SUMMARY

The title of the master's degree work is: THE ANALYTIC CONTROL OF THE BIODIESEL QUALITY. CONTRIBUTIONS TO THE IMPROVEMENT OF PHYSICO-CHEMICAL SPECIFIC FEATURES.

The present master's degree work contains 202 pages, these being structured in four chapters: 1 – Introduction; 2 – Experimental part;
3 – Conclusions; 4 – Bibliography.

Chapter 1 – Introduction, contains 37 pages and refers to the following aspects:

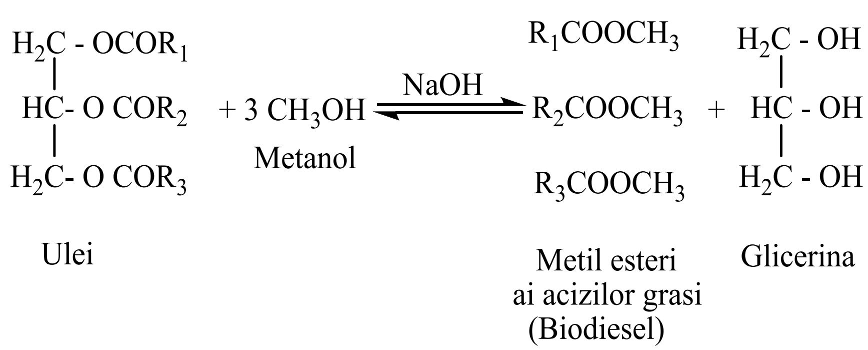
1.1. The necessity of production and use of biofuels. In international plan, the diminution of crude oil reserves and the consecutive increase of its price, created favourable prerequisites for the approaching of making alternative fuels. In the same advantageous way are also acting the antipollution legislations, which sternly limit the quantity of polluted emissions from the escapement gases of the engines with internal burning.

1.2. Types of extant biocarburants.The biofuels are remade resources which help to the reduction, in the atmosphere, of the emissions of dioxide of carbon and of other gases. In the present moment, the ethanol is the most used biofuel, the biodiesel is the second biocarburant used now, and the biogas is the third biocarburant used now, but its using is more limited than that of the ethanol and biodiesel.

1.3. Raw materials used to obtain the biofuels. The biomass can be used as a resource to produce biofuels. This includes any regenerate material of organic type, containing the terrestrial vegetables (agricultural cultures of food use, trees and cultures destinated to produce energy, industrial plants, fodders) and aquatic (algas, sea plants), but also the ensemble of offals and organic rests from agriculture, fishry, forestry, city offals and other offals.

Biodiesel, from chemical point of view, is a mixture of monoalchiles esters of the fatty acids, obtained in an usual manner through the reaction of transesterification of triglycerides with an inferior alcohol. The usual sources of triglycerides used to obtain the biodiesel are represented by the vegetable oils and animal fats.

1.4. Processes and technologies to obtain the biodiesel. Biodiesel is obtained into a chemical technological process of transesterification, through which the glycerine is extracted from fats or vegetable oils used as raw material. From this chemical process, result - methyl esters - the biodiesel and the glycerine:



oil | methanol | methyl esters of fatty acids (Biodiesel) | Glycerine

The reaction of transesterification is reversible and temperately exoterm.

Nowadays there are different industrial processes and with their help biodiesel can be obtained. The most important processes are:

- Base – base process, through which a basic catalyzer is used, the hydroxide. This hydroxide can be Hydroxide of sodium (sodium hydroxide) or Hydroxide of potassium.

- Acid – base process, is the process in which is made for the first time an acid esterification and then it continues with the normal base-base process; generally are used acids with a high level of acidity.

- Supercritical processes – in these processes we don't need the presence of a catalyzer, because these processes are produced at high temperatures in which the oil and the alcohol react without the necessity of an external agent, such as the hydroxide, to act in reaction.

- Enzymatic processes – nowadays some enzymes are studied, those which can be used as reaction accelerators oil-alcohol.

1.5. Physico-chemical changes which take place during the storage period of biodiesel. The chemistry degradation of biodiesel is the same as that of the oils from which it comes. The oxidation of lipids is done through three mechanisms:

- Autooxidation: *The reaction of autooxidation* is radical and passes through three stages: initiation, propagation and interruption.

- Photooxidation: *The forming of hydroperoxides through photooxidation* from unsaturated fatty acids is accelerated by the exposition at light. This acceleration can be explained on the one hand by direct photooxidation (photochemical oxidation) and on the other hand by photosensitized oxidation of the unsaturated fatty acids.

- Enzymatic oxidation: *The forming of hydroperoxides through enzymatic oxidation* is catalyzed by the presence of the lipooxygenase enzymes. These catalyze the peroxidization of fatty acids with a forming of hydroperoxides.

1.6. Advantages and disadvantages of the biodiesel utilization.

Advantages: it reduces easily the emission of dioxide of carbon in the atmosphere; it reduces with 100% the emission of dioxide of sulphur (it doesn’t contain sulphur); it reduces the emissions of particles in the atmosphere; it can be mixtured with gas oil in any percent; it is less inflamable; it is obtained from regenerate resources (vegetable oils); the smell of emanations is pleasant (smell of pop-corn or of doughnut); it degrades itself four times faster than the usual diesel (maximum 28 days); the energetic performances are comparable to those of the classic gas oil; it is ten times less toxic comparatively with the cuisine salt.

