



REVIEW

by **Assoc. Prof. Dimitrinka Aleksieva Nikolova, PhD**
Institute of Catalysis, Bulgarian Academy of Sciences
member of a scientific jury of the University "Prof. Dr. Asen Zlatarov" - Burgas,
regarding the dissertation of Eng. Ivan Petrov Petrov
head of the "Quality" group at "LUKOIL NEFTOHIM BURGAS" JSCo

Topic: **Impact of the H-Oil tar hydrocracking process on the action of other oil refining processes in a modern underwater oil refining refinery (Lukoil Neftohim Burgas Ad)**

Supervisors:

1. Associate Professor Dr. Dobromir Yordanov - Asen Zlatarov University
2. Prof. DSc. Dicho Stratiev - "LUKOIL NEFTOHIM BURGAS" JSCo

for the acquisition of an educational and scientific degree " doctor " in a professional field 5.10.
Chemical technologies, scientific research specialty 02.10.23 "Technology of natural and synthetic fuels"

I. General presentation of the candidate.

Eng. Ivan Petrov Petrov was born on June 30, 1975. He completed his higher education in 1999 at "Prof. Dr. Asen Zlatarov" University, Burgas, where he obtained a master's degree in engineering, majoring in materials technology and materials science.

Engineer Petrov's professional development began in 2001 as a Catalytic Reforming Plant Operator. Subsequently, Engineer Petrov held the following positions:

- Shift manager in production "Catalytic processing of fuels";
- Production technologist "Catalytic processing of fuels";
- Fuel technology engineer;
- Senior engineer on catalytic refining processes;
- Deputy Chief Technologist for Engineering and Technical Estimates.

The PhD student currently works as the Head of the "Quality" group of manufactured products at "LUKOIL NEFTOHIM BURGAS" JSCo. The researches were carried out in the Research Laboratory and the industrial installations of "LUKOIL NEFTOHIM BURGAS" JSCo.

Eng. Petrov has won competition "Best Scientific and Technical Development" in "LUKOIL NEFTOHIM BURGAS" JSCo in the period 2015-2019 years.

The biographical data of Eng. Petrov show his professional development and impressive experience in the field of oil refining, management and organization of technological processes in "LUKOIL NEFTOHIM BURGAS" JSCo.

II. Actuality of the problem developed in the dissertation work in scientific and scientific-practical terms

The topic of the dissertation work of Eng. Ivan Petrov is relevant due to the growing requirements in modern oil refining for the utilization of heavy, residual oil fractions. The importance of H-Oil hydrocracking technology is determined by the possibility of the process providing high conversion of residual oil fractions to light oil products. The efficiency of the hydrocracking process of tar, a residue of oil after distillation, depends on various parameters such as the quality of the raw material used, the type of catalyst and the operating conditions for H-Oil hydrocracking realization.

The target of the dissertation work is determined by the lack of sufficient data in the literature on the quality of the products obtained from the hydrocracking process depending on the quality of the raw material, the properties of the catalyst used and the operating conditions applied, as well as the impact of the hydrocracking process on the other processes involved in a technological scheme. The aim formulation is "to evaluate the impact of the hydrocracking process of H-Oil tar, included in the oil processing scheme in the refinery of "LUKOIL NEFTOHIM BURGAS" JSCo on the action of the other processes involved in the technological scheme of the refinery of "LUKOIL NEFTOHIM BURGAS" JSCo".

III. General characteristic of the dissertation

The dissertation is written in a very good professional language, technically it is very carefully designed and includes an introduction, a literature review, an experimental part, results and discussions, conclusions, contributions and references. It contains 169 pages, in which 39 tables are included. It is illustrated with 66 figures, which represent technological schemes, graphs with obtained results and photographs, allowing a correct perception of the information. A list of abbreviations used is included, which makes reading easier.

IV. Problem status and creative evaluation of literary material

In the literature review, a very high level of scientific awareness and ability to successfully deal with the scientific literature is demonstrated. Of the total of 315 cited sources, 225 refer to the literature reference. A large part of them are from the last decade, which is a clear indicator of knowledge of the current state of the problem under consideration.

