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Analysis of Treatment Methods of Coal Crude Benzene

E. S. MIKHAYLOVA¹ and Z. R. ISMAGILOV^{1,2}

¹Institute of Coal Chemistry and Material Science, Siberian Branch, Russian Academy of Sciences, Kemerovo, Russia

E-mail: MihaylovaES@iccms.sbras.ru

²Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia

E-mail: IsmagilovZR@iccms.sbras.ru

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Abstract

Organic synthesis products are widely used in the daily life beginning with medicinal, sweet preparations, lacs, dyes up to plastic, rubber, *etc.* Benzene that is amongst the top ten largest of the biggest substances of the chemical industry being highly liquid and high priced products. In this regard, this product is manufactured both at petrochemical enterprises and their by-product coking plants. Coal crude benzene contains unsaturated and sulphur compounds and it is required to preliminarily purify it from these undesirable impurities to obtain pure products from it. Even insignificant amounts of sulphur in benzene and toluene when using them in organic synthesis processes cause fast poisoning of the catalyst, and resinous substances formed resulting from polymerization of unsaturated compounds cover the catalyst surface and thereby deactivate it. Analysis of the published works on treatment methods of coal crude benzene from unsaturated and sulphur compounds was performed in the present review. The advantages and shortages of the known methods were considered. Prospects of catalytic ozone treatment of coal crude benzene were demonstrated.

Kew words: coal crude benzene, sulphuric acid refining, catalytic hydrorefining

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MAJOR TECHNOLOGIES OF BENZENE MANUFACTURE AND CONSUMPTION AREAS

Benzene is among top ten substances of the chemical industry being a highly liquid and expensive product and is widely used in organic synthesis [1-3].

Manufacturing benzene is based on processing of a variety of raw components: the product of catalytic reforming, pyrolysis gasoline, vapour-phase cracking, and crude benzene of by-product coke plants (Fig. 1) [4].

Depending on preparation and destination technology, the following benzene grades are distinguished: petroleum and high purity coal, for synthesis, highest, first, for nitration, technical, crude [5].

Global demand for benzene is currently over 40 million tons a year and its major volume (over 95 %) is manufactured from petrochemical raw materials, as a rule, using hydrofining technology. At the same time, four plants operate on coal-tar raw material in Europe (Germany, Poland, Czechia, and Belgium). The world leaders in manufacturing benzene are Exxon Mobil Chemical, Dow Chemical, and Shell Chemical companies.

Russian processing companies produced in 2015 approximately 1.38 million tons of benzene, herewith, the proportion of coal benzene reached 25 % (Fig. 2).

According to research, manufacturing benzene in Russia increased by 5 % from 2010 to 2014. It is noteworthy, annual production volumes of benzene in this period reached 1073-1214 t. An increase of production volumes in 2015 was 13.8 % [6].

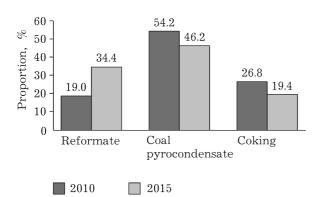


Fig. 1. Sources of aromatic hydrocarbons in the world.

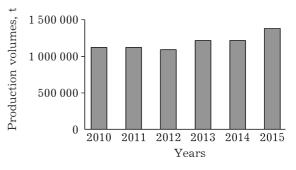


Fig. 2. Dynamics of manufacturing benzene in Russia.

The following JSCs are the major producers of coal benzene in Russia: Altay-Koks (45 thousand t), Severstal', Koks, Kuznetsk Metallurgical Combine, West Siberian Metallurgical Complex (80 thousand t), Novolipetsk Metallurgical Combine (400 thousand t), Mechel and Magnitogorsk Metallurgical Combine (Fig. 3).

