REVIEW

By Prof. Dr. Silvia Zhivova Todorova, Institute of Catalysis - Bulgarian Academy of Sciences

of a dissertation for awarding the educational and scientific degree **' doctor'**

in the field of higher education "Technical Sciences",.
professional direction *5.10. "Chemical technologies".*
doctoral program 02.10.23 *"Technology of natural and synthetic fuels "*

Author: magister Eng. Vasil Kotsev Yankov

Title: *DEPENDENCE OF THE PERFORMANCE OF THE PROCESSES HYDROCRACKING OF VACUUM RESIDUE H-OIL AND CATALYTIC CRACKING OF VACUUM-GASOIL ON THE PROPERTIES OF THE RAW MATERIAL AND THE HARDNESS OF THE MODE IN H-OIL.*

Scientific supervisors

Associate Professor. Dobromir Yordanov, PhD

Prof. DS Dicho Stratiev

1. General description of the presented materials

The author of the dissertation is Vasil Kotsev Yankov – PhD student at the University "Prof. Dr. Asen Zlavacuum residueov , Burgas with learned supervisors Dobromir Yordanov , Ph.D. , and Prof. Dr Dicho Stratiev to Faculty of Social Sciences, Department of " Industrial Technologies and Management"

Presented by Vasil Yankov a set of materials are in accordance with the Regulations for the conditions and order for acquiring scientific degrees and occupying of academic positions in University "Prof. Dr. Asen Zlavacuum residueov, Burgas. The PhD student presents 5 publications.

The documents are submitted on time and are well formatted

2. Brief biographical data of the PhD student

Vasil Yankov completed his higher education in 2002 at Higher Institute of Chemical Technology "Prof. Dr. Asen Zlavacuum residueov , Burgas, specialty "Oil and Gas Technology" with an educational degree "Master of Engineering". Two specializations in leading companies for the production of catalysts can also be considered as part of his training: AXENS IFP Group Technologies and " Haldor Topsoe ".

From March 1998 until now, Vasil Yankov has been employed at "LUKOIL Neftohim Burgas" AD, having successively held the following positions: Compressor operator in the "Catalytic reforming and hydrogenation of pyrolyzed gasoline" workshop; Operator of "Catalytic Reforming " installation; Shift manager in " Xylol " production; Head of installation "Catalytic

reforming and hydrogenation of pyrolyzed gasoline"; Senior engineer on catalytic beneficiation processes ; Deputy head of production " Catalytic processing of fuels 2"; Deputy Chief Technologist; Group Quality Manager; Chief technologist of the "Primary oil processing" complex.

By order No. UD-307 of 16.12.2020. of the Rector of the University "Prof. Dr. Asen Zlavacuum residueov ", Prof. Dr. Magdalena Mitkova, Vasil Yankov has been enrolled as a doctoral student of independent preparation with the topic of the dissertation work "Dependence of the action of the hydrocracking processes of H-Oil vacuum residue and catalytic cracking of vacuum gas oil on the properties of the raw material and hardness of the mode in H-Oil"

The doctoral student's personal skills include working with modern computer programs, including CHEMCAD- chemical process simulator and good written and spoken English and Russian language

3. Actuality of the topic and appropriateness of the goals and tasks

The research is directly related to current societal challenges, namely energy and energy efficiency and environmental protection. Fluidized bed hydrocracking has gained even greater importance in recent years due to the reduced demand for heavy petroleum products, the increasing proportion of heavy petroleum types undergoing processing and the ever-increasing requirements for fuel quality and environmental protection. Heavy oil are characterized by a high content of sulfur, nitrogen, metals, and asphaltenes, which have a strong negative impact on the activity and stability of catalysts used for hydroprocessing .

