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The compliance assessment of petroleum products supplied on state defence order

Keywords: petroleum products, compliance assessment, State Defence Order, permission for the application.

Abstract. The operating system of petroleum products compliance assessment, based on Federal Law of RF on «technical regulation» and Customs Union Technical Regulations TR TS 013/2011 and 030/2012, specifies the requirements for the limited number of quality indexes, which characterize man and environment vital activity security. Machinery operation safety issues, application efficiencies of petroleum products within the framework of Technical Regulations are not considered. So a consumer, using such production, assumes all the risks, associated with a possible breakdown of machinery operation because of inferior POL quality.

Considering the importance of reliable and trouble-free war materiel operation for the country safety support, the compliance assessment alternative system of defense production generally and petroleum one, in particular, was developed by Government Decree №1036 in 2012. The main point of Decree is the following: the Government establishes the necessary requirements for the whole range of production quality indexes, primarily, for those indexes, which characterize production application efficiency and only after that for other indexes, which characterize man and environment vital activity security. It makes possible to reduce and minimize the risks, associated with a possible breakdown of machinery operation because of insufficient level of indexes, which characterize production efficiency.

The compliance assessment new system of petroleum products, supplied on State Defence Order, is based on the following principles:

- a new form of compliance assessment, concerning petroleum products, is put into effect: admission in war materiel, which includes plant technological readiness for production of declared products; proficiency (laboratory-bench) tests, bench tests and proving ground tests of petroleum products;
- authorized government bodies (military representative offices on plants and FAI "The 25th State Research Institute of Chimmotologos of the Russian Ministry of Defence") implement a constant control over production state, so that petroleum products, approved for application in war materiel, continue to correspond the established requirements and their physical-chemical and performance properties correspond to the approved ones during conducting of application approval procedure.

The military representative offices implement a constant control over adherence to production technology, check the quality of each shipped petroleum product batch. More than that, annually, thorough check of production is carried out with the participation of military representative offices and FAI "The 25th State Research Institute of Chimmotologos of the Russian Ministry of Defence". The check comprise test conducting of production samples, taken from commercial batches, control over constant state of production composition and adherence to technological conditions during production making. Requirements of the compliance assessment system of petroleum products, supplied on the State Defense Order, are mandatory only for those petroleum product producers, who deliver their products to the Ministry of Defence of the Russian Federation. Each producer independently decides the question of joining to this system, agrees to the constant monitoring over the production process on the part of authorized government bodies. High-quality dual-use products (both military and civil) will appear on the market as a consequence of this system. The quality of these products will be confirmed comprehensively both in terms of indexes characterizing man and environment vital activity security and indexes defining efficiency of petroleum product application on machinery.

For unstructured petroleum product consumers (motor transport establishments, bunkering companies, etc.) the claiming on valid solution to petroleum application in war materiel (as one of the contract conditions) will make it possible to get POL materials with a guaranteed quality. For petroleum producers a valid admission of petroleum products application in war materiel will be a kind of kite mark, which is a significant argument in competition for customers.

References

1. Safonov A.S., Ushakov A.I., Grishin V.V. *Khimmotologiya goryuche-smazochnykh materialov*. [Khimmotologiya of combustive-lubricating materials]. Moskow: NPIKTs, 2007. – P. 16

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Study and optimization of operation of the straight-run naphtha separation isomerization unit of JSC «ANKhK»

Keywords: gasoline fractions, straight-run naphtha, raw materials for the isomerization unit, rectification column, reflux ratio, the temperature of the feed, the temperature of hot jet.

