results of chromatography analysis

triglycerides were lumped into a common component, which was the tri-oleate.

To design our process, we consider in more detail the composition of the raw material [5]. Thus, we perform and report results of experiments in which the amount of various triglycerides in several oils were determined. Among them we choose rapeseed oil, most common in Romania, as raw material and base our simulation on the experimentally-determined composition.

The third element of novelty concerns the calculation of physical properties. Simulation of previous processes used the UNIFAC estimation method to obtain the interaction parameters of UNIQUAC activity coefficient models [6]. Our simulation, performed in AspenPlus v22, uses the NIST database for a more accurate representation of the physical properties and interaction parameters.

The article is organized as follows. First we report the experimental results concerning the composition of several oils, in order to characterize the raw materials used for biodiesel production. Then, considering that the accurate knowledge of physical properties is the basis for successful flowsheet simulation, we discuss the methods used for estimating the physical properties required. The next section presents the design and simulation of an integrated biodiesel production process. The paper ends with conclusions.

Considerations regarding process simulation

In a typical approach to process design, several alternatives are generated and analyzed, and the best one is selected for further development. For simple processes, experimental testing of the alternatives in a pilot plant is a plausible and responsible decision. Unfortunately, most processes involve many reactants, products and byproducts, reactions and separation operations, therefore being too complex for a pilot plant investigation. Today fast computers and advanced flowsheeting environments are available. These are the tools that can be employed in order to minimize the human effort for assessing the commercial feasibility of various process alternatives

Flowsheeting (process simulation) is a complex activity describing a chemical process with the goal of acquiring

Table 1
COMPOSITION OILS OF DIFFERENT TYPES

Oil	Palmitic [%]	Stearic [%]	Oleic [%]	Linoleic [%]	RicinOleic [%]
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	

knowledge about the process which can be used for various activities such as evaluation, optimization, risk analysis, process control, etc [7]. Process simulation is very advantageous because precious information is obtained without the cost of experimental setups. Simulation helps to identify the experimental conditions which lead to information that is relevant for process understanding. Today's process flowsheet simulators have sophisticated user interfaces, large physical properties databanks and many thermodynamic models. They use estimation methods for the unknown properties and models of various degree of accuracy for mass and energy balance of process units. In this context, today's chemical engineer can be compared with a house builder. The builder knows that the pylons and the bricks are the essential elements of a house. He can design any shape, any size and any color of the house if the pylons are stable and the bricks are arranged in a right way. For a chemical engineer, the pylons are the fundamental laws of chemistry and physics and the bricks are the unit operations. A chemical engineer can generate any plant if the laws of chemistry and physics are obeyed and the unit operations are combined in the right way. So we call a talented house builder or a talented engineer the one who use his creativity in a responsible way.

However, it should be remarked that running sophisticated process simulations does not always guarantee correct results [8,9]. For example, the simulator often accepts a wrong choice for the thermodynamic model or the user can specify a unit operation model based on assumptions that are not valid for the process considered. The simulator issues no warnings about these but produces erroneous results. In conclusion, we always need to ask if the process flowsheet simulators provide a reasonable description of the reality.

Experimental part

Cetene number (CN) is the most important combustion characteristic of biodiesel fuel. It increases with the chain length, but decreases with the unsaturation of the fatty esters. It is considered that Oleic acid is the best fatty acid for biodiesel quality. For this reason, the composition of raw materials is very important for the biodiesel quality and should be taken into account during process design.

In this section we will present results of experimental studies aiming to determine the composition of various oil types which are used as raw material in biodiesel production. This composition will be used during process simulation.

Gas chromatography is a common method for composition characterization [10]. However it cannot be applied to vegetal oils because of the very high boiling point. In the method employed in this study, methyl esters of fatty acids (FAME) are obtained by the transesterification reaction of oils and methanol. Then, the composition of FAME mixture is determined by gas chromatography. This way, the amounts of various fatty acids in the original oil can be assessed.

Different oils were studied: Soybean, Ricin, Saffron, Rapeseed (two types), Sunflower and Camelina. 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 hour. 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.

