Relation between quality and production cost for pure biodiesel bases on the mixes of raw materials

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Abstract. Nowadays biodiesel has become more attractive because it is made from renewable resources. The main ingredients of industrial biodiesel are rap oil, sun oil, fat acid, olive oil cooked. In this study we verify that, the proportion of these components sets the qualitative composition and energy efficiency of the final product. Essential we link the raw materials (rap oil, sun oil, fat acid, olive oil cooked) used in the manufacture of industrial biodiesel the proportion of mixes, with the variation of physicochemical properties of biodiesel produced. According to the quantitative analysis we notice that the physiochemical properties which alter the value for example humidity, acidity, while a large number of physicochemical properties do not change their value depending on the ratio of raw materials in each mixture. The analysis of these changes seems that the presence of fat acids is negative for the quality of the mixture. From the analysis of the cost of the final mixtures that lower cost is achieved in the mixture was 10 and the highest cost was in the mixture 3. Based on a study of the cost of the mixtures can determine a basic relation between the quality and the cost of the final product.

1. Introduction
It is generally accepted that biodiesel as a renewable energy product is clean, non-toxic and biodegradable, contains no aromatic compounds and emissions of the pollutants sulfur oxides, carbon monoxide, unburned hydrocarbons and soot from the burning of the diesel engines are very low. The presence of sulfur in fuels is responsible oxides of sulfur in the exhaust gas which are one of the main pollutants of diesel. In biodiesel the sulfur density is very small, almost zero.

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The biodiesel is commonly produced by the transesterification of the vegetable oil or fat acid feedstock. The material used for the production of fatty acid methylester is oil. This oil comes from various kinds of oils such as olive oil cooked and fat acids, vegetable oils which content sunflower, cottonseed, rapeseed, soybean and vegetable oil who comes from energy crops and is already prepared when they arrive at the plant as a raw material.

Nevertheless the problems which have to be solved, in relation to the production route, are many but the most important are the cost and the quality of the final products. Biodiesel is categorized as one of the liquid biofuels, an alternative diesel fuel, derived from renewable biological sources such as virgin oil feedstock, waste vegetable oil, algae, oil from halophytes and fat acids [1–3]. It is generally known that this approach comes from the period when Rudolf Diesel tested vegetable oil as fuel for his engine, more than one century ago[1].

During the decades of 1930s and 1940s vegetable oils were used as diesel fuels but usually only in emergency situations. Because of the continuous growing demand for energy, the scientific community, the oil companies as wells as the governments worldwide, are looking for new energy sources including the biofuels. In recent years up to 16 % of global final energy consumption comes from renewable sources [4] and this figure is continuously increasing.

Because of the way of the production of biodiesel inevitably the final mixture contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. Even refined oils and fats contain small amounts of free fatty acids and water [5]. The diesel fuels, both conventional diesel fuels as well as biodiesel/diesel blends, need to satisfy a wide range of engine types. Alongside it must be on top for different operating conditions and duty cycles, as well as in variations of fuel system technology, at the engine temperatures and fuel system pressures. It must also be suitable for a variety of climates. The properties of each grade of diesel fuel must be balanced to provide satisfactory performance over an extremely wide range of circumstances. In some respects, the prevailing quality standards represent certain compromises so that all the performance requirements may be satisfied. By controlling specifications and properties, it is possible to satisfy the requirements of millions of compression ignition engines with a single grade of diesel fuel.

The study of physicochemical properties of biodiesel has become much written lately [6-13], but there are not references to the effect of mixing the raw materials on properties of biodiesel produced as well as the correct mixture that gives the balance between quality and production cost of the final product.

In this study it is easily understood that the values of the properties of pure biodiesel are dependent on the mix of raw materials. Specifically the quality of the final biodiesel is directly affected by the analogy of raw material such us fat acid and olive oil cooked. When the values are increased the final product is not good from qualitative point of view. With the methodology developed in this work is given the possibility to determine the blending limits of raw materials (rap oil, sun oil, fat acid, olive oil cooked) for the production of industrial biodiesel before the production process, identified and costs in relation to raw materials, the produced biodiesel.

The production of the mixtures made by mixing the raw materials which came from the energy plant oils, oils from fat acids and oils cooked. The finished biodiesel depends on the value of the acidity and the water present in the raw materials used for mixing.