Over 95 % benzene produced in Russia is consumed inside of the country. Finland, mainly buying crude (impure) benzene from metallurgical companies, is the largest importer of Russia Benzene. Russia annually imports almost 15 thousand tons of benzene (mainly from the Ukraine and Kazakhstan), which is less than 2 % from production volumes (Fig. 4) [2].

It is expected that the annual demand for benzene will increase for almost 4 %, since the market of the final products, such as polystyrene, polycarbonates, phenol resins and nylon is quickly developed [3]. Average prices of producers for benzene increased by 31.8 % over a period of 2011-2014: from 23365.4 to 30.7963 rub./t. The peak increase of average prices by producers was registered in 2013 and was 15.1 %. The expected level of manufacturing benzene in Russia reaches 1.3 million t in 2016, including by-product coke – about 140 thousand t, and consumption – 1.19 million t.

Crude coal benzene is required to preliminarily purify from unsaturated and sulphur compounds, since even insignificant sulphur impurities in benzene and toluene used in organic synthesis processes cause fast poisoning of a catalyst, and resinous substances formed as a result of polymerization of unsaturated compounds coat the catalyst surface and deactivate it.

The present review is devoted to analysis of the known purification methods of coal crude

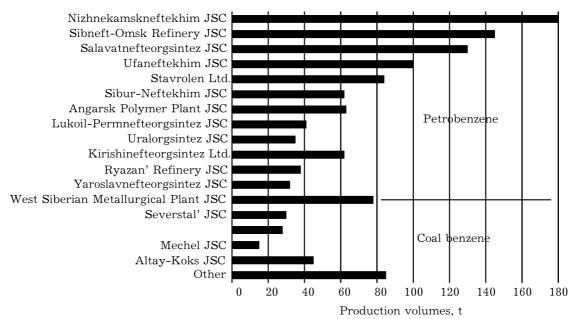


Fig. 3. Manufacturing benzene in Russia.

benzene. An opportunity to use its catalytic ozone treatment was demonstrated.

Composition and properties of coal crude benzene

Coal crude benzene is a mixture of aromatic hydrocarbons, mainly benzene (55–57 %), toluene (10–18 %), xylene (2.5–6.0 %), trimethylbenzenes and ethyltoluenes (1.0–2.0 %), unsaturated compounds (cyclopentadiene, styrene, indene in total, 7–10 %). Sulphur compounds (carbon bisulphide, thiophene), saturated hydrocarbons, phe-

nol, pyridine enter into the composition of coal crude benzene as admixtures [4, 5].

It is isolated from coke oven gas through adsorption at atmospheric pressure by scrubbing oils of coal or oil origin followed by evaporation with live steam and distillation with isolating the product with the end boiling point of 200 °C. It presents a transparent liquid from the light colour to dark brown, does not contain suspended particles, with the smell of hydrocarbons. The boiling point is 150-200 °C, the freezing point is from -20 to -25 °C, the density at 20 °C is 0.9 kg/dm³[7].

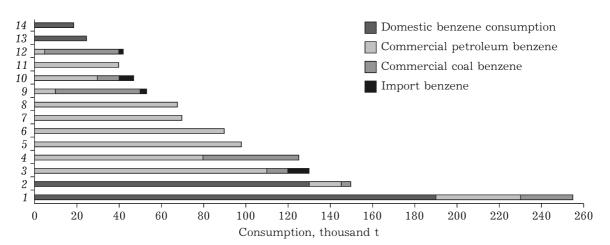


Fig. 4. Benzene consumption in Russia: 1 – Nizhnekamskneftekhim JSC, 2 – Salavatnefteorgsintez JSC, 3 – Kuybyshevazot JSC; 4 – Kemerovoazot JSC; 5 – Sibur-Perm JSC; 6 – Ufaorgsintez JSC; 7 – Shchekinazot JSC; 8 – Omsk Kauchuk JSC; 9 – Samaraorgsintez JSC; 10 – Orgsintez JSC (Kazan'); 11 – Saratovorgsintez Ltd.; 12 – Promsintez JSC (Chapaevsk); 13 – Angar, Rinko-Yukos Co.; 14 – Kirishinefteorgsintez Ltd.

