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SUMMARY OF THE MAIN RESULTS

I. Production of low and ultra low sulfur fuels using alternative hydrodesulfurization methods.
II. Preparation and application of biosorbents (activated carbon) based on waste biomass.
III. Preparation and application of modified nanocomposite materials in water purification.
IV. Research in laboratory and industrial conditions of the influence of technological factors on the yield and quality of the products of the hydrocracking; reactivity of heavy oils in catalytic and thermal cracking.
1. Influence of technological factors on the parameters of the hydrocracking in the processing of heavy oil fractions.
2. Influence of technological factors on the parameters of catalytic and thermal cracking.
3. The possibility of obtaining bitumen from vacuum residue from the H-Oil process in LNB.
4. Environmental problems in oil refining
V. Other research.

I. Production of low and ultra low sulfur fuels using alternative hydrodesulfurization methods

Oxidation desulphurization [1, 4, 33].

The study describes oxidative desulfurization of a model mixture of fluid-catalytic-cracked light cycle oil (LCO). Oxidations of the sulfur compounds have been monitored by FTIR spectroscopy. Oxidized sulfur compounds and degree of desulfurization by oxidation have been determined by gas chromatography-mass spectroscopy (GC-MS).

It has been established that after oxidation and proper extraction process about 90% of the highly refractive by HDS (hydrodesulfurization) sulfur compound like 4,6-Dimethyl-dibenzothiophene (4,6-DMDBT) is removed from the oxidized model mixture. **[1].**

The objective of the present study is to decrease the sulphur content of heavy gas oil by oxidation-extraction desulphurization which is one of the alternative methods which are aimed at. An adequate mathematical model is developed on the ground of a planned experiment approach which describes the effect of a number of factors (a temperature, contact time, and a peroxide-to-formic acid molar ratio) on the rate of sulphur content decrease. The optimal values of the variables are found to provide sulphur decrease in the heavy gas oil raffinates of up to 87 %. The process is monitored by FTIR and NMR spectroscopy, and gas chromatography equipped with sulphur chemiluminescence detector (SCD) **[4, 33].**

Studies on adsorption desulfurization of petroleum fuels and model mixtures with biosorbents obtained on the basis of waste biomass [3, 34].

Rice husks pyrolysed at different temperatures in the range of 250–700°C were investigated as adsorbents for thiophene removal from a model fuel. The adsorption ability of the samples was evaluated under both static and dynamic conditions. It was found that pyrolysed rice husks without any pretreatment are a promising adsorbent for the removal of sulphur-containing molecules from the model fuel. Removal of 92% of the sulphur from the fuel was achieved. The adsorption capacity of the pyrolysed rice husks correlates with their textural and chemical characteristics which strongly depend on the pyrolysis temperature. The adsorption of thiophene is influenced by the initial sulphur concentration level, the fractional composition of the adsorbent, the temperature and the adsorbent/fuel volume ratio. The adsorption capacity of the pyrolysed rice husks is higher under static than under dynamic conditions.

The adsorption desulfurization of model fuel was performed with a biosorbent modified with zinc and copper **[34]**. The modification of the adsorbent was performed by impregnation with solutions of copper carbonate and zinc oxide. The adsorption of dibenzothiophene (DBT) from the model fuel is performed under static conditions and under the influence of ultrasound to intensify the process. The change in sulfur content of the model fuel after adsorption was monitored by UV spectroscopy by observing the intensity of the peak characteristic of the sulfur compound. The influence of the particle size distribution of the modified adsorbent was also studied. The results showed that the method is promising and applicable for the removal of dibenzothiophene from the model fuel.

Desulphurisation of a liquid product by pyrolysis of used tires [16, 32].

In recent years, the recycling of used car tires by pyrolysis has aroused considerable scientific interest due to the energy and environmental significance of the problem. This process releases about 40% liquid product (pyrolysis oil), with a sulfur content of about 1%, which requires its purification. In this regard, a systematic literature review was made on the basis of published data on possible options for desulfurization of pyrolysis oil and its fractions. The summarization of the scientific results showed the possibility of alternative methods, incl. and oxidative desulfurization to refine liquid pyrolysis products that are competitive with conventional hydrodesulfurization [16].

Studies have been carried out on the chemical composition of pyrolysis oil fractions and it has been found that some of them have properties similar to those of petroleum fuels of the 'industrial gas oil' type and meet the requirements for sulfur content up to 1%. Fractions can be used as conventional fuel after reprocessing (desulfurization or after mixing with petroleum fractions) [32].

