REVIEW

on the PhD thesis:"Impact of H-Oil vacuum residue process on the performance of other refinery processes in a modern refinery (Lukoil Neftohim Burgas AD), presented by MSc Ivan Petrov Petrov, applicant for a PhD degree in the professional field 5.10 Chemical technologies (Technology of natural and synthetic fuels)

Scientific organization. University "Prof. Dr. Asen Zlatarov", Burgas

Scientific supervisors: Assoc. Prof. Dr. Dobromir Yordanov and Prof. DSc Dicho Stratiev

Reviewer: Assoc. Prof. Dr. Kiril Stanulov, member of the scientific jury, appointed by Order No. UD- 258/ 27.09.2022 of the Rector of the University

Biographical details of the applicant

Eng. Ivan Petrov was born on June 30, 1975. He graduated in 1999 from the University "Prof. Dr. Asen Zlatarov" in the specialty of Materials Technology and Materials Science with a degree of Master of Science. In 2001 he joined Lukoil Neftohim Burgas (LNB), where he is currently working as the head of the Quality Group (management and organization of the quality control of the products produced by LNB). He started his professional development in the refinery as an operator of the unit "Catalytic reforming", after which he held positions in various production plants as shift supervisor, production technologist "Catalytic processing of fuels", fuel technology engineer, senior engineer for catalytic processes, deputy chief technologist for engineering and technical calculations. Eng. Petrov has also acquired several certificates from training in hydroprocess efficiency, catalysts and catalytic processes and other specializations in leading companies in the field of oil refining (UOP, Axens IFP, Haldor Topsoe, etc.). Ivan Petrov's professional profile defines him as an engineer with extensive experience and high qualifications in the field of refining and more specifically in hydroprocessing.

Structure, aim and relevance of the PhD thesis

The PhD thesis of Eng. Petrov's has 169 pages, including 66 figures, 39 tables and 315 cited references. It consists of 6 chapters, which include an introduction, literature review, experimental part, results and discussion, conclusions, contributions and declaration of originality.

The aim of the PhD thesis is to evaluate the impact of the H-Oil residue hydrocracking (HC) process on the performance of other processes included in the technological configuration of the Lukoil Neftohim Burgas refinery.

Hydrocracking is distinguished by its versatility, which allows the production of any light fuels - from gas to diesel fuels and oils. Due to the increasing trend of heavy oil processing and the changing quality of the raw materials for HC, the quality of the cracking products is also changing, which are subjected to further processing in other installations of the refinery scheme such as catalytic cracking, catalytic reforming, etc. This dependence of the processes requires a thorough analysis of the experimental data of the plants and optimization of the processes in order to improve the quality and economic indicators of the production, which I find a relevant and useful study for the refining industry.

Literature review and rationale for the research

The literature review of the thesis includes brief historical data on the technological development of hydrocracking of heavy oil residues, chemistry and kinetics of the process and a description of the technologies used in petroleum refining.

In the review, the PhD student focuses on the chemical transformations of vacuum residues (hydrocarbons) from primary refining, in particular their aromatic and naphtheno-aromatic structures and heteroatoms, which undergo thermal conversion under hydrocracking conditions to form aromatic and aliphatic radicals. The reference states that, despite uncertainties in the reaction mechanism of hydrocracking of petroleum residues, it is based on the carbenim ion theory of hydroprocesses, which has been confirmed in the hydrogenation of asphaltenes. Studies by a number of authors have been cited, according to which the breaking (cracking) of C-C bonds between aromatic rings in asphaltenes and aliphatic chains, with hydrogenation of the aromatic structures taking place on the acid sites of the catalyst, and desulfurization and demetallization taking place on its metal sites. In this part of the review, the graduate also cites research on the coking ability of heavy oil residues and more specifically the asphaltenes content, their structure and molecular size, which also implies selective selection of a catalyst with balanced structural characteristics. Data of different authors on the kinetic modeling of hydrocracking based on the method of discrete grouping of residue types by boiling points (Fig. 3) and on the reactivity of different SARA fractions (Fig. 4) are commented. In the analysis of the kinetic characteristics of the hydrocracking reactions, the Ph.D. student points out significant differences in the values of the activation energies of the same reactions according to the data of different authors. A similar effect is observed for the influence of the type of catalyst on the rate constants and activation energies for identical reactions, necessitating a more thorough generalization of the experimental data for hydrocracking of vacuum residues of different compositions.