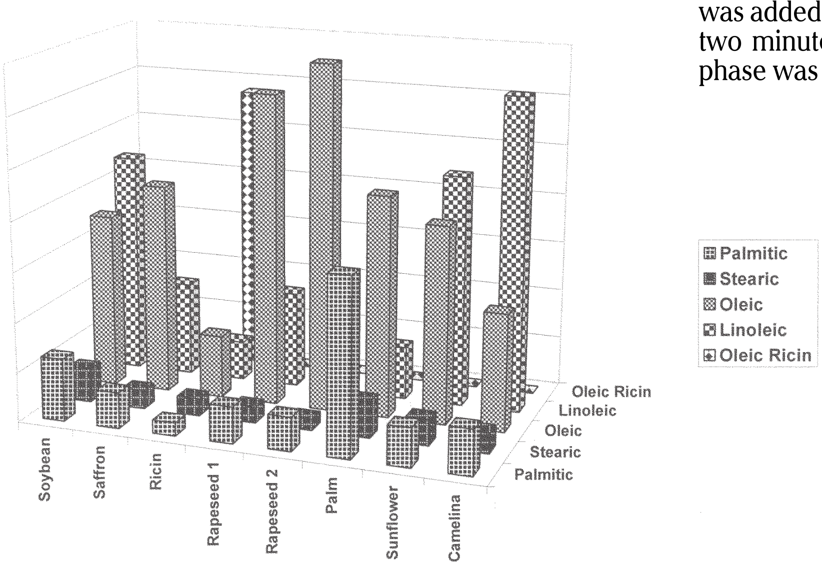

Fig. 2. Comparison of acid content in oils of different type

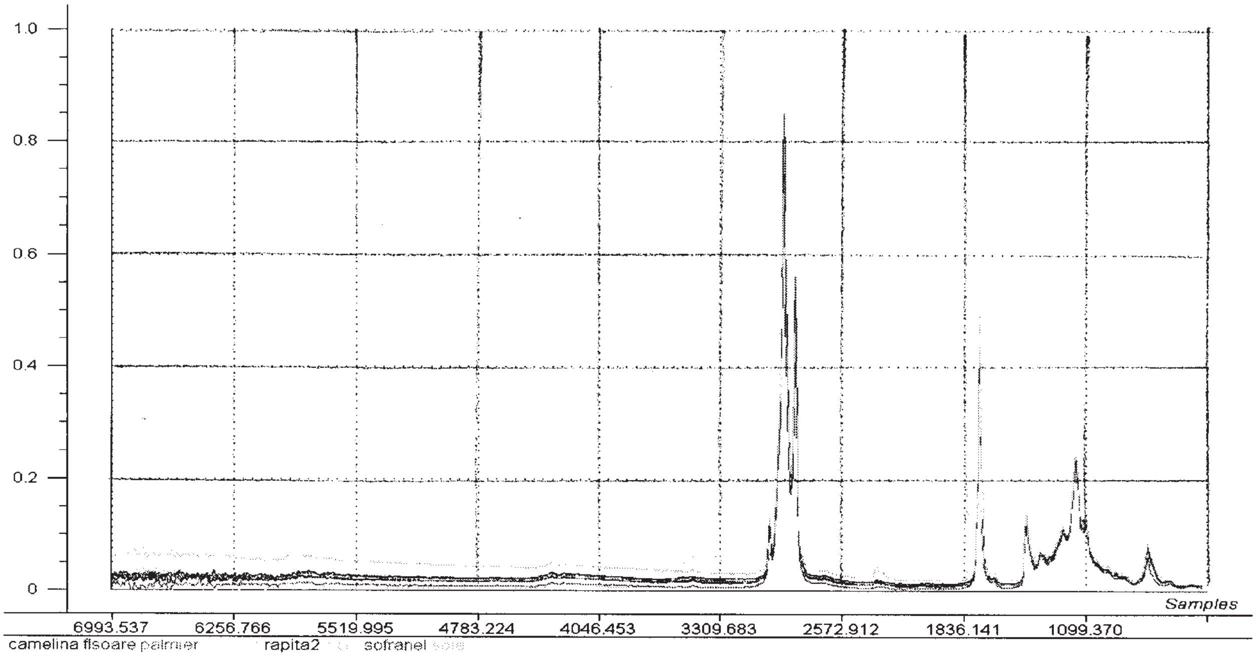

Fig. 3. Comparison of IR spectra for oils of different types

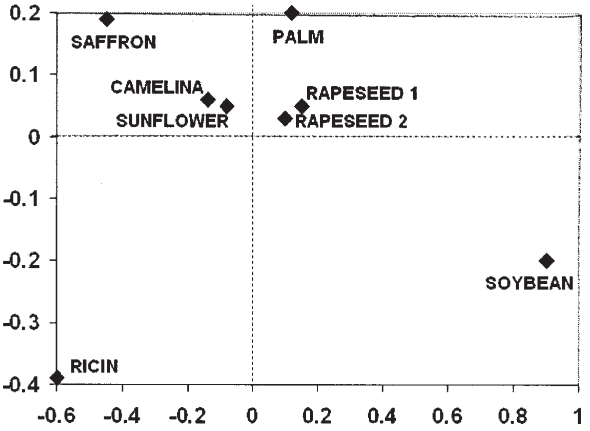

Fig. 4. Results of PCA analysis

Methyl esters characterization

The methyl esters obtained by transesterification reaction were characterized using GC-MS. A GC-MS (Saturn IV) was equipped with a HP5-MS 30 meters column. The initial temperature was 60°C. This temperature was maintained for two minutes and then increased with 5 °C per minute until the temperature reached 280°C (in 44 min). The final temperature of 280°C was maintained for another minute. Figure 1 shows typical chromatograms.

Table 1 and figure 2 present 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. However, the fraction does not exceed 70% and, for this reason, considering the triglyceride of oleic acid as the unique component of oil might not be a reasonable assumption. 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.

We conclude that Rapeseed oil, having 69% oleic acid, is a raw material which is suitable for the biodiesel production. Therefore, the composition experimentally obtained will be used for the design of the process.

FTIR-ATR spectroscopy

FTIR-ATR spectroscopy [11] performed in the range 7000 - 400 cm^{-1} confirms chromatography results. The spectra of different oils (fig. 3) appear similar. However, the Principal Component Analysis (PCA) can transform a number of possibly correlated variables into a smaller number of uncorrelated variables, called principal components. PCA method was used in a range of 7000-400 cm^{-1}. The results (fig. 4) show that the two rapeseed oils are similar. The same conclusion applies for Camelina and Sunflower oil. Ricin and soybean oils appear to be quite different compared to the other types.

Physical properties

In this section we will demonstrate that physical and thermodynamic properties are relevant information for de simulation activity [12].

Let us assume that the vapor pressure of a species is needed during simulation. The simulator can calculate the values for vapor pressure using two routes [13,14]. First route starts from experimental data and the parameters of Antoine or Wagner equation can be obtained by regression. The second route is based on estimation methods. For example, the Antoine equation parameters are estimated by Li-Ma or Riedel methods. In turn, Li-Ma method requires boiling point (T_b) and molecular structure. Riedel method needs boiling point (T_b) and critical points (T_c,P_c). The values of the boiling point and critical points can be obtained by using experimental data or by estimation. The estimation methods for the boiling point and critical parameters are Gani and Joback. The information required for the Joback and Gani methods is molecular structure. For Wagner equation, critical properties are the required, parameters which can be estimated by Gani and Joback method. The diagram presented in figure 5 summarizes the routes and the interdependence between different estimation methods.

Knowledge of the calculations done by the simulator and of the assumption on which the calculations are based is essential for choosing the right estimation route and for assessing the accuracy of the results.