II. Preparation and application of biosorbents (activated carbon) based on waste biomass.

Preparation of adsorbents from rice husks and their application in oil spill purification and non-stick coating [2, 9, 31].

Pyrolyzed rice husks, in addition to being an adsorbent for desulfurization, could also be used to remove oil spills. Carbon/SiO2-containing natural composite material is obtained by slow pyrolysis of rice husks at 350 ◦C. The pyrolyzed rice husks acquired structural and surface characteristics which rendered them a suitable material for the purification of waters from crude oil. In order to improve the adsorption characteristics of the pyrolyzed rice husks they were modified with: 5% H2SO4 solution, 1M 12-stearic acid and hydroxystearic acid, as well as with different amounts of fluids extracted with acetone from the solid pyrolysis residue. A comparative assessment of the effect of modifiers and fluids on the sorption efficiency of the pyrolyzed rice husks toward oil and water was made. On the basis of the results obtained, the factor of effectiveness of the adsorbent was determined as a quantitative measure of the efficacy of materials used for cleaning spills of oil and oil products from water surfaces **[2]**.

In the study **[9]** an attempt was made to describe the kinetics and mechanism of oil and oil products' sorption from aqueous surface on pyrolyzed rice husks. The pseudo-first order and second order kinetic models, Elovich equation and intraparticle diffusion model were applied to describe the kinetics and estimate the rate-limiting stage of the process. The best-fit model was selected based on the linear regression method. The effect of the sorbent granulometry, the density of oil pollutants and the presence of surface functionalities on sorption kinetics was investigated**.**

Burnt-on sand is a layer molding mixture strongly connected to the surface of the castings. This is the reason for the recall or at least a sharp increase in costs for cleaning of their surface. Additives to molding mixtures and / or dispersion coatings applied to the working surface of the mould are used to prevent its formation. The product, obtained according to the regime of the pyrolysis of rice husks contains SiO2, solid carbon and volatile hydrocarbons in different ratios, and can be used for anti-burnt-on sand coating. In this work has been investigated the possibility of using pyrolyzed rice husks as a material for creating anti-burnt-on sand coatings for sand molds for the iron and steel castings production. **[31]**.

Preparation of adsorbents from algae [5, 14].

A procedure has been developed for the recovery of algae waste used in the production of biodiesel by pyrolysis at 550 ° C. The solid pyrolysis product was characterized by elemental analysis, differential thermal and thermogravimetric analysis. The composition of gaseous and liquid products (group chemical composition and oxygen-containing compounds) was determined. The carbonized product was subjected to physical activation with water vapor at different temperatures. The porous texture of the obtained samples was studied by low-temperature nitrogen physisorption. The results showed a moderately developed specific surface area and porosity (micro- and meso-) in the process of obtaining the samples. The presence of surface oxygen groups was determined by Böhm's method. The obtained results regarding the adsorption-texture parameters of the samples, as well as the characteristics of the chemical nature of their surface, give reason to consider the obtained carbon samples as promising sorbents for treatment of organic pollutants and metal ions from wastewater.

Preparation, characterization and application of activated carbon from lignocellulosic biomass [19, 20, 28].

Activated carbons were prepared based on hydrolyzed lignocellulosic biomass, and were chemically activated with potassium hydroxide and phosphoric acid **[28]**. The texture parameters of the adsorbents obtained were determined by low-temperature nitrogen adsorption; their thermal stability was studied by DTA/ TG and the surface functional groups - by FTIR spectroscopy. The adsorption properties of the obtained activated carbons toward perrhenate ions from an aqueous solution were investigated at three different pH values. The adsorbent obtained after activation of hydrolyzed lignin with KOH was found to have significantly better adsorption capacity than that obtained after activation with H_3PO_4. The maximum adsorption value of the perrhenate anion: 95.7% was obtained at a concentration of rhenium in the solution 5 mg l^{-1} and pH 2. Results from this study indicated that waste-derived activated carbon can act as an effective adsorbent for perrhenate ions from acidic wastewater.