The yield of coal crude benzene at coking coals is varied within 0.8–1.1 % per initial anhydrous coal and on average is about 1 %. According to the yield and composition, coal crude benzene obtainable at various plants is almost identical, which is driven by uniformity of instrumentation of the coking process and high end temperature of pyrolysis in a coking chamber. Minor changes in the composition and yield of crude benzene are due to the nature of coked coals, the temperature mode of coking and the design of coking furnaces.

Effect of benzene and its derivatives on the environment

The major sources of the anthropogenic impact on the atmospheric air, water and soil resources are enterprises that perform extraction and processing of hard coal. By-product coke plants send to dumps significant amounts of sour tar formed when processing of coal crude benzene, which leads to pollution of the environment and degradation (destruction) of ecological systems. For this reason, development of alternative and ecological methods of low-tonnage treatment coal crude benzene is of actual relevance.

METHODS OF TREATMENT CRUDE BENZENE

Processing of coal crude benzene suggests the isolation from it of pure aromatic hydrocarbons: benzene, toluene, a solvent (a mixture of di- and trimethylbenzenes) that is a BTX fraction, as well as indene-coumarone fraction (ICF). To prepare pure products from benzene its preliminary treatment from unsaturated and sulphur compounds that exert negative effects in organic synthesis processes is required [8].

In this regard, any processing scheme includes preliminary preparation stages that ensure the removal until the required depth of admixtures of sulphurous unsaturated and saturated hydrocarbons. Quality requirements of pure products of benzene series are regulated by State Standard GOST 84448-78.

Sulphuric acid refining

Analysis of methods for isolating and treatment coal benzene demonstrates that brand new processes have not been developed, and perfection of the sulphuric acid method is proposed to perform by treatment narrow fractions and its addition by the stage of extractive rectification to isolate thiophene concentrates and nonaromatic hydrocarbons [9, 10]. Implementing these proposals allowed increasing the efficiency of the sulphuric acid method [11, 12]. Sour tar is also proposed to use for treatment crude benzene [13]. Methods for treatment crude benzene based on using acid agents are widely known. Crude benzene containing thiophene and unsaturated compounds is treated with sulphuric acid in the presence of phenols and aliphatic aldehydes, the content of which in the acid layer is 5–15 % [14].

The sulphuric acid method of treatment coal crude benzene dominates so far in the by-product-coking industry. Difficulties with the preparation of deep treatment grades of benzene and waste utilization emerged in the middle of the last century were overcome due to implementation of continuous cleaning using static mixers [15] and the application of two-stage treatment sulphuric acid with additives of unsaturated compounds instead of treatment oleum [16], the development of recycling technologies of acid tar and still bottoms as air-oil emulsions supplied to a batch [17]. Currently, the sulphuric acid refining is applied in two options for treatment a BTX fraction [18] and when preparing benzene for synthesis [19].

Typically, crude benzene is preliminarily separated for the light part that boils out before 150 °C and the residue (heavy benzene). After separation of low-boiling hydrocarbons, the presence of which complicates treatment, the residue that is a fraction of benzene-toluene-xylenesolvent (BTXS) is directed to sulphuric acid refining. Treatment is performed in a continuous process in the system of static mixers (one option is vapour mixers). Sulphuric acid in this process acts as a catalyst. The consumption of concentrated sulphuric acid reaches 70 kg/t of raw materials.

The purified fraction after separation from the spent acid, acid tar, neutralization, and steam stripping is separated for marketable products: benzene, toluene, a mixture of xylenes and an aromatic solvent that is a solvent. Herewith, benzene meets market requirements for nitration. To increase the depth of treatment from thiophene benzene is subjected to repeated treatment with sulphuric acid with additives of unsaturated compounds and extracting rectification to decrease the content of saturated hydrocarbon impurities.

