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CHANGE OF COALS SUPRAMOLECULAR STRUCTURE DURING ACTIVATION BY POTASSIUM HYDROXIDE

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The aim of the work is to study the effect of coal rank (CR) on changes in coal supramolecular structure during transformation into activated carbons (ACs) under potassium hydroxide activation. The main criterion selected is the carbon content being varied in the interval $C^{daf}=70,4-95,6\%$.

Alkaline treatment of coal was performed by impregnation with the same ratio of KOH/coal (1 g/g). ACs were prepared in argon atmosphere by thermoprogrammed heating (4 deg/min) to 800 °C, isothermal exposure for 1 h, cooling, washing from alkali and drying. The yields (29,5-82,8 %) and the specific surface area of ACs (323-1547 m²/g) were determined. Diffractograms (Bruker D8 diffractometer) of initial coal and ACs were obtained. They were deconvoluted into Gaussians corresponding to the γ -band and (002) and (100) reflexes.

The following parameters of the supramolecular structure of aggregates of intraframework polyarene fragments (crystallites) were determined: the interlayer distance d_{002} , height L_c , diameter L_a , volume V_{cr} , number of polyarene layers $N=(L_c/d_{002})+1$ and intensity I_{002} of the (002) reflection. By comparing these characteristics for coal and ACs, changes in the supramolecular structure during alkaline activation are estimated.

It has been established that during the conversion of coals to ACs, the distance d_{002} in crystallites increases (by 5–13), and the height of crystallites L_c decreases (by 6–32) due to the fact that KOH makes the supramolecular structuring complex. For ACs, the d_{002} dependence on C^{daf} shows a plateau with C^{daf} 80-90 % ($d_{002}=0.430\pm 0,006$ nm) and a sharp decrease in the region of $C^{daf}=90,0-95,6\%$.

The dependence of L_c on C^{daf} is characterized by the L_c decrease in the range of $C^{daf}=70-83\%$ and a subsequent increase in the transition to anthracite. Under conditions of alkaline activation (combined action of heat and KOH), ACs crystallites are more spatially disordered in comparison with coals crystallites. When transforming coals into ACs, the disordering degree was proposed to estimate by the parameter Δd_{002} – the ratio of the difference between the interlayer distances of the AC and coal to the d_{002} value of coal. It is extremely dependent on CR: it decreases on going from lignite to bituminous coal (with C^{daf} growth from 70 to 80 %), increases to a maximum for coal with $C^{daf}=90\pm 1\%$ and then decreases to anthracite. The average diameter L_a of ACs crystallites significantly (15-2,4 times) exceeds the L_a values of coals. The L_a values of ACs changes along a curve with a minimum for coals with $C^{daf}=80-82\%$.

Hydroxide KOH does not prevent the growth of polyarene layers due to thermally initiated condensation reactions. It was concluded that during the ACs formation, supramolecular structural fragments are formed and include “extended” polyarene (graphene) layers. They are aggregated in 2-4 layers into spatially disordered crystallites and are connected by macromolecular chains into a three-dimensional porous framework.

Keywords: coal, alkaline activation, activated carbon, supramolecular structure, crystallites, polyarene fragments, condensation, graphene layers, interlayer distances.

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PRODUCTION OF HIGH-QUALITY COKE FROM THE COAL BLENDS WITH INCREASED CONTENT OF GAS COALS USING THE METHOD OF PARTIAL BRICKETING OF THE BLENDS.

Report 1. The study of the possibility of using as a binder for briquetting hydrocarbon products of coke production

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The briquettes were produced on the basis of the commercial coals blend, in which 5 and 10 % of coals grade K and OS were replaced with the same amount of gas coals. Thus, the content of gas coals in the experimental coal blends was 30 and 35 %, respectively.

As binders for briquetting, pitch screenings, coal tar, tar and oil from the biochemical installation, acidic tar from the trapping shop, as well as their blends in different ratios were used.

Along with the assessment of technological and chemical properties, an assessment of the physicochemical properties of hydrocarbon products used as additives was made. Recommendations for the preliminary preparation of additives before being fed into the briquetting blends are given.

Briquetting was subjected to 20 % of the experimental mixture.

The compaction pressure in the laboratory press was 20 MPa. The briquette density was 1019 kg / m³.

The most durable briquettes were obtained when using as a binder mixture of coal tar sludge and coal tar. The number of undestructed briquettes after dropping twice from a height of 1.5 m amounted to 89.6 %.