The possibility of obtaining activated carbon from lignocellulosic waste biomass (beech, oak, banana and pine sawdust) by KOH activation was studied **[19, 20]**. The obtained cheap and available adsorbents were characterized by scanning electron microscopy (SEM), elemental analysis, infrared spectroscopy (FTIR) and their adsorption-texture parameters were determined by the method of low-temperature nitrogen adsorption. ABs with a high specific surface area (1200 to 1600 m^2g^{-1}) were obtained and the highest ABET (1663 m^2g^{-1}) was found in AB obtained from beech waste biomass. The large volume of micropores (about 70% of the total pore volume) and the large specific surface area suggest their suitability for use in gas phase adsorption or in a new aspect as gas storage, which outlines guidelines for continuing these studies in this direction.

Utilization of coffee waste products [11, 30].

The study reports on the preparation of activated carbons based on biomass (spent coffee brew) and on the characterization of their porous texture. The developed laboratory technology appropriate for the purpose included (1) extraction of coffee grounds biomass to remove coffee oil residue; (2) carbonization of extracted biomass – individual or in mixture with 10, 20 and 30 mass % Bulgarian lignite coal and (3) chemical activation by potassium hydroxide.

The results obtained show the activated carbons prepared by the activation procedure used to have very high specific surface area (from 1600 to 2200 m^2 g^{-1}), with high microporous volume (0.600 – 0.800 cm3 g-1) and with homogeneous mesoporous size distribution (max. ~ 2 nm) **[30].**

A method has been developed to utilize coffee by-products (sludge and coffee husks) to produce renewable fuel additives (biodiesel) and adsorbents. The extraction of these waste products is the first step towards their recovery. Oils from spent coffee grounds and flakes, raw materials for biodiesel production were extracted by various solvents, and the remainder of the extraction is a suitable precursor for AB **[11]**.

III. Preparation and application of modified nanocomposite materials in water purification [18, 26].

The risk of spills of oil and oil products exists at every stage of their life cycle related to their production, transportation, storage and use. This pollution leads to serious environmental, economic and social problems. The application of sorbents is considered the most effective method, characterized by simple and easy use, directly on the affected area.

Studies on the purification of oil and petroleum products from water surfaces with pyrolyzed rice husks were continued with experiments to obtain composite materials from biodegradable and environmentally friendly products with in situ zinc oxide particles, which are suitable for sorption of oil spills. The sorption capacity in relation to dye, crude oil and oil products (diesel fuel and motor oil) was studied **[18, 26]**. The possibility of composite material regeneration and reuse was also investigated.

In recent years, it has been of interest to obtain superhydrophobic and oleophilic materials from natural products. The study is based on the fact that the modification of cotton fabric with crosslinked polymer can create suitable active centers for adsorption of contaminants. In the presence of a suitable layer with a corresponding structure of the pores, it is possible for oil to penetrate into them and be absorbed. By creating a rough surface, the wetting properties of the material could also be improved.

A better alternative for modification from an ecological point of view is the use of biopolymers from renewable sources. Chitosan, the second most commonly used biopolymer, was selected in the study. It can be easily crosslinked with glutaraldehyde and this further stabilizes the structure of the resulting film and controls the degree of its swelling. Further improvement of the materials is achieved by combining natural polymers (in this case chitosan) with metals or metal oxides. ZnO was used in the work due to its good photocatalytic activity, stability, antibacterial properties and non-toxicity. After the addition of NaOH, an unstable compound is formed - zinc hydroxide, which after heat treatment is converted into ZnO-nanoparticles, the aggregation of which is prevented by chitosan.

Of the composites studied, the one containing chitosan and zinc (ChZn) showed the best sorption capacity relative to oil and the worst for the dissolved dye Drimarene K-7B. This material acts as an adsorbent and its sorption capacity is better than the more viscous motor oil, which contains long chain hydrocarbons and a package of additives. Chitosan composite material (Ch) adsorbs the dissolved dye faster than other materials, as it changes the surface of the cotton fabric and reduces the repulsion of the dye molecules from the fabric. This improved its adsorbing properties. With regard to the possibility of regeneration and reuse, it was found that the ChZn material was successfully regenerated with hexane and used repeatedly until the oil spill was completely eliminated **[18]**.

IV. Research in laboratory and industrial conditions of the influence of technological factors on the yield and quality of the products of the hydrocracking; reactivity of heavy oils in catalytic and thermal cracking.

1. Influence of technological factors on the parameters of the hydrocracking in the processing of heavy oil fractions [6, 7, 21, 23, 30].

