REVIEW
Of dissertation for the acquisition of educational and science degree
"DOCTOR"

Scientific field: 5. Technical sciences
Professional field: 5.10. Chemical technologies
Scientific specialty: Technology of natural and synthetic fuels
Author of the dissertation: mag. eng. Vasil Kotsev Yankov
Topic of the dissertation: Dependence of the operation of the processes "Hydrocracking of heavy oil 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"
Member of the scientific jury: assoc. prof. PhD eng. Todor Vasilev Palichev

1. BIOGRAPHICAL DATA

Vasil Kotsev Yankov graduated in 2002 as a chemical engineer, master in "Oil and Gas Technology", at the University "Prof. Dr. Asen Zlatarov"-Burgas. He improved his qualifications in various international organizations, from which he has the relevant certificates. From February 2022 until now, chemical technologist of the "Primary oil processing" complex in "LUKOIL Neftochim Burgas" AD, as his activity includes management and organization of the production activity, including daily monitoring of the technological process and analysis of the work of the technological installations.

2. STRUCTURE AND RELEVANCE

The work presented to me for review is written on 165 pages and contains 52 figures, 28 tables and a bibliography of 286 literary sources. The work includes: introduction - 2 pages, literature review - 53 pages with 286 - literary sources, experimental part - 20 pages, results and discussion - 55 pages, conclusions - 2 pages and contributions 1 page.

The list of publications includes articles in full text in specialized magazines with an impact factor and an Internet edition - a total of 5 nos. The candidate is third author on three papers and fourth and sixth on the remaining two. Co-authorship with the supervisors and other researchers shows the importance of the conducted research, but it would be more correct to publish a part of the dissertation showing the personal contribution of the doctoral student in a separate article.

The dissertation is designed according to the requirements and traditions in this field and covers the scientometric requirements.

In 2015, the "H-Oil heavy oil residue Hydrocracking" complex was put into operation at "LUKOIL Neftochim Burgas" AD, and the assimilation of the technology of hydrocracking of heavy oil residue in a pseudo-fluidized bed H-Oil is associated with many difficulties and challenges. Despite the accumulated experience from the operation of a "Catalytic Cracking" plant and the continuous research of the H-Oil technology on a global

scale, the influence of the type of raw material and the hardness of the regime on the conversion of heavy oil residue and the quality of the obtained products has not yet been fully clarified. In this regard, the topic of the dissertation and the conducted research are extremely relevant from a scientific and applied point of view.

3. LITERATURE REVIEW

In the literature review, the PhD student very well describes the theoretical foundations of the hydrocracking and catalytic cracking processes, their varieties, the types of catalysts, the types of industrial installations, the influence of the type of raw material and the technological parameters on the ongoing physicochemical processes. Attention is also paid to the influence of nitrogen and sulfur compounds and metal pollutants on the catalyst, and hence on the operation of the catalytic cracking plant.

From the analysis of the literature, it has been established that the reactivity of the raw material for hydrocracking depends on its physicochemical properties and composition, and they, in turn, on its origin. The reason is that certain compounds act as initiators for the formation of free radicals and thus increase the conversion, while others, on the contrary, slow down these processes.

In the literature, there is no unambiguous definition of the process of sedimentation in the hydroprocessing of oil residues, and regardless of extensive research in this direction, no clear relationships have been established for quantitative prediction of this phenomenon in industrial conditions, and there is not enough information on how the quality of the raw material and its reactivity affect the precipitation of asphaltenes and sedimentation.

The PhD student studied a large number of literature sources and did not find enough information on how the regime hardness, expressed by increasing the temperature and increasing the contact time, affects the sedimentation in the hydrocracking of tar in a pseudo-fluidized bed of the H-Oil catalyst. It also did not find how the addition of HCAT nanocatalyst to the conventional catalyst affects the performance of H-Oil heavy oil residue hydrocracking and related processes in a refinery process.

At the same time, it is clear from literary sources that the composition and properties of the raw material are a key factor for the operation of the "Catalytic Cracking Installation". Correlations between various physical properties and the content of certain components in the feedstock or relationships between them with the conversion and quality of catalytic cracking products have also been established.

In the literature, however, 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 heavy oil residue on the performance of catalytic cracking. No information was found on how the regime stiffness in the tar hydrocracking plant affects the quality of the gas oil fractions that are used as feedstocks for catalytic cracking and how this change affects the cracking processes.

4. AIMS AND TASKS

As a result of the findings and conclusions from the literature review, the doctoral student sets

himself the following goal: Study of the influence of the type of raw materials and the hardness of the regime on the ongoing processes in the installations "Hydrocracking of h-oil heavy oil residue and "Catalytic cracking of vacuum-diesel".

