Waste animal fats as renewable and friendly environmental energy resource

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Abstract: - The paper presents in the first part, step by step, the necessary procedures to be accomplished in order to produce the alternative fuel bio-diesel, starting from waste animal fats with high free fatty acid concentration, and applying the transesterification. Based on the experimental results, one performed further a comparative study concerning the generated impact on air quality, bio-fuel versus normal diesel, when they would be utilized as main fuel for the vehicles in real traffic. The CALROADS software was used. The simulation scenarios were conducted to 2 major crossroads in the city of Timisoara. The simulation results demonstrate clearly that air quality is improved when biofuel is used.

Key-Words: - RES, bio-diesel, transesterification, alternative fuels, air quality.

1 Introduction and scope

Air pollution is a major concern for all nations, with a higher or lower development level. The rapid increase of the industry sector and urban development had generated substantial quantities of substances and poisonous materials, witch are, mostly evacuated in the atmosphere. The human society was not willing to recognize that the environment has only a limited capacity to process all this waste, without major changes. As a consequence we are able to observe disfunctionalities in the health degree, deterioration of flora and fauna, materials, buildings, in parallel with the lost of natural resources. Each of us is a polluter but also a victim of pollution.

The globalization process stimulates fast development, economic and financial, for all the countries. On the other hand, the globalization process can bring to some negative effects like global warming, terrorism, pollution, etc. Accepting this aspects the international community as acknowledge that one of the major problems of this period is to find ways to maximize the benefits of globalization on all countries, and to minimize the negative effects such as erasing as cultural specifity.

With exception of hydroelectricity and nuclear energy, the major part of all fossil energy quantities consumed worldwide is based on petroleum, charcoal and natural gas. However, these sources are limited, and will be exhausted by the end of this century, despite the ever growing energy demand worldwide. Thus, looking for alternative sources of energy to replace the classic ones is of vital importance.

The promotion of renewable energy has an important part to play in redefining the European strategy in the energy sector. Since 1997, the EU has been working towards the ambitious target of a 12% share of renewable energy in gross inland consumption by 2010. In 1997 the share of renewable energy was 5.4% and by 2001 it had reached 6% (Figure 1.1). Bio-energy already provides 64% of all renewable energy sources (RES) of the European Union, thus leading the way to a sustainable pattern of energy generation. In spite of the advance already gained in the bio-energy sector, the overall development lags far behind the goals fixed in the White Paper of the European Commission. According to this document the contribution of bio-energy should increase from 45 Mtoe in 1995 to 135 Mtoe in 2010. However, it won't be possible for the EU-15 to achieve such targets alone, due to the scarce national biomass resources existing in some countries (e.g. the Netherlands). Today, the inclusion of ten new members gives the opportunity for reaching the European goals, since the New Member States bring to the EU a significant bio-energy potential.

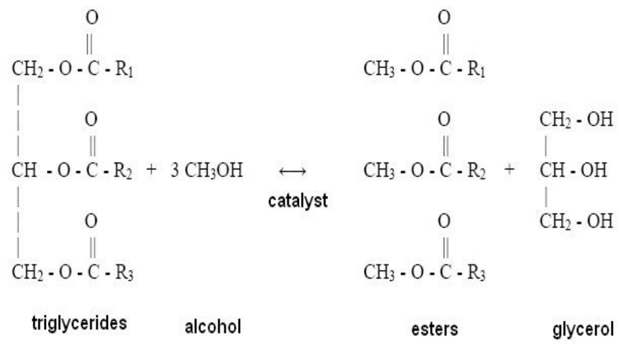
To meet rising energy demands and compensate for diminishing the fossil reserves, fuels such as biodiesel and bio-ethanol are in the forefront of alternative technologies. It is well known that the transportation system is almost totally dependent on fossil-, particularly petroleum-, based fuels such as gasoline, diesel fuel, liquefied petroleum gas, and natural gas. An alternative fuel to petro-diesel must be technically feasible, economically competitive, environmentally acceptable, and easily available. Accordingly, the viable alternative fuel for compression-ignition engines is bio-diesel [1].

Vegetable oils and animal fats are a promising renewable and potentially inexhaustible source of energy with an energetic content comparative to diesel fuel. It contributes to the fuel cocktail of the future that will support the new concept of the transportation.

The physical characteristics of fatty acid ester (bio-diesel) produced by a relative simple technology – the transesterification - are close to those of fossil diesel fuel. Furthermore, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation and not major impacts on the air quality.

Transesterification is the general term used to describe the important class of organic reaction where an ester is transformed into another, through interchange of the alkoxy moiety. When the original ester is reacting with an alcohol, the transesterification process the transesterification is called alcoholysis.

The general transesterification reaction equation is:



The transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the presence of the catalyst (typically a strong acid or a base) accelerates considerably the adjustment of the equilibrium. In order to achieve a high yield of the ester, it is recommended using the alcohol in excess.