Abstract. The straight-run naphtha separation block was monitored and its operation was studied. The composition of raw materials was studied by GCMS and gas chromatography methods, the distillation curves were built, operation scheme of the raw materials separation unit was analyzed, the existing equipment of the separation unit was calculated. Operation efficiency of the straight-run naphtha separation unit rectification column was illustrated based on the content of the key components of the collected fractions. Analysis of the models of different separation variants for fraction 30–180°C showed that it is possible to considerably improve the quality of the collected fractions and to increase the 30–70°C fractions selection by reducing the reflux ratio from 5.2 (in the current variant) to 2–3. Mathematical modeling of the rectification process showed that optimal temperature of the raw in the input to the column should be 115–120°C. It was shown that with increasing hot jet temperature, selection of C₅ hydrocarbons in the fraction 30–70°C was increased insignificantly whereas the C₆ hydrocarbons selection was increased about two times. C₆ Hydrocarbons content increase in the fraction 70–95°C with increasing of hot jet temperature was negligible. Growth of the hot jet temperature increases the C₇ hydrocarbons concentration in the fraction 70–95°C which is the raw material for pyrolysis installation. Thus, the recommended hot stream temperature without significant increase in the furnace load, should be in the interval 160–165°C. It was shown that in order to optimize operation of the straight-run naphtha separation block and to increase efficiency of the fraction 30–180°C separation as well as to achieve maximum yields of the fractions 30–70°C it was necessary to reduce the reflux ratio and to increase the temperature of the raw materials feeding.

References

1. Mirimanyan A.A., Vikhman A.G., Mkrtychev A.L. Industrial experience of the isomerization of pentane-hexane fraction [Promyshlennyy opyt raboty ustanovok izomerizatsii pentan-geksanovoy fraktsii]. *Neftepererabotka i neftekhimiya – Petroleum Refining and Petrochemicals*, 2006, no. 4, pp. 22–31.
2. Bashinskiy A.I., Vikhman A.G., Mirimanyan A.A., Savvateyev M.A., Kiyevskiy V.Ya., Yampol'skaya M.Kh., Karapertyan I.N., Yenukova I.Yu., Danilyan M.Yu., Yolshin A.I., Krashchuk S.G., Design solutions for the development of a combined isomerization unit with blocks of raw material preparation at Refinery JSC «Angarskaya Neftekhimicheskaya Kompaniya» [Proektnye resheniya po razrabotke kombinirovannoy ustanovki izomerizatsii s blokami podgotovki syrja na NPZ OAO «ANKhK»]. *Neftepererabotka i neftekhimiya – Petroleum Refining and Petrochemicals*, 2006, no. 9, pp. 9–14.
3. GOST 52714-2007. Automobile gasoline. Determination of individual and group hydrocarbon composition by capillary gas chromatography.

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Optimization of the process demercaptanization of the light fraction of catalytic cracking gasoline obtained from the mixture of Azeri oil

Keywords: catalytic cracking gasoline, demercaptanization, mercaptan sulfur, octane number, optimization, statistical treatment, regression mathematical model.

Abstract. One of the main problems of oil refining is remove mercaptan sulfur from petroleum, lead to corrosion equipment. To this end, we conducted the demercaptanization process light fraction of catalytic cracking gasoline. As feedstock for the process demercaptanization is selected light fraction (IBP–130°C) FCC obtained from the mixture Azeri oils with content the total and mercaptan sulfur, respectively, 88 and 30 ppm, olefins 24,6% (wt).

Studies were carried out on a flow-type installation in a temperature range of 70–150°C, a pressure of 0,5–1,0 MPa, the volume ratio of hydrogen to feedstock 0,5:1–1:1, volume rate of feed of the raw material – $\nu = 1,0 \text{ h}^{-1}$.

For establish quantitative ratio reflecting the influence of the main factors of technological regime (temperature – X_1 , °C, pressure – X_2 , MPa, the volume ratio hydrogen to feedstock – X_3) at process indicators (the content total sulfur – Y_1 , ppm; the content mercaptan sulfur – Y_2 , ppm, octane number by MON – Y_3 , the content of unsaturated hydrocarbons – Y_4 , wt %) was used the method of active planning of the experiment.

The processing of experimental data allowed us to determine the value of coefficients of the regression equation. The hypothesis about the adequacy of the model has checked by criterion Fisher.

