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Waste Animal Fats with High FFA as a Renewable Energy Source for Biodiesel Production - Concept, Experimental Production and Impact Evaluation on Air Quality

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1. Introduction

This chapter presents one method to obtain the renewable "biodiesel" energy source through animal fats transesterification with high free fatty acid content. The authors tested different methods to produce biodiesel from waste animal fats. The purpose of research was to use the byproduct from the meat industry, the wastes in form of fats with high free fatty acid content (FFA), fats that cannot be used in other sectors, like supplement in animal food, due to high contamination and FFA content.

The research underlines a correlation between social-economic development and air quality in an urban area. We also intend to improve the knowledge in the field of alternative fuels, field not well covered in Romania, especially if the waste management and potential are in sight. 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. (Popescu, 2009)

The chapter will follow three directions: first will describe the research conducted in order to obtain an "receipt" to produce the biodiesel from waste animal fats; second will describe the pilot installation constructed to improve the biodiesel production receipt and third will describe some research conducted in order to prove (or validate) the positive impact on the urban environment if the biodiesel is used instead of regular diesel.

In a broad sense, *energy conversion* is the capacity to promote changes and/or actions (heating, motion, etc.), and *biomass* includes all kinds of materials that were directly or indirectly derived not too long ago from contemporary photosynthesis reactions, such as vegetal matter and its derivatives: wood fuel, wood-derived fuels, fuel crops, agricultural and agro-industrial by-products, and animal by-products. *Bioenergy* is the word used for energy associated to biomass, and *biofuel* is the bioenergy carrier, transporting solar energy stored as chemical energy. (Ionel, 2008) *Biofuels* can be considered a renewable source of energy as long as they are based on sustainable biomass production. The style will adjust your fonts and line spacing. Improving the efficiency of the existing power-plants using fossil fuels, the use of renewable fuels and renewable energy sources and the increased use of nuclear power are all considered to be important means of reducing greenhouse-gas emissions. One possibility to reduce greenhouse-gas emissions is to substitute biomass for

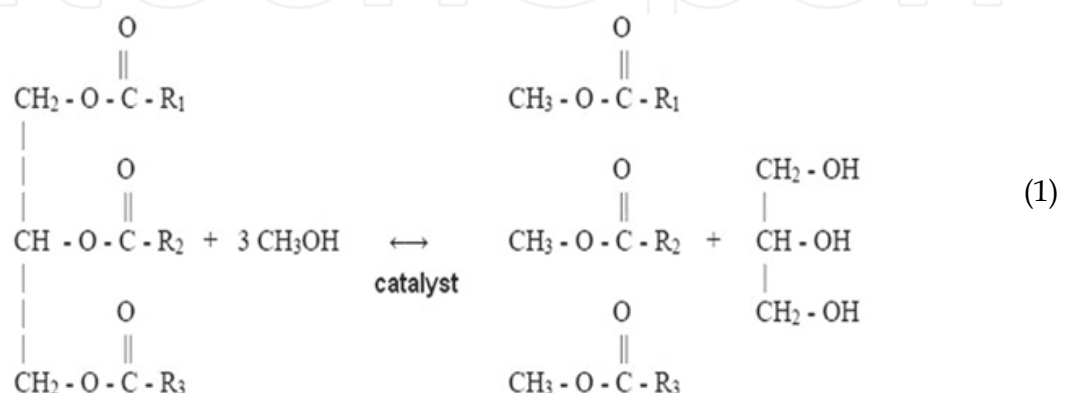
coal in energy units or to add in a restrictive amount biofuel to fossil fuel, in internal engine combustion systems. The use of biomass in energy plants or of liquid biofuels in engines also offers advantages associated with emissions, other than reducing greenhouse-gas emissions. These are due to the low sulphur and low nitrogen contents of biomass. Also it is worth to notice that liquid biofuels are of interest as well, despite the present debate of not affecting price and production of food products. Not at least supplementary problems that must be solved are attested (emission of CO, unburned hydrocarbons, etc.). There is evidence that power generation from biomass is an attractive technology that utilizes agricultural residual waste. It is evident from research that efficient co-firing of biomass with coal can be achieved with minimal modifications to existing coal-fired boilers; as well existing engines might run, with minimum investment costs, using a blended fossil flue with biofuel. (Ionel 2008)

Among the available alternative energy sources, including hydro, solar, wind etc. to mitigate greenhouse emissions, using biofuels is the only carbon-based sustainable option. It is increasingly understood that 1st-generation biofuels (produced primarily from food crops such as grains, sugar beet and oil seeds) are limited in their ability to achieve targets for oil-product substitution, climate change mitigation, and economic growth. Their sustainable production is under review, as is the possibility of creating undue competition for land and water used for food and fibre production. A possible exception that appears to meet many of the acceptable criteria is ethanol produced from sugar cane. The cumulative impacts of these concerns have increased the interest in developing biofuels produced from non-food biomass. With exception of hydroelectricity and nuclear energy, the major part of all energy quantities consumed worldwide comes 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 a renewable and potentially inexhaustible source of energy with an energetic content close to diesel fuel. The physical characteristics of fatty acid ester (bio-diesel) resulted in the end of 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.

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 reacted with an alcohol, the transesterification process is called alcoholysis.

The general transesterification reaction equation is:



To meet rising energy demands and compensate for diminishing petroleum reserves, fuels such as bio-diesel and bio-ethanol are in the forefront of alternative technologies. It is well known that transport 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.

Thus, it is obvious that 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 base) accelerates considerably the adjustment of the equilibrium. In order to achieve a high yield of the ester, the alcohol has to be used 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 course of the transesterification.

One popular process for producing bio diesel from fats/oils is transesterification of triglyceride by methanol (methanolysis) to make 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), sodium hydroxide (NaOH) and sulphuric acid or heterogeneous catalysts such as metal oxides or carbonates. (Popescu, 2009)

The transesterification process of the fresh fats and vegetable oils is an easy one with no complications. It is more difficult to control the transesterification process when the raw materials are waste fats with animal origin and very high content of free fatty acids. The scope of this paper is to provide a 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, that otherwise must be incinerated/destroyed in special conditions with high costs, as a renewable energy source.