The total losses during treatment are usually 3-5 %. The yield of clean products under operational conditions is 91-93 % from the amount of benzene distilled of before 180 °C, which is driven by significant losses during processing the head fraction.

Excessive losses of clean products, the formation of production wastes as sour tar and the preparation of spent (regenerable) acid, the use of which for the production of ammonium sulphate is difficult, are referred to disadvantages of sulphuric acid refining [20].

Catalytic hydrorefining

Catalytic hydrogenation that, alongside with deep treatment from sulphur and unsaturated compounds, ensures deep removal of hydrocarbons is one of the methods of treatment coal crude benzene.

Hydrogenation treatment methods are based on hydrogenation reactions of sulphur and unsaturated compounds admixtures to gaseous or volatile compounds separated from benzene hydrocarbons by simple methods. Treatment of benzene hydrocarbons in the presence of hydrogen in the gas phase over a catalyst is performed under pressure. Hydrogen-containing gases, alongside with hydrogen, are used as a hydrogenation agent, in particular, coke-oven gas with a hydrogen content of no less than 60 % – in the by-product coking industry. Process conditions (temperature, pressure, hydrogen/raw materials molar ratio, contact time, catalyst type) are selected in such a way to ensure almost entirely hydrogenolysis of sulphur, unsaturated, oxygen- and nitrogen-containing impurities and exclude the course of hydrogenation reactions of aromatic hydrocarbons. Hydrogen is mainly consumed for destructive hydrogenation of thiophene and carbon disulphide and hydrogenation of cyclopentadiene and styrene. Practically, amounts of the consumed hydrogen-containing gas and the gas discharged into the fuel system are approximately equal

(150–180 m³/t of raw materials). The waste gas is depleted in hydrogen from 58-60 to 48-50 vol. % and enriched in methane, butane, ethane, water vapours, hydrogen sulphide.

A plenty of options of catalytic hydrorefining coal crude benzene is known. The most common from them is medium temperature (350-380 °C) hydrorefining that was performed in the USSR as early as 1968, which ensures the preparation of benzene with a content of thiophene of 0.0001-0.0004 % and the crystallization temperature of 530-535 °C [21]. A method for hydrorefining at 250-400 °C and 25-60 atm pressure in the presence of a catalyst containing 0.3 mass % Pd over Al₂O₃ is known [22]. The method requires complex instrumental design and use of costly catalysts, and therefore, is uneconomical. Other technological solutions that allow obtaining benzene by hydrorefining without involving additional technologies are also known: decreasing of pressure to 10 atm at 480-500 °C [23, 24], using zeolite-containing catalyst at 450-480 °C at the second stage [25] or at 475–480 °C using mixtures of crude benzene/naphthalene fraction as raw materials for hydrorefining [26].

A reduction in the content of impurities, the amount of which and thiophene increases in the hydrorefining process up to a level of the required norm for high-grade benzene after purification was reached with increasing a temperature to 400 $^{\circ}$ C and using extractive rectification at the stage of isolation of benzene [27].

The process in a high-temperature hydrorefining installation is carried out over an alumocobalt-molybdenum catalyst under 4 MPa pressure and a temperature above 550 °C. This creates the conditions for hydrocracking of saturated hydrocarbons, and consequently, for improving the quality of benzene and increasing its yield to 98 % [20, 28–35].

To obtain benzene products not containing saturated hydrocarbons combination of catalytic hydrorefining with extractive rectification is foreseen [36].

There are numerous works on developing hydrorefining catalysts. For example, a series of works [37–42] is devoted to the development of platinum catalysts for hydrodesulphurization.

Hydrogenation treatment methods allow minimizing the content of sulphur, unsaturat-

ed impurities, and in a number of modifications of the process – and saturated compounds, and obtaining high quality products almost without residuals. Disadvantages of the methods are related to high capital costs because of the need to conduct operations under pressures up to 40 atm at high temperatures (to 400 °C) and use hydrogen or purified hydrogen-containing gases. In this regard, process benefits are better displayed for large centralized installations.