For solve the problem of optimization was used program Matlab-6, containing modern algorithms for solving linear programming problems. Solving the optimization problem showed that a minimum content of the total and mercaptan sulfur (respectively $Y_1 = 24,1$ ppm and $Y_2 = 1,92$ ppm) can be obtain at a temperature of 65°C , at system pressure – $0,5$ MPa, at the volume ratio of hydrogen to feedstock – $1:1$. In these values of the input variables the octane number was equaled – 80 p. by MON (Y_3) and also the content of unsaturated hydrocarbons – $24,5\%$ wt (Y_4) .

Thus, the developed mathematical model the process demercaptanization the light fraction of the FCC in the form of a polynomial regression allowed to find optimal values of the input variables which the content of mercaptan sulfur was equaled to $1,92$ ppm and octane number – 80 p. by MON.

References

1. Guseynova I.S., Mirzoeva L.M., Yunusov S.G., Kazimova A.N., Alieva N.R., Guseynova A.D., Rustamov M.I. The obtaining automobile gasoline perspective quality [Poluchenie avtomobilnogo benzina perspektivnogo kachestva]. *Abstracts & Proceedings of the 1st International chemistry and chemical engineering conference*, Baku, Azerbaijan (2013), pp. 683–686.
2. Merpeisov Kh.S., Isichenko I.V., Konovalov A.V. The new technology alkali-free demercaptanization of hydrocarbons based catalyst MARS [Novaya tekhnologiya besschelochnoy demerkaptanizatsii uglevodorodnogo syrya na osnove katalizatora MARS]. *Oil. Gas*, 2007, no. 3 (31), pp. 50–52.
3. Akhmedova Yu.I., Serebryakov O.I. Modern geochemical studies and forecasting the content homologues hydrogen sulfide and its organic derivatives in gas condensate systems [Sovremennye geokhimicheskie issledovaniya i prognozirovaniye sodержaniya gomologov serovodoropda i ego organicheskikh proizvodnykh v gazokondensatnykh sistemakh]. *Geology, geography and global energy*, 2010, no. 4 (39), pp.29–35.
4. Ruzinov L.P., Slobodchikova R.M. Planirovanie eksperimenta v khimii i khimicheskoy tekhnologii (Design of experiments in chemistry and chemical technology). Moskow, Khimiya, 1980. 280 p.
5. Tikhomorov V.B. Planirovanie i analiz eksperimenta (Planning and analysis of the experiment). Moskow, Legkaya industriya, 1974. 260 p.
6. Bondar A.G. Matematicheskoe modelirovanie v khimicheskoy tekhnologii (Mathematical modeling in chemical engineering). Kiev, Vischa shkola, 1973. pp.192–225.
7. Vasilev F.P. Chislennyye metody resheniya ekstremalnykh zadach (Numerical methods for solving extremal problems). Moskow, Nauka, 1988. 552 p.
8. Matlab-6,5. The Math Works. Inc. All Right Reserved, USA, 2000.

ANALYTIC METHODS FOR OIL and PETROLEUM PRODUCTS

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Separation of stable water-oil emulsions using ultrasound

Keywords: oil, water-oil emulsion, dewatering, ultrasound, CDU, demulsification.

Abstract. In laboratory studies of oil and oil products (especially in the laboratories involved in the identification expertise petroleum), researchers are often faced with the problem of high water content in the sample oil. Its presence makes it difficult or impossible to determine many of the characteristics and physico-chemical properties of the sample. So the definition of fractional composition, kinematic viscosity, pour point, flash point, and many other characteristics may exercise only the dehydrated sample.

Classical methods of dewatering described in the standards, solves the problem of poorly irrigated study samples with a water content of up to 4% by weight. These methods are in water sorption precalcined inorganic salts (e.g., sodium sulfate). At a higher water content, these methods do not work, and remove the water in this way is not possible.