Several aspects, including the type of catalyst (alkaline or acid), alcohol/fat molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on the curse of the transesterification.

One popular process for producing bio diesel from fats/oils is the transesterification of triglyceride by methanol (methanolysis), resulting methyl esters of straight-chain fatty acids. The purpose of the transesterification process is to lower the viscosity of oil. The transesterification reaction proceeds well in the presence of some homogeneous catalysts such as potassium hydroxide (KOH) or sodium hydroxide (NaOH) and sulphuric acid or heterogeneous catalysts, such as metal oxides or carbonates.

The transesterification process of fresh fats and vegetable oils is not a complicate proceedure. But it is more difficult to control the transesterification process when the raw materials are waste fats of animal origin, characterised by much higher content of free fatty acids. The first scope of this paper is to provide an original receipt, based on authors experiences, to succeed in the transformation of waste fats to bio-diesel and to use the energy contents of waste fats. Normally this organic waste is expected to be incinerated and thus destroyed in special conditions with higher costs, as a renewable energy source. No use for animal sector is allowed any more.

The second scope focuses on the utilisation of the bio-diesel in a comparative study regarding air quality impact of its utilisation as main fuel in a real fleet in urban area, in comparison to the present situation, when fossil diesel is used.

The relevance of this research theme in the knowledge development is related to the fact that studies regarding environment protection are not an objective but a dynamic process that requires adequate instruments and concrete actions in the frame of a coherent legislative frame.

2 Fats used in experiments

In this section the properties of 11 old fats sample provided by the same manufacturer are presented. It may be interesting to mention that the fats were formerly used as food in animal farms. Presently the qualities of the fats are below the current norms (for animal use GROFOR-norm is active), and that is a very good reason and argument to use the fats waste for bio-diesel production. Measurements have been accomplished for: iodine number (DGF-Methoden C-V 11b), sulphuric ash (DIN 51 575), total contamination (DIN 51419-A), peroxide number, cinematic viscosity (DIN 51 562 part 1) and free fatty acid FFA (DIN 51 558 part 1, Ref.1).

In the next figures and table 1 some pictures taken during the experiments are shown and a synthesis of the resulted waste fat proprieties is given.

Fig. 1. Determination of sulphuric ash content.

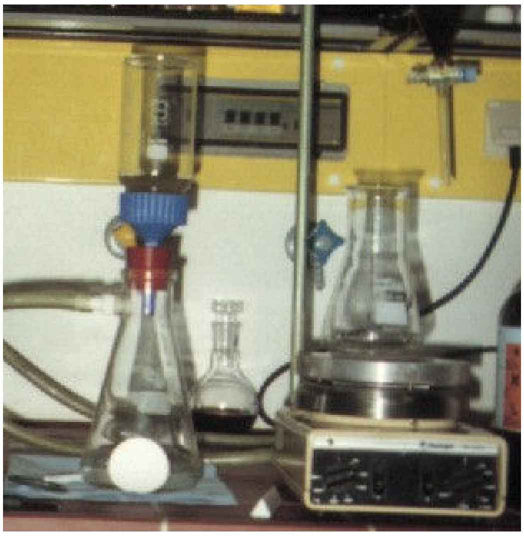


Fig. 2. Measurement of total contamination.

Fig. 3. Determination of free fatty acid number.

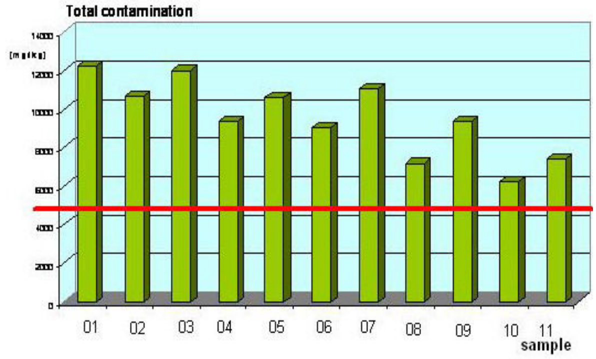


Fig. 4. Mass concentration of total contaminants in the samples.

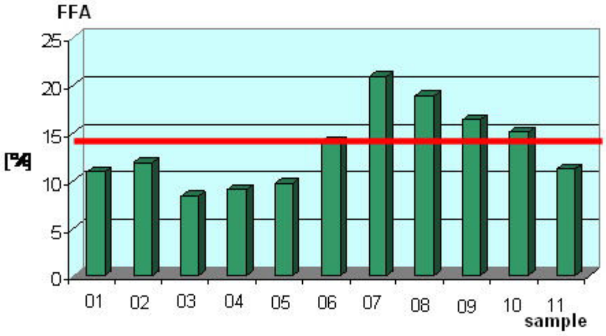


Fig. 5. Volume concentration of free fatty acid content of the samples.