Physicochemical treatment methods

The following methods refer to physical methods: rectification (azeotropic), crystallization [45], adsorption (chemisorption) [46], treatment with anhydrous aluminium chloride and its complexes at 35-80 °C [47], treatment with gaseous or liquid hydrogen fluoride at increased or normal pressures, boron trifluoride or its complexes [48], gas chlorine treatment under anhydrous conditions [49, 50], oxidative treatment with active oxygen, hydrogen peroxide or electrochemical oxidation over an anode [51, 52], over a skeletal nickel catalyst [53], treatment with mercury [54], sulphuryl chloride in the presence of pyridine or its derivatives [55], extraction with phenylacetonitrile [56], treatment with sodium or potassium metal or their alloys at increased temperatures and pressures [57].

The physicochemical methods turned out unsuitable for separation, since thiophene and benzene form mixed crystals [59]. The reagents proposed for the chemical treatment do not ensure the required treatment depth; processes are notable for duration and multiple repetitions of treatment operations and therefore did not find industrial applications.

Physicochemical methods make up another group of techniques, the base of which is the principle of the chemical impact for thiophene followed by physical separation of benzene and products of thiophene rectification. The vast number of works related to physicochemical methods is devoted to methods of treatment for benzene from saturated and heteroatomic hydrocarbons by extractive rectification and liquid extraction techniques [59].

Use of oxidative methods

There is a thorough research in the area of developing non-traditional desulphurization processes. Since the composition of undesirable petroleum and coal liquid products is similar, the regularities obtained [60] are advisable to consider when developing ozonolysis technology of coal crude benzene.

Currently, many methods for oxidative desulphurization of petroleum products that suggest their direct treatment by oxidation and subsequent extraction or adsorption isolation of polar oxidation products (sulphones and sulphoxides) or their thermal decomposition to sulphur dioxide and a hydrocarbon are known [61–63].

Oxidation of sulphur compounds of oil fractions by hydrogen peroxide and alkyl hydroperoxides was considered in works [64–74] using various catalysts: Mo, V and W compounds, organic acids, *etc.* Despite a high treatment degree from sulphur compounds, these processes have not been technically applied in industry because of a high cost of oxidants and the formation of stable water-oil emulsions.

Presently, methods of desulphurization of oil products have been proposed using ionic liquids containing Cu (I) and Ag (I) ions [64–75]. Owing to the formation of π -complexes of Cu and Ag ions with thiophene derivatives, adsorption of ions and subsequent regeneration of ionic liquids by low molecular mass paraffinic hydrocarbons happen. Combination of this method with oxidation in the presence of hydrogen peroxide allows removing from a mixture (oil products) to 99 mass % of sulphur; however, lack of large-tonnage productions of ionic liquids hinders its application.

Methods of deep treatment of diesel fuels from total sulphur are known. Thus, deep desulphurization in work [64] was reached due to combination of electrochemical catalytic and liquid-phase plasma oxidation in the presence of oxygen at 85 °C with extraction of sulphur oxidation products.

Oxidation methods of black oil fuel with air oxygen are known, with an increase in the yield of light low sulphur distillates during subsequent cracking of the oxidation reaction mixture [76–81]. However, the oxidation process is performed at a high temperature (450 °C) and increased

pressure, which is unsafe due to the danger of ignition of oil products.

Promising research on desulphurization was performed using ozonation of oil products. This oxidation method is based on selective electrophilic addition of ozone to sulphur compounds and polycyclic arenes entering into the composition of fuel fractions [64, 82]. The method allows desulphurization heavy oil fractions, destroying condensed sulphur compounds and polyarene structures without using catalysts and hydrogen-containing gas [64, 83–90]. Research was related to extraction of oxidized sulphur compounds using extraction and thermal methods of their removal [91–97].