Purpose of the present work was to investigate the possibility of separation of oil-water emulsions (with a water content of 5% by weight. Above) using ultrasound. In addition, in this work was to evaluate the effect of ultrasound (frequency 35 kHz) to the qualitative composition of oil samples before and after sonication. The influence of ultrasound on the qualitative composition of oily samples rated chromatography-mass spectrometry on an Agilent 6850 / 5973N, equipped with chromatographic silica capillary column HP1-MS 60m x 0,25mm x 0,25mkm. Composition of the samples was studied before and after sonication.

Thus, this study is to evaluate the use of ultrasound (with a frequency of 35 kHz) for laboratory analysis for the treatment of severely cut oil. It has been shown that treatment of oil samples indicated frequency ultrasound does not affect the composition of the test oil (which is an important factor in determining the physical and chemical parameters of oil), and will not cause a significant overestimation or underestimation of any determined in the laboratory measure. Laboratory method proposed dewatering water emulsions with a high water content (more than 5 wt.%) Combining the sample treatment with ultrasound at a frequency of 35 kHz, followed by final drying by classical methods (water sorption precalcined inorganic salts – the sample was

shaken with anhydrous sodium sulfate or other appropriate desiccants and after settling separate sample from the dryer by decantation).

References

1. Klokoval T.P., Volodin Yu.A., Glagoleva O.F. Effect of ultrasound on the properties of colloidal-disperse oil systems [Vliyaniye ultrazvuka na kolloidno-dispersnyye svoystiya neftyanykh sistem] *Khimiya i tekhnologiya topliv i masel – Chemistry and technology of fuels and lube oils*, 2006, no. 1, pp. 32–34.
2. Kirillova L.B., Pivovarova N.A., Vlasova G.V., Schugorev V.D. Investigation of the influence of parameters and wave processing adjuvants on the particle size of the dispersed phase of paraffin oils [Issledovanie vliyaniya parametrov volnovoy obrabotki i aktiviruyuschikh dobavok na razmer chastits dispersnoi fazy parafinistykh neftey]. *Neftepererabotka i neftekhimiya – Petroleum Refining and Petrochemicals*. 2011, no. 1, pp. 13–16.
3. Afanasiev E.S., Rimarenko B.I., Yasiyan Yu.P., Gorlov S.G. Effect of ultrasonic treatment on the process of destruction of oil-water emulsions [Vliyaniye ultrazvukovogo vozdeystviya na protsess razrusheniya vodoneftyanykh emulsiy]. *Neftepererabotka i neftekhimiya – Petroleum Refining and Petrochemicals*, 2009, no. 9, pp. 39–41.
4. GOST 2477-65. Oil and oil products. Method for determination of water content.
5. GOST 3900-85. Oil and oil products. Methods for determining the density.
6. GOST 33-2000 (ISO 3104-94). Petroleum products. Transparent and opaque liquids. Determination of kinematic viscosity and calculation of dynamic viscosity.
7. Pastukhov M.O., Okhlopkov A.S., Zarubin O.P. *Issledovanie bituminoznoy nefti v tamozhennykh tselyakh: Metodicheskoe posobie* [Research bituminous oil for customs purposes: the developers]. Moscow: TsEKTU, 2010.
8. Pastukhov M.O., Okhlopkov A.S., Zarubin O.P. *Identifikatsionnoe issledovanie nefty i nefteproduktov v tamozhennykh tselyakh: Metodicheskoe posobie* [Identification study of oil and petroleum products for customs purposes: the developers]. Moscow: TsEKTU, 2012.

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New composite materials for purifying petroleum from heteroorganic compounds

Keywords: Petroleum, heteroorganic compounds, metallic powder.