A history of hydrocracking technology, chemistry, and various kinetic models of vacuum residue hydrocracking are described. Oil refining schemes involving the tar hydrocracking process are explained and illustrated. The influence of the catalyst, the operating conditions of the tar hydrocracking process and the quality and origin of the raw material on the conversion, yields and quality of the products are critically analyzed

The literature review and summarization of the existing information helped the doctoral student to formulate concretely and clearly the tasks to achieve the set goal, shows the necessary literary awareness of Eng. Petrov.

V. The experimental part

The experimental part is based on a detailed presentation of several technological schemes:

- Simplified technological scheme of the refinery of "LUKOIL Neftohim Burgas" representing the location of the H-Oil installation for hydrocracking in a pseudo fluidized bed of tar;
- The principle technological scheme of hydrocracking of tar in "LUKOIL Neftohim Burgas" - working conditions, raw materials, yields and characteristics of the products;
- Technological scheme of the Catalytic Cracking industrial complex in "LUKOIL Neftohim Burgas" processing mixtures of directly distilled vacuum gas oils and gas oils from hydrocracking;
- Schematic of the laboratory installation ACE (Advanced cracking equipment), where the cracking experiments were carried out;
- Schematic diagram of the Catalytic Reforming installation in "LUKOIL Neftohim Burgas";
- Technological diagram of the hydrotreatment plant of primary and secondary diesel fractions;
- Technological diagram of the section for desalination of crude oil in the installation for atmospheric distillation of oil - AVD-1.

The methods used to characterize the petroleum derivatives investigated in the present dissertation are summarized in Table 15.

VI. Research methodology and main results

The obtained results of the scientific studies are presented and discussed in six sections corresponding to the formulated tasks.

In the present work, a complex approach is applied focused on:

1. Investigation of the dependence of the quality of tar hydrocracking products on the types of oil processed in the refinery, the properties of the mixed feedstock and the operating conditions of the process. The Kw-characterizing factor of the mixed tar feedstock and the Kw-characterizing factor of the vacuum gas oil from the hydrocracking process of tar with a pseudo fluidized bed of the catalyst were analyzed

2. Laboratory studies on the performance of the Catalytic Cracking process as a function of the performance of various catalysts in the processing of vacuum gas oils containing H-Oil gas oils of variable quality and variable quantity. Six industrial zeolite catalysts containing oxides of rare earth elements in the range of 1.6-2.9 wt% were investigated. Catalysts with the highest rare earth content were found to be the most active and most coke-selective in the processing of vacuum gas oils

containing vacuum gasoil from catalyst pseudo-fluidized tar hydrocracking. One of the investigated catalysts containing 1.6 wt% rare earth oxide (catalyst D) showed less dependence of the FCC efficiency on the change of the quality of the raw materials, confirming that the performance of the catalyst depends on the raw materials.

3. Research and evaluation of the influence of the structure of the various types of oil processed in the Lukoil Neftohim Burgas refinery, the properties of the catalysts and the properties of the vacuum gas oils from the hydrocracking process of tar with a pseudo fluidized bed of catalyst on the operation of the industrial installation for catalytic cracking. It was found that the most active and most selective Δ coke catalyst can provide higher conversion in an industrial catalytic cracking plant, regardless of the lower catalyst/feed ratio resulting from the higher Δ coke, if the plant does not is limited by reaching the maximum allowable temperatures in the regenerator.

4. Study of the influence of the improved action of the hydrocracking process of tar with a pseudo fluidized bed of the catalyst on the cetane number of the motor diesel fuel produced in the refinery of "Lukoil Neftohim Burgas"

5. Investigating the possibilities of controlling the level of sodium in the raw material for the hydrocracking process of tar in a pseudo fluidized bed of the catalyst during the primary oil refining process. It was found that the sodium content above 20 ppm in the tar accelerates the deactivation of the solid catalyst and does not allow the use of liquid nano-dispersed HCAT catalyst in the hydrocracking process of tar in a pseudo fluidized bed of the catalyst. Its removal depends on the operation of the crude oil desalination unit and the cost of injecting caustic soda into the desalted crude oil. Maintaining a crude oil desalination rate of about 90% can provide sodium content in the vacuum residue in the 3-7 ppm range.