CATALYTIC OZONE TREATMENT OF COAL CRUDE BENZENE

Reaction of hydrocarbons with ozone

Works [62, 83, 84, 88, and 98] demonstrate an opportunity of a significant increase in the yield of distillate fractions from oils and natural bitumens, as well as from brown coal liquefaction products at relatively low-temperature thermal destruction initiated by ozonides and sulphoxides.

Two mechanisms of chemical transformations are probable during ozonation of organic substances: electrophilic addition of ozone at π -bonds in molecules of unsaturated compounds or reactions proceeding by the radical-chain mechanism. The probability of the availability of the both reactions types during ozonation of crude benzene is almost the same [99].

Ozone is able to interact with any organic compounds either entering with them into electrophilic addition or radical-chain reactions.

Electrophilic addition reactions. Addition reactions of ozone at π -bonds in molecules of unsaturated and aromatic hydrocarbons and heteroorganic compounds are specific and most important in practical terms.

Ozone in unsaturated compounds is added to the O-C bond with the formation of ozonides that are easily destroyed during heating or under the action of chemical reactants. This enables to sort of cut the hydrocarbon skeleton along the place of the double bond. Ozonides are unstable and already at room temperature, break up into two fragments, one of which contains the carbonyl group, the second one – a bipolar ion. The formation of the end products happens resulting from connection of fragments after a change in their mutual orientation and during various transformations of the bipolar ion [100].

Typically, other functional groups react slower than C=C bonds. Reacting with ozone, aromatic compounds also form ozonides [101, 102]. Benzene reacts with difficulty, since the formation of intermediate and final compounds is related to the violation of the π -conjugated system and requires significant energy costs (in an inert medium, $K = 0.06 \text{ L/(mol } \cdot \text{s})$). As a result, saturated ozonides that decompose under the action of temperature with the formation of glyoxalic acid are the final product.

Oxidative radical-chain reaction. All aromatic hydrocarbons and heteroatomic compounds containing unsaturated fragments in molecules may be subjected to radical-chain oxidative rearrangements during treatment with ozone/oxygen mixtures. Ozone molecules act as an oxidizing agent, and salts initiate chain reactions. As a result, various carboxylic acids, carbonyl compounds, alcohols and peroxides are formed. The attack of free radicals in oxidative processes may be oriented at any C-H bonds in saturated fragments of molecules. As a result, hydrogen atoms split off and appropriate peroxide radicals are formed. Decay of the latter contributes to generation of new alkyl, alkoxyl and other radicals that continue the development of the chain process, as well as of various molecular products. Hydrogen separation from the initial molecule is the limiting step of the oxidation process.

Oxidation at primary carbon atoms in saturated fragments of molecules proceeds extremely slowly (oxidation rates of C_5-C_{14} *n*-alkanes change from 0.015 to 0.036 L/(mol \cdot s)). The oxidation rate of methyl groups increases abruptly, when they are bound directly with aromatic rings and increases symbatically to the number of such substituents (e. g., for toluene, $K = 0.17 \text{ L/(mol \cdot s)}$, and for hexamethylbenzene – 245 L/(mol \cdot s). During splitting of the C–C π -bond, aromatic acids (derivatives of benzoic, naphthenic acids, and etc.) and aliphatic or alicyclic acids and aldehydes are formed in the carbon chain.

Oxidation of alcohols and ethers proceeds with breaking the C-H bond and is accompanied by the formation of mixtures of aldehydes, ketones, acids, esters and peroxides.

Reaction with sulphur compounds. Work [99] describes reactions with unsaturated sulphides, disulphides and polysulphides. It was demonstrated that sulphides reacted easily with ozone (rate constant $K = (1.5-1.9) \cdot 10^3 \text{ L/mol} \cdot \text{s}$)). It is noteworthy that the rate constant for the interaction of ozone and sulphides is comparable with that for phenols $(1