Disadvantages: being a better solvent than the classic gas oil, it brushes away the deposits from the engine and brings these particles to the level of injectors, blocking up the injection pump or the injectors, producing even “the drowing” of the fuel filter with these types of deposits; it dissolves easily any fiting or caoutchouc connection; it produces with 5% more oxides of azote comparatively with the gas oil (because of the content in the oxygen atoms which oxydates easier the azote in the air introduced into cylinders); it presents great addiction to the cost of raw material; it generates the glycerine as a subproduct, whose purifying is viable only for great productions; it presents reduced fluidity at low temperatures; the maximum period of storage is less than six months.

1.7. Determination of the level of biodiesel oxidation. The most used methods of appreciation of the level of autooxidation in lipids are the following – sensorial (subjective) methods and physico-chemical (objective) methods, the latter ones offering the posibility of appreciation of the oxidation level after the size (values) of some indexes such as: the acidity index, the refraction index, the peroxide index, the iodine index, the saponification index, the disturbance point, the cetanic number, the stability in oxidation, the cromatographic analysis, the thermogravimetrical analysis.

1.8. Function of the antioxygens in the process of biodiesel storage. The antioxygens have a large domain of use, including animal fats, vegetable oils, products with a varied content of lipids, packings for fats or food products rich in fats, cereal products. The most used antioxygens are the tocoferrols and the ascorbic acid. Taking into account the great interest to use natural antioxygens (flavonoides, phenolic compounds from plants, fruit, seeds etc) in stead of synthetic antioxygens it was registered on a large scale an intensive activity of research in utilization of some natural compounds with antioxygen function.

Chapter 2 – The experimental part, contains a number of 136 pages, being structured as it follows:

2.1. The detaching of samples. In order to achieve the experimental part were used:

- biodiesel samples obtained from sun-flower oil – HELIANTHUS ANNUUS; *The biodiesel* used was obtained from sun-flower oil esterificated with methanol using a basic-type catalyzer (NaOH).

- seeds of Vitis vinifera; *The extracting of oil from the Vitis vinifera seeds* was done with the help of the apparatus type Soxhlet, using as a solvent – the petroleum ether.

- plants of Medicago sativa; *The extracting of oil from Medicago sativa*. The material (gathered in the period of blossoming) dry and broken up (2-3 mm) of Medicago sativa was introduced into the Soxhlet apparatus, where the oil was extracted, using as a solvent the petroleum ether.

The forming of work samples – There were formed three sets of samples:

- a set formed by biodiesel obtained from sun-flower oil;
- a set formed by biodiesel obtained from sun-flower oil additived with 1% oil obtained from Medicago sativa;
- a set formed by biodiesel obtained from sun-flower oil additived with 1% oil obtained from Vitis vinifera.

2.2. The classic analysis of biodiesel. As it concerns this subchapter of the experimental part were determined the qualitative indexes of biodiesel during the storage period, being studied in this way the main properties of the fuel:

- **determination of the refraction index with the Abbe refractometre** – through the determination of this index we wanted to monitorize the behaviour of the simple biodiesel and the behaviour of that additived with antioxygens, during a year of days, for a strict evaluation of behaviour in oxidation of these samples. The refraction index was monthly read and the obtained results were satisfactory: for the samples of additived biodiesel it was registered a diminution of the refraction index because of the reduced accumulation of oxidation products, comparatively with the unadditived samples with antioxygens.

- **determination of the stability in oxidation through Rancimat method** – Through Rancimat method of determination of the stability in oxidation of biodiesel, we proposed to follow the antioxydant action of poliphenols contained in the seeds of Vitis vinifera and Medicago sativa, by measuring the induction period, during a year of storage of the biodiesel and additived biodiesel samples. This method consits in the oxidation of Biodiesel in accelerated conditions. The method allows the establishment of induction period which corresponds with the initiation stage of the biodiesel autooxidation. The antioxidant action of the poliphenols contained in the Vitis vinifera and Medicago sativa seeds leads to the diminution of the speed steadfastness value for the oxidation reaction of the lipids from the biodiesel samples. The smaller value of speed steadfastness makes that the biodiesel samples with antioxygen present a value of the induction period bigger than in the additived samples.

- determination of the freezing point and of trouble point – Using the antioxygens, the freezing temperature or the freezing point is favourable to the samples of additived biodiesel, because the forming of oxidation compounds during the storage period in smaller. The changing of trouble point leads to the appearance of some problems concerning the diminution of debit through the injection pump (diminution of the engine power), the stopping up of filters and of supplying conductors.

- determination of the inflamability point – Through the determination of inflamability point we suggested a comparative analysis of the simple biodiesel and additived with antioxygens, thinking that the volatile products of oxidation appeared during the storage period, can raise the danger of kindling of the liquid fuel. We proved the fact that the additivity with antioxygens reduces the composition in volatile products of oxidation, so the kindling risk, during a large period of storage.