2. Experiments to obtain a “receipt” for biodiesel production from waste fats

In this paragraph the properties of 11 old fats sample provided by the same manufacturer will be presented. It may be interesting to mention that the fats were originally produced to be used as a food in animal farms. The qualities of the fats are below the in force in Germany at the time of experiments, GROFOR - that stipulates the acceptable limits for the quality of animal food - and that is a very good reason and argument to try to use the fats for bio-diesel production. Measurements have been made for: iodine number (DGF-Methoden C-V 11b), sulfuric ash (DIN 51 575), total contamination (DIN 51419-A), peroxide number, kinematic viscosity (DIN 51 562 part 1) and free fatty acid (DIN 51 558 part 1). In Table 1 a synthesis of the old fat proprieties used in experiments are given.

In figures 1 and 2 the total contamination and free fatty acid number are presented in correlation with the admissible limits according to GROFOR norms for animal foods.

The fat must be heated until it becomes liquid and then might be filtered. Two stages (acid-catalyzed stage and base-catalyst stage) should be accomplished. (Trent, 2002)

For a successful reaction the oil must be free of water. There are two common methods of removing the water content:

- Boiling the water off: heating to 100 °C. As the heat raises the water, it separates out and falls to the bottom. The water is then drained out to avoid steam explosion. The temperature (> 100 °C) should be maintained until no bubbles are rising any more.

- Settling the water out: This method saves energy. The fats must be heated to 60 °C and to keep this temperature for 15 minutes. After this one pours the fats into a settling tank and lets it settle for at least 24 hours. The water will separate and fall to the bottom.

Sample	Iodine number	Acid number	Total contamination [mg/kg]	Viscosity [mm ² /s]	Sulfuric Ash [%]	FFA [%]	Peroxide number
S1	64,76	21,63	12227	44,136	0,6839	10,87	58,4
S2	66,12	23,56	10709	43,084	0,4328	11,85	2,9
S3	69,7	16,59	12028	43,264	0,4344	8,34	9,1
S4	66	17,93	9385	42,666	0,3332	9,02	1,5
S5	58,7	19,51	10598	49,592	0,3674	9,8	177,8
S6	61	27,89	9026	41,373	0,3465	14,02	146,1
S7	57	41,59	11050	49,59	0,6218	20,91	116,9
S8	61	37,58	7177	44,978	0,475	18,89	1,4
S9	53,4	32,84	9351	46,278	0,4934	16,5	13,3
S10	66,7	29,99	6243	41,819	0,2988	15,08	28,9
S11	58,9	22,3	7426	43,569	0,3715	11,21	14,5

Table 1. Main properties / characterization of fats used in experiments

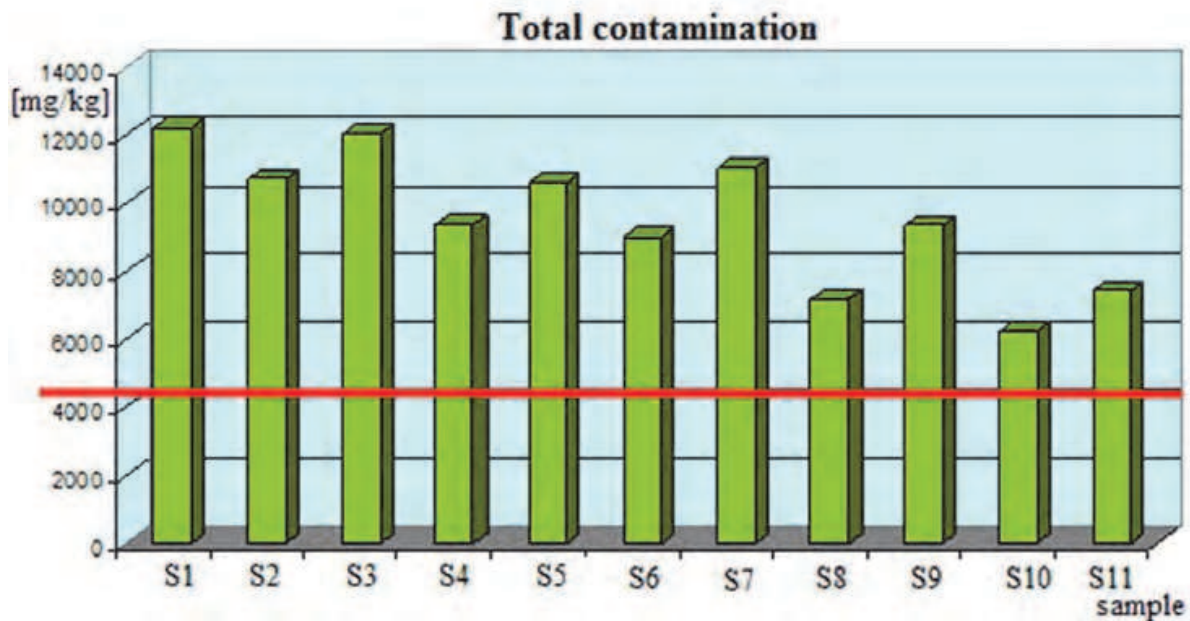


Fig. 1. Total contamination of the probes used in experiments, expressed in mg of contaminants in one kg of waste fats. (e.g. bone residues)