Figure 6 presents the dependence of vapor pressure

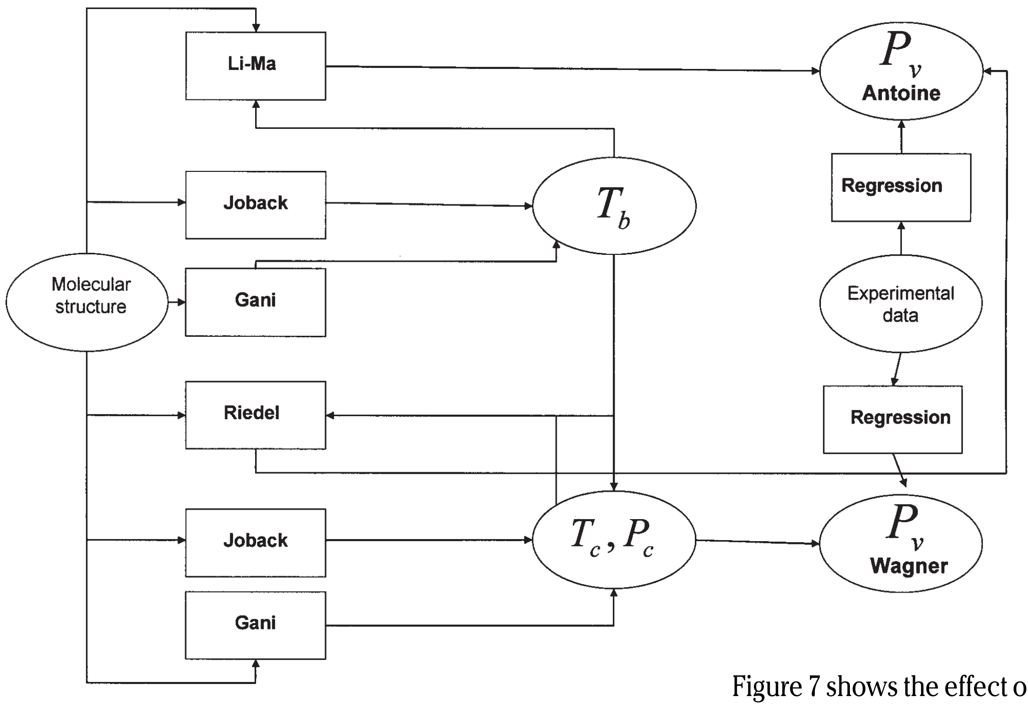

Fig. 5. Routes for calculating various physical properties

versus temperature, for methyl-oleate, calculated by various routes. Firstly, the Antoine equation with coefficients from the database of the simulator was employed (1). Because these coefficients are based on experimental results, we regard this method as being the most accurate. Secondly, the Antoine coefficients are estimated by Riedel method [15] while the required parameters (T_b, T_c, P_c) were estimated by a first-order method (Joback, 2) [15] and a second-order method (Gani, 3) [6]. Then, Li-Ma method [15] was employed, with the required parameter (T_b) estimated again by Joback (4) and Gani methods (5). Figure 6 shows that using a second order method and a minimum number of parameters estimated from the molecular structure gives the best predictions.

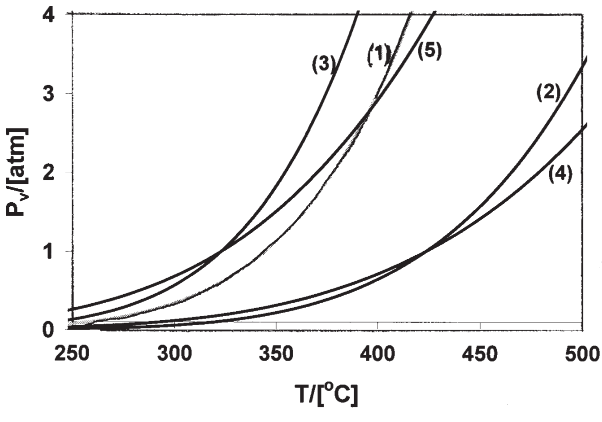

Fig. 6. Different methods of estimation for methyil-oleate
The predictions of the estimation methods depend on the source of parameters

(1)- All the properties, vapor pressure (P_v), boiling point (T_b), critical parameters (T_c, P_c) are from data base (DB)

(2)- P_v is estimated by Riedel method and T_b, T_c, P_c, are estimated by Joback method

(3)- P_v is estimated by Riedel method and T_b, T_c, P_c, are estimated by Gani method

(4)- P_v is estimated by Li-Ma method and T_b is estimated by Joback method

(5)- P_v is estimated by Li-Ma method and T_b is estimated by Gani method

Figure 7 shows the effect of including additional known values in the estimation procedure. Thus, the vapor pressure was estimated by Riedel and Li-Ma methods when the boiling point was estimated by Gani method (3, 5) or when the exact value was taken from the database (3a, 5a). Comparing with figure 6, it is obvious that knowledge of the boiling point improves the estimation accuracy. We conclude that any experimental data that is available must be used to enhance the accuracy of property estimation.