6. Evaluation of the impact of replacing NaOH with an organic agent used for neutralization in the primary oil processing plant, in order to achieve a low level of Na in the tar (a requirement imposed by the application of the HCAT nano-catalyst in H-Oil and lowering of the poisoning of the solid catalyst with Na) on the action of the catalytic reforming process. It was found that the replacement of NaOH with organic nitrogen compounds with alkaline properties in the unit for the primary distillation of oil, in order to reduce the sodium content of the feedstock for the pseudo-fluidized bed tar hydrocracking process, caused poisoning of the catalytic system of a plant Catalytic reforming with basic nitrogen, deactivates the catalyst and lowers the octane number of the reformer.

VII. Main contributions of the dissertation

Based on the detailed and in-depth research done by Eng. Ivan Petrov, the dissertation has significant contributions with completely industrial application for the successful operation of the modern refinery of "LUKOIL NEFTOHIM BURGAS" JSCo.

They are expressed in:

1. The operation of the oil desalination and dewatering unit has been improved and the sodium content of the tar has been minimized from 40 to below 20 ppm.

2. The use of an expensive caustic replacement chemical in the oil desalination and dewatering unit to reduce sodium in the tar below 20 ppm has been discontinued.

3. The octane number of the reformer has been increased due to the discontinuation of the organic base compound replacing NaOH in the primary oil processing plant.

4. The composition and properties of the catalyst for catalytic cracking were optimized when processing raw material with different quantity and quality of vacuum gas oil from hydrocracking of tar in a pseudo-fluidized bed of the catalyst.

5. The planning of a cetane-increasing additive for the production of commodity diesel fuel fulfilling the specification of EN 590 for a cetane number not lower than 51 has been optimized.

The achieved results show the professional growth of engineer Ivan Petrov.

VIII. Scientific indexes

The results obtained during the preparation of the dissertation are reflected in 8 scientific papers published in the journals: *Oxidation Communications (2020-JCR Q3)*, *Oil Gas, Oil Gas European Magazine (2021-JCR Q4)*, *Processes (2021-JCR Q2)*, *Resources (2021-JCR Q2)*, *Petroleum and Coal (2020-JCR Q3)*, *Journal of Chemical Technology and Metallurgy (2021-JCR Q3)*.

The number and time for which all articles were published, within only 2 years (2020-2021), is an indicator of very high publication activity.

IX. Remarks and recommendations

The presented dissertation is based on publications that have been reviewed by international experts in the field. My only comment is that the submitted dissertation format lacked a conclusion on the impact of higher volumes of tar hydrocracking diesel, higher aromatic hydrocarbon content, on the cetane number of motor diesel fuel produced at the Lukoil Neftohim Burgas refinery.

The conclusion was added after the filing of the documents and its wording is:

"The application of an intercriteria analysis to assess the reasons for the approximately doubling of cetane raising additive consumption in the production of stock diesel fuel for automotive engines revealed that as the stiffness of the operating mode in H-Oil increases, the amount of diesel fraction produced increases and its cetane index decreases. As a result of the increased proportion of H-Oil diesel fraction and its lower cetane number in the refinery's diesel pool, an increase in the rate of cetane raising additive from 236 to 550 ppm is required to produce a product with a cetane number no lower than 51.0 conforming to the requirements of EN 590."

X. Description of the main results and scientific contributions of the dissertation work in the abstract

The abstract is very well designed and fully and correctly reflects the results of the research. After a short introduction, the goal and main tasks are formulated. The main results are discussed and the scientific contributions are presented.

XI. Conclusion

After reviewing the presented dissertation, I can conclude that topicality, volume of investigations, achieved results and scientific contributions of this PhD thesis fully corresponds to the requirements of the Regulations on the terms and conditions for acquiring scientific degrees and holding academic positions at the University "Prof. Dr. Asen Zlatarov" - Burgas. I give my positive assessment and I suggest with conviction of the members of the Jury and to the Scientific Council of at the University "Prof. Dr. Asen Zlatarov" - Burgas to vote positively for awarding the educational and scientific degree "doctor" to Eng. Ivan Petrov Petrov.

Date 16. 12. 2022

Reviewer:

Подпис заличен
Чл.2 от ЗЗЛД

/Assoc. Prof. Dimytrinka Nikolova, PhD/