REVIEW

by Prof. Dr. Magdalena Sabeva Mitkova

of a dissertation work "Improving the effect of the hydrocracking process of tar in LUKOIL Neftohim Burgas" for the acquisition of an educational and scientific degree " Ph.D" in the doctoral program "Technology of natural and synthetic fuels", professional direction 5.10 "Chemical technologies", field of higher education 5. Technical sciences of full-time doctoral student Ivan Atanasov Ilchev with supervisors: Prof. Dr. Dobromir Ivanov Yordanov and Prof. Dicho Stoyanov Stratiev.

By order No. UD-255/15.07.2024 I was appointed as a member of the jury that will examine the dissertation work of Ivan Atanasov Ilchev, and by order No. UD-270/23.07.2024 I was assigned to prepare a review.

Biographical data

Ivan Atanasov Ilchev was born on June 11, 1991. He completed his secondary education at "Dr. Petar Beron" Secondary School, Svilengrad. From September 2010 to September 2014, he studied "Industrial Management" and received a bachelor's degree at the University "Prof. Dr. Asen Zlatarov", Burgas. From September 2014 to July 2016, he continued his studies in the master's program "Industrial Design in Oil Refining and Petrochemistry" at the University "Prof. Dr. Asen Zlatarov", Burgas and received the Master's degree. Since January 2020, he is a full-time doctoral student in the doctoral program "Technology of Natural and Synthetic Fuels". He has worked successively as: administrator at Atlantis Bulgaria, designer-technologist at Himproekt, Devnya, refinery operator at Lukoil Neftohim Burgas AD, designer-technologist at Promproekt Varna EOOD and is currently a Supply Chain Specialist of export oil products at Lukoil Neftohim Burgas AD.

Relevance of the topic developed in the dissertation work

In 2015 in "LUKOIL Neftohim Burgas" AD, the complex "Hydrocracking of tar H-Oil" was put into operation and the assimilation of the technology of hydrocracking of tar in a pseudo-fluidized bed H-Oil began. One of the main problems after the start-up turns out to be the recovery of the heavy vacuum residue (VTB). This intermediate product is mostly suitable for blending to obtain boiler fuel. But the low cost price of the boiler fuel product makes a team of technologists

at Lukoil Neftohim Burgas ambitious to tackle thedifficulttask of utilizing the heavy vacuum residue in the production of a product with a higher cost price, such as road bitumen. Scientific research on the possibilities of applying hydrocracked unconverted vacuum residue in the production of road bitumen gradually began, which subsequently progressed to laboratory, semi-industrial and industrial experiments to reach its application in the production of bitumen.

The lack of scientific data in the literature regarding the input of hydrocracked unconverted vacuum residue and what blends of which crudes, what percentage of primary and secondary vacuum residues, what additives aid the process and under what operating regime will not there are production safety issues in the production of road bitumen have determined the aim of the present dissertation to improve the action of the hydrocracking process of tar in order to obtain a hydrocracked unconverted vacuum residue with indicators suitable for the production of road bitumen.

To achieve this goal, the following goals are formulated in this dissertation:

1. Investigation of the incorporation of atactic polypropylene (aPP) and elemental sulfur to improve the quality of the finished product with maximum incorporation of vacuum residues of secondary origin.

2. Investigating the application of H-OIL VTB and FCC SLO in different percentage ratios (oxidized and non-oxidized) and adding sulfur in the production of road bitumen and comparing their quality indicators to obtain an optimal commodity product.

3. Study of the optimal percentage of VTB that can be added for the production of bitumen without interfering with the standardization of the product according to BDS, consistent with the constantly changing blended oils processed in the refinery of Lukoil Neftohim Burgas AD and optimal mode of operation of the installation for hydrocracking of tar.

Dissertation review and analysis of results

The dissertation is presented in 149 pages, includes 42 figures, 28 tables and a bibliography of 154 literary sources. The structure of the dissertation follows the generally accepted norms, introduction, literature review, experimental part, results and discussion, conclusions, contributions and used literature.

