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CHEMISTRY and TECHNOLOGY of CARBON MATERIALS

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Managing the process of oxidation of the bitumen in a tubular reactor in the production of road bitumen high-performance 4-10

*Keywords***:** road bitumen, tubular reactor, vacuum column, West Siberian oil, Vankor oil, group chemical composition of bitumen, fractional composition of bitumen.

Abstract. Joint Stock Company «Achinsk oil Refinery of the Eastern oil company» is the largest supplier of road bitumen in Eastern Siberia of the Russian Federation and the only one in the Krasnoyarsk region. Organization of production of road bitumen meeting the requirements of FRA «Rosavtodor», namely, GOST 33133 «Automobile roads of general use. Viscous road petroleum bitumens. Technical requirements» was very important for the needs of the road construction industry of the Russian Federation in this region.

The quality of feedstock, temperature, air consumption and oxidation duration are the main factors determining the efficiency of the oxidation process in bitumen production. However, oxidizing devices because of their different design features create different conditions for the oxidation process.

Oxidation in a tubular coil reactor occurs under conditions of intensive mixing of the feedstock with air due to the high rates of the reaction mixture. The vertical arrangement of the tubes prevents separation of gas and liquid phases, therefore, improves the conditions of their contact. The main advantage of using a tubular reactor is low air consumption. Due to the existence of a developed heterogeneous phase contact surface, reactions are accelerated both in the production of road and construction bitumen. This leads to a reduction in operating costs for air supply, but the large flow rate of the recirculation makes the process energy-intensive, and the formation of coke in the evaporator reduces the overhaul interval.

A comparative analysis of the physical and chemical properties of road bitumen obtained in the standard and recommended technological modes showed that the bitumen obtained after the adjustment of technological parameters, namely: increasing the viscosity of bitumen to 39 c, reducing the multiplicity of recirculation to 2,3, reducing the temperature in the reaction zone to 260°C, increasing the relative air flow to 114 $m^3/m^3/h$; have an increased range of plasticity and resistance to the processes of thermo-oxidative aging. Oxidation of the feedstock at a soft temperature (260°C) allowed to keep the penetration of oxidized bitumen at a high level. This behavior is typical only for bitumen obtained from light raw materials. The higher content of tars and asphaltenes in the feedstock allowed to increase the dynamic viscosity of bitumen, which predicts its better resistance to shear loads during exploitation in the asphalt-concrete mixture.

The results obtained made it possible to make a reasonable choice of the parameters of the tubular reactors, combined with the vacuum unit of the bitumen facility, and to obtain road binders in full compliance with modern requirements of regulatory and technical documentation.

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Application thermodestruction processes in the preparation of the waxy oil to pipeline transport 11-15

Keywords: high-viscosity and high-oil, pipeline transport, oil preparation for transportation, methods of preparation.

Abstract. In connection with the development of oil fields containing significant amounts of paraffins, the creation of technologically and cost-effective methods of their preparation for transportation through the pipeline is an urgent task. Among the traditional methods of pumping paraffin and heavy oils the most promising is their mixing with organic solvents, gas condensate or low-viscosity oil or oil products. However, this does not exclude the loss of phase stability of the mixture, and as a consequence of precipitation, which leads to clogging of the pipeline. In addition, the need to build a special solvent pipeline parallel to the oil pipeline, which serves to feed the regenerated solvent in the opposite direction and the construction of mixing bases lead to an increase in capital costs. In the oil refining industry,

distillate fractions used to dilute the components of the boiler fuel are obtained at the plant itself at the visbreaking units of fuel oils and tars. It follows that the production of its own lightweight fraction through the use of thermal processes for processing high-paraffin oil and its supply for mixing with paraffin raw materials can be one of the effective ways to solve the problem of transportation of such oils. The paper proposes a method of reducing the viscosity of oil in field conditions by thermal destruction of paraffin-containing fractions of oil, which ensures its transformation into light hydrocarbon fractions, which will provide the possibility of oil transportation to the plant. The application of the method will reduce the need for light oil or condensate as a solvent, as well as enable the processing of high-paraffin oil at the refinery according to the traditional scheme.

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PETROCHEMISTRY

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Keywords: ESR spectroscopy, catalyst, dimerization, tetratriphenylphosphine nickel (0), bis-1,5-dicyclooctadiene nickel (0).