The work describes in detail the technological schemes of vacuum residue hydrotreating processes and their combination with hydrocracking. For this purpose, Petrov has used a considerable amount and quality of scientific, technical, company, etc. information, showing analytical skills and good process awareness in its generalization. He has been able to present the state of the art of technologies and their varieties for hydrotreating heavy oil residues with a fixed catalyst bed, fluidized bed schemes, those with a suspended catalyst (slurry hydrocracking), H-Oil processes with a three-phase catalyst beds, and combined hydrocracking schemes with other processes (deasphalting , coking, desulfurization, etc.). It has also been found that the quality of the hydrocracking feedstock is a determinant of the thermos-catalytic conversion of the residues and the properties of its products (Tables 4-9).

Based on the thorough analysis of data from 315 literature sources on the topic of this dissertation, the Ph.D. student summarized his findings from the review and formulated the objectives of his research in the experimental part of the work.

Experimental part and research results

The research on the topic of the thesis includes the evaluation of the impact of hydrocracking of heavy oil residues on the performance of major units of the technological configuration of the LNHB refinery. In this regard, Chapter III of the thesis describes a simplified block diagram of the refinery (Fig. 23), as well as the process flowsheets of the plants that are the objects of experimental investigations, namely: hydrocracking, catalytic cracking (laboratory and industrial plants), catalytic reforming, hydrodesulfurization of primary and secondary distillates, and the crude oil desalination section. The investigations of the influence of hydrocracking on the above processes are based on data on the main process parameters of the H-Oil process (Table 10), with 10 different feedstock compositions for hydrocracking selected by the PhD student and 36 cases of operating conditions listed in Tables 11 and 12. In the analysis of the characterization indices of the hydrocracking products used as raw materials for the other processes, the PhD student found significant deviations in the minimum and maximum values of the indices, e.g. for the heavy vacuum gas oil, vacuum residue, cetane index, etc. (Table 13). These deviations have a direct impact on the processing of the products in the other plants, which calls for more in-depth studies of the factors influencing these processes. The results are summarized in Chapter IV of the thesis as follows:

1. The dependence of the quality of hydrocracking products on the types of oil processed in the refinery, the properties of the mixed feedstock of the H-Oil process and the operating conditions of vacuum residue hydrocracking was investigated. As a result, correlations were developed between the density, K_W-characterization factor and hydrogen content of the hydrocracking mixed feedstock (Mixed feed), the straight-run vacuum residue (SRVRO) and of the H-Oil products atmospheric residue (ATB) and unconverted vacuum residue VTB (Fig. 29). The correlations derived by the PhD

student confirm the results of other authors, according to whom the density and K_W-characterization factor of heavy residues are indicators of feedstock quality, respectively of aromaticity and hydrogen deficiency. Using multiple linear regression for the 36 cases studied, equations were developed and it was found that the K_W-characterization factor of the mixed hydrocracking feedstock depended more on the percentage of catalytic cracking (FCC) slurry oil (SLO) and less on the contribution of the partially blended fuel oil (PBFO) recycle to the mixture. A correlation between the quality of the unconverted hydrocracked vacuum residue (VTB = vacuum tower bottom product), the plant capacity and the percentage participation of FCC SLO and recycle is derived and it is shown that the VTB is enriched in hydrogen with increasing throughput and decreasing reactor temperature, FCC SLO and the amount of PBFO recycle. A similar relationship was found for the cetane index of the hydrocracked diesel, which increased with increasing throughput, and decreasing reaction temperature and the percentage of FCC SLO in the blended feedstock. These qualitative changes in the hydrocracking products, the author explains by an increase of content of alkanes in them and a decrease of arenes in the course of the reaction. The dependence of density, kinematic viscosity and vacuum residue softening temperature on Conradson carbon content (CCR) content was investigated (Fig. 32). It was found that the viscosity and softening point of the residue increased exponentially with increasing CCR and density of the unconverted residue. It is shown that for the same density of VTB and SRVROs, the H-Oil VTB is higher in CCR content, i.e. contains more condensed aromatic structures. The high softening point of the unconverted hydrocracking residue is problematic for its use as a feedstock for bitumen production, which requires its reduction to acceptable values. In his work, Eng. Petrov has investigated the possibility of such reduction by mixing the residue with heavy vacuum gas oil (HVGO) and has found that with increasing content of HVGO the softening point of the mixture linearly decreases (Fig. 33).