It is shown that the used hydrocarbon additives in some cases change the technological properties of partially briquetted blends, but not so much as the change the properties of coke obtained from them.

It is shown that obtaining sufficiently strong briquettes is possible under the accepted briquetting conditions (P = 20 MPa) when using acid binder and coal tar sludge with coal tar as a binder mixture.

Resins and oils of biochemical plants are less effective as a binder than coal tar.

The use of pitch screenings as a binder is impractical due to the fact that the briquettes obtained with its participation are completely destroyed already at the first dumping.

The following options for additives in the briquetted part of the coal blend were developed and the quantity of such additives in percent was determined:

- the pressing pressure in the laboratory press was 20 MPa, the density of briquettes was 1019 kg/m³;
- the most durable briquettes are obtained using a blend of coal tar sludge and coal tar as a binder;
- the number of undestructed briquettes after dropping twice from a height of 1,5 m is equal to 89,6 %.

Keywords: hydrocarbon products of coke production, coal concentrates, coal blend, briquetting, strength of briquettes.

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APPLICATION OF COUMARONE-INDENE RESINS FRACTION FOR ADHESIVE ADDITION TO OIL ROAD BITUMES

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The article is devoted to the study of the possibility of using of the indene-coumarone resin with methacrylate fragments as a polymeric additive to petroleum road bitumen.

As the raw material for the preparation of indene-coumarone resin with methylacrylate fragments the indene-coumarone fraction has been selected, obtained from PJSC "Zaporizhkoks" (Ukraine). This material contained 6.73 % styrene by weight, 5.75 % wt. of coumarone and 44.45 % wt. indene. To obtain modified bitumen, oxidized bitumen was produced by PJSC "Transnational Financial and Industrial Oil Company Ukratnafta" (Ukraine, Kremenchuk), which had the following characteristics: softening temperature - 46 ° C, penetration - 70 • 10⁻⁴ m, elongation - 63 • 10⁻² m, adhesion to glass - 33 %.

It was shown that coumarone-indene fraction with methyl methacrylate on radical cooligomerization using 2-methyl-propionitrile as the initiator, forms coumarone-indene resins with methacrylic fragments. The structure of the synthesized substance has been confirmed by infrared spectroscopy. The effect has been investigated of composition of coumarone-indene resins with methacrylic fragments, the temperature and reaction time on the yield of polymer modified bitumen. It has been installed the optimal conditions of preparation of polymer modified bitumen and proposed the using of resins as the adhesive additive for petroleum road bitumen.

On the basis of experimental studies, it can be concluded that the best adhesion results are achieved with an coumarone-indene resin with methyl methacrylate content in bitumen of 3 wt % with the help of its heat treatment by temperature of 190 °C during 60 min. Under these conditions, the final mixture according to it softening point and penetration practically coincides with the characteristics of bitumen, which does not contain a polymer component, but has an increased adhesion and the elasticity. It has been concluded that the resin obtained from the indene-coumarone fraction with the addition of methyl methacrylate and 2-methyl-propionitrile can be used as an adhesive additive to petroleum road bitumen.

Keywords: coumarone-indene resins, coal tar, methacrylic fragments, bitumen, polymer-modified bitumen.

INFLUENCE OF THE AMOUNT OF CATALYST ON THE PROCESS OF RECEIVING MODIFIERS OF ROAD BITUMES FROM PHENOL FRACTION OF COAL TAR

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It has been shown, that traditional asphalt concrete based on unmodified bitumen is not able to provide the necessary physical and mechanical properties of road surfaces and their durability. Therefore, it is necessary to improve the quality of materials and the operational reliability of layers of road clothing. An effective way of accomplishing this task is to improve the structure and properties of bitumen by using inexpensive modifiers of various types. The Department of Chemical Technology of Petroleum and Gas Processing at Lviv Polytechnic National University has been conducting research into obtaining cheap and effective modifiers of petroleum bitumen from liquid coal coking products in recent years. Previous studies have shown that phenol-cresol-formaldehyde resin (PhCR-F), obtained from the phenolic fraction of coal tar and synthesized by the method of polycondensation of "crude" phenols with formaldehyde, is an effective modifier for road petroleum bitumen. However, the impact of technological factors on the process of PhCR-F obtaining has not been studied in terms of their further use as a modifier of road oil bitumen. This is precisely the purpose of the research, outlined in this article.