Abstract. The work considers the research results of the influence of composites based on coarsely dispersed metal powders on petroleum composition. The relevance of this work was defined by the need to obtain new materials for petroleum refining and processing, based on metal powders. The main work objective was to analyze the influence of coarsely dispersed iron and copper powders, modified by cobalt and nickel ions, on the chemical composition of petroleum crudes in the process of their treatment. Researches were carried out with a variety of analytical methods: elemental analyses, IR- and NMR-spectrometry, Chromato-Mass-Spectrometry. Composites prepared on the basis of: copper powder, modified with nickelous ions (sample 1); iron powder, modified with nickelous ions (sample 2); copper powder, modified with nickelous and cobaltous ions (sample 3); iron powder, modified with nickelous and cobaltous ions (sample 4) were used. Metallic powders were obtained by the method of electric explosion of conductors in argon. The modification of powders with Ni²⁺ and Co²⁺ ions was carried out from the saturated solutions of nickelous and cobaltous chlorides. Usinsk field and all kinds of westsiberian petroleum crudes that have different chemical types and vary in n-paraffin content and distribution pattern, resinous-asphaltenic materials and heteroatom were processed. It was specified that in the process of treatment, the qualitative composition of light crude petroleum, typical for West Siberia practically did not change. The treatment by composites of Usinsk heavy crude petroleum that typically has high concentration of nitrogen and organosulfur compounds led to their weakening. The introduction of studied composites into the system decreased the portion of alkyl-based benzothiophene, quinoline, thiophen-quinoline and carbazole in the composition of heteroatomic compounds. The change of chemical composition of Usinsk field petroleum must be due to the chemisorption of heteroorganic compounds on composites' surface. It was shown that composites based on coarsely dispersed iron and copper powders, modified with nickelous and cobaltous ions, could be used for primary purification of hydrocarbon crudes with high concentration of heteroatomic compounds. Table 6, picture 1, bibliography 13 names.

References

1. Bagriy E.I., Nekhaev A.I. Petroleum Chemistry and Environmental Protection (review) [Neftekhimiya i zashcha okruzhayushchey sredy (obzor)] *Neftekhimiya - Petroleum Chemistry*, 1999, v.39, no. 2, pp. 83–97.
2. Radchenko E.D., Zelentsov Yu.N., Chernakova G.N. *Vliyaniye organicheskikh azotsoderzhashchikh soedineniy na gidrogreking neftyanykh fraktsiy na tseolitsoderzhashchikh katalizatorakh* [The effect of organic

- nitrogen-containing compounds on hydrocracking of petroleum fractions on the zeolite catalysts]. Moscow: TsNIITEneftkhim, 1987.
3. Schmitter J.M., Arpino P.J. Azaarenes in fuels // Mass spectrometry reviews. 1985. V. 4, № 1. P. 87-121.
 4. Tolbanova L.O., Mostovshchikov A.V., Ilin A.P. Structural and chemical transformations in copper nanopowders at air heating [Strukturnye i khimicheskie prevrashcheniya v nanoporoshkakh medi pri nagrevanii v vozduhe]. *Izvestiya tomskogo politekhnicheskogo universiteta – Bulletin of the Tomsk Polytechnic University*, 2008, V. 312, no. 3, pp. 16–18.
 5. Petrov A.A. *Uglevodorody nefii*. [Petroleum hydrocarbons]. Moscow: Nauka, 1984, 264 p.
 6. Smit A. *Prikladnaya IK-spektroskopiya: Per. s angl* [Applied Infrared Spectroscopy: Fundamentals, Techniques, and Analytical Problem-solving]. Moscow: Mir, 1982, 328 p.
 7. Ogorodnikov V.D. NMR-spectroscopy as method of research of a chemical composition of the oils. [YaMR-spektroskopiya kak metod issledovaniya khimicheskogo sostava neftey]. *Instrumentalnye metody issledovaniya nefii. Pod red. G.V. Ivanova – Instrumental methods for studies of petroleum*: ed. G.V. Ivanov. Novosibirsk: Nauka, 1987, pp. 49–67.
 8. Mossner S.G., Lopez de Alda M.J., Sander L.C., Lee M.L., Wise S.A. Gas chromatographic retention behavior of polycyclic aromatic sulfue heterocyclic compounds, (dibenzothiophene, naphtho[b]thiophenes, benzo[b] naphthothiophenes and alkylsubstituted derivatives) on stationary phases of different selectivity *J. of Chromatogrphy A*, 1999, V. 841, p. 207–228.
 9. Lopez Garcia C., Becchi M., Grenier-Loustalot M.F., Paisse O., Szymanski R. Analysis of aromatic sulfur compounds in gas oil using GC with sulfur chemiluminescence detection and high-resolution MS. *Anal. Chem.*, 2002, V. 74, no. 15, pp. 3849–3857.
 10. Clegg H., Wilkes H., Oldenburg T., Santameria D., Horsfield B. Influence of maturity on carbazole and benzocarbazole distributions in crude oils and source rocks from the Sonda de Campeche, Gulf of Mexico. *Org.Geochem.*, 1998, V. 29, no. 1–3, pp. 183–194.
 11. Schmitter J.M., Colin H., Excoffier J.L., Arpino P.J., Gulochon G. Identification of triaromatic nitrogen bases in crude oils. *Anal. Chem.*, 1982, V. 54, no. 4, pp. 769–772.
 12. Schmitter J.M., Ignatiadis I., Arpino P.J. Distribution of diaromatic nitrogen bases in crude oils. *Geochim. Cosmochim. Acta*, 1983, V. 47, no. 14, pp. 1975–1984.
 13. Bolshakov G.F. *Infrakrasnye spektry arenov* [Infrared spectra of arenes]. Novosibirsk, Nauka, 1989, 230 p.
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EQUIPMENT AND DEVICES