Due to the fact that in hydrocracking in a pseudo- fluidized bed there is the possibility of continuous replacement of the spent catalyst with fresh, this allows to raw materials with a high content of impurities are also processed. The catalyst used in pseudo-fluidized bed is supported on an aluminum oxide support whose pore sizes are small and does not allow the largest asphaltene molecules to reach the active centres. However, the operation of this process at a longer reaction time shows results comparable to those of the latest suspension processes, hydrocracking, which use nano-catalysts. As noted by the PhD student, the level of vacuum residue conversion in the hydrocracking plant is critical to the economics of refining, as a 1% variation in conversion is equivalent to a USD 15,000/day change in refinery profit. The operation of the vacuum residue hydrocracking plant must be in sync with the operation of the other process for the conversion of heavy oil fractions - fluid catalytic cracking, since these two processes are the main driving force for improving the economic performance of modern oil refining.

The aim of the dissertation is: to study the dependences of the action of the processes " Hydrocracking of vacuum residue H-Oil" and "Catalytic cracking of vacuum-diesel " on the properties of the raw material and the hardness of the regime in H-Oil.

To achieve this goal, the following tasks were formulated:

1. Study of the dependence of reactivity and sedimentation rate in the hydrocracking process of H -Oil vacuum residue on the properties of vacuum residues of different origin;

2. Study of the influence of the hardness of the regime during hydrocracking of vacuum residue - H-Oil on the rate of sedimentation.

3. Investigation of the combined effect of a solid catalyst on an alumina support and a liquid nanocatalyst containing molybdenum on the performance results of the industrial H-Oil vacuum residue hydrocracking plant and on those of fluid catalytic cracking.

4. Study of the influence of the hardness of the mode in hydrocracking of vacuum residue - H-Oil on the operation of the installation for catalytic cracking of fluid type.

5. Investigation of the reactivity of vacuum gas oils obtained from the Hydrocracking process of H-Oil vacuum residue in the processing of vacuum residues from different types of oil and different hardness of the operating mode in the fluid type catalytic cracking process.

From the above mentioned, the aims and objectives of the dissertation are undoubtedly in a modern, current and promising field.

4. Knowing the problem

The dissertation contains 6 chapters and is based on a review of 286 literary sources, contains 165 pages, includes 52 figures, 28 tables. The introduction gives a brief but meaningful picture of the advantages of fluidized bed hydrocracking . The relevance of the conducted research is shown and the guidelines of the research are clearly justified. In the literature review, a detailed analysis of the state of research regarding hydrocracking of vacuum residue is made and in addition to the chemistry and mechanism of the process, its brief history is also given. Hydrotreating and hydrocracking reactions are described in detail. They are described the varieties of the vacuum residue hydrocracking process and the types of reactors as well as the types of catalysts. A brief review of industrial flow charts for fixed-bed, moving-bed, and fluidized-bed hydrocracking is given . An overview of the influence of the properties of the raw material on the conversion and sedimentation in hydrocracking was made, as well as the influence of the hardness (temperature in the catalyst bed and the volume velocity) of the regime in hydrocracking of vacuum residue on the content of asphaltenes , sedimentation , conversion and distribution of yields and the quality of the products.

Catalytic Cracking process is described along with its history, design of the reactor-regenerator system, influence of the operating conditions, structure and chemical composition of the catalysts for this process. The influence of feedstock on the distribution and quality of catalytic cracking products, as well as the influence of contaminants on the catalyst and catalytic cracking performance, are examined.

Based on the literature review, some lacks of information were found, such as there is no information about the precise quantitative dependences on the influence of the quality of the raw material on its reactivity during the hydrocracking of vacuum residue ; there is insufficient information on how the quality of the raw material and its reactivity affect the precipitation of asphaltenes and sediment formation; there is not enough information on how the hardness of the regime affects the sediment formation during hydrocracking of vacuum residue in a pseudo-fluidized bed of the H-Oi catalyst ; there is insufficient information on how the addition of HCAT nano -catalyst to conventional catalyst affects the performance of H-Oil vacuum residue hydrocracking and related processes in a refinery process; in the literature, there is not enough information on the influence of the composition and content of catalytic poisons in raw materials of secondary origin and more specifically from hydrocracking of H-Oil vacuum residue on the performance of catalytic cracking; there is no information on how the rigor of the regime in the vacuum residue hydrocracking plant affects the quality of the gas fractions that are used as

feedstocks for catalytic cracking and how this change affects the performance of the catalytic cracking.