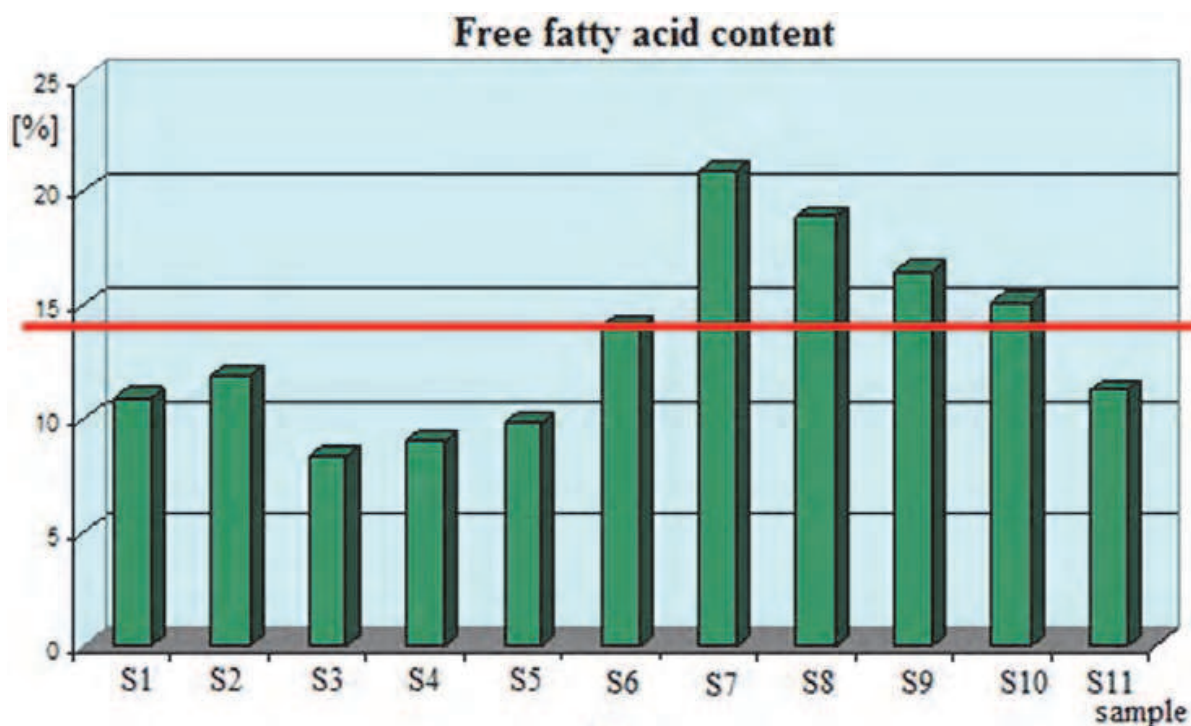
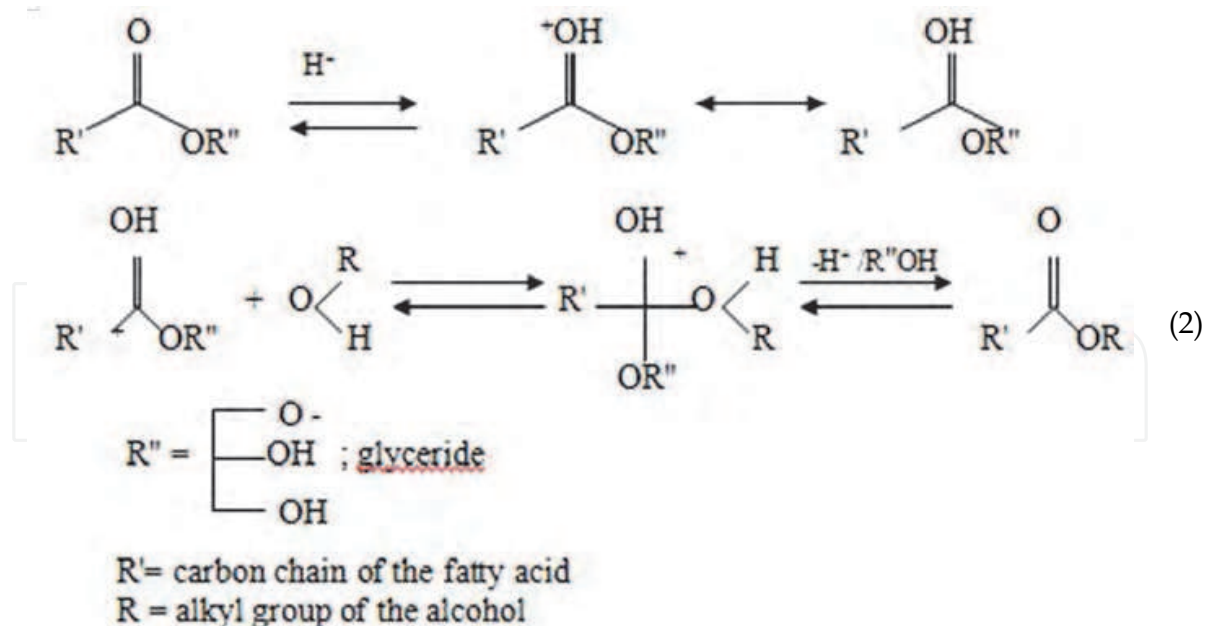


Fig. 2. Free fatty acid (FFA) content of the probes used in experiments.

The following strategy/receipt must then be fulfilled, step-by-step, for accomplishing successfully the fats preparation. First described is the acid-catalyzed stage, giving the basic acid stage reaction.



Bellow is given the First stage (acid-catalyzed stage), in detail:

- Measuring the volume of oil/fats to be processed (preferably in liters).
- Heating the oil/fats to 55 °C - all solid fats must be melted.
- Measure out the methanol and add 0.1 liter of methanol for each liter of oil/fats (10 % by volume). Add the methanol to the heated oil.

- Mixing for 5 minutes; the mixture will become murky because of solvent change (methanol is a polar compound, oil is strongly non-polar and a suspension will occur).
- Adding for each liter of oil/fats the quantity of 1 milliliter of 95-97 % sulfuric acid (H_2SO_4). A graduated eyedropper, a graduated syringe or a pipette should be used.
- Mixing gently at low rotation speed (rpm), while keeping the temperature at 55 °C. The rotation of the stirrer should not exceed 500 to 600 rpm.
- Maintaining the temperature at 55 °C for 50 minutes then stop heating. Continuing stirring.
- Preparation of the sodium methoxide that consists of adding 0.1 liter of methanol for each liter of oil/fat (10 % by volume) and 3.1 grams of 99 % pure sodium lye (NaOH) per liter of oil/fat. Finally mixing the lye into the methanol until the lye is completely dissolved.
- Pouring half of the prepared methoxide into the mixture after 1.5 hours (oils only or oils plus fats) or 2 hours (for fats that are solid at room temperature). This will stop the acid-catalyzed reaction and prevent ester back splitting. Mixing for 5 more minutes, then stop.
- Allowance to the mixture to settle for 6 to 12 hours, then draining off the glycerin. (the brown or dark brown compound at the bottom).

Bellow is given the Second stage (base-catalyzed stage), in detail:

- Heating the mixture to 55 °C. Make sure that any remaining room-temperature solid fats are melted.
- Adding the second half of the prepared sodium methoxide to the heated mixture and start mixing at the same low speed of not more than 500 to 600 rpm. Mix for 1 hour.
- Allow settling for 6 to 12 hours.
- Drain off the glycerin. The biodiesel is now obtained.