Abstract. The formation of paramagnetic Ni (I) complexes with square-planar structures under interaction of zerovalence nickel complexes with β-diketones and diethylaluminium chloride in benzene and toluene solvents are studied by ESR-spectroscopy. Magnetic resonance parameters of Ni (I) and their adducts with lower olefins (ethylene, propylene) are characterized. The catalytic properties of 1,5-cycloalkadienyl Ni (I) hexafluoroacetylacetonate complexes in the dioligomerization reaction of ethylene and propylene are investigated. It has been shown that, besides of hexafluoroacetylacetone Ni (I) complex other β-diketones complexes are not active or low active in the dimerization of ethylene (propylene) and require an organometallic activator. Studies of the effect of the nature of the transition metal azo- and azomethine complexes on their activity have shown, that the copper (II) compounds are not active, the Co (II) complexes exhibit a low and Ni (II) compounds high activity in the ethylene dimerization. The nature of the substituents in the organic part of the complexes has a noticeable effect in the discussion of their catalytic activity. Electron-donor substituents in azo complexes of Ni (II) increase the yield of butenes. In the case of azomethine complexes, the yield of hexenes and octenes increases. To stabilize the paramagnetic complexes of Ni (I), organophosphorus compounds (triphenylphosphine or 1,2-bis-diphenylphosphineethane) are added to the system. The reaction of the tetratriphenylphosphine complex of Ni (0) – Ni $(PPh_3)_4$ – with β-diketones is also accompanied by the formation of a paramagnetic metal-olefin complex of Ni (I). The nickel (I) – olefin complex with one phosphorus atom was identified by the EPR method. A scheme for the formation of Ni (I) – olefin complex and the dimerization of ethylene with its participation was proposed. The EPR spectroscopy method showed that the reaction of coordination of ethylene with a monovalent nickel complex is reversible character. We believe that the square-planar complexes of Ni (I) are active in the dimerization reaction of the lower olefins. The ones of that are more active, which are characterized by the lesser covalency of the M-L bond.

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Keywords: alkylation, benzene, ethanol, H-ultrasil, borum, selectivity.

Abstract. The effect of boron concentration on physicochemical and catalytic properties of H-ultrasyle in the benzene alkylation by ethanol in the temperature range from 300 to 350°C at the ideal displacement flow-through installation was studied. In the studied temperature range H-ultrasyle shows low selectivity for ethyl benzene (EB) that equal 43,5–50,3%. It has been confirmed that in the presence of H-ultrasyle the products of benzene alkylation by ethanol consist from toluene, EB, xylene, diethyl benzenes, triethyl benzenes and aromatic hydrocarbons C_{9+}. Distribution of reaction products points out also to intensive proceeding of side reactions – trans-alkylation of benzene, ethyl benzene and obtained products. The chemical modification of H-ultrasyle by boron bring to sharp decreasing of side products and promote the increasing of selectivity on ethyl benzene. On the sample containing 2,0% mass of boron

the temperature increasing from 350 up to 500°C bring to increasing of EB yield from 20,9 up to 36% mass and the increasing of selectivity on ethyl benzene from 54,5 up to 62%. The increasing of boron concentration in H-ultrasyle up to 5% mass sharp inhibits the proceeding of side reactions. On the samples containing 4 and 5% mass of boron the formation of not desirable products – m- and o-xylenes haven't been observed. The highest selectivity on EB (69,5%) was reached on the sample containing 4% mass of boron. It was shown that the chemical modification leads to change of the strength of acidic centers and micro porous structure of zeolite.

On the basis of adsorption investigations of water vapor, n-heptane and benzene have been confirmed that with the increasing of boron concentration in H-ultrasyle its sorption capacity on water vapor, n-heptane and benzene have been decreased. The increasing of boron concentration in H-ultrasyle up to 5% leads to decreasing of sorption capacity on n-C_7H_{16} from 0,164 up to 0,074 g/sm^3, and on benzene from 0,08 up to 0,055 g/sm^3. Obviously, as a result of the modification, a narrowing of the zeolite channels occurs.

It was shown that the change of activity and selectivity of ultrasyles modified with boron have been also promoted by change of concentration and strength of acidic centers. By the increasing of boron concentration up to 4% mass in the samples the concentration of strong acidic centers has been decreased from 528 up to 105 mcmol/g. The increasing of selectivity in formation of EB concern to the decreasing of strength and concentration of strong acidic centers and also sorption capacity as a result of H-ultrasyle modification by boron.

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MATHEMATICAL SIMULATION TECHNOLOGICAL PROCESS

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Pimenov Yu.M., Sereda V.A.

Automotive fuels' evaporation discharge process modeling under conditions of longterm storage **26-35**

Keywords: automotive fuels, evaporation discharge, storage, resemblance, modeling, experiment, integral estimate.

Abstract. The article presents the current issues of the chimmotology process modeling with regards to the automotive fuels' evaporation discharge under long-term storage conditions caused by the demand for composition (brandmark) interaction formalization, automotive fuels' properties and storage conditions, which produce an effect on storability during a long-term storage period of the fuels intended for the national needs.

The modeling of the automotive fuel evaporation discharge process under conditions of long-term storage is carried out on the basis of the common factors well-known in chimmotology and incorporates the construction of the structural and functional, physical and mathematical process models. The similarity parameters were suggested for the evaporation discharge process conditions intended for the tanks and physical models.