2. Six industrial catalysts (Table 16) were investigated in a laboratory catalytic cracking plant ACE (Advanced Catalytic Evaluation) for cracking three types of vacuum gas oils containing between 20 and 32 % H-Oil VGO of different quality (Table 17). The rare earth oxide content of the catalysts (RE_2O_3) was found to be a determining factor for their activity and selectivity, which increased with increasing oxide content (Fig. 37). It has been shown that the higher the RE_2O_3 content in the catalysts, the higher the feedstock conversion is, i.e., the less the amount of heavy catalytic gas oil in the cracking products and the less the alkenes in the C_3-C_4 fraction (Figs. 40, 41) are. More active catalysts were found to improve the quality of gasoline by reducing the alkenes in it and increasing the arenes and iso-alkanes and improving the motor octane number (Table 18, Figs. 42-44). It has also been noted that a targeted improvement in the catalyst formulation to suppress bimolecular hydrogen transfer reactions between alkene and coke can reduce its selectivity over coke and deviate from the typical linear relationship of increasing selectivity over coke with increasing RE_2O_3 content (Fig. 37b).

3. The influence of the structure of 16 types of crude oil and one atmospheric residue processed in LNB refinery, the properties of the 26 straight run vacuum gas oils (SRVGOs) obtained from them and their blends with H-Oil vacuum gas oils, and the properties of 4 types of catalysts on the performance of the industrial catalytic cracking unit in the refinery was studied (Tables 20-28). By using correlation matrices to determine the influence of factors affecting the performance of the FCC, it was found that the quality of the SRVGOs varied within a narrow range and did not significantly affect the conversion and yield of cracking products. The only variable found to be related to conversion was the K_W-characterization factor of the H-Oil vacuum gas oils, or their quality, which is strongly influenced and degraded by the slurry content of the hydrocracking feedstock (Figs. 46, 47). The risks of increased activity and selectivity of the catalysts with respect to the maximum Δcoke due to the danger of exceeding the permissible temperature in the regenerator of the plant are also pointed out.

4. The influence of H- Oil hydrocracking on the cetane number of diesel fuel produced at LNB was investigated. For this purpose, 10 diesel fractions used for the production of automotive diesel fuel were characterized and correlations between the properties of the fractions were evaluated by intercriteria analysis. The cetane number and cetane index of the hydrocracked diesel fractions were found to decrease due to an increase in their aromatic hydrocarbon content. It is shown that increasing the conversion of hydrocracking not only increases the diesel production but also decreases its cetane index, respectively lowers the cetane number of the commodity diesel, which requires additional consumption of cetane improver to achieve the standard requirements of EN 590.

5. The possibilities of controlling the Na level in the H-Oil feedstock during the primary oil processing due to its negative influence on the activity of the nano-dispersed liquid catalyst (HCAT) in the hydrocracking plant were investigated. On the basis of summary data on the Na content of crude oil and its tar, it was found that after desalting about 90% of the crude oil, the fraction of sodium remaining in the tar increases by about 20% and almost all of it (about 5 ppm) goes to the vacuum residue (Table 35, Fig. 57). It was found that a desalination rate of about 90% was sufficient to provide a sodium content in the tar of 3-7 ppm and the increase above these values was due to injection of NaOH into the desalted oil.