2. Materials and methods

2.1. Materials

All the experiments were performed employing fuel samples from commercial sources. Especially, the vegetable and fat oil based biodiesel was procured from ELIN OIL A.C.company.

Oils from energy crops for the production of mixtures used, rap, sun oil, and oils from fat acid, fat acid, and olive oil cooked. Especially vegetable blends are derived from rapeseed and soybean oil. In particular were generated 10 mixtures of raw materials (rap oil, sun oil, fat acid, olive oil cooked) in various proportions as shown in table 1.
Table 1. Mixing of raw materials (rap oil, sun oil, fat acid, olive oil cooked) to create mixtures produced pure biodiesel

| Properties       | Unit | Mix 1 | Mix 2 | Mix 3 | Mix 4 | Mix 5 |
|------------------|------|-------|-------|-------|-------|-------|
| Olive oil cooked | %    | 50%   | 40%   | 37%   | 50%   | 30%   |
| Rap oil          | %    | 20%   | 42%   | -     | 20%   | 25%   |
| Sun oil          | %    | -     | 25%   | 16%   | 10%   | -     |
| Fat acid         | %    | 30%   | 35%   | 5%    | 40%   | 50%   |

Then, after appropriate treatment of the mixtures were determined the values of the physicochemical properties of biodiesel produced by the method EN ISO [14-42]. These values are also the properties of the produced industrial pure biodiesel.

3. Results and discussion
After the creation of the mixtures were determined values of physicochemical properties and forming properties of the produced pure biodiesel industry, as shown in table 2 and table 3.

3.1. Physicochemical properties of mixtures.
In table 2: Prices physicochemical properties of raw material mixes (rap oil, sun oil, fat acid, olive oil cooked) in various ratios to prepare pure industrial biodiesel.

Table 2.A. Values physicochemical properties of raw material mixes (rap oil, sun oil, fat acid, olive oil cooked) in various ratios to prepare pure industrial biodiesel (remains stable during the experiment).
Table 2.B. Values physicochemical properties of raw material mixes (rap oil, sun oil, fat acid, olive oil cooked) in various ratios to prepare pure industrial biodiesel (remains stable during the experiment).

| Properties                  | Unit | MIN | MAX | Method                                      | Mix 6 | Mix 7 | Mix 8 | Mix 9 | Mix 10 |
|-----------------------------|------|-----|-----|---------------------------------------------|-------|-------|-------|-------|--------|
| Density                     | Kg/m³ | 860 | 900 | ENISO 12185                                 | 881,2 | 881,5 | 881,5 | 881,1 | 881,1  |
| Viscosity                   | mm²/s | 3.5 | 5   | ENISO 3104                                  | 4,5   | 4,5   | 4,5   | 4,5   | 4,5    |
| Total sulfur                | mg/kg | 10  |     | ENISO 20846                                 | 4,8   | 4,8   | 4,8   | 4,8   | 4,8    |
| Carbon residue              | %m/m  | 0,3 |     | ENISO 10370                                 | -     | -     | -     | -     | -      |
| Sulphated ash               | %m/m  | 0,02|      | ENISO 3987                                 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01  |
| Solid                       | mg/kg | 24  |     | ENISO 12662                                 | 10    | 10    | 10    | 10    | 10     |
| Phosphorus                  | mg/kg | 4   |     | ENISO 12185                                 | 1,2   | 1,2   | 1,2   | 1,2   | 1,2    |
| Na                          | mg/kg | 5   |     | ENISO 12185                                 | 0,1   | 0,1   | 0,1   | 0,1   | 0,1    |
| K                           | mg/kg | 5   |     | ENISO 12185                                 | 0,3   | 0,3   | 0,3   | 0,3   | 0,3    |
| Ca                          | mg/kg | 5   |     | ENISO 12185                                 | 0,2   | 0,2   | 0,2   | 0,2   | 0,2    |
| Mg                          | mg/kg | 5   |     | ENISO 12185                                 | 0,2   | 0,2   | 0,2   | 0,2   | 0,2    |
| Methanol                    | %min  | 0,2 |     | ENISO 12185                                 | 0,03  | 0,03  | 0,03  | 0,03  | 0,03   |
### Table 3.A. Values physicochemical properties of raw material mixes (rap oil, sun oil, fat acid, olive oil cooked) in various ratios to prepare pure industrial biodiesel (change during the experiment).