According to the EU norms the fats with FFA over 15 % by mass and total contamination over 5,000 mg/kg are not suitable for use as food for animals. This value is highlighted by a horizontal line in the graphics. Thus, this category of waste can only be exploited in industry (for soap, pharmaceuticals, lubricants products, etc.) or for bio-diesel production, as fuel for the internal combustion engines, for example.

Table 1. The properties of the fats used in experiments.

Sample	Iodine number	Acid number	Total contamination (mg/kg)	Viscosity (mm^2/s)	Sulphuric ash (%)	FFA (%)
S1	64.76	21.63	12227	44.136	0.6839	10.87
S2	66.12	23.56	10709	43.084	0.4328	11.85
S3	69.7	16.59	12028	43.264	0.4344	8.34
S4	66	17.93	9385	42.666	0.3332	9.02
S5	58.7	19.51	10598	49.592	0.3674	9.8
S6	61	27.89	9026	41.373	0.3465	14.02
S7	57	41.59	11050	49.59	0.6218	20.91
S8	61	37.58	7177	44.978	0.475	18.89
S9	53.4	32.84	9351	46.278	0.4934	16.5
S10	66.7	29.99	6243	41.819	0.2988	15.08
S11	58.9	22.3	7426	43.569	0.3715	11.21

3 Bio diesel production tests

Two different methods to produce bio diesel where preliminary tested: the first is in accordance to the European patent application 0 249 463 A2 and the second is a similar method, according a WEB resources [2]. As none proved to be efficient for fats with high free fatty acid contend an updated novel method was planned, resulted not empirically but base on numerous bench experiments [3].

This is a two-stage procedure, acid-first stage and base-second stage. It is based on transesterification of waste animal fats (with high FFA content) but it can be applied also on waste cooking oils.

3.1 Preparation of fats

The fat must be heated until it becomes liquid and then might be filtered. Two stages (acid-catalysed stage and base-catalysed stage) should be carried out [4].

For a successful reaction the oil must be free of water. Only such a procedure one may turn the fats ready to be used in the transesterification process.

There are two ordinary methods of removing the water content:

- Boiling off the water meaning the heating to 100 °C. The heat determines the separation of the water, which is further drained out, to avoid steam explosion. The temperature regime (> 100 °C) should be maintained until no bubbles are rising any more.
- Settling the water out is the second possibility. This method saves energy. The fats must be heated to 60 °C and this value is then kept for 15 min. The fats are sent into a settling tank for at least 24 h in order to separate to the bottom

The fats are now ready to be used in the transesterification process. [5]

3.2 First stage (acid-catalyzed stage)

After the fats preparation and the removal of all waster content the first stage of the transesterification can begin. It is called acid-catalyzed stage and the following steps are to be fulfilled:

- Measuring the volume of oil/fats to be processed (preferably in litters).
- Heating the oil/fats to 55 °C as all solid fats must be melted.
- Measuring out the methanol and providing 0.1 l of methanol for each litter of oil/fats (10% by volume). Add the methanol to the heated oil.
- Mixing for 5 min until the mixture will become murky because the solvent change. This action is necessary because the methanol is a polar compound, oil is strongly non-polar and a suspension will always occur if no special care is taken.
- Adding for each litter of oil/fats the quantity of 1 ml of 95-97 % by volume sulphuric acid (H_2SO_4). A graduated eyedropper, a graduated syringe or a pipette should be used. Special care when handling the concentrated sulphuric acid is to be taken.
- Mixing gently at low rotation speed (rpm), while keeping the temperature at 55^{o}C. The rotation of the stirrer should not exceed 500 to 600 rpm, as speed is not crucial and splashed oil is a mess to clean.
- Maintaining the temperature at 55^{o}C for 50 min then stop heating but continuing stirring.
- Preparation of the sodium methoxide that consists of adding 0.1 l of methanol for each litter of oil/fat (10% by volume) and 3.1 grams of 99% by volume pure sodium lye (NaOH) per liter of oil/fat. Further step consists of the lye into the methanol until the lye is completely dissolved.
- Pouring half of the prepared methoxide into the mixture after 1.5 h (oils only or oils plus fats) or 2 h (for fats that are solid at room temperature). This will stop the acid-catalyzed reaction and prevent ester back splitting. Mixing for 5 more min, then stop.
- Allowance to the mixture to settle for 6 to 12 h, then draining off the glycerine, meaning the brown or dark brown compound at the bottom.

After the settling the FAME (Fatty Acid Metil Ester) and glycerine must be separated and the FAME is ready to be used in the next transestrification step, the base-catalyzed stage.