With this goal set, the doctoral student sets himself the following tasks:

- to conduct research and establish dependencies on the influence of the properties of the heavy oil residue and the hardness of the regime on the reactivity and the rate of sedimentation in the process "Hydrocracking of heavy oil residue H-Oil";
- to investigate the combined action of a solid catalyst on an aluminum oxide support and a liquid nanocatalyst containing molybdenum on the performance of the industrial plant for "H-Oil heavy oil residue Hydrocracking" and on those of "Fluid Type Catalytic Cracking";
- to investigate the reactivity of vacuum gas oils obtained from the "H-Oil heavy oil residue Hydrocracking" process in the processing of tars from different types of oil and different operating mode hardness in the "Fluid Type Catalytic Cracking" process.

5. EXPERIMENTAL

The research was done on laboratory and industrial installations. Hydrocracking of 26 tar samples was carried out in the "H-Oil" industrial installation in "LUKOIL Neftochim Burgas". The mixtures of tars originating from different types of crude oil are processed in the hydrocracking installation in the pseudo-fluidized bed of the catalyst - H-Oil in LUKOIL Neftochim Burgas (LNB). A Ni-Mo catalyst with a low sedimentation potential as well as a nano-dispersed Mo-catalyst HSAT were used in the study. The heavy oil residue samples were characterized by determining the physical properties affecting the processes and the content of saturates, arenes, resins and asphaltenes. The content of nitrogen, sulfur and metals, which negatively affect the activity of the catalyst, was also determined. The conversion of each heavy oil residue sample was calculated and the reactivity index was determined using it, using the conversion of a reference vacuum gas oil. The sediment content and relative sediment content were also determined.

The effect of regime stiffness on sedimentation rate was investigated using data from laboratory and industrial tar hydrocracking plants. The conversion of the raw material and the conversion of the asphaltenes were calculated. Total Sediment Existing (TSE) and Total Sediment Potential (TSP) were determined for blends of partially blended boiler fuel with distillate oil fractions.

Hydrocracking experiments with the addition of the HCAT nanocatalyst were also conducted in pilot and industrial plants with a pseudo-fluidized bed of the solid catalyst.

The laboratory cracking experiments were carried out with the three gas oils from H-Oil: heavy atmospheric gas oil (HAGO), light vacuum gas oil (LVGO), heavy vacuum gas oil (HVGO) and with deasphalted product from the bottom of the vacuum column. An industrial equilibrium cracking catalyst was used. Its characteristics are indicated in the dissertation. The industrial experiment in the "Catalytic Cracking Installation" was conducted with the same catalyst. The raw material for catalytic cracking is directly distilled vacuum gas oil (fraction 360-540°C) and gas oil from H-Oil, which is a mixture of the three gas oils TAGO, LVGO and TVGO.

In order to fulfill one of the set tasks, namely the study of the reactivity during

cracking of vacuum gas oils from H-Oil, obtained from different raw materials at different hardness of the regime, laboratory cracking experiments were conducted with 12 samples obtained from different types of oil.

6. RESULTS

1. Dependence of reactivity and rate of sedimentation in the H-Oil heavy oil residue hydrocracking process on the properties of tars of different origin and interrelationship between the different properties of the feedstock for H-Oil tar hydrocracking.

The first step in determining the influence of feed mixture properties on reactivity in heavy oil conversion processes is to characterize the feedstock. The characterization of the data for the 26 VRs shows a wide range of variation in their properties and composition. It has been established that the reactivity and tendency to form sediments during hydrocracking in a pseudo-fluidized bed of the H-Oil catalyst of heavy oil residues originating from different types of oil depends on the composition and properties of the tar, namely: density (content of saturated components), content of sulfur, nitrogen and asphaltenes. Increasing density (decreasing saturates) and sulfur content have been shown to increase the reactivity of the tar and lower its tendency to form sediments in the hydrocracking of H-Oil heavy oil residue. Arene compounds increase the rate of chain reactions. This is thought to be a result of their higher reactive sulfur content. Nitrogen has been shown to act as an inhibitor. Asphaltenes can form stable radicals and therefore reduce the cracking rate.

A relationship was established between the reactivity of the raw material and the formation of sediments during hydrocracking of heavy oil residue. It is likely that the increase in the rate of reactions has a suppressive effect on the precipitation process.

2. Effect of regime stiffness in hydrocracking of heavy oil residue (H-Oil) on sedimentation rate.

It was found to be preferable to increase the stiffness of the regime in the H-Oil fluidized bed heavy oil residue hydrocracking plant by increasing the reaction time (decreasing the volumetric velocity), since a higher conversion is achieved in this mode of operation at the same or lower sediment content in the residual hydrocracked fractions.

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

It has been proven that, under other conditions being equal, the content of sediments in the hydrocracked residual fractions from H-Oil increases linearly with increasing content of asphaltenes.