Final stage is represented by the washing out the biodiesel and the pH of the FAME (fatty acid methyl ester) should be known. The receipt comprises the following steps: Put the FAME in one vessel with $\frac{1}{2}$ water or the same quantity of water as the FAME to wash. The FAME and water must have the same temperature (room temperature). The water pH must have as many units under 7 as the FAME pH is above 7. Use strong vinegar to obtain lower pH for water. Use compressed air to create bubbles in the vessel ho contains the FAME/water mixture. Let it bubble for up to 6 hours. The bubbles will carry the water up. When this water falls down again, it washes the soaps and surplus methanol out of the FAME and the vinegar neutralizes the remaining lye. After settling for 12 hours the water will fall to the bottom, turning completely white and the bio-diesel will look much lighter in color now (Figure 3).

In Table 2 are presented the chemicals (CH_3OH - methanol, H_2SO_4 - sulphuric acid, NaOH - sodium hydroxide, KOH - potassium hydroxide) and their concentration values used in the tests for producing the bio-diesel.

The most successful test was No 6, realized with an extra-step with KOH. The viscosity of the bio-diesel obtained was 5.3 mm²/s. Also test No 7 was a partial success. It should be mentioned that for the last step (KOH) for No 6 it was used just 188.28 g collected at the end of the second step. Figure 3 is a view over samples from biodiesel No 6. Note the lighter colors and no depositions.

Implementing the process described above results in the process flow shown in the figure 4.

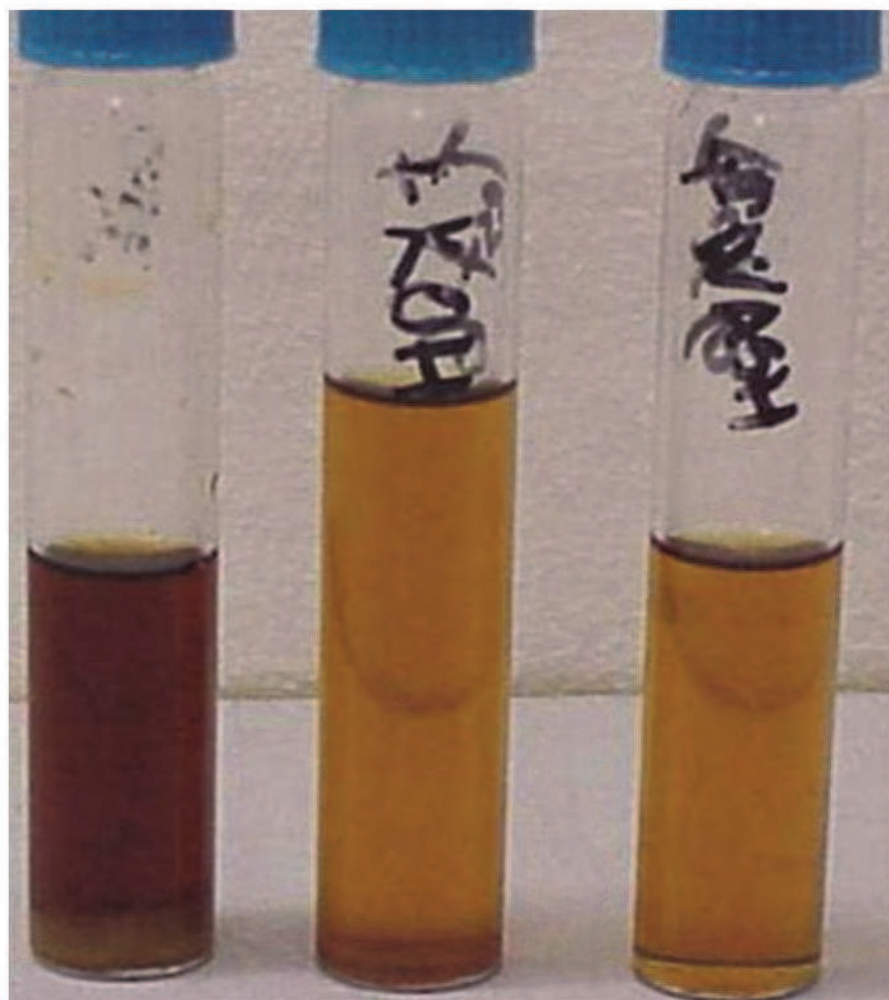


Fig. 3. Biodiesel sample after second stage (left), before (middle) and after washing (right)

Test No	Fats (ml)	CH ₃ OH (ml)	H ₂ SO ₄ (ml)	NaOH (g)	CH ₃ OH (ml)	Stage I (h)	Stage II (h)	KOH (g)	CH ₃ OH (g)	Reaction time (min)
1	500	50	0,5	3,5	50	2	1			
2	500	50	1	3,5	50	2	1			
3	500	50	1	5	50	2	1			
4	500	60	1	4	50	5,3	1			
5	260	25	1	1	25	2	1			
6	250	40	2	1,5	40	2	1	2,53	26,35	25
7	250	40	2,5	2,65	40	2	1			