3.3 Second stage of the transesterification

It is named the base-catalyzed stage and consists of several steps:

- Heating the mixture to 55 ^{o}C. Make sure that any remaining room-temperature solid fats are melted.
- Adding the second half (left from the first stage) of the prepared sodium methoxide to the heated mixture and starting mixing for more than 1 h, at the same low speed of not more than 500 to 600 rpm.
- Allowing settling for over 6 to 12 h.
- Draining off the glycerine.

The bio-diesel is obtained finally, after the implementation of all mentioned steps of the first and second stage.
The washing of the bio diesel can be achieved in several ways; the preferred method is the water wash. The biodiesel is placed in one vessel with about ½ water contend as the bio diesel to be washed. The biodiesel and water must have the same temperature (room temperature). It is recommended that the water pH should have as many units under 7 as the bio diesel pH is above 7. Using strong vinegar has as result obtaining lower pH for water. By applying compressed air to create bubbles in the vessel which contains the biodiesel/water mixture a more appropriate medium is created. Following, one has to let it bubble for up to 6 hours. The bubbles will carry the water up. When this water descends again, it washes the soaps and surplus methanol out of the fame, and the vinegar neutralises the remaining lye. After settling for 12 h, the water will fall to the bottom, turning completely white, and the resulted bio-diesel will take a much lighter colour (Fig. 6).

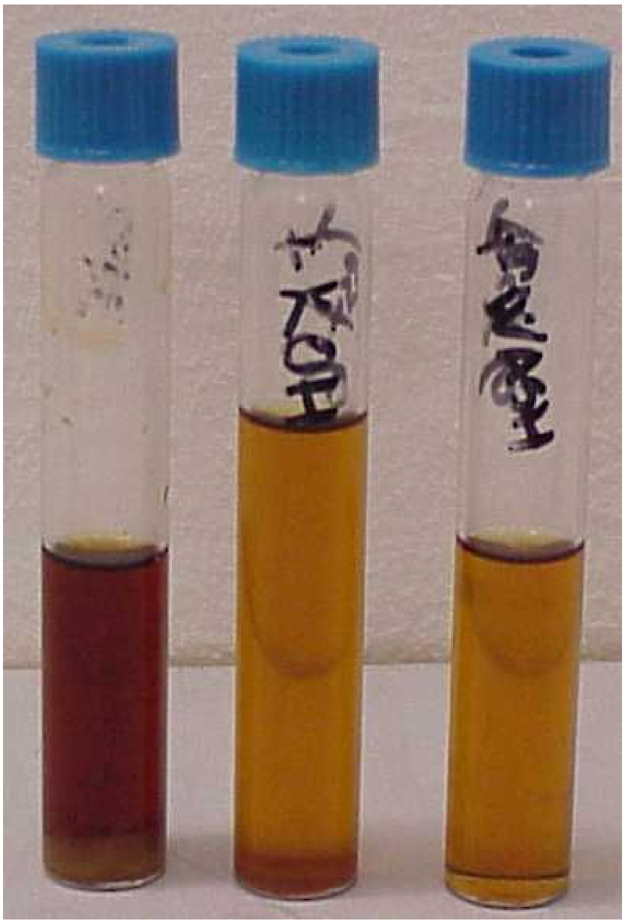


Fig. 6. Bio-diesel sample after second stage (left), before (middle) and after washing (right).

Biodiesel is the only alternative fuel for unmodified conventional diesel engines using low concentration biodiesel-diesel blends. It can be stored anywhere that petroleum diesel fuel is stored. Biodiesel can be made from domestically produced, renewable oilseed crops such as soybean, rapeseed, and sunflower. However there a major disadvantages in the production of biodiesel from vegetable oils, especially given by the need to close large areas of land from traditional agriculture and to use this lend for crops used in biodiesel production. The risks of handling, transporting, and storing biodiesel are much lower than those associated with diesel. Biodiesel is safe to handle and transport because it is as biodegradable as sugar and has a high flashpoint compared to petroleum diesel fuel. Biodiesel can be used alone or mixed in any ratio with petroleum diesel fuel. The most common blend is a mix of 20% biodiesel with 80% petroleum diesel, or B20 according to recent scientific investigations [12]; however, in Europe the current regulations foresees a maximum 5.75% biodiesel.
Combustion of biodiesel alone provides over a 90% reduction in total unburned hydrocarbons, and from 75 to 90% reduction in polycyclic aromatic hydrocarbons (PAHs). [12] Biodiesel further provides significant reductions in particulates and carbon monoxide compared to petroleum diesel fuel. Biodiesel provides a slight increase or decrease in nitrogen oxides depending on the engine family and testing procedures.
The major disadvantages of biodiesel are higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxides (NOx) emissions, lower engine speed and power, injector coking, engine compatibility, high price, and higher engine wear.
Neat biodiesel and biodiesel blends increase nitrogen oxides (NOx) emissions compared with petroleum-based diesel fuel used in an unmodified diesel engine. The peak torque is less for biodiesel than petroleum diesel but occurs at lower engine speed, and generally the torque curves are flatter. The biodiesels on the average decrease power by 5% compared to diesel at the rated load. [12]