- **Effect of catalyst condition on sedimentation and conversion in the ebullated bed vacuum residue H-Oil hydrocracking [7, 23].**

This study highlights the importance of the condition of the catalytic system in the ebullated bed vacuum residue hydrocracker on the performance of the unit, proving that not only feedstock quality but also catalytic system quality are the single variables which have the biggest impact on residue hydrocracker performance. During processing of the same vacuum residual oil in the LUKOIL Neftochim Burgas H-Oil ebullated bed hydrocracker a variation of conversion between 56.6 and 73.0% was observed. A higher sedimentation and the resulting decreased reaction severity were provoked by a higher vanadium content in the catalyst in the second reactor and a higher arsenic determinant in the whole catalytic system.

The reduction of the second reactor catalyst vanadium content along with a decrease of the arsenic determinant in the whole catalytic system allowed recovering the 16.4% loss of conversion during processing the same feedstock. The increase of reaction temperature at constant liquid hourly space velocity (LHSV) increases aromaticity of the unconverted vacuum residual oil product, most probably due to dealkylation of the side alkyl groups attached to the aromatic cores. The rise of temperature also had an effect on the increase of asphaltene conversion, a fact that is not always observed during EBRHC of vacuum residual oils from different origins. **[7].**

In addition to the state of the catalyst, the particle size of the catalyst also plays an important role **[23]**. The LUKOIL Neftochim Burgas (LNB) refinery, which features the H-Oil ebullated bed vacuum residue hydrocracking in its petroleum refining processing scheme, employs HCAT, HTI’s proprietary dispersed nano-size catalyst technology, to boost the H-Oil performance. The positive results from HTI’s pilot plant hydrocracking experiments were confirmed at the commercial LNB H-Oil hydrocracker, registering a conversion increase of about eight per cent without penalizing the sediment formation rate. The increased H-Oil vacuum residue conversion led to increased density, viscosity, and softening point of the unconverted hydrocracked vacuum residue which require further optimization of the utilization of this product. The increased H-Oil vacuum residue conversion as a result from the use of HCAT did not have an impact on the performance of the fluid catalytic cracking unit that processes a blend of straight run vacuum gas oil (VGO) and H-Oil VGO.

- **Petroleum crude slate effect on H-Oil performance [21]**

Sixteen petroleum crudes and an imported atmospheric residue originating from Russia, Azerbaijan, Greece, Italy, Kuwait, Iraq, Iran, Saudi Arabia, Tunisia, and the USA have been processed in the LUKOIL Neftochim Burgas (LNB) refinery, and their effect on the ebullated bed vacuum residue H-Oil hydrocracking (EBVRHC) performance has been evaluated. The vacuum residue conversion in the LNB H-Oil EBVRHC varied between 55% and 82% depending on the crude blend processed in the LNB refinery. It has been established that among all vacuum residue SARA fractions during EBVRHC, the resins have the highest conversion, followed by the naphtheno-aromatics while the saturates show the lowest conversion. Depending on the petroleum crude origin the behaviour of the most problematic VR asphaltene fraction has been found to be different suggesting distinct propensity of the asphaltenes from the different petroleum crudes to participate in radical recombination reactions leading to the formation of additional amounts of core-condensed asphaltenes

- **Effect of commercial additives to reduce sediment formation in the ebullated vacuum residue H-Oil hydrocracking [6]**

The problems associated with formation of deposition of asphaltenes and waxes generate significant production loss and involve expensive corrective measures in both oil production and oil refining. Many studies have been dedicated to elucidating the mechanisms of deposit formation from asphaltene aggregation and precipitation and from wax precipitation with the aim to find corrective measures to mitigate and prevent deposition from asphaltenes and waxes in the oil industry. One of the promising strategies to mitigate deposit formation from waxes and asphaltenes has been found to treat the oils by chemical additives. The synthesized additives have been found to retard the process of aggregation of asphaltenes and waxes inhibiting the deposit formation rate.

Ten H-Oil residual oils and eleven commercial additives inhibiting the asphaltene agglomeration were explored in this work **[6]**. It was found that the tendency to form sediments from the asphaltenes in the H-Oil residual oils was different for the distinct feed blends processed in the LNB H-Oil vacuum residue hydrocracker. The performance of the additives was found to be specific to the alloyed H-Oil residual oils. The additive based on the polyisobutylene succinimide was found to be capable of reducing the sediment content in the H-Oil residual oils produced from all feedstock blends studied in this work. The efficiency of its performance however was different for the studied residual oils being the highest for the residual oil obtained from the feedstock blend 70 % Urals/30 % El Bouri (with the highest tendency to form sediment). This additive has also good efficiency against the H-Oil residual oil obtained from the feed 100 % Urals (with lower tendency to form sediment) but diluted with the high aromatic heavy cycle oil from fluid catalytic cracking.