- determination of the acidity index – The presence of antioxygen establishes a reduced accumulation of oxidation products. This reduced accumulation establishes a diminution of the acidity index for the biodiesel samples with antioxidant.

- **determination of the peroxide index** – Although the peroxide index is less suit for the monitorization of the oxidation process of biodiesel [102] and is not specified in the standards of biodiesel fuel, this parametre influences the cetanic number (a parametre which is specified in standard by carburant). An increase of peroxide index involves an increase of cetanic number, and therefore, can reduce the time interval necessary to the kindling process which takes place into engine.

- **determination of the saponification index** – After a year storage period of the biodiesel, we established the saponification index, as a measure conversely proportional with the molecular mass of fatty acids from the triacilglycerols composition.

- **determination of the iodine index** – It presents a decreasing variation during the storage of samples, because of the fact that, with the beginning of the oxidation processes, the level of unsaturation is reduced because of the oxidation of unsaturated fatty acids.

2.3. Determination of the gaseous emissions. The presence of the oxidation compounds appreciably modifies the CO accumulation from the value of 0,076% for the biodiesel samples to 0,061% and 0,059% for the additived biodiesel samples, from 1,94% CO2 for the biodiesel samples to 1,93% and 1,92% for the additived biodiesel samples, from 53 ppm HC for the biodiesel samples to 51 ppm and 50 ppm for the additived biodiesel samples.

2.4. Thermogrevimetrical analysis. The thermic grevimetry developed proper from the classic method of warming-up and of weighing into steps of a solid sample.Warming a substance at different temperatures, this substances suffers a series of changes, some of them being also related to weight changes. Following the weight variation in accordance with temperature, we could have some conclusions about the changes appeared in the researched material. Outlining graphicly these weight variations in mass coordinations in accordance with temperature (m=f(t)) is obtained the curve of thermic grevimetry. Thermogrames were done for the additived and unadditived samples, in the beginning and in the end of the storage period of 12 months.

2.5. Cromatographic analysis. The analysis of biodiesel samples was done on a cromatograph type FOCUS GC bounded with a spectometre of DSQ II mass. The results of the cromatographic analysis point out the additive function obtained from seeds of Vitis vinifera and plants of Medicago sativa through the values of concentrations of the principled esters copounds of biodiesel in the end of the experiment.

2.6. Comparative analysis of the natural antioxygens used and of synthetic antioxygens. The researches made in the samples of biodiesel obtained from sun-flower (HELIANTHUS ANNUUS) and additived with natural antioxygens extracted from Medicago sativa and Vitis vinifera, pointed out the antioxidant capacity of these, through the modification of the principled qualitative parametres. To establish certainly this antioxidant capacity we done a comparative analysis of the of using of these natural antioxygens concomitantly with two synthetic antioxygens used in world plan, Ionol BF 200 and Irgastab 100, produced by the Ciba Corporation company. The comparative study was made in the samples of biodiesel obtained from sun-flower, colza and palm tree oil. For the comparative study of the natural antioxygens with those synthetic were used the following determinations:

1. Determination of the induction period; The value of induction period in the three types of biodiesel used in the experimental activity and additived with natural and synthetic antioxygens presents an increse of this which

allows a comparison of the antioxygen function on the oxidation reactions during the storage period.

2. Determination of the acidity index before and after the establishment of the Induction period; The modification of acidity in biodiesel samples because of the accelerated oxidation reaction presents higher values in the unadditived samples. The samples additived with a natural antioxygen obtained from Vitis vinifera present closed values of those additived with a synthetic antioxygen, which makes advisable its use.

3. Determination of the peroxide index before and after the establishment of the Induction period; The near values of the Peroxide index in the end of the accelerated oxidation reaction of the samples of biodiesel additived with a natural antioxygen, with those obtained in the samples additived with a synthetic antioxygen, point out the role of the natural antioxygen extracted from Vitis vinifera.

4. Determination of the gaseous emissions before and after the establishment of the Induction period; The gaseous emissions obtained in all samples of researched biodiesel don't present essential changes between them.

2.7. Comparative analysis in the using of biodiesel and of classic fuels.

The utilization of biodiesel as a substitute of the gas oil presents a series of advantages, such as:

- it generates a short cycle of carbon;
- it presents a high biodegradation;
- does not contain sulphur, allowing the utilization of catalyzers for a better improvement of burning and for a diminution of gaseous emissions;
- it reduces the danger of explosion owing to the emanations of gases during the storage;

- the accumulation of the principled gases emanated during the burning process are smaller than in the case of gas oil.

Afterwards the examination of the burnt gases, done in the biodiesel and gas oil samples, is pointed out by the meaningful reduction of its concentrations, especially in the biodiesel samples towards those of gas oil.

Chapter 3 – Conclusions, contains 14 pages, and the confirmation of all experimental events obtained during the examinating activity in the three types of biodiesel (sun-flower, colza and palm tree) leads to the fact that vinifera presents an antioxidant activity, which means an using of these in the storage process of biodiesel.

Chapter 4 – Bibliography.