4 Application of the Biodiesel versus Diesel in road traffic. Timisoara air quality case study.

In the next paragraph and figures 7 to 9 one presents the results upon air quality when bio-diesel is used replacing the fossil diesel, in real case traffic episodes, in urban areas. The simulation was accomplished using the numerical simulation of the pollutant dispersion for one major Timisoara crossroad, Michelangelo. Such numerical dispersion models are used by several authors to make a good comparison or establish relevant action according the results, more for prevention and strategy base. The values for emission factors both for diesel and bio-diesel fuels are used as provided by the CORINAIR database. [11] Traffic structure and meteorological date were measured in situ and used correspondently.

The used software CALROADS consists of a modeling code CALINE 4 (US EPA approved) and the areas studied was the vicinity of the Michelangelo crossroad, a major polluting surface area source in the city of Timisoara. The traffic surveillance and cars characterizations have been conducted for the time frame considered in both crossroads. [7] The medium number of cars in this intersection was around 45 000 vehicles/day from witch about 30% are diesel powered vehicles. The diesel emission factors have been taken from Corinair database and biodiesel from literature.

In figure 7 an example of road traffic structure measured in the Michelangelo crossroad is given. The figure shows the traffic structure over one hour period from a typical day in a time frame with medium traffic intensity.

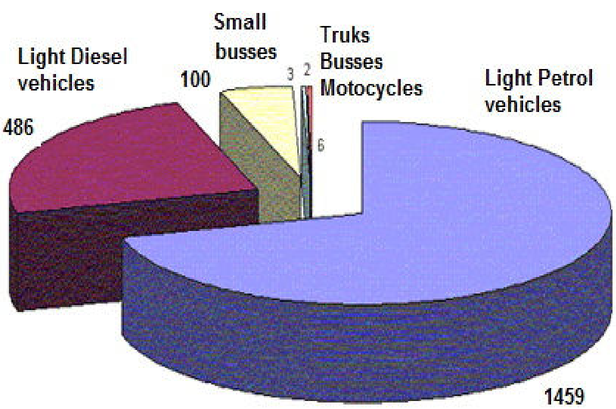


Fig.7. Road traffic structure for one hour period in Michelangelo crossroad

The most relevant results of the simulations are presented in figures 8 to 12.

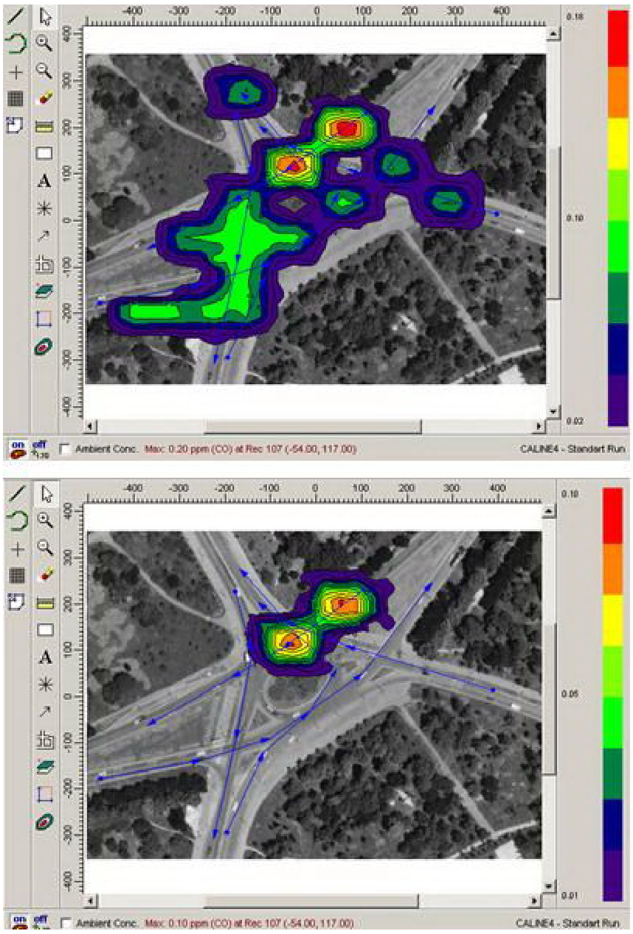


Fig. 8. CO concentrations for the Michelangelo crossroad: diesel (*up*) versus bio-diesel (*down*)

The road traffic measurements and fleet characterization has been done over a week period, the results for total road traffic number in the Michelangelo crossroad is given in table 2.