3. Study of the influence of HCAT nanocatalyst on sedimentation, conversion, yields and quality of products in the hydrocracking of H-Oil heavy oil residue, and on the operation of a "Catalytic Cracking" (CCF) plant.

Through research conducted in a laboratory pilot plant, it was found that the application of nano-dispersed molybdenum-containing HCAT catalyst significantly reduced the formation of sediments in the atmospheric residue (from 0.33 to 0.07%), allowing an increase in the reaction temperature and an increase in the hydrocracking conversion of H-Oil tar. At the same time, the conversion of asphaltenes in the hydrocracking of H-Oil heavy oil residue is not affected by the use of HCAT.

In an analysis of the operation of the "Catalytic Cracking" (CCF) installation with raw material containing vacuum gas oil from H-Oil without and with HCAT catalyst, it was found that, at a content of 28% HC with HCAT, the conversion into CCF is reduced by 3-4%.

4. Influence of the hardness of the regime in hydrocracking of heavy oil residue - H-Oil on the operation of the installation for catalytic cracking of fluid type.

It was found that increasing the reaction temperature in hydrocracking in a pseudo-fluidized bed of the H-Oil catalyst leads to an increase in the content of aromatic components in H-Oil gas oils, which lowers the conversion level of vacuum gas oil in catalytic cracking and increases the temperature in the regenerator in " Installation catalytic cracking" due to the greater coke formation.

5. Reactivity of vacuum gas oils from H-Oil obtained during the processing of heavy oil residues from different types of oil and different hardness of the mode in H-Oil in the fluid catalytic cracking process.

Through the study of 12 types of raw materials for CCF, it was found that the most reactive vacuum gas oils are the direct-distillate ones. The influence of the type of raw material on the quantity and quality of the products obtained at CCF was also studied. The reactivity of heavy oil fractions originating from "H-Oil heavy oil residue Hydrocracking" has been shown to correlate with their 50% boiling point (T50%), which is new to world science in this field.

The abstract is very well designed and correctly reflects the results of the research.

7. CONTRIBUTIONS

The results of the PhD student's research have scientific and applied contributions, some of which can be summarized as follows:

- a regression equation was derived describing the dependence between the reactivity and the properties of the raw material for hydrocracking H-Oil, which can be used to evaluate the economic efficiency of processing new alternative types of oil and their mixtures in the "Lukoil Neftochim Burgas" refinery and for daily monitoring;
- the influence of the quality of the raw material and the hardness of the regime on sediment formation during hydrocracking of H-Oil heavy oil residue has been proven;
- the influence of the stiffness of the regime in the H-Oil heavy oil residue hydrocracking plant on the yield and quality of gas oil fractions-raw materials for catalytic cracking has been established, which allows to predict the behavior of the catalytic cracking plant and to optimize the joint action of the two economic the most effective deep processing processes Hydrocracking and Catalytic Cracking at the Lukoil Neftochim Burgas refinery.

The contributions in the dissertation are of great scientific and practical value and their use contributes to the realization of a significant economic effect in "Lukoil Neftochim Burgas".

8. TECHNICAL DESIGN, RECOMMENDATIONS, AND NOTES

The thesis is very well laid out. There are no spelling and punctuation errors. In places, names outside the IUAPAC nomenclature are used, but the names used are extremely popular in practice. Several tables (Tables 9, 10, 11, 14, etc.) are incorrectly titled. They are entitled "Physico-chemical properties", and it is about hydrocarbon composition and other indicators. In some tables and figures, it is not clear what kind of percentages we are talking about.

A large number of experiments, both laboratory and industrial, have been carried out. Despite the difficulties in conducting industrial experiments, the doctoral student managed to collect very valuable information from a scientific and practical point of view. The experimental data are very well

analyzed and relevant conclusions are drawn. However, they lack quantitative results, although they are present in the dissertation.

The mentioned remarks and recommendations do not change my high assessment of the dissertation work, which impresses me with the volume, the quality of the experimental work performed and the analysis of the results. The PhD student successfully coped with his tasks, showed a very good knowledge of thermocatalytic processes in the deep processing of oil, which he successfully applied in the development of the dissertation work.

9. CONCLUSION

In terms of volume, quality, and achieved scientometric indicators, the dissertation work fully meets the requirements of Law on the development of academic staff and the Regulations for the acquisition of scientific degrees and holding academic positions at the University "Prof. Asen Zlatarov"-Burgas. These findings and the contributions of the dissertation give me reason to confidently propose to the Honorable Scientific Jury to award Master of Engineering Vasil Kotsev Yankov the educational and scientific degree "PhD" in the scientific specialty "Technology of Natural and Synthetic Fuels".

Burgas, November 2022

Signature: Подпис заличен чл.2 от ЗЗЛД

/Assoc. Prof. PhD Todor Palichev/