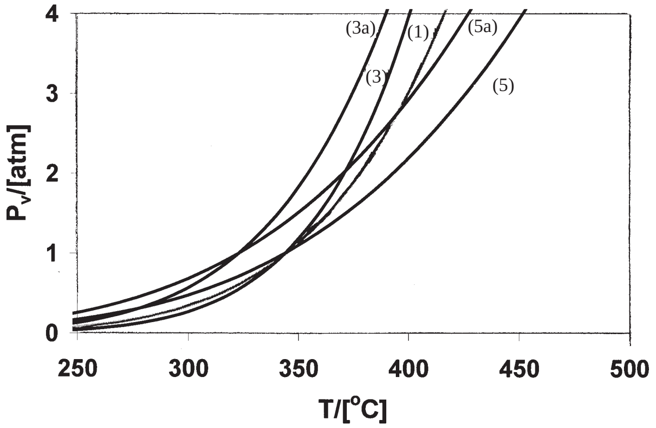

Fig. 7. Different methods of estimation for methyil-oleate knowing boiling point
This figure shows the importance of the experiment. Knowledge of the boiling point improves the accuracy of the estimation methods.

(1)- All the properties, vapor pressure (P_v), boiling point (T_b), critical parameters (T_c, P_c) are from data base (DB)

(3)- P_v is estimated by Riedel method and T_b, T_c, P_c, are estimated by Gani method

(3a)- P_v is estimated by Riedel method, T_b is from DB and T_c, P_c are estimated by Gani method

(5)- P_v is estimated by Li-Ma method and T_b is estimated by Gani method

(5a)- P_v is estimated by Li-Ma method and T_b is from DB

Figure 8 considers fours different species: triolein (which has the more complex molecular structure), diolein, monooelein and methyl–oleate (the simplest molecular structure). The vapor pressure is estimated by Riedel method and the other necessary properties are estimated by Gani method. It can be seen that estimation methods work better for smaller, simpler molecules.

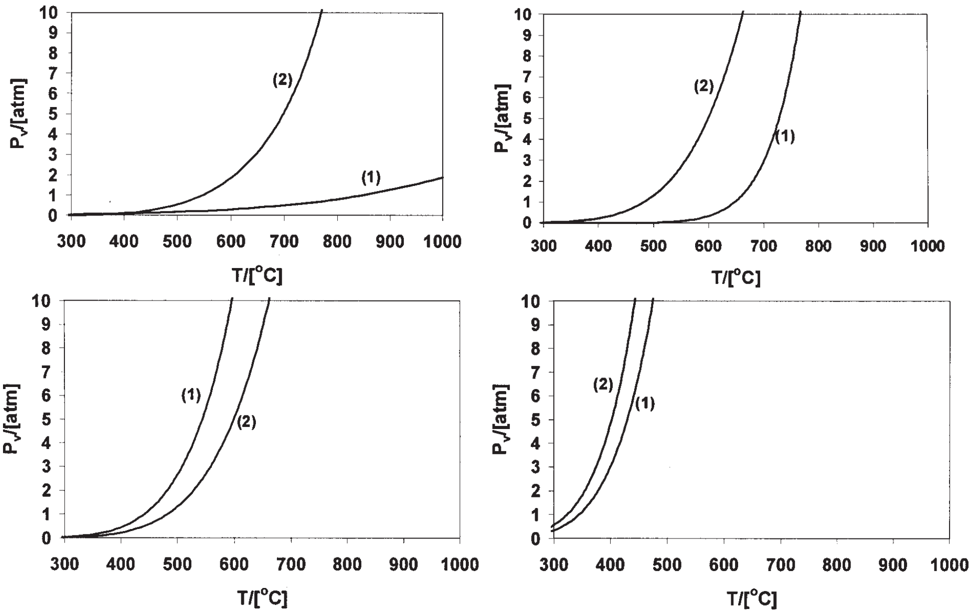

Fig. 8. Riedel estimation for different molecules. From left to right: triolein, diolein, monooelein, methyl-oleate The molecular structure influences the accuracy of the estimation. Riedel method works best for methyl-oleate and worst for triolein.
(1)- All the properties, vapor pressure (P_v), boiling point (T_{b0}), critical parameters (T_c, P_c) are from data base (DB)
(2)- is estimated by Riedel method and T_b, T_c, P_c, are estimated by Gani method