Table 2. Measured data for total road traffic in Michelangelor crossroad

Day		Road traffic [veh. tot.]
15.05.2007	Thursday	49430
16.05.2007	Wednesday	50601
17.05.2007	Thursday	50077
18.05.2007	Friday	50990
19.05.2007	Sunday	41256
20.05.2007	Saturday	32105
21.05.2007	Monday	50589
22.05.2007	Thursday	48883
23.05.2007	Wednesday	40101

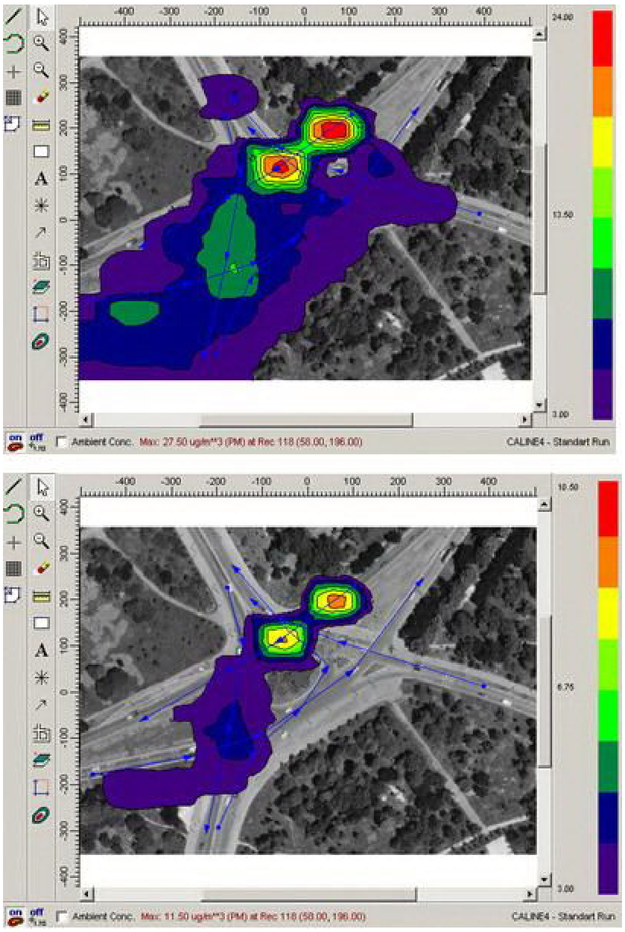


Fig. 9. Particles concentrations for the Michelangelo crossroad: diesel (*up*) versus bio-diesel (*down*)

In all simulations charts, figures 8 to 12, the road fleet is structured thru direct measurements as in/out system and represented by the blue arrows. The dispersion maps are on top of a base map with an aerial view of the crossroads. In the right side pf the charts the level of pollutants concentration are represented in a graphical mode, the color representing a low concentration and the red color high concentration. At the bottom of the figure the maximum obtained concentration for a specific pollutant is given, but also in table 2.

Similar results were accomplished for the particles in another cross road with high traffic, namely Marasti (figures 10, 11 and 12). In all cases, the episodes were considered the same, in terms of fleet, meteorological data and topography, all being based on real data inputs, as determined and established by the authors.

The simulations for NOx were also done but the results have been similar for both diesel and biodiesel, presented in table 3.

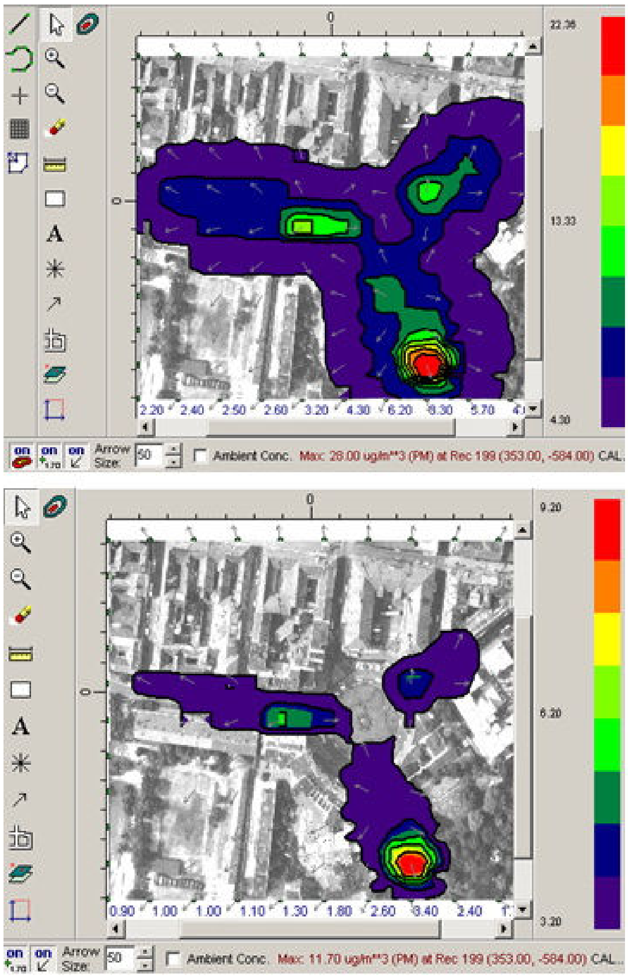


Fig. 10. Particles concentrations for the Marasti crossroad: diesel (*up*) versus bio-diesel (*down*)