2. Effect of technological factors on the parameters of catalytic and thermal cracking [8, 12, 13, 17, 22].

- **Reactivity of heavy oils in catalytic and thermal cracking, impact of refinery economics [8, 12, 13]**

This paper **[8]** presents results of cracking experiments performed with blends of typical feed (hydrotreated vacuum gas oil) and atmospheric gas oil, slurry and slop wax in a commercial fluid catalytic cracking (FCC) unit. The commercial FCC tests showed that the addition of the FCC slurry obtained at higher conversion to the hydrotreated feed led to a decreased LPG, gasoline and diesel selectivities at the expense of increased coke and dry gas selectivities. Processing of the slurry along with the FCC feed resulted in lower hydrogen transfer reaction rate and higher C4 olefinicity. Adding only 2% slop wax to the FCC feed led to conversion decreasing and lower gasoline and diesel yields. Slop wax adding to the FCC feed resulted in higher delta coke and fast deterioration of e-cat properties. Atmospheric gas oil processing along with the FCC feed resulted in an increase of conversion, gasoline and diesel yields. C3 and C4 products had a lower olefinicity when 3% atmospheric gas oil is added to the FCC feed which is related to higher hydrogen transfer reaction rate.

The economical evaluation made by Honeywell RPMS software showed that adding atmospheric gas oil in a commercial FCC unit is the best profitable option from investigated cases and can improve the overall refinery margins with 5.4%. Economic benefit of slop wax adding in the commercial FCC unit is commensurable with increased fresh catalyst expenses. Increased FCC slurry recycling in a commercial FCC unit doesn’t seem profitable and can lead to lower overall refinery margins of 4.9%.

- The modern heavy oil conversion technologies are generally based on two processes: catalytic cracking and thermal cracking. They are the backbone of the modern refining business. Considering that the feedstock quality is the single variable that most affects the heavy oil conversion unit performance, and that the heavy oils are very complex mixtures, consisting of myriad components we have focused on the published results about catalytic and thermal cracking of individual hydrocarbons (n-alkanes, cycloalkanes, alkyl aromatics and polynuclear aromatics). The catalytic cracking proceeds through carbocation chain reactions, while the thermal cracking based processes proceed via free radical chain reactions. The reactivity of different hydrocarbon classes in terms of catalytic and thermal cracking increase with enlargement of molecular weight and follows the order: n-alkanes (alkanes) < cyclic alkanes (naphthenes) < alkylbenzenes < naphtheno-aromatics. The polynuclear aromatic hydrocarbons are the least reactive individual hydrocarbons **[12]**.

The second part of this study **[13]** was about reactivity of heavy oil SARA (saturates, aromatics, resins, asphaltenes) fractions during thermal and catalytic cracking, and the relations of heavy oil SARA composition to conversion level in both thermal and catalytic cracking.

It was found that reactivity decreases in the order: saturates > aromatics > resins > asphaltenes. The highest reactivity of the heavy oil saturate fraction was due to its lowest activation energy. During thermal cracking based processes, a definite order in the reactivity of the different SARA fractions was not observed. The reason for the disorder in the thermal reactivity of the different SARA fractions might be rooted in the lack of order in the content of the free radical accelerators naturally present in the different heavy oil SARA fractions. We suppose that in the presence of free radical accelerators like peroxides for example the higher hydrogen content of heavy oils and oil fractions would achieve a higher thermal conversion.

- **Investigation of Fluid Catalytic Cracking catalyst performance [17, 22]**

Another important factor influencing the FCC parameters is the type and composition of the catalyst **[17].** Three vacuum gas oils containing different amounts of H-Oil VGO (between 20 and 32%) having different H-Oil quality have been cracked on six commercial catalysts in a laboratory ACE FCC unit. It was found that the catalyst rare earth (RE2O3) content is the main factor controlling the catalyst activity and selectivity. The highest RE2O3 content catalysts were the most active and most coke selective. The higher the catalyst RE2O3 content, the higher the conversion, the lower the HCO cut yield, the lower the LPG olefins content, the lower the cracked naphtha naphthenes content and the higher the naphtha aromatics content are. An improvement in the catalyst formulation directed to suppressing the bimolecular reactions of hydrogen transfer between alkene and coke could decrease the coke selectivity and deviate from the typical linear relation of increasing of coke selectivity with magnification of the catalyst RE2O3 content in a direction of coke selectivity reduction.