| Properties                  | Unit | MIN | MAX | Method                                      | Mix 1     | Mix 2     | Mix 3     | Mix 4     | Mix 5     |
|-----------------------------|------|-----|-----|---------------------------------------------|-----------|-----------|-----------|-----------|-----------|
| Ignition point              | °C   | 101 | -   | ENISO 3679                                  | 180       | 164       | 172       | 176       | 178       |
| Water                       | mg/kg| -   | 0,02| ENISO 12937                                 | 289,7     | 269       | 230       | 300,1     | 250,1     |
| CFPP                        | °C   | -   | =5/-5| EN116                                       | 0         | -1        | 0         | 0         | 0         |
| Methylester                 | %m/m | 96,5| -   | EN1403                                      | 97,08     | 96,98     | 97,05     | 96,03     | 97        |
| Acid methyl. His linolenikou acid | %m/m | -   | 12  | EN1410 3                                   | 2,61      | 3,18      | 3,08      | 3,08      | 3,01      |
| Acidity                     | mgKOH/g | -   | 0,5 | EN1410 4                                   | 0,12      | 0,13      | 0,08      | 0,13      | 0,12      |
| Iodine Value                | g iodine / 100g | -   | 120 | EN1411 1                                   | 99,5      | 99,7      | 99,7      | 99,4      | 99,6      |
| Monoglycerides              | %m/m | -   | 0,8 | EN1410 5                                   | 0,285     | 0,329     | 0,305     | 0,3       | 0,299     |
| Diglycerides                | %m/m | -   | 0,2 | EN1410 5                                   | 0,079     | 0,079     | 0,079     | 0,077     | 0,076     |
| Triglycerides               | %m/m | -   | 0,2 | EN1410 5                                   | 0,087     | 0,087     | 0,088     | 0,088     | 0,087     |
| Free glycerol               | %m/m | -   | 0,02| EN1410 6                                   | 0,008     | 0,004     | 0,001     | 0,001     | 0,001     |
| Total glycerol              | %m/m | -   | 0,25| EN1410 5                                   | 0,101     | 0,108     | 0,1       | 0,1       | 0,101     |
Table 3.B. Values physicochemical properties of raw material mixes (rap oil, sun oil, fat acid, olive oil cooked) in various ratios to prepare pure industrial biodiesel (change during the experiment).

| Properties                  | Unit | MIN | MAX | Method                                      | Mix 6 | Mix 7 | Mix 8 | Mix 9 | Mix 10 |
|-----------------------------|------|-----|-----|---------------------------------------------|-------|-------|-------|-------|--------|
| Ignition point              | °C   | 101 | -   | ENISO 3679                                  | 181   | 180   | 180   | 175   | 180    |
| Water                       | mg/kg| -   | 0,02| ENISO 12937                                 | 257,9 | 279,9 | 249,9 | 305,9 | 232,9  |
| CFPP                        | °C   | -   | -5/5| EN11 6                                     | 0     | 0     | 0     | 0     | 0      |
| Methylester                 | %m/m | 96,5| -   | EN14 03                                    | 96,09 | 97,01 | 98,01 | 96    | 98     |
| Acid methyl. His linolenikou acid | %m/m | 12  | 3,03| EN14 103                                   | 3,03  | 3,01  | 3,01  | 3     | 3,01   |
| Acidity                     | mgKOH| -   | 0,5 | EN14 104                                   | 0,14  | 0,14  | 0,13  | 0,14  | 0,07   |
| Iodine Value                | g iodine / 100g | - | 120 | EN14 111                                   | 98,6  | 98,2  | 98,7  | 97,7  | 98,8   |
| Monoglycerides              | %m/m | -   | 0,8 | EN14 105                                   | 0,382 | 0,389 | 0,229 | 0,399 | 0,231  |
| Diglycerides                | %m/m | -   | 0,2 | EN14 105                                   | 0,091 | 0,094 | 0,094 | 0,294 | 0,097  |
| Triglycerides               | %m/m | -   | 0,2 | EN14 105                                   | 0,087 | 0,087 | 0,087 | 0,087 | 0,087  |
| Free glycerol               | %m/m | -   | 0,02| EN14 106                                   | 0,001 | 0,001 | 0,001 | 0,003 | 0,001  |
| Total glycerol              | %m/m | -   | 0,25| EN14 105                                   | 0,101 | 0,101 | 0,101 | 0,102 | 0,101  |

From analysis of the above tables it is apparent that the physicochemical properties of table 3 are those which are altered by the creation of mixtures of blending raw materials. From these properties we observe that the greatest change occurs, humidity and acidity. These properties are expected to be altered because it is directly associated with the percentage of animal fatty acids that contained into fat acid (fat assets). The result of those that mentioned above is that with the increasing of the percentage of animal fats in the mixture we have a comparable change in the cost of the final product. This is a first conclusion from the analysis of the tables on the qualitative analysis as far as the final product.
**4. Presentation of cost mixtures**

Taking as a base the table 2A, table 2B and table 3A and table 3B we can observe the properties of the final product the values that remain constant or vary depending on the mix.