In the literary review, the doctoral student describes the application of bitumen in historical terms, dwells on the principle scheme for its production, the chemistry and technology of the

process, the influence of individual factors on it. 6 commercial brands of road bitumen are described and the main characteristics of bitumen are graphically compared for the two most popular indicators characterizing bituminous binders - Penetration and Softening Temperature.

In the experimental part, the possibility of increasing the share of the unconverted vacuum gas oil from the H-Oil process by oxidizing the mixtures in a laboratory reactor, semi-industrial, and also in an industrial installation for the production of bitumen in LUKOIL Neftohim Burgas AD was considered. Commercial samples of straight distillate tar (SRVGO) and hydrocracked tar (H-Oil VTB) obtained during the processing of a blend of 70% Urals and 30% Middle East crude oil at the LNB refinery were also examined. The tested bituminous mixtures were analyzed for penetration at 25°C according to EN 1426, softening temperature by the ring-ball method as described in EN 1427 and fracture point according to Fraass - EN 12593. The durability expressed by resistance to hardening at 163° C (RTFOT) is rated in accordance with EN 12607-1. Density was measured according to the procedure in which dilution with toluene was used. The repeatability of the density measurement by dilution with toluene was 0.0035 g/cm3 for all vacuum residues. The distillation characteristics of the studied samples were determined by gas chromatography simulation at high temperature distillation according to ASTM D-7169. A laboratory and industrial study of the production of road bitumen from mixtures of straight-distilled and hydrocracked tar in various ratios is described. An experiment was conducted to find the optimal parameters for obtaining road bitumen brand 50/70 according to BDS EN12591&2009/NA&2017/Amendment 1:2017.

In the "Results and discussion" section, before discussing the obtained experimental results, the doctoral student again dwells on the objectives and background of the experiment, which repeats part of the content of the literature review. In my opinion, this is unnecessary and complicates the presentation, but does not reduce the value of the results obtained.

It is known that bitumen must meet the specification requirements for hardness (softening temperature and penetration). Since neither the direct distillate vacuum residue SRVGO nor the unconverted vacuum residue VTB were sufficiently hard, an attempt was made to harden both and their mixtures by oxidation with air. Air oxidation was found to increase the softening temperatures of both types of residues. To compare the curing rate for these two residues with increasing oxidation time, a first-order reaction kinetics of the air oxidation process is assumed. Hydrocracked residues have been shown to be more sensitive to solidification.

The summary of laboratory, semi-commercial and commercial results for one year of production of bitumen for road pavements with a penetration degree of 50-70 shows that the increase in the softening temperature of the ring-ball method after curing can be mainly related to the content and properties of VTB . Industrial results confirm the possibility of applying hydrocracking residue in bitumen production in an amount of up to 37%. It is shown that from the point of view of maximizing the amount of cheap VTB flow in bitumen, the optimal way is not to oxidize the latter and the hardness of the blend with SRVGO is reached as oxidation of only SRVGO before mixing (blending). In an attempt to find a solution to the increase in the softening temperature of VTB after curing resistance, the addition of a plastomer - atactic polypropylene (aPP), which is a by-product of isotactic polypropylene produced at LNB, was investigated. Another way to improve the properties of the binder through chemical modification is explored by the dissertation student, using a chemical agent to modify the properties of pure bitumen. One such chemical agent introduced for the purpose of bitumen modification is sulphur.

It is discovered that the addition of sulfur simultaneously increased the softening temperature of VTB blends at a low amount (1.63%) and decreased the softening temperature at higher amounts of 4 and 8%.

The thesis examines changes in H-Oil VTB quality as a function of tar conversion, H-Oil plant operating conditions and crude oil processed at the LNB refinery, and attempts to relate them to the potential use of H-Oil VTB as a source for the production of road asphalt. The data obtained show that increasing H-Oil conversion worsens the Fraass breaking point of VTB. The addition of FCC SLO to H-Oil VTB appears to slightly improve the Fraass breaking point.