Table 2. Chemicals needed for bio-diesel preparation

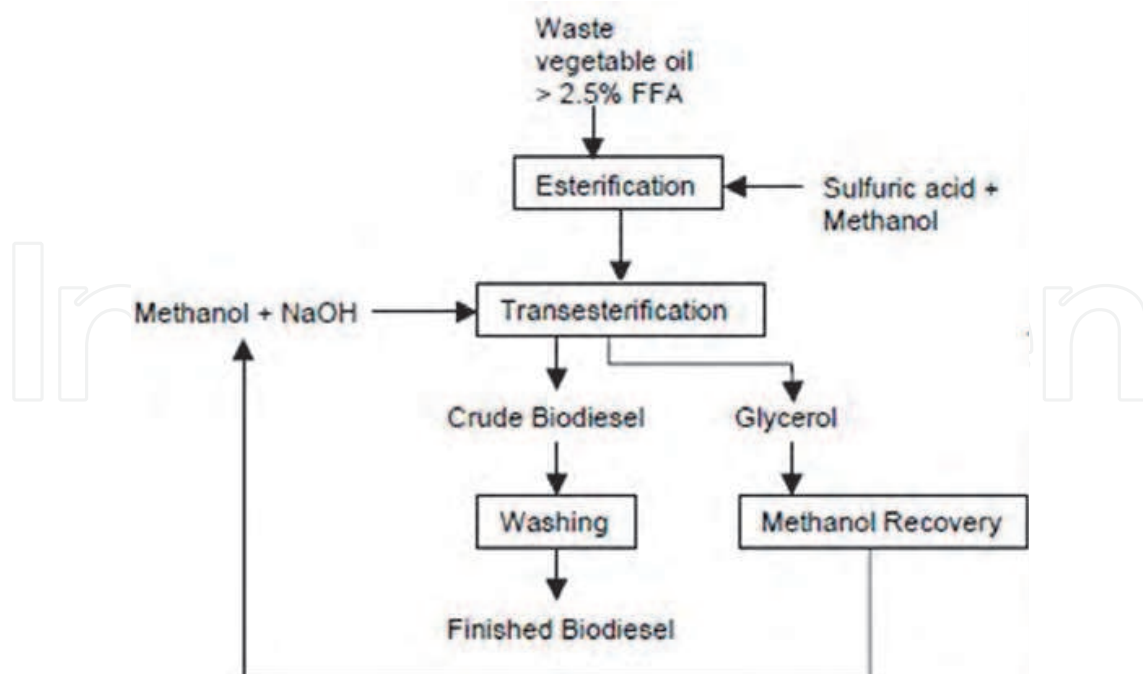


Fig. 4. Biodiesel production flow-chart

Based on the experiments described above and on the derived flow chart of the process, the pilot station presented in figure 5 was built at “Politehnica” University of Timisoara. The control of the installation and transesterification process is fully automated and design to use waste animal fats from meat processing industry. The ration between raw fats introduced and biodiesel produced is up to ~ 50% for waste fats with the FFA content higher than 12% and is getting higher as the FFA content in the raw material decreases. The installation capacity is 20 liters of fats and the processing time is from 3 to 10 hours, depending on the FFA content of the fats

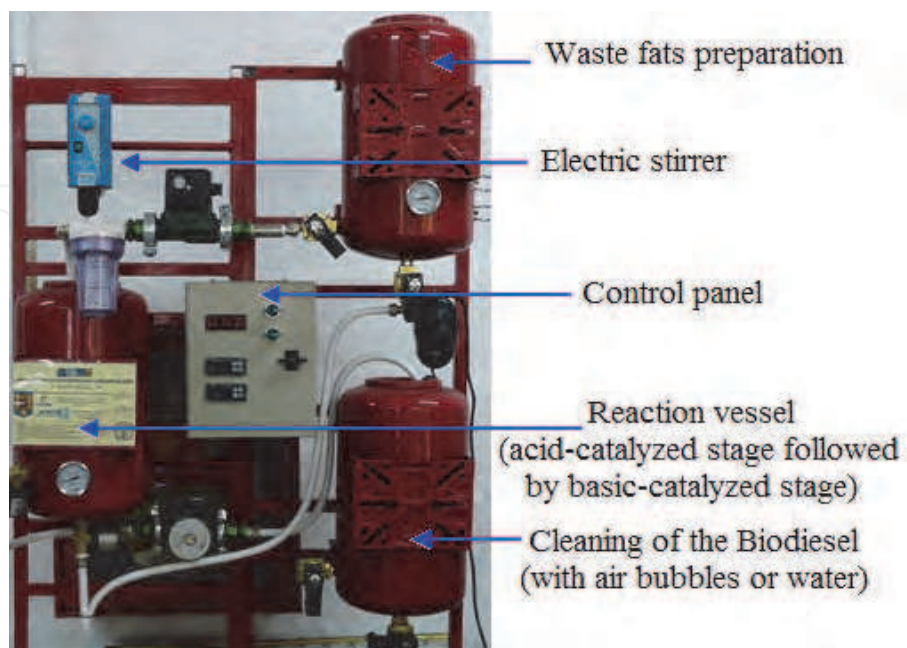


Fig. 5. Pilot installation for Biodiesel production from waste fats with high FFA content.

3. Advantages in the use of biodiesel in an typical urban vehicles fleet

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, which 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 loss of natural resources. Each of us is a polluter but also a victim of pollution. (Ghani, 2009)

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

Further examples of how air quality might be determined by numerical modeling in order to establish if new industrial sources (that are also polluting sources) might affect the quality of air. One knows that the total air concentration is a sum of the natural pollution and the induced anthropic pollution. In order to modernize a city it is necessary to build new industrial areas that are simultaneously also polluting. By numerical simulation the strategy might be optimized. (Silva, 2010)

In the next paragraph and figures is presented the simulation in the case that all diesel engines are using the bio-diesel fuel, for one major Timisoara crossroad, M. The values for emission factors both for diesel and bio-diesel fuels are extracted from Corinair database and traffic structure and meteorological data were measured *in situ*. The CORINAIR - CORE INventory of AIR emissions - was a project performed since 1995 by the then European Topic Centre on Air Emissions under contract to the European Environment Agency. The aim is to collect, maintain, manage and publish information on emissions into the air, by means of a European air emission inventory and database system. This concerns air emissions from all sources relevant to the environmental problems of climate change, acidification, eutrophication, tropospheric ozone, air quality and dispersion of hazardous substances.

The software used was CALROADS with modeling code CALINE 4 (US EPA approved) and the areas studied were Michelangelo crossroad and Marasti crossroad, both major polluting area points in the city of Timisoara. The traffic surveillance and cars characterizations have been conducted for the time frame considered in both crossroads. The medium number of cars in both intersections was around 45 000 vehicles/day (about 30% diesel powered vehicles). The diesel emission factors have been taken from Corinair database.

In figure 6 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.

The road traffic measurements and fleet characterization has been done over a week period, the results for total road traffic in the Michelangelo crossroad is given in table 3.

In figure 6 the road traffic structure is given for one hour period, for the Michelangelo crossroad, as the concentrations resulted after the simulations are one hour mean values.

The formulas used to calculate the emission factors for CO, NO_x and particles is in accordance to Corinair methodology and the estimated results for diesel and biodiesel are calculated. (EMEP, 2007)

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

Table 3. Measured data for total road traffic in Michelangelo crossroad.

