OPINION

for the PhD thesis of MSc Vasil Kotsev Yankov on the topic "Dependence of performance of the processes "H-Oil vacuum residue hydrocracking" and "Catalytic cracking of vacuum-gas oil" on the feedstock properties and the severity of operation in H-Oil", submitted for obtaining PhD degree in the professional field 5.10 Chemical technologies (Technology of natural and synthetic fuels)

by Assoc. Kiril Stanulov - member of the Scientific Jury, according to the Order № UD-257/ 27.09.2022 of the University "Prof. Dr. Asen Zlatarov" – Burgas

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

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Eng. Vasil Yankov was born in 1975. He graduated in 2002 from University "Prof. Dr. Assen Zlatarov" with a MSc degree and a qualification of chemical engineer in the specialty "Technology of Oil and Gas". He has been working at Lukoil Neftohim Burgas since 1998, initially as an operator in the "Catalytic reforming and hydrotreatment of pyrolysis gasoline" unit, and subsequently he held the positions of head of the "Catalytic reforming" installation, senior engineer "Catalytic processes", deputy head of production "Catalytic processing of fuels", deputy chief technologist, etc. Currently he is in the position of Chief Technologist of the complex "Primary Oil Processing". He has also acquired several training certificates from leading companies in the field of oil refining. The above mentioned data from the professional development of Eng. Yankov characterize him as an engineer with high qualification and extensive experience in the field of petroleum technology.

The dissertation of Eng. Yankov is written in 165 pages, includes 52 figures, 28 tables and a bibliography of 286 references. It is structured in six chapters, including introduction, literature review, experimental part, discussion of results, conclusions and contributions.

The main objective of the thesis is to investigate the dependencies of the performance of the processes "Hydrocracking of vacuum residue H-Oil" and "Catalytic Cracking" on the properties of the feedstock and the severity mode of operation in the H-Oil process. The theme is topical due to the increasing trend to use heavy oils in refining.

In the literature review, the PhD student has focused on the chemical, technological and design features of the two processes, demonstrating good awareness and competence on the subject matter. He has presented sufficient data on the historical development of hydrocracking as a process for the treatment of heavy oil, and residues, the peculiarities in the chemistry and mechanism of hydrotreating and hydrocracking, and the typical reactions for these processes. The varieties of hydrocracking, the types of reactors, their characteristics and operating conditions, as well as the advantages of ebullated bed systems due to the possibility of continuous regeneration of the catalyst are indicated. The bi-functional

performance of hydrocracking catalysts, their requirements and reasons for their deactivation are commented on, as well as a brief reference to fixed and moving bed catalyst reactors and processes and those with a ebullated three-phase bed. In his reference, Eng. Yankov has studied, analyzed and summarized literature data on the quality of feedstocks for hydrocracking and its influence on conversion and sedimentation, emphasizing the role of asphaltenes in their formation. An in-depth analysis of data on the influence of the severity mode of operation, reaction temperature and space velocity (LHSV) of hydrocracking on asphaltene content, sediment formation, conversion and distribution of cracking products has been carried out.

The review provides data on fluid catalytic cracking (FCC), the historical development of the process, the description of the scheme and the operating conditions of the process. The types of catalysts, their requirements and also their structure and chemical composition are discussed. An analysis of the feedstocks for FCC including vacuum gas oils and their blends, pilot plant data on the use of biofuels, vegetable oils and other feedstocks, and an assessment of their influence on the cracking products is presented, The negative role of catalytic poisons contained in the feedstocks such as nitrogen and sulphur compounds and metals (V, Ni, Fe, Na) is highlighted.

In writing the review, the PhD student has used a significant amount of scientific information, analyzed and summarized sufficient data, based on which he formulated the tasks on the topic of his dissertation.

The experimental part of the dissertation includes a study of the dependence of the performance of the processes "Hydrocracking of vacuum residue H-Oil" and "Catalytic cracking of vacuum gas oil" on the properties of the feedstock and the severity mode of operation in H-Oil. The results of these studies can be summarized as follows:

The dependence of the reactivity and rate of sedimentation in hydrocracking on the properties of vacuum residues of different origin was investigated. For this purpose, 26 vacuum residues (VRs) were characterized by 14 parameters, and it was found that the properties of VRs varied over a wide range, including density, sulfur, and C_7 asphaltenes contents. The correlation between the properties of the residues was investigated using a correlation matrix and it was found that density correlated strongly with Conradson carbon, sulfur, saturates contents and with asphaltenes, and C_7-asphaltenes correlated with C_5-asphaltenes, indicating interchangeability of these indicators. An equation was derived by regression analysis of the VR data, which shows the dependence of the cracking ability (reactivity index) on the density, sulfur, nitrogen and asphaltenes in the feedstock. It is shown that the reactivity of the VRs increases with increasing density and sulfur, while sediment formation decreases due to enhanced initiation of the cracking chain reactions.