It will be very useful to investigate the effects on the total cost of the final product when specific properties change their values because we believe that this variation, based on the cost of raw materials, will define the price of the final product.

Alongside the purpose of this study is to ascertain what mixing ratio of raw materials will produce a final product of biodiesel based on the features of maximum quality and minimum cost. To do that we take the Greek Market in order to investigate the reaction of the minimum and maximum values in raw materials but it is obvious that this approach can be adapted to any country.

An analysis of table 2 and table 3 shows that mixing of raw materials for the creation of mixtures affect the physicochemical properties of ignition point, water, methylester and acidity which constitute essential characteristics of the suitability of the produced net biodiesel.

According with our methodology there is a relationship among growth limits of animal oils in order not to adversely affect the properties of mixtures and final cost. We know that animal oils are cheaper for biodiesel production but at the same time reduce the quality of biodiesel produced.

For the vegetable blends the production cost is a priori very high. The problem occurs in animal mixes, as we already mentioned above, where the product is cheaper but low quality product produced is observed. Depending on the prices of raw materials and the area where it operates the biodiesel industry may be, making use of the conclusions of this work and of the methodology that proposed, to carve the biodiesel production policy accordingly. We can observe from the Scatter plot in figure 1 the relation of between the mixtures and the production cost. At the same time by the diagrammatic illustration it is obvious that the increasing of % of fat acid gives cheaper final product but short on quality. We should mention that the use of vegetable oil meaning sun oil gives quality in product, but make it more expensive for the producer and consequently for the final consumer. In conclusion it is easily understood that with this resolution by changing the % of oils in the mixtures we can receive each time a different product from qualitatively point of view. Alongside we could know the cost of the final product by choosing the quality of our blends.

![Scatter plot of the mixtures](image)

**Figure 1.** Scatter Plot. Representation of the Mixtures mixtures costs in Euro/liters.
Based on the above values investigation table 4 shows, with regard to the final produced biodiesel, the relation between quality and cost.

**Table 4.** Relationship between quality and cost based on the mixing ratio of raw materials (in liters)

| Mix 1 | Mix 2 | Mix 3 | Mix 4 | Mix 5 |
|-------|-------|-------|-------|-------|
| Compositon measured on liters | 50% Olive oil cooked | 40% Olive oil cooked | 37% Olive oil cooked | 50% Olive oil cooked |
| | 20% Rape Oil | 25% Sun Oil | 16% Sun Oil | 30% Olive oil cooked |
| | 30% Fat acid | 35% Fat acid | 5% Fat acid | 10% Sun Oil |
| Cost (€) / lit | Min | Max | Min | Max | Min | Max | Min | Max | Min | Max |
| Olive oil cooked | 0.325 | 0.375 | 0.260 | 0.195 | 0.241 | 0.278 | 0.330 | 0.380 | 0.195 | 0.225 |
| Rape | € | € | € | € | € | € | € | € | € | € |
| Fat acid | 0.160 | 0.190 | 0.000 | 0.000 | 0.336 | 0.399 | 0.000 | 0.000 | 0.160 | 0.190 |
| Sun Oil | 0.165 | 0.210 | 0.193 | 0.135 | 0.220 | 0.280 | 0.275 | 0.350 |
| Total Cost | € | € | € | € | € | € | € | € | € | € |

While we are using larger precedence of raw materials the properties that determine the quality of the finished biodiesel are low acidity values for example water but we have large production cost as we can see on the mixes 1, 3 and 6 from the table 4. In contrast when we are using higher precedence of fat acids then we lower cost and at the same time low quality biodiesel produced because the values of the examined properties are undesirable high. This can be found on the mixes 2, 4, 8 and 10 from the table 4. This encourages, in general, finding the best mixing ratio of raw materials to ensure a balance between cost and quality of raw materials.