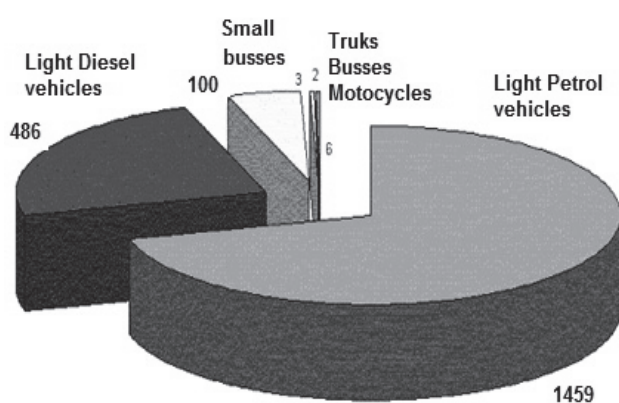


Fig. 6. Road traffic structure for one hour period in Michelangelo crossroad

$$E_{CO} = 5.41301 \cdot V^{-0.574} \quad [g / km] \quad (3)$$

$$E_{NOx} = 1.331 - 0.018 \cdot V + 0.000133 \cdot V^2 \quad [g / km] \quad (4)$$

$$E_{PM} = 0.45 - 0.0086 \cdot V + 0.000058 \cdot V^2 \quad [g / km] \quad (5)$$

In the formulas above V is the mean speed of the vehicles. The calculated results for a typical mean vehicle speed in Michelangelo crossroad is about 30 [km/h] are presented. Emissions factors for diesel fuel, for each vehicle, are:

$$E_{CO}^{diesel} = 0.7683 \quad [g / km] \quad (6)$$

$$E_{NOx}^{diesel} = 0.91 \quad [g / km] \quad (7)$$

$$E_{PM}^{diesel} = 0.2442 \quad [g / km] \quad (8)$$

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

$$E_{CO}^{biodiesel} = 0.30732 \quad [g / km] \quad (6)$$

$$E_{NOx}^{biodiesel} = 0.93 \quad [g / km] \quad (7)$$

$$E_{PM}^{biodiesel} = 0.09768 \text{ [g / km]} \quad (8)$$

The most relevant results are presented in figures 8, 9 and 10 and in table 4 the maximum values obtained for considered pollutants, after dispersion, are given.

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 [$\mu\text{g}/\text{m}^3$]
	Biodiesel	11.70 [$\mu\text{g}/\text{m}^3$]

Table 4. Maximum values obtained for considered pollutants, after simulation.

4. Conclusion and discussions

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 physical characteristics of fatty acid ester (bio-diesel) resulted in the end of 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.

It is quite visible from Figures 7, 8 and 9 the advantages of using bio-diesel in diesel engines and that if all diesel engines will use bio-diesel fuel the reduction of emitted CO and particle concentration is up to 50%.

As it is known the crude oil world reserves will not last forever and it is necessary to obtain alternatives fuels for piston engines. Another aspect is the more decent impact of these fuels on the environment. The search for alternative fuels is on wide spread in all developed countries. The advantage of bio-diesel as an alternative fuel relies first of all on its physical properties, similar with those of diesel fuel so that bio-diesel can be used directly in diesel engines with no essential modification. Second advantage is the very low impact on environment, and the third advantage is the accessibility of the breeding materials like old animal fats and a large variety of vegetable oils.

The tests described above are a real success and a step forward in developing new alternative fuels for piston engines.

This paper brings in attention an 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. Also, gives an example on how numerical simulations with software approved by international institutions can be used by local urban and environment authorities in order to control pollutants emissions in urban or industrial areas, with an emphasis on sustainable and eco-friendly urban development. The advantage of numerical simulations is given by fast results, low cost and possibility to evaluate different pollution reduction scenarios.