The exploitation of H-Oil fluidized bed tar hydrocracking under more severe conditions and the processing of higher viscosity direct distillate vacuum residue SRVGO results in the production of H-Oil unconverted vacuum residue VTB, which is characterized by high density, high Conradson carbon and high hardness (high softening point and Fraass breaking point and low penetration). After extensive experimentation, it was concluded that commercial antioxidants were unable to retard the setting resistance of road bitumen containing H-Oil VTB, H-Oil HVGO, FCC HCO and SRVGO.

A serious experiment was carried out on blending direct distilled vacuum residue SRVGO and unconverted vacuum residue VTB in the ratios: 100:0, 75:25, 65:35 and 50:50. Incorporating 35%

heavy oil residue of secondary origin into the production of road bitumen and obtaining a standardized product is a major success in this study. As a result of the research, four conclusions were drawn. In my opinion, they are too descriptive and could be refined.

Basic scientific and scientific-applied contributions

The presented dissertation has scientific and extremely scientific and applied contributions.

1. The oxidation kinetics of the two residues SRVGO and VTB with air were investigated and a first-order reaction kinetics of the air oxidation process was assumed. Rate constants are derived.

2. Permanent implementation of VTB in the production of road bitumen in compliance with all production and state standards. In this way, the conversion of H-Oil is significantly increased and the operation process of the Hydrocracking of tar plant on the territory of LNHB is improved.

3. A scheme of work with the addition of non-oxidized VTB in the production of road bitumen has been successfully implemented. The low-value semi-product VTB without any further processing is added to the stock road bitumen and increases the bitumen yield.

4. A scheme of work with the addition of oxidized VTB in the production of road bitumen has been successfully implemented. This scheme of operation replaces part of the SRVGO, which instead of going to the production of road bitumen, goes to the production of light fuels of a much higher value in an H-Oil plant without disturbing the operation mode of the Bitumen installation.

5. Due to the seasonal nature of the production of bituminous products, a large part of the experiments were used by the production team to prepare the operating mode of the installation before start-up. This provided preliminary data according to the current types of oil being processed at the refinery, which scheme of operation would be most suitable for operation and would bring the most revenue to the company.

Description and evaluation of the presented materials

The doctoral student has presented 5 scientific articles, 3 of which are indexed in the Scopus database. In one article (#5) he is the sole author, in two of the articles (#1 and #2) he is in seventh place, in one article (#3) he is in fourth place and in one article (#4) he is in fifth place place as an author. Working in large teams is typical for researchers from Lukoil Neftohim AD, Burgas considering the scale of laboratory, semi-industrial and industrial experiments. From the

way the doctoral thesis is presented, it is clear and leaves no doubt that the doctoral student has carried out a large-scale experiment in laboratory and industrial conditions.

The quantitative requirements for groups of indicators for obtaining the ESD "doctor" have been met, namely the sum of the points for indicators 1 and from 5 to 11 is 96.1 points out of the required 80 points.

Critical remarks

There are few technical errors in the thesis that are easy to fix. I have no primary objections to the research done and its interpretation. I am impressed by the large number of experiments, both in laboratory and industrial settings, where valuable information for both science and practice has been collected, which should be more concisely reflected in the conclusions. The mentioned remarks do not change my high evaluation of the dissertation work. The doctoral student has coped very successfully with his tasks.

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 acquired scientific degrees and holding academic positions at the University "Prof. Dr. Asen Zlatarov", Burgas. These findings and the contributions of the dissertation allow me to confidently propose to the Honorable Scientific Jury to award Master Engineer Ivan Atanasov Ilchev the educational and scientific degree "- Ph.D" in the scientific specialty "Technology of Natural and Synthetic Fuels".

Reviewer: Подпис заличен чл.2 от ЗЗЛД

Prof. Dr. Magdalena Mitkova

September 20, 2024 Burgas