In the basis of the methodology was developed it becomes evident-clear that the presence of raw materials, fat acid, olive oil cooked, determines the change of physicochemical properties of mixtures and quality in the produced pure biodiesel.
materials. An explanation it can be given an explanation in the result of low quality in the final product of biodiesel when we are using higher precedence of animal raw materials because of the composition of raw materials, fat acid, olive oil cooked, since they contain a large proportion of unsaturated fatty organic acids with negatively affect to the quality of the fuel.

Table 5. Chemical composition of biodiesel

| Caprylic  | C8/0  | CH3(CH2)6COOH |
|----------|-------|---------------|
| Capric   | C10/0 | CH3(CH2)8COOH |
| Lauric   | C12/0 | CH3(CH2)10COOH |
| Myristic | C14/0 | CH3(CH2)12COOH |
| Palmitic | C16/0 | CH3(CH2)14COOH |
| Palmitoleic | C16/2 | CH3(CH2)14CH=CH(CH2)7COOH |
| Stearic  | C18/1 | CH3(CH2)16COOH |
| Oleic    | C18/1 | CH3(CH2)16CH=CH(CH2)7COOH |
| Linoleic | C18/2 | CH3(CH2)16CH=CHCH2CH=CH(CH2)7COOH |
| Linolenic| C18/3 | CH3(CH2)16CH=CHCH2CH=CHCH2CH=CH(CH2)7COOH |
| Arachidic| C20/0 | CH3(CH2)18COOH |
| Eicosenoic| C20/1 | CH3(CH2)18CH=CH(CH2)10COOH |
| Behenic  | C22/0 | CH3(CH2)20COOH |
| Eurcic   | C22/1 | CH3(CH2)20CH=CH(CH2)12COOH |

In general we know that the presence of unsaturated carbon chains imparts non-stability in the fuels used. It is also known that conventional fuels such as diesel, there are unsaturated hydrocarbons in the final product. Their presence is detected only on biodiesel and thus the possible mixtures diesel-biodiesel. Thus, the higher rate will have to biodiesel, the higher rate will have the final mix and so therefore the low stability of fuel should I use with corresponding negative effects on the environment.

Since the unsaturated hydrocarbons are concentrated in the fat acid and cooking oil, we understand that as they are used as starting material, the above problems will be presented.

The main criterion for the quality of biodiesel is the agreement regarding the corresponding specifications (standards). Generally the quality of the fuel can be influenced by several factors including the quality of the raw materials, the content of fatty acids, oils or fats, the production process, other materials used in the process and the post-production parameters. Specifically these parameters are the physicochemical properties that certify the suitability of the product and directly related to the type of raw materials, for example, animal or vegetable biodiesel. Furthermore with this study we know which of the properties altered and therefore affects the production and the cost of biodiesel production.

Concluding our analysis we know that animal oils are cheaper for biodiesel production but at the same time reduce the quality of biodiesel produced. With the equations that we mention in this study we can know the percentage of animal biodiesel that can be used in order to reduce the production cost and alongside to have a suitable product produced.

5. Conclusions
The analysis in these tables is proved, that the results of each mixture biodiesel regarding the properties affected by the quality of raw materials purchased by the factory, as in laboratory biodiesel. Soybean oil, rapeseed oil and sunflower oil is of very good quality oil and therefore the biodiesel containing a large percentage of them have excellent results compared to those containing cooked oil and fat acid, which is lower class raw materials. In particular as far as the quality of the pure biodiesel the presence of raw materials derived from fats acids affect the quality because increase properties such as acidity, triglycerides, methylester and monoglyceride. Similarly, the cost analysis have showed that the raw materials derived from fats acids are cheaper but do not contribute to the quality of the finished product. Contrasting the use of vegetable raw materials enhances the quality but charged to the final cost. So on the
basis of cost analysis table we must find the mixture to be equilibrium between quality and cost to a finished biodiesel industry. Generally, the above methodology can be a manual production process in this direction.

Alongside biodiesel could be used with all the other forms of energy meaning supplementary energy for electricity generation, household applications and transportation modes in accordance with the European Directive 2020. According with this Directive by 2020 the use of biodiesel must get to 20%. Currently on the market the Industries are using 8% in order to produce biodiesel. Consequently the proposed application can be used as tool in order to cover the remaining 12% according with the European Directive.

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