Based on the identified deficiencies, the above-mentioned tasks were also formulated.

5. Research methodology

Based on the in-depth analysis of the literature and the previous experience of the scientific supervisors, the aim of the PhD thesis was formulated, and several specific tasks were defined, which were mentioned above. To realize the set tasks, the research was carried out both in laboratory and pilot installations, as well as in industrial ones, which makes the achieved results particularly valuable. t. e.g. mixtures of vacuum residues originating from different types of crude oil were processed in the hydrocracking installation in a pseudo-fluidized bed of the catalyst - H-Oil in LUKOIL Neftohim Burgas (LNB) and their physico-chemical properties were analyzed; Hydrocracking experiments were carried out with the addition of HCAT nano-catalyst in pilot and industrial plants with a pseudo fluidized bed of the solid catalyst; A laboratory and industrial experiment were conducted in a catalytic cracking plant .

6. Characterization and evaluation of the PhD thesis

Prepared by Vasil Yankov thesis meets the requirements of Regulations for the conditions and order for acquiring scientific degrees and occupying of academic positions and contains: Introduction, Aims and objectives, Literature review, Experimental part, Results and discussion, Conclusions, and Cited literature, List of scientific publications related to dissertation work. The dissertation work is presented on 165 pages, includes 52 figures, 28 tables. The bibliography covers 286 titles. Most are from recent years, but older literature is also used, which testifies to the detailed examination of the problem and allows a more comprehensive view.

The dissertation is clearly structured with logically connected chapters. The presented figures, tables and diagrams are designed strictly and precisely and allow a very quick reading of the information. The topic of the dissertation fully corresponds to the scientific specialty. Scientific results have a certain value and are achieved through appropriate methods and approaches. The reliability of the obtained results is also guaranteed by a comparison of the results of clarifying the same problem, obtained by different research methods.

7. Contributions and significance of the results for science and practice

The dissertation has contributions of a theoretical and scientific-practical nature. The main conclusions can be the following:

As a result of the conducted research, the following conclusions can be drawn:

1. The density (content of saturated components) of sulphur , nitrogen and asphaltenes are factors determining the reactivity and the tendency to form sediments during hydrocracking in a pseudo- fluidized bed of the H-Oil catalyst of vacuum residues originating from 26 different types of oil.

2. Increasing the density (reducing the content of saturated components) and the sulphur content increase the reactivity of the vacuum residue and lower its tendency to form sediments in the hydrocracking of H-Oil vacuum residue .

3. By increasing the reaction time (decreasing the volumetric rate) a higher conversion is achieved at the same or lower sediment content in the residual hydrocracked fractions.

4. Asphaltenes have been confirmed to be the main cause of sediment formation in H-Oil hydrocracked residual fractions.

5. Under the same other conditions, the content of sediments in the hydrocracked residual fractions from H-Oil increases linearly with increasing content of asphaltenes.

6. The application of nano - dispersed molybdenum-containing HCAT catalyst significantly reduces the formation of sediments in the atmospheric residue, allowing an increase in the reaction temperature and an increase in conversion in the hydrocracking of H-Oil vacuum residue.

7. The use of molybdenum HCAT does not affect asphaltene conversion in vacuum residue hydrocracking H-Oil is not affected by.

8. The increase in the reaction temperature during hydrocracking in a pseudo- fluidized bed of the H-Oil catalyst leads to an increase in the content of aromatic components in the H-Oil gas oils, which lowers the conversion level of the vacuum gas oil during its catalytic cracking and increases the temperature in the regenerator in a catalytic installation cracking due to greater coke formation .

9. It was established for the first time in world practice that the reactivity of heavy oil fractions originating from " H-Oil Vacuum residue Hydrocracking" correlates with their 50 % boiling point (T50%).

10. Heavy oil fractions of H-Oil origin are characterized by a higher nitrogen and aromatic content than heavy oil fractions of primary origin and, for this reason, they are less reactive and more prone to coke formation in their catalytic cracking.