An important result is that one of the investigated catalysts (catalyst D) demonstrated a lower dependence of FCC performance on feedstock quality variation, confirming earlier findings that the catalyst performance is feedstock dependent.

The performance of the commercial LUKOIL Neftochim Burgas fluid catalytic cracking unit (LNB FCCU) during processing 24 blends of straight run vacuum gas oils originating from 16 petroleum crudes and an imported atmospheric residue and employment of four catalysts was evaluated **[22]**. It was found that the nature of the petroleum crudes processed in the ratios employed had no effect on the LNB FCCU performance. Instead, the content of the H-Oil vacuum gas oil (VGO) and its quality quantified by Kw-characterization factor was found to control the LNB FCCU conversion level. Based on the LNB FCCU commercial data a regression was developed quantifying the effect of equilibrium catalyst activity, H-Oil quality, and quantity in the fluid catalytic cracking (FCC) feed, and catalyst-to-oil ratio on the level of conversion. The regression was used to evaluate the impact of catalyst activity and catalyst-to-oil ratio, that is known to be a function of catalyst Δ coke selectivity, on the FCC conversion.

All these investigations regarding the relationship between the type and composition of feeds and the parameters of the catalysts have important practical significance for optimizing the technological parameters of the industrial plants in the LNB refinery.

3. The possibility of obtaining bitumen from vacuum residue from the H-Oil process in LNB [15, 27].

The possibility of obtaining bitumen from vacuum residue from the H-Oil process in LNB (HCVR) was studied **[15]**. The influence of the addition of residual slurry oil from catalytic cracking (FCC SLO) and sulfur on the properties of viscosity, softening temperatures and Fraass breaking point of the obtained bitumen blends was monitored.

The addition of FCC SLO to vacuum residue (HCVR) reduces the Fraass breaking point temperature, but impairs oxidative aging and increases mass loss. The addition of 1.5% sulfur to HCVR-FCC and SLO-OSRVR (oxidized straight run vacuum residue) reduces the rate of oxidative aging and increases the softening temperatures of bitumen blends due to the increase in the content of C7 asphaltenes. The observed effect of the addition of sulfur decreases linearly with increasing OSRVR content in the road bitumen mixture.

A summary of the results **[27]** with the commercial production of road pavement bitumen with involvement of H-Oil VTB revealed that the SRVR share in the bitumen blend can be decreased from 82 to 76% at the expense of H-Oil VTB/HVGO when non-oxidized SRVR is employed. The use of commercial antioxidant additives cannot inhibit the process of oxidative ageing of the bitumen blend containing H-Oil VTB. Mixing of bitumen blends with fluid catalytic cracking gas oils (HCO, and slurry oil) accelerates the oxidative ageing. A straight run vacuum gas oil and H-Oil heavy vacuum gas oil added to bitumen blend do not accelerate the oxidative ageing. The treatment with sulphur of bitumen blends containing H-oil VTB/HVGO retards the process of oxidative ageing if it is performed at good stirring and temperature of 140°C for 2 h. Unfortunately, the bitumen treatment with sulphur is accompanied by H_2S release that requires special care to safely evacuate. Bitumen blends containing H-Oil VTB and having lower softening points are easier to oxidise. The relation of the first order kinetic constant of oxidation to the bitumen blends softening point is described by a power function.

4. Environmental problems in oil refining [24, 25].

The odor is a property of a mixture of different volatile chemical species (sulfur, nitrogen, and volatile organic compounds) capable of stimulating the olfaction sufficiently to trigger a sensation of odor. The impact of odors on the surrounding areas depends on different factors, such as the amount of odors emitted from the source, the distance from the source, weather conditions, topography, odors sensitivity and tolerance of the neighbourhood. Due to the complexity of the odor issue, the aim of this project was to give an overview of techniques (sensorial and analytical) that can be used to determine a qualitative and quantitative characterization of odor emissions in oil refineries.