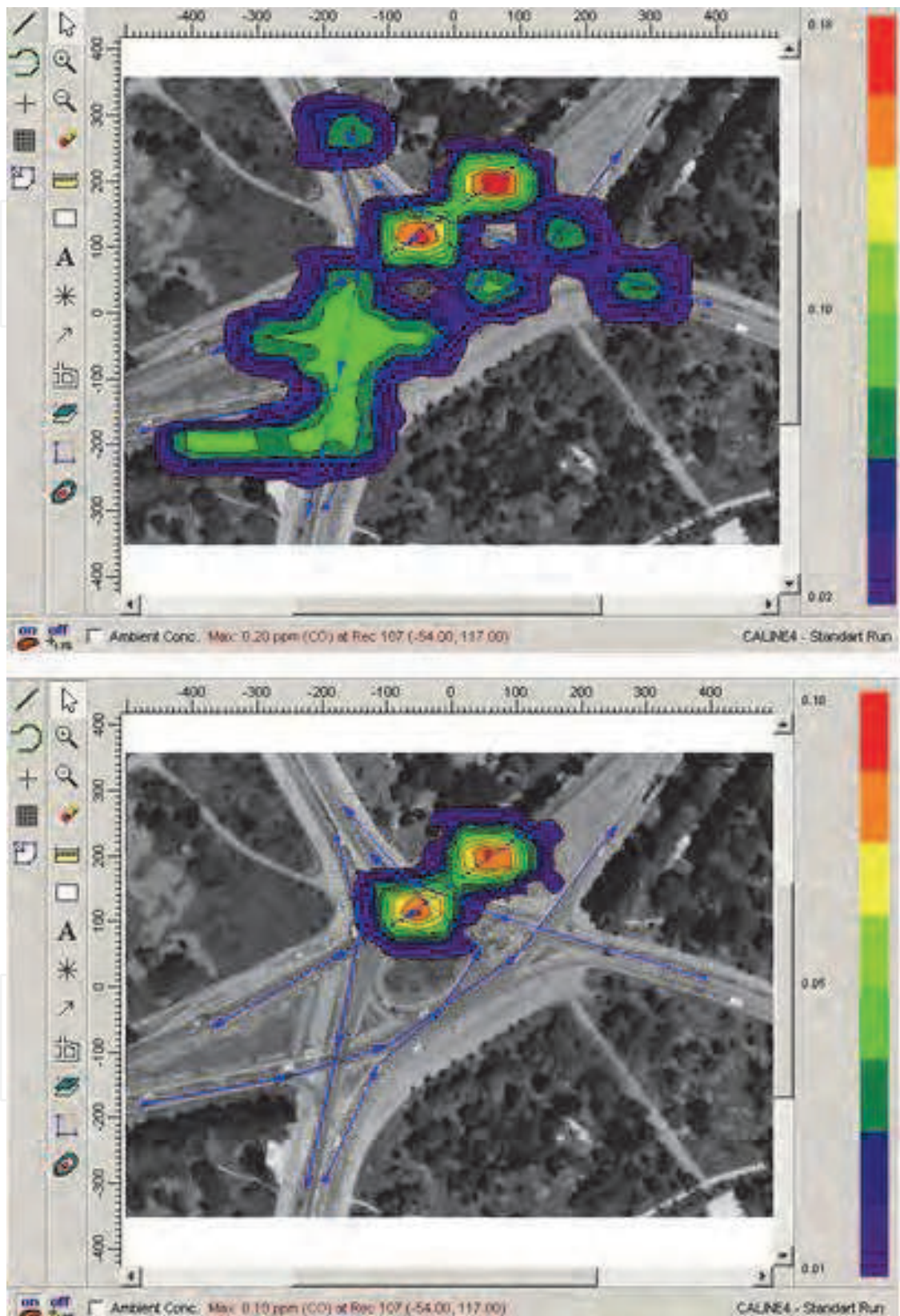


Fig. 7. CO concentrations for the Michelangelo crossroad: diesel (*up*) versus bio-diesel (*down*), where red color represents highest values and violet lowest values. The maximum resulted value for CO concentration in ambient air is in red, in the figure bottom.

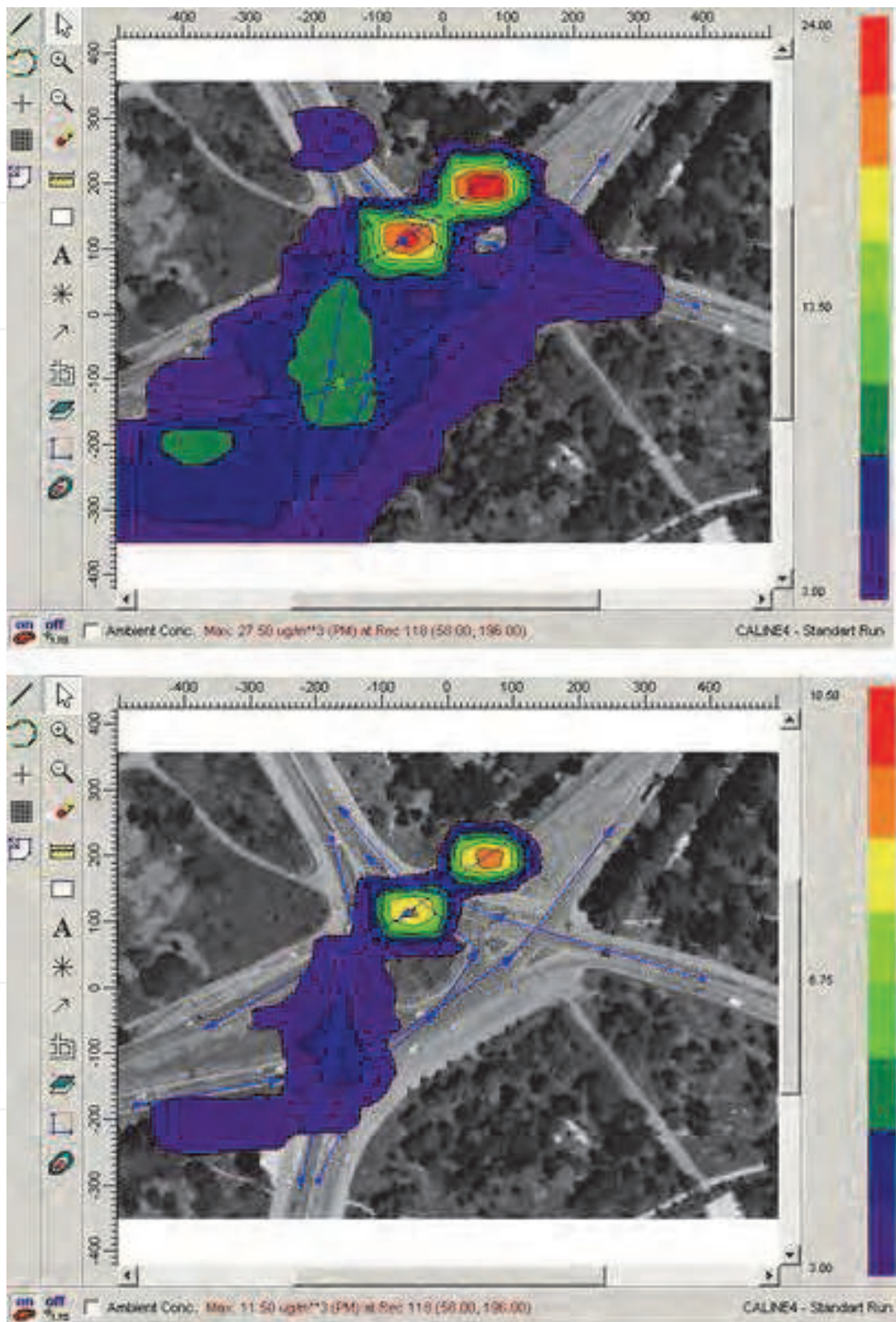


Fig. 8. Particle (PM) concentrations for the Michelangelo crossroad: diesel (*up*) versus biodiesel (*down*), where red color represents highest values and violet lowest values. The maximum resulted value for PM concentration in ambient air is in red, in the figure bottom.