11. Heavy oil fractions with the highest content of condensed aromatic structures and with higher density derived from H-Oil are more likely to accelerate catalyst deactivation due to coke formation in catalytic cracking. This is associated with higher selectivity to dry gas production, lower selectivity to gasoline, lower selectivity to C4 hydrocarbons and higher normal paraffin content in gasoline and lower motor octane.

12. From the raw materials for hydrocracking of H-Oil vacuum residue, which contain vacuum gas oil during hydrocracking, vacuum gas oil richer in saturated components is obtained. This has a positive effect on their reactivity in catalytic cracking.

The main contributions of the dissertation are as follows:

1. The derived regression equation describing the dependence between the reactivity and the properties of the raw material for hydrocracking H-Oil can be used to evaluate the economic efficiency of processing new alternative types of oil and their mixtures in the "Lukoil Neftohim Burgas" refinery. Also, the derived dependence can be used for daily monitoring and evaluation of the reactivity of the hydrocracking feedstock, allowing prediction and timely optimization of the technological regime of the H-Oil vacuum residue hydrocracking plant .

2. Establishing the influence of the quality of the raw material and its reactivity, as well as the stiffness of the regime, expressed by the reaction time (volumetric rate) and temperature, on the sediment formation in the hydrocracking of H-Oil vacuum residue allows timely and correctly managing the content of sediments - the main and the most difficult to control quality indicator of commodity boiler fuel.

3. Establishing the influence of the regime stiffness in the H-Oil vacuum residue hydrocracking plant on the yield and quality of gas oil fractions - raw materials for catalytic cracking allows to predict the behavior of the catalytic cracking plant and to optimize the joint action of the two most economically - efficient processes for deep processing Hydrocracking and Catalytic Cracking in the "Lukoil Neftohim Burgas" refinery.

The high competence of the scientific supervisors undoubtedly contributes to the correct approach and interesting results Dobromir Yordanov, Ph.D., and Dicho Stratiev, Ph.D., Chief Technologist of Lukoil Neftohim Burgas, the largest oil refining company on the Balkan Peninsula .

8. Evaluation of publications on the dissertation work

Materials including research presented in the dissertation are published in 5 articles belonging to the category Q 3 . In 3 of the presented articles, the doctoral student is in third place, in one in fourth place and in one in fifth place. This shows that his contribution to the development of scientific research is significant.

9. Personal participation of the doctoral student

Appreciating the fact that the doctoral student is in 3rd author in three of the presented articles, in one is in fourth place and in one in fifth place , I can accept that the dissertation is his work under the guidance of the scientific supervisors. A declaration of originality of the research presented in the dissertation is also attached

10. Abstract

The presented abstract reflects objectively the structure and content of the dissertation work. The abstract was prepared in accordance with the requirements of ZRAS, the Rules for its application.

11. Critical remarks and recommendations

The dissertation is written in good language and technical errors are few enough. The dissertation reads with ease. The presented figures and tables are designed strictly and precisely and allow a very quick reading of the information. I have no principled objection to the material in the dissertation.

12. Personal impressions

I have no personal impressions.

CONCLUSION

The dissertation ***contains scientific, scientific-applied and applied results, which represent an original contribution in science*** and practice and **meet all** the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria, the Regulations for the Implementation of ZRASRB and **University "Prof. Dr. Asen Zlavacuum residueov, Burgas.**

The dissertation shows that the PhD student Vasil Kotsev Yankov **has** in-depth theoretical knowledge and professional skills in the scientific specialty *"Technology of natural and synthetic fuels* " . by **demonstrating** qualities and skills for independent conduct of scientific research.

Due to the above, I confidently give my ***positive evaluation*** of the conducted research presented by the above-reviewed dissertation work, abstract, achieved results and contributions,

and I ***offer to the honorable scientific jury to awarded the educational and scientific degree 'doctor'*** of Vasil Kotsev Yankov in the field of higher education: " Technical Sciences ",. professional direction " *Chemical technologies* " doctoral program " *Technology of natural and synthetic fuels* ".

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... Prof. Dr. Silvia Todorova