6. A systematic analysis has been carried out to identify the causes leading to the decline in octane numbers (MON and RON) of reformate from the catalytic reformer for the period 2018-2020. The influence of a number of factors affecting the octane characteristics has been investigated and it has been found that the main cause of the deterioration in octane numbers of reformate is the increased nitrogen content in the reformate feedstock due to the use of a nitrogen-based chemical (containing ethylamine) in the desalination of the oil. The basic nitrogen of the chemical used deactivates the reforming catalyst and reacts with the chlorides deposited on it to form

ammonium salts. Identification of this effect led to an increase in sodium control in crude oil by optimizing the NaOH dosing system in the crude oil.

Scientific and applied contributions of the dissertation

The contributions of the dissertation are of scientific and applied nature, which can be summarized as follows: Based on the functional necessity of minimizing the sodium content in the H-Oil hydrocracker, the operation of the oil dewatering and desalting unit is optimized. As a result, it was possible to reduce its content in the tar from 40 to below 20 ppm, which is important for maintaining the catalytic activity of the liquid nano dispersed hydrocracking catalyst. It has been shown that increased nitrogen content in reformer gasoline deactivates the reformer catalytic system and degrades the octane characteristics of the reformer, thus confirming other authors' reports of a similar effect in catalytic cracking catalysts. This research has led to the discontinuation of the use of nitrogen-containing chemicals in oil desalination. Based on catalytic cracking catalyst selection studies, a catalyst formulation with balanced activity and selectivity over coke for feedstocks of different quality has been found, which is a preferred approach in modern petroleum refining. The scheduling of a cetane improver for diesel blends with increased H-Oil diesel fractions has been optimized, which stimulates production and improves the quality of automotive diesel.

Critical comments and recommendations on the thesis

I have the following comments and recommendations on the formatting and writing of the dissertation: 1. The literature review should have commented on the data from the studies of foreign authors in the sections of the dissertation, rather than noting and discussing them in the experimental part, which makes the presentation short. 2. I think that the diagrams in Figs. 24, 26-28 are better presented as block diagrams rather than describing the process plants in detail. 3. Some omissions have been made, such as: on p. 17, Table 1, there is no dimension for activation energy; on p. 73, the temperature at which the viscosity was measured is not given, on the same page it is correctly "Conradson carbon" and not "Conradson coke"; on p. 124 and elsewhere, instead of "boiling point", it is incorrectly written "boiling temperature"; on p. 126 NaOH should be used instead of ' caustic '.The omissions noted are editorial and do not detract from the merits of the thesis.

I have the following questions related to the PhD thesis:

1. On what basis does the dissertation recommend catalyst type D for catalytic cracking, since the quality of LPG and gasoline deteriorates when cracked with it (Fig. 41)?

2. The reduction of amount of NaOH in the desalinated oil does not lead to enhancement of equipment corrosion in the primary oil processing, does it?

I do not know the candidate personally, but I appreciate the results and contributions of the thesis. In his work, Eng. Ivan Petrov has shown knowledge and skills to analyze and summarize experimental data and to successfully apply the methods of mathematical analysis in assessing the impact of H-Oil hydrocracking of hydrocarbons on the performance of a number of installations of the technological configuration of LNCB.

Abstract and publications on the dissertation

The abstract and conclusions correctly reflect the results of the dissertation research, but some of the conclusions could have been more specific. There are 8 papers published on this dissertation in journals that are refereed and indexed in world renowned databases, including 1 publication in *Processes* (IF = 3.35) and the rest in journals such as *Oxidation Communications, Oil Gas Journal of Chemical Technology and Metallurgy*, etc.

Conclusion: The PhD thesis of Ivan Petrov is an in-depth study of the effect of hydrocracking of vacuum residue H-Oil on the performance of other petroleum refining processes in LNB. The PhD student has achieved the aim and objectives of the dissertation and has obtained results that exceed the minimum requirements of the Law on the Development of Academic Staff in the Republic of Bulgaria, the Regulations for its application and the Regulations of the University "Prof. Dr. Asen Zlatarov" for the acquisition of the requested scientific degree. These findings and the mentioned contributions of the dissertation give me reasons to confidently propose to the Honorable Scientific Jury to award to MSc Ivan Petrov Petrov the scientific degree PhD.

Подпис заличен
Чл.2 от ЗЗЛД

20.11.2022 г. **Reviewer:**