Process design

This section presents the assumptions and the results of the design of an integrated biodiesel process. The process takes place in two steps: acid catalysis followed by basic catalysis.

Today, the high production cost caused by the raw materials is the major impediment for large biodiesel marketing [16,17]. Many research activities are focused on finding cheaper raw materials and better catalysts. In basic catalysis [18], the reaction rate is high, a conversion of 95% being achieved in one hour. The reaction conditions are accessible and the molar ratio alcohol/ oil is reasonable. However, the vegetal 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. Therefore, the requirement of pure raw materials increases the production cost.

A biodiesel production process that uses an acid catalyst accepts raw materials with more than 4% free fatty acids [19,20]. This happens because the esterification of free fatty acids and the transesterification of triglycerides occur simultaneously. Therefore, residual oil can be used resulting in decrease of the production cost. At the same time the saponification reaction is excluded with beneficial effects on the easiness of separation. 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, a large molar ratio alcohol/oil and is sensitive to the water concentration 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 previously described, and integrated alternative appears attractive. An integrated process consists in a pre-esterification step that uses an acid catalyst (sulfuric 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 22.0 was used.

The procedures for process simulation mainly involve defining chemical components, selecting a thermodynamic model, checking up on properties required, choosing proper operating units and setting up input condition (flow rate, temperature, pressure and other condition). Information on most components, such as methanol, glycerol, sulfuric acid, sodium hydroxide and water is available in the ASPEN PLUS component library [21].

The rapeseed oil is considered as raw material because this is the major oil used in Romania. The composition of the rapeseed oil is presented in table 1. Triolein, trilinolein, tripalmitin, tristearin and oleic acid define the raw material. Methyl-oleate, methyl-linoleate, methyl-palmitate and methyl-stearate are the biodiesel components. All these chemical species are available in the ASPEN PLUS database.

Due to the presence of the highly polar components, universal quasi-chemical (UNIQUAC) thermodynamic/ activity model was used. The unavailable interaction parameters coefficients such as methanol/methyl-linoleate, glycerol/methyl-linoleate, etc were estimated using UNIFAC method.

Other pure component properties that are not available in the ASPEN PLUS database were estimated by adequate methods, for example critical volume estimated by Joback method, vapor pressure estimated by Riedel method or ideal gas heat capacity estimated by Benson method [6].

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

Distillation was 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 9 and will be described in the rest of this section. Table 2 and table 3 will present a detailed mass balance.