The demands for environmental pollution from the oil industry are constantly growing and this is a serious challenge for refineries. Purposeful work continues in the field of studying and researching the emissions of odors into the environment. New solutions to these environmental problems are being sought by applying sensory and analytical methods to detect pollution emissions. There are different approaches to their evaluation, which continue to develop and have not been the subject of in-depth research. Missing or not fully developed methodologies and characteristics. Emission control requires a systematic approach to a sustainable solution to the problems that arise with them. According to the different sources of odor emissions and according to the composition of the emissions of pollutants into the atmosphere, specific actions and strategies are proposed to reduce their concentration in the environment.

There are models that predict the directions of pollution with different accuracy. Some of them can be useful in developing guidelines for developing odor reduction strategies in neighboring refinery settlements. The odor management plan reflects the current state of operation of the process unit and covers all aspects of its design, operation and maintenance.

Due to the complexity of the odor issue, the aim of this project was to give an overview of techniques (sensorial and analytical) that can be used to determine a qualitative and quantitative characterization of odor emissions in oil refineries.

V. Other studies.

- Reduction of sulfur content in coal combustion emissions **[36]**

The results of the work on the project "Reduction of emissions from burning lignite coal in Maritza-East 2 and 3" showed that a promising method in this direction is the conversion of pyrite sulfur into sulfate by its oxidation with air at high temperature before the combustion of coal.

- **Effect of additives to improve the properties of lubricants [10, 29, 35, 37]**

The aggregation of detonation nanodiamonds hinders their wider implementation and requires application-oriented studies and selection of stabilizers, which do not interfere with the rest of the components in the product in which they are used.

The aim of this work **[10]** was to study the effect of typical lubricant additives on the sedimentation stability of nanodiamond powders in non-polar media (liquid paraffin). The low temperature stability of lubricating oils with nanodiamonds was also evaluated experimentally.

The used powders (nanodiamonds, ND and nanodiamonds with 40 % soot, NDS 40) were with sizes typical for commercial industrial nanodiamonds. Experimental evidence is presented that they contain a significant amount of aggregates larger than nano-sizes.

Conventional laboratory mechano-chemical disaggregation, in the presence of experimentally selected best additives, ensures that more than 50 % of the NDS stays in the upper-most layer of the paraffin concentrate after 90 days of storage.

The mechano-chemical disaggregation was not so effective for ND. Similar stability was achieved when it was combined with a technology in which the concentrate was prepared from water suspension, by evaporation of the water in the presence of the stabilizer and some paraffin. The NDS and ND powders slightly influence the low temperature stability of automotive oils.

The work **[35]** investigates the influence of suspensions with nanodiamonds on the oxidation stability, and lubricating properties of an automotive gear oil and a motor oil.

- The blend of soot and 40 % diamond showed a very significant pro-oxidation effect in the gear oil, but the stability of the motor oil practically remained unchanged. The pure nanodiamond concentrates improved twice the oxidation stability of the motor oil. In the formulated gear oil the concentrate with a polysuccinimide stabilizer did not change the oxidation stability, while that with a sulfonate stabilizer impaired it.
- The tested suspensions did not show an impressive positive influence on the lubricating properties, except in a few cases. The explanation of the obtained results seems to lie in the relatively small amount of really nano-sized fraction in the powders. The successful deaggregation is important not only for the physical stability of the concentrates, but also a prerequisite for a breakthrough in improving the properties of lubricants containing them.

Improvement of the properties of lubricants (viscosity index) was studied in [**29**] and the effect of Polybutene 30 (PIB30) on the rheological characteristics was monitored experimentally with mineral oil type AN46. The results showed that the tested samples of mineral oil with different concentrations of the polymer additive have a typical pseudoplastic fluid behavior. With increasing concentration, a decrease in viscosity and an increase in shear stress are observed.

The study **[37]** focused on boron compounds as additives to improve the anti-wear and anti-seizure properties of lubricants (the topic of the candidate's thesis).

- **Influence of microorganisms on the physicochemical and operational properties of petroleum fuels**

All types of petroleum fuels under certain conditions can change their quality under the action of microorganisms, which not only absorb hydrocarbons from fuels, but change their composition, and deteriorate their physico-chemical and operational properties. The purpose of the review **[38]** is to study the mechanism of action of microorganisms and their influence on the physicochemical and operational properties of jet and diesel fuels.