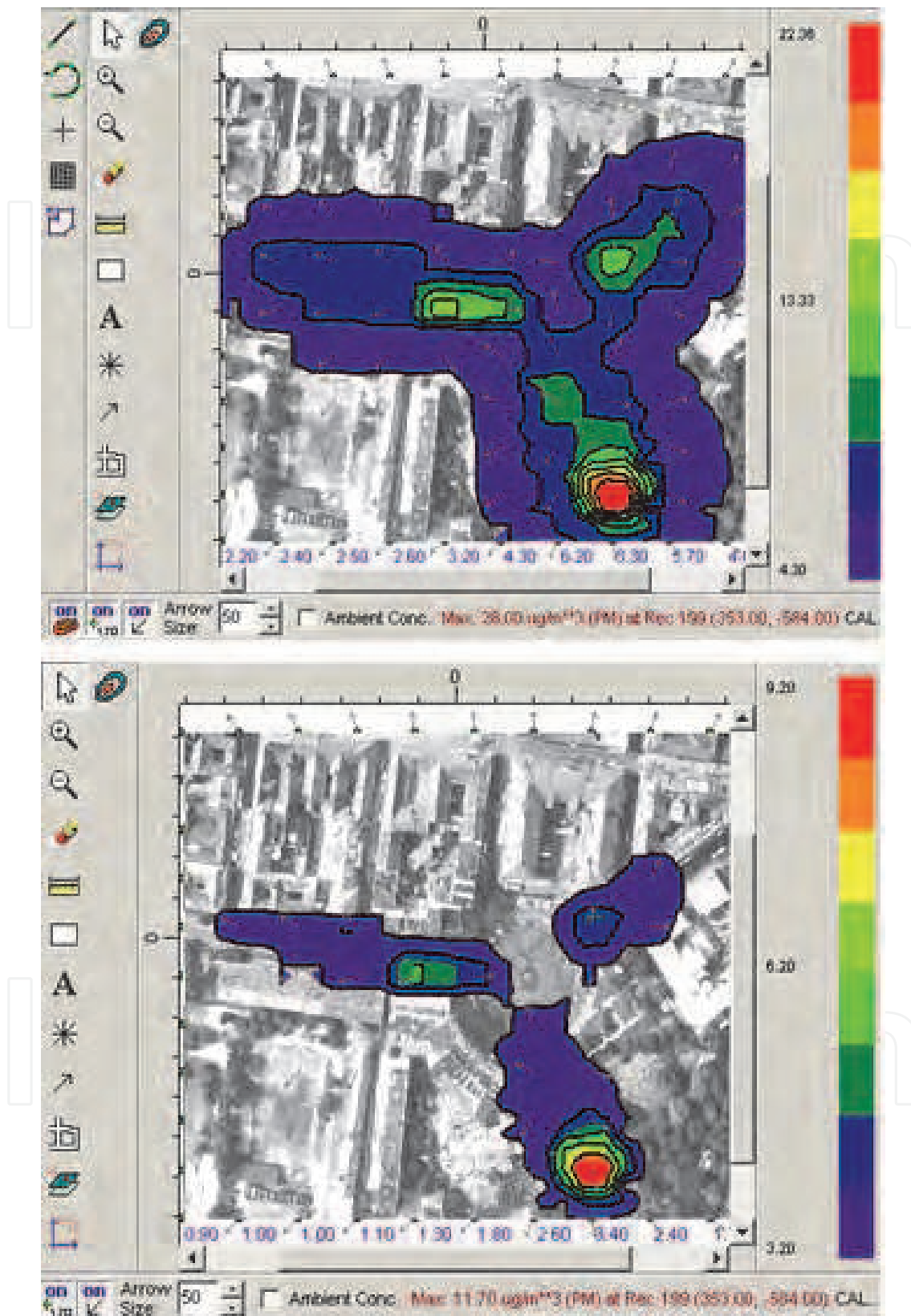


Fig. 9. Particles concentrations for the Marasti crossroad: diesel (*up*) versus bio-diesel (*down*), where red color represents highest values and violet lowest values. The maximum resulted value for PM concentration in ambient air is in red, in the figure bottom.

Worldwide, there is a growing interest in the use of solid, liquid and gaseous biofuels for energy purposes. There are various reasons for this, such as:

1. Political benefits (for instance, the reduction of the dependency on imported oil);
2. Employment creation – biomass fuels create up to 20 times more employment than coal and oil; and
3. Environmental benefits such as mitigation of greenhouse gas emissions, reduction of acid rain and soil improvements.

The advantage of biofuel as an alternative fuel relies first of all on its physical properties, similar with those of diesel fuel so that biofuels (biodiesel or buthanol) can be used directly in diesel engines with no essential modification. Second advantage is the very low impact on environment, and the third advantage is the accessibility of the breeding materials like old animal fats and a large variety of vegetable oils.

In this respect, knowledge exchange as well as the creation of conducive market mechanisms and legislation is essential for a more widespread introduction of biomass and biofuels energy systems.

5. Acknowledgment

All tests presented where successfully made by the authors in the frame of several projects of the hosts, "Politehnica" University of Timisoara and T.U. München with the financial support of Alexander von Humboldt Foundation, Romanian National Council for Scientific Research and Balkan Environmental Association for which deep thanks are expressed.

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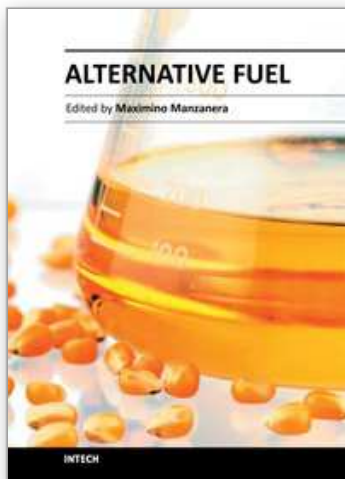
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*** DIN 51419-A, DIN 51575, DIN 51562-Teil 1.

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Alternative Fuel

Edited by Dr. Maximino Manzanera

ISBN 978-953-307-372-9

Hard cover, 346 pages

Publisher InTech

Published online 09, August, 2011

Published in print edition August, 2011

Renewable energy sources such as biodiesel, bioethanol, biomethane, biomass from wastes or hydrogen are subject of great interest in the current energy scene. These fuels contribute to the reduction of prices and dependence on fossil fuels. In addition, energy sources such as these could partially replace the use of what is considered as the major factor responsible for global warming and the main source of local environmental pollution. For these reasons they are known as alternative fuels. There is an urgent need to find and optimise the use of alternative fuels to provide a net energy gain, to be economically competitive and to be producible in large quantities without compromising food resources.

How to reference

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Francisc Popescu and Ioana Ionel (2011). Waste Animal Fats with High FFA as a Renewable Energy Source for Biodiesel Production - Concept, Experimental Production and Impact Evaluation on Air Quality, Alternative Fuel, Dr. Maximino Manzanera (Ed.), ISBN: 978-953-307-372-9, InTech, Available from: <http://www.intechopen.com/books/alternative-fuel/waste-animal-fats-with-high-ffa-as-a-renewable-energy-source-for-biodiesel-production-concept-experi>

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