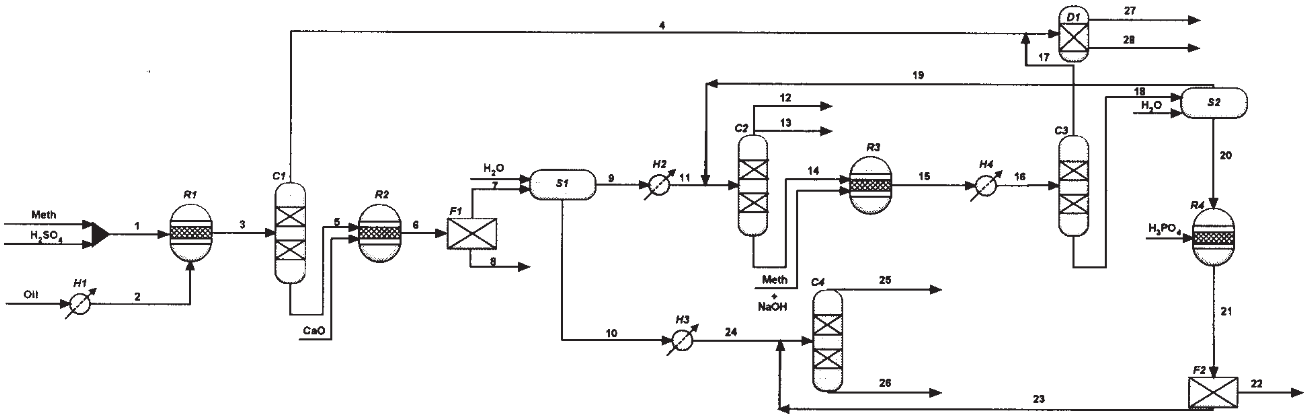

Fig. 9. Flowsheet of the integrated biodiesel production plant

Esterification (R1)

The 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 sulfuric 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 sulfuric acid to oil molar ratio. For this reactor we used a 50% oil conversion and a 100% free fatty acid conversion.

Methanol recovery (C1)

The distillation column *C1* separates the methanol from the reaction mixture. It has seven theoretical stages and the reflux ratio was set to 2. Stream 4 recovers 99% of the methanol. For this reason, the recovered methanol is dried in *D1*. The bottom product of the column is directed to the acid removal unit. For this column the condenser duty is 14.75×10^6 kcal/h and the reboiler duty is 15.70×10^6 kcal/h.

Acid removal (R2, F1)

In reactor *R2*, sulfuric acid is completely neutralized with calcium oxide (1620 kg/h) to produce $CaSO_4$ and H_2O. Calcium oxide was used primarily due its low-cost relative to other alkali substances. A gravity separator *F1* removes the $CaSO_4$.

Table 2

MASS BALANCE

Stream name	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
Temperature (°C)	20	80	80	82	232.5	60	60	60	29	20	160	100	100
Mass flow/ (1000 kg/h)	21.6	10.3	31.9	19.4	12.5	13.6	11.1	2.44	10.4	0.785	10.4	0.049	10.3
Component mass fraction													
Methanol	0.92	0	0.60	0.99	0.002	0.002	0.0025	0	0.0012	0.0199	0.0012	0.22	0.0002
Triolein	0	0.62	0.1	TRACE	0.25	0.23	0.28	0	0.30	TRACE	0.30	TRACE	0.0004
Trilinolein	0	0.19	0.003	TRACE	0.08	0.07	0.09	0	0.095	TRACE	0.095	0	TRACE
Tristearin	0	0.03	0.05	0	0.01	0.012	0.015	0	0.016	TRACE	0.016	0	0
Tripalmitin	0	0.07	0.018	TRACE	0.03	0.027	0.036	0	0.036	TRACE	0.036	0	TRACE
Methil-Oleate	0	0	0.12	TRACE	0.32	0.29	0.36	0	0.39	TRACE	0.39	0.0028	0.70
Methil-Linoleate	0	0	0.03	TRACE	0.08	0.07	0.09	0	0.096	TRACE	0.096	0.001	0.19
Methil-Stearate	0	0	0.005	TRACE	0.013	0.012	0.015	0	0.016	TRACE	0.016	0.0001	0.03
Methil-Palmitate	0	0	0.018	TRACE	0.03	0.027	0.034	0	0.036	TRACE	0.036	0.001	0.07
Oleic acid	0	0.078	0	0	0	0	0	0	0	0	0	0	0
Glycerol	0	0	0.015	TRACE	0.03	0.036	0.045	0	TRACE	0.63	TRACE	0.001	TRACE
H_2O	0	0	0.016	0.002.	0.0002	0.02	0.026	0	0.0028	0.43	0.0028	0.76	0.00046

Table 2 (continued)