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Modernization of water filtration system to reduce sediment in the refrigerator equipment of isomerization unit

Keywords: water recycling, refrigerator equipment, water quality, chemical treatment of water, corrosion, isomerization unit.

Abstract. Actuality of the problem is caused by that the use of water as a cooling agent authorizing leads to problems of corrosion, scaling, pollution, development and growth of microorganisms in the water cycle. These issues have a major impact on the production process, reducing the efficiency of heat transfer, increasing energy consumption and increasing operating costs.

Given the seasonality, the heat load on the cooling tower is changing, resulting in evaporation coefficient (Ku) reduced in the winter to 2.0 in summer, on the contrary, the heat load is increased, resulting in Ku rises to 3.0-3.8. As a result of water recycling unit at the optimal mode in the winter it can work with a smaller number of blowdown system, and in the summer requires increasing the number of blowdown system. Feed water characterized by stable quality throughout the work unit of water recycling, quality indicators meet regulatory requirements, with the exception of suspended solids. Suspended solids concentration exceeds the limit, especially in the spring-summer time. Recycled water for its quality does not always meet the regulatory requirements for the quality of recycled water. In the summer time when enthusiasm for the temperature of the ambient air, there was an increase in the proportion of water evaporated, causing the growth of the carbonate hardness, evaporation rate in this case is - 3.0-3.8. Elevated levels of hardness salts (carbonate hardness) in circulating water leads to the formation of a layer of scale and as a consequence of the deterioration of cooling refrigeration isomerization unit. Heat deterioration caused by the fact that the layer of scale has low thermal conductivity. And to cool the top product of columns K-2 and K-5 K-6 to the desired temperature, a larger coolant flow. The heat transfer coefficient depends on the thickness of scale and may deteriorate to 50% depending on the thickness of the layer of scale.

Most rational way to solve these problems is possible by installing additional filter by make-up water, the purge valve and control system salinity. Make-up water will be filtered from suspended solids through an additional filter, and the content will be governed by hardness and in-line salinometer using the purge valve will be purged from the system hard water. Just need to add more fine cleaning filter through bulk. This we can achieve better water purification from harmful contaminants, bacteria, and thereby reduce its corrosive properties, having a negative impact on heat transfer equipment and pipelines.

STUDYNG TOGETHER

Abridged English-Russian dictionary of Chimmotologos terms and expressions: V-W

The Compiler – Danilov A.M.

MATERIALS of the PETROCHEMICAL and REFINERS ASSOCIATION

Extracts of the protocol #120 of ANN board meeting of 25.06.2014 / Subject –State of industrial safety and ecology at the Gazpromneft-Omsk Refinery JSC and Gazpromneft-Moscow Refinery JSC