The effect has been investigated of the catalyst amount on the process of obtaining phenol-cresol-formaldehyde resin, which is used as a modifier of petroleum road bitumen. As a raw material in the process, the phenolic fraction of coal tar was used. By the method of polycondensation of "raw" phenols with formaldehyde (with different amounts of catalyst - concentrated hydrochloric acid), phenolic-cresol-formaldehyde resins of novolac type (PhCR-F) has been obtained. The oxidized petroleum bitumen has been modified by the obtained resins (at 190 ° C and a modifier content of 2.4 % per the mass of the mixture).

Modified oxidized petroleum bitumen was used to obtain the resulting resins. It has been found that the optimal concentration of the catalyst should be considered as 3 % by weight, since with such a catalyst amount high yield (94,3 % by mass per raw material) and optimal temperature of softening of the resin (110 °C) has been observed. Increase in catalyst content up to 6 % by mass per "raw" phenols during the obtaining PhCR-F, practically do not affect the characteristics of modified bitumen.

Keywords: phenol fraction, catalyst, phenol-cresol-formaldehyde resin, modified bitumes..

APPLICATION OF VACUUM DISTILLATION FOR OBTAINING A DISPERSION MEDIUM OF GREASES

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The article is devoted to the problem of plastic greases production at the base of the regenerated (utilising) materials.

It has been proved, that as the dispersion medium or base component occupies at least 80 % of the mass in the composition of grease, its properties largely determine the properties of the final product. This, in turn, determines the requirements for the quality of the base component. To date, the main component in the production of greases are distillate and residual oil fractions after selective purification from paraffin and tar-asphaltene substances. Due to the fact that these fractions are in demand in the production of lubricating oils and greases for various functional purposes and have a considerable cost, the search for a cheaper alternative that meets the requirements for quality level seems to be a very actual task.

Vacuum distillation, which can be used as an independent technologie, is known as a well-established process for the regeneration of used motor oils, but in most cases it is still the final stage of any technological scheme of regeneration. In this article the possibility of obtaining of a base component for greases from used motor oils of various natures with the help of vacuum regeneration in laboratory conditions is considered. In order to study the possibility of using of the obtained samples as a dispersion medium of plastic greases, some physicochemical quality indicators were determined for them, which are comparable with the quality indicators of distillate oil of selective purification of grade

I-40A. This industrial oil is often used as a base component in the production of lubricating oils and plastic greases. The best results, from the point of view of the study of low-temperature properties (viscosity index 127, pour point - 25 ° C) has been obtained by using waste engine oils on synthetic base.

Regeneration of used motor oils with the use of vacuum allows obtaining a base component for the production of greases, which, by its physico-chemical characteristics, is identical to the distillate oil of selective purification, brand I-40A.

By the value of the sulfate ash index, one can judge the absence of metal-containing additives in the regenerated oils, which is fully consistent with industrial oil.

Keywords: used motor oil, grease, regeneration, vacuum, viscosity, viscosity index, basic component.

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DEVELOPMENT OF A DEVICE FOR PYROLYSIS OF CARBON-CONTAINING MATERIALS

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The aim of this work is to improve the structural and technological solutions for the development of a pyrolysis device for carbon-containing materials, that will ensure the durability and safety of maintenance of the main units of the installation. The described method of pyrolysis of carbon-containing materials, its implementation, which becomes available through the use of the developed device, will allow a creating of a highly efficient, environmentally friendly process for producing products of the required quality.

The problem is related to the nature protection and rational use of its resources. The main technical solutions for the efficient processing of wood waste are given. It is shown that pyrolysis is widely used in the modern industry for the processing of carbon raw materials. The disadvantages of the currently known structures have been analyzed and an advanced installation has been proposed that allows a highly efficient, environmentally friendly and safe process for the production of pyrolysis products of carbon-containing materials.

The developed device for pyrolysis of carbon-containing materials due to its structural implementation provides effective regulation of the temperature regime in the working chambers under the modes of drying and pyrolysis, the possibility of redistribution of heat between the chambers if necessary, which in turn ensures high quality of the resulting product.

Increasing / decreasing the flow of pyrolysis gases into the furnace, as well as increasing / decreasing the flow of flue gases through an isolated heat exchanger with the help of slides allows technologically and quickly adjust the volume of coolant supplied to the working chambers.

The role of preliminary preparation of raw carbon-containing materials has been shown. As a such preparation can be used any kind of handling, carried out before loading raw materials in the device, for example – grinding raw materials to the required size. Preferably, the pre-treatment of the raw material is carried out by drying before loading into the device using residual heat of the flue gas.

Keywords: device, wood waste, pyrolysis, carbon-containing materials, efficiency of process, ecological safety.

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