Stream name	14	15	16	17	18	19	23	24	25	26	27	28
Temperature (°C)	357	60	125	64	235	20	20	105	100	225	64	64
Mass flow/ (1000 kg/h)	5.09	6.15	6.15	0.53	56.1	5.13	0.98	1.77	0.78	0.99	19.8	0.048
Component mass fraction												
Methanol	TRACE	0.087	0.087	0.99	0.0004	TRACE	0.0022	0.01	0.02	TRACE	0.99	0
Triolein	0.66	0.027	0.027	TRACE	0.03	0.032	TRACE	TRACE	TRACE	0	TRACE	0
Trilinolein	0.20	0.0085	0.0085	TRACE	0.009	0.01	TRACE	TRACE	0	0	0	0
Tristearin	0.03	0.0014	0.0014	TRACE	0.0015	0.0017	TRACE	TRACE	0	0	0	0
Tripalmitin	0.07	0.003	0.003	TRACE	0.003	0.0038	TRACE	TRACE	0	0	0	0
Methil-Oleate	0.01	0.53	0.53	TRACE	0.58	0.64	TRACE	TRACE	TRACE	TRACE	TRACE	0
Methil-Linoleate	0.004	0.16	0.16	TRACE	0.18	0.19	TRACE	TRACE	TRACE	TRACE	TRACE	0
Methil-Stearate	0.001	0.028	0.028	TRACE	0.03	0.03	TRACE	TRACE	TRACE	TRACE	TRACE	0
Methil-Palmitate	TRACE	0.06	0.06	TRACE	0.06	0.07	TRACE	TRACE	TRACE	TRACE	TRACE	0
Glycerol	TRACE	0.08	0.08	TRACE	0.08	TRACE	0.50	0.56	0.006	1	TRACE	0
H_2O	TRACE	0	0	0	0	0.002	0.49	0.42	0.97	TRACE	0	1

Water washing (S1)

The purpose of this step is to separate 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 (stream 10), respectively 45% unconverted oil and 54% FAME (stream 7). Before entering the FAME distillation column, the stream 9 is brought at the boiling temperature in the heat exchanger *H2*.

FAME purification (C2)

In order to obtain a final biodiesel product with high purity, the distillation column *C2*, with eight theoretical stages, partial condenser and a reflux ratio of 2, was used. *C2* was operated under vacuum to keep the temperature low enough to prevent degradation of the biodiesel product. Water and methanol are removed in stream 13 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 interesting to mention that this column processes FAME – oil mixture resulting from both steps of the process (the acid and the basic catalysis). This integration reduces the investment and energy costs. The condenser duty is 4.93×10^6 kcal/h and the reboiler duty is 5.51×10^6 kcal/h.

Transesterification (R3)

The stream 14 from the FAME distillation column containing 66% triolein and 20% trilinolein is fed into reactor *R3* which was modeled as a stoechiometric 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 second methanol recovery (C3)

This unit 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 in the feed stream 9 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 0.42×10^6 kcal/h and the reboiler duty is 0.80×10^6 kcal/h.

The second water washing (S2)

The purpose of this step is to separate 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.

Sodium hydroxide removal (R4)

The next step is to remove the basic catalyst. Phosphoric acid (20.66 kg/h) is used to neutralize the sodium hydroxide. The resulting Na_3PO_4 is removed in a gravity separator.

Glycerol purification

Glycerol purification column has eleven theoretical stages and a reflux ratio of 2. The column is operated under vaccum to keep temperature low enough to prevent degradation of the glycerine product. Glycerol product (99.5%) was obtained in stream 26 as residue liquid. The distillate liquid contains 97% water. As for FAME purification, in order to reduce the cost 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 2.06 x 106 kcal/h and the reboiler duty is 1.83 x 10^6 kcal/h.

Conclusions

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. The method combined transesterification with methanol and GC-MS analysis of the resulting mixture. The composition was confirmed by IR spectroscopy and Principal Component Analysis.

Accurate physical properties are required for a realistic simulation of biodiesel production. Although the databases in the recent version of the process simulator AspenPlus contain many components relevant in biodiesel production, many physical properties must be estimated. In this article, we demonstrate that any experimental data available contributes to better estimation of unknown properties. Because most of the estimation methods use the molecular structure, the complexity of the molecule affects the estimation accuracy.

An integrated biodiesel production process, using rapeseed oil as raw material, was designed and an AspenPlus simulation was built. The process uses a pretreatment step with the acid-catalysis and a transesterification step with basic-catalysis. The separation operations that are common to the acid- and alkali-catalyzed step are preformed in the same unit allowing a decrease in the energy and equipment costs.

Future work will consider developing a process simulation for biodiesel production using a kinetic model of the esterification and transesterification reaction, with information from literature and experiments performed in our laboratory as source of data.

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