The influence of space velocity (LHSV) and reaction temperature on conversion and sedimentation was investigated. It was found that with decreasing space velocity (increasing reaction time), the conversion of vacuum residue and that of asphaltenes follow the same trend. The conversion of asphaltenes is best

described by a first order equation. By processing literature data from laboratory and industrial studies, it was found that an increase in the conversion leads to an increase in the density of asphaltenes and sediments in the atmospheric residue of H-Oil hydrocracking of goutron and to an increase in the saturated compounds of the SARA fractions. It was found that the asphaltene content in the residue is a determinant of sedimentation which was confirmed by studying mixtures of partially blended fuel oil (PBFO) with middle distillate fractions (diluents). As a result of pilot and industrial studies, it was found that with increasing reaction temperature, the saturate compound content of the vacuum residue decreases and the content of aromatic structures, resins and asphaltenes increases. An equation has been derived that conclusively shows an increase in sediment in atmospheric residues with increasing hydrocracking reaction temperature and can be used in practice to predict sediment formation rate for any operating temperature.

By hydrocracking of vacuum residues in laboratory (pilot) and industrial conditions, Eng. Yankov has investigated the influence of HCAT nano-catalyst on sedimentation, conversion, yields and quality of products in hydrocracking of VR H-Oil and on the performance of fluid catalytic cracking (FCC) process. In laboratory tests, he found that the use of the nano-catalyst in the hydrocracking feedstock significantly reduced the sediment in the atmospheric residue, which allowed an increase in the reaction temperature by 14 °C and subsequently in the conversion by 15%. It was shown that the yields of gas, naphtha and diesel increased with increasing conversion , while the yield of vacuum residue decreased linearly. The maximum yield of vacuum gas oil was obtained at a conversion of about 60%. In industrial conditions, the use of HCAT showed that the total amount of sediments in the atmospheric residue did not increase, which allowed to increase the temperature of the catalyst bed by 7°C and increase the conversion by 6.7% without increasing the sediments in the atmospheric residue. As a result, it was found that the use of nano-catalyst does not deteriorate the quality of diesel, does not affect the conversion of asphaltenes, reduces the amount of vacuum residue, but increases their softening temperature. A significant decrease in FCC conversion (3-4%) was found when increasing the proportion of vacuum gas oil from H-Oil to 28%, as well as the need to reduce the FCC slurry oil (SLO)content in the hydrocracking feedstock. By laboratory FCC of H-Oil heavy oil fractions and H-Oil VTB (vacuum tower bottom product) deasphalted oil, it is shown that the T50% of these fractions, or their molecular weight, correlates with their conversion, which is a novelty in assessing their reactivity. Using a correlation matrix, FCC data of heavy oils from H-Oil under industrial conditions are summarized, and it is found that the conversion in FCC is most strongly influenced by the Δ coke, vacuum gas oil content and conversion from hydrocracking, and the reaction temperature in H-Oil. In a pilot-scale ACE catalytic cracking plant, the reactivity of 12 hydrocracking vacuum gas oils derived from different oil types and severity mode of operation in H-Oil unit was investigated. By investigating correlation relationships between feedstock quality, conversion, FCC products and their quality, it was found that the determining factor for the crackability of the feedstocks was their nitrogen content, while the characterization factor and heavy aromatic hydrocarbon content were less significant. The relationships between

the plant's product selectivity and the properties and composition of the feedstock (vacuum gas oils) were found to be important for the economic efficiency of FCC.

The dissertation of Eng. Vasil Yankov is a thorough and systematic study of the feedstock and product interrelation between the most cost-effective H-Oil and FCC processes in LNB refinery. The scientific and applied contributions of the research can be summarized as follows: Optimal solutions were found to control the sedimentation by controlling the severity mode of operation and selection of feedstocks for hydrocracking. The ability to predict the performance of the FCC depending on the severity mode of operation in the H-Oil hydrocracker, yield and quality of the vacuum gas oils from hydrocracking is found, allowing functional optimization of the two refinery-defining structural processes.

The abstract and conclusions correctly reflect the results of the research in this dissertation. In the formatting and writing of the dissertation some omissions were made such as "molecular weight" instead of "molecular mass", the names of the hydrocarbon groups are not according to IUPAC and other editorial errors, which do not change my excellent impression of the PhD research.

The thesis has been published in 5 publications that have been refereed and indexed in world databases, including 2 in Oxidation Communications, 2 in Petroleum and Coal and 1 in Petrol Science Technology .

In conclusion, I consider that the PhD student has fulfilled the aim and objectives of his thesis. He has achieved the results that according to the requirements of the Law for the Development of Academic Staff in the Republic of Bulgaria, the Regulations for its implementation and the Regulations of the University "Prof. Dr. Asen Zlatarov" has reached and exceeded the minimum requirements for the acquisition of the PhD degree. These findings give me the reason to confidently propose to the Honorable Scientific Jury to award to M.Eng. Vasil Yankov the PhD degree

30.11-2022 г. The opinion was written by:

Подпис заличен
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