The comparative analysis of the same episodes reveals in all cases the advantages upon air quality of replacing the classic fossil based diesel with biodiesel. Similar results have been notes also by other authors [1] [12]. In reality it is not possible to immediately change the strategies to turn to biofuels but it is obviously that even a small percent of bio origin introduced is applied in reality as basic fuel certain improvements in air quality will result.

Urban areas are mostly characterized by higher level of pollutants concentration even under the maximum allowed limit in comparison to non-urban regions. That's way even small improvements are salutary. Another argument for the use of biofuel is the local circuit of the money, as normally such biofuels are produced and utilized in the same (limited) area. Thus the benefits upon air quality improvements are directed generally to the same area determining the inhabitants to work and struggle more and with conscience for applying economics and main idea concerning biofuel development.

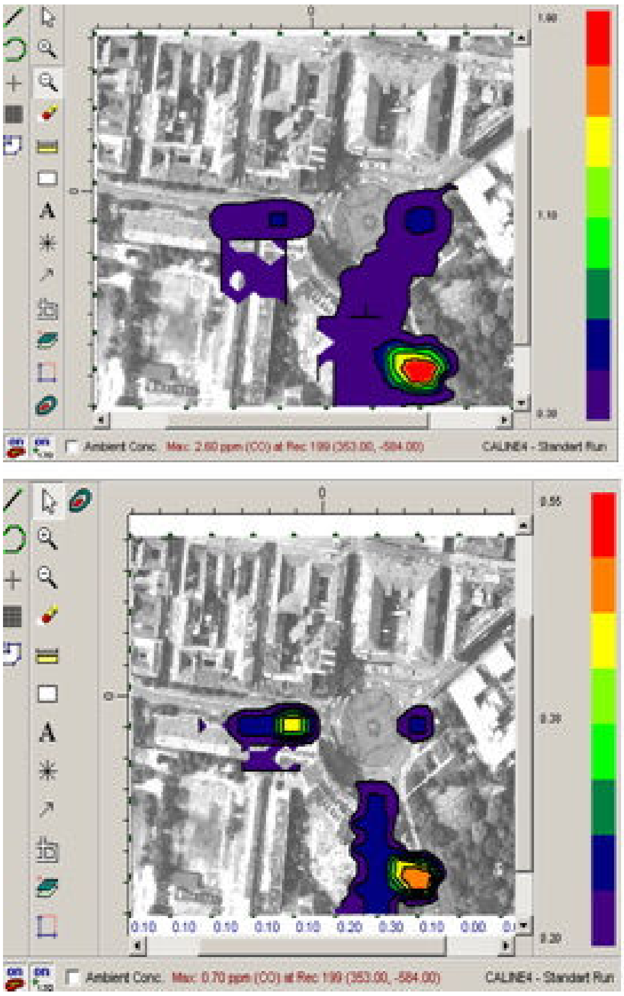


Fig. 11. CO concentrations for the Marasti crossroad: diesel (*up*) versus bio-diesel (*down*)

The formulas used to calculate the emission factors for CO, NOx and particles is in accordance to Corinair methodology [11] and the estimated results for diesel and biodiesel are calculated.

$$E_{CO} = 5.41301 \cdot V^{-0.574} \quad [g/km]$$

$$E_{NOx} = 1.331 - 0.018 \cdot V + 0.000133 \cdot V^2 \quad [g/km]$$

$$E_{PM} = 0.45 - 0.0086 \cdot V + 0.000058 \cdot V^2 \quad [g/km]$$

In the formulas above V is the mean speed of the vehicles, expressed in km/h.

The calculated results for a typical mean vehicle speed in the Michelangelo crossroad is about 30 [km/h] and all figures presented are based on this input data.
Emissions factors for diesel fuel, for each vehicle, are, according to Corinair methodology:

$$E_{CO}{}^{diesel} = 0.7683 \quad [g/km]$$

$$E_{NOx}{}^{diesel} = 0.91 \quad [g/km]$$

$$E_{PM}{}^{diesel} = 0.2442 \quad [g/km]$$

Emission factors for biodiesel fuel (B100 blend), for each vehicle, are:

$$E_{CO}{}^{biodiesel} = 0.30732 \quad [g/km]$$

$$E_{NOx}{}^{biodiesel} = 0.93 \quad [g/km]$$

$$E_{PM}{}^{biodiesel} = 0.09768 \quad [g/km]$$

Fig. 12. NOx concentrations for the Marasti crossroad: diesel (*up*) versus bio-diesel (*down*)