The physical model is performed in a form of a pilot unit incorporating the design models of tanks, fuel mass measuring devices, fuel supply packages, registration, operation and control panels, parameter analysis and visualization devices. The construction of the pilot unit ensures an independent variation of the factor values for evaporation discharge process according to the test plan that allows evaluating the separate and joint effect of the factors onto the fuel evaporation discharge.

On the basis of the mathematical modeling of the fuel evaporation discharge process as per the results of the active experiment of the response surface investigation and the fuel testing in the physical model, the authors have obtained the common factors of interconnection between the fuel composition, its storage conditions and the results of the fuel evaporation discharge process submitted as multi-factor non-linear regression models.

It is suggested to characterize the fuel's potential property for evaporative losses as a new aggregated indicator (an integral estimate) of evaporation discharge and to evaluate a relative degree of "superiority" of one fuel over another as per evaporative criterion, which is a ratio of an integral estimate of evaporation of any fuel type under testing to the integral estimate of the standard of comparison.

The modeling allows studying the history of fuel evaporation discharge in tanks and obtaining the quantitative and predictive assessment of fuel evaporation losses focused on the fuel composition variety and conditions of their long-term storage in the land storage tanks.

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QUALITY: documents and comments

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Keywords: automobile and aviation gasoline, diesel, marine and boiler fuels, standards.

Abstract. The article discusses changes made to interstate fuel standards, developed in connection with changes in international fuel standards and test methods. Changes are made to GOST 32513-2013 for motor gasoline, GOST 1012-2013 for aviation gasoline, GOST 32511-2013 for diesel fuel EURO, GOST 32510-2013 for marine fuels and GOST 10585 for fuel oil.

For motor gasolines a change in the requirements for their evaporation at narrower intervals to meet the requirements of the TS CU is introduced. A breakdown of the norms has been introduced for the indicator «Saturated vapor pressure», which makes it possible to classify gasoline to a specific class of evaporation in order to determine its seasonal use.

For EURO diesel fuels, a warranty period of storage is established and test methods are specified. In accordance with the change, the warranty period of storage is 1 year - for fuels without WAFI and 6 months for fuels made with the addition of WAFI additives. Because the methyl esters of fatty acids are not applied on the territory of the Russian Federation, additional requirements for methyl esters of fatty acids and other biocomponents in the change to GOST are not considered. Discussed were test methods for quality indicators not accepted by the interstate standard, such as simulated distillation for determining fractional composition, method for determining ignition delay and combustion delay using constant volume direct injection chamber for determining cetane number, as well as additional requirements for plugging filter at positive temperatures, existing in the English EN 590, and a method that determines the tendency to clog a cold filter required when using bio-components in the composition of the diesel fuel.

In the standard for marine fuels, the addition of a table of technical requirements with 2 quality indicators for evaluating low-temperature properties: cloud point and limiting filterability temperature, which will allow consumers to navigate relative to the temperature of use of marine fuel.

The change to the standard for fuel oil refers to the actualization of test methods and the addition of GOST to the section «Precision of test methods».

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ANALYTIC METHODS FOR OIL and PETROLEUM PRODUCTS

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Keywords: automatic analyzer, petroleum, petroleum products, cold filter plugging point, gasoil, heating oil, flash point (Pensky-Martens).

Abstract. The Techno company developed an automatic analyzer to determine the fractional composition (DIST-A1) 2 years ago. DIST-A1 is a great success in the market of the Russian Federation. At the moment, another 2 devices for determining the quality of petroleum products have been developed and tested - an automatic analyzer of the limiting temperature of filterability (PTF) and an automatic analyzer of flash temperature in a closed crucible (Pensky-Martens). We created analyzers using the experience of foreign manufacturers such as Anton Paar Gmbh, ISL, PAC, Orbis BV, Normalab Analis, Herzog, Tanaka Scientific.

On the territory of the Russian Federation, the ambient air temperature is in the range from (-64.4 to + 45.2)°C. The fuel must operate at these temperatures – pump through the filter at low temperatures and comply with safety requirements (flash point) at high temperatures. The limiting filterability temperature is the main indicator of fuel properties at low temperatures. Its definition is long and laborious, so process automation is very important. The flash point in a closed crucible is the main indicator, together with the indicator of the fractional composition of petroleum products (at atmospheric pressure) in determining the safety of fuel use. Its automatic detection significantly reduces time and increases the accuracy of the analysis. Therefore, domestic base improvement of testing equipment is very important for simplification

and automation of tests. It is particularly important that domestic analyzers are not only highly competitive with foreign counterparts in terms of metrological characteristics, but also exceed them for a number of factors. The paper contains test results of the new Russian automatic analyzer CFPP-A1, PMA-A1 using commercial oil products and certified reference materials as well as metrological characteristics of the analyzer that were received from tests in comparison with the requirements of effective normative documents by the test method.

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