Table 3. Maximum values obtained for considered pollutants, after simulation, for Marasti crossroad

Pollutant	Fuel	Maximum obtained value
CO	Diesel	2.60 [ppm]
	Biodiesel	0.70 [ppm]
NOx	Diesel	0.02 [ppm]
	Biodiesel	0.02 [ppm]
Particles	Diesel	28 [µg/m^3]
	Biodiesel	11.70 [µg/m^3]

Comparing the results from figures 8 to 12 and the maximum values for concentrations from table 3 one conclude that the environmental impact on air quality in the case of the use of biodiesel in urban auto-fleet is significant lower that the impact of the regular diesel fuel. Not only that the maximum values are lower in case of CO and particles but also the impact area (dimension of affected region) is reduced.

4 Conclusion

With exception of hydroelectricity and nuclear energy, the major part of all energy is produced from petroleum, charcoal and natural gas. However, these sources are limited, and will be exhausted by the end of this century. Thus, looking for alternative sources of energy is of vital importance.

Vegetable oils and animal fats are renewable and potentially inexhaustible sources of energy with an energetic content close to diesel fuel.

The procedure described generates bio-diesel from a waste source. The resulted renewable fuel (RES) has certain advantages as alternative fuel, first of all based on its physical properties, similar with the fossil Diesel fuel properties. Thus bio-diesel can be used directly in Diesel engines with no essential modification of these. The physical characteristics of fatty acid ester (bio-diesel) resulted from the transesterification are very close to those of diesel fuel and the process is relatively simple. Furthermore, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation. Another advantage consists of a very low impact on environment trough combustion, generally exhausting trough combustion no more pollutant concentrations. The third advantage relays in the accessibility to the raw materials like old animal fats and a large variety of vegetable oils.

The tests described and the results of the novel technology proposed represent a success and surely will be followed, attesting the qualities of the alternative fuel resulted from waste fat transesterification, meaning thus the bio-diesel.

The bio-diesel is proper to replace the normal diesel for the fleet, and in urban areas one demonstrated that by this way a significant reduction of the impact upon air quality is reached, in terms of maximum values, but also in terms of dimensions of the relevant dispersion area. Due to the exponential increase of people living in cities and the consequent associated degradation of quality of life due to air quality damaging due to the traffic intensity, serious concern and strategic measures grow continuously, applying pressures over resources, infrastructures and facilities, for stopping affecting negatively the standard of living in cities [9].

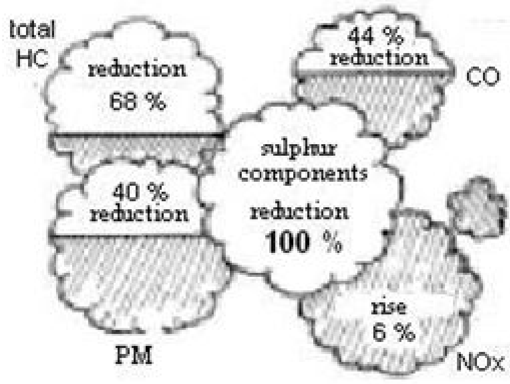


Fig. 13. A plastic representation for Biodiesel advantages and disadvantages

In this context, the search for new and renewable energy resources, with a minimum impact on urban environment is more then justified, especially if this sources are waste material, with recoverable energy content. Based on the method described concerning the comparative study of fuel quality influence upon air pollution, and starting from urban vehicles traffic counters, emission factors databases and simulation, general prediction of the future urban planning strategies for clean sustainable development are enforced. General speaking, the article deals not only with a novel simple method of bio-diesel production from waste as RES resource, but also demonstrates that the generated fuel is environmentally friendly, when it replaced the fossil diesel.

Biodiesel has got better lubricant properties than fossil diesel. Its oxygen content improves the combustion process, leading to a decreased level of tailpipe polluting emissions. Biodiesel is non-toxic and quickly biodegrades. The risks of handling, transporting, and storing biodiesel are much lower than those associated with fossil diesel. The competitiveness of biodiesel relies on the prices of biomass feedstock and costs, which are linked to conversion technology. Depending on the feedstock used, byproducts may have more or less relative importance. Biodiesel is not competitive with fossil diesel under current economic conditions, where the positive externalities, such as impacts on the environment, employment, climate changes, and trade balance, are not reflected in the price mechanism.

This paper brings in attention of example of possible strategy in order to meet the general EU strategy concerning the RES utilization and percentage support for the total energy consumption by 2020.

Maybe it is time to close the circle. In 1900, Rudolf Diesel was presenting his engine in Paris. His chosen fuel: vegetable oil. After 100 years it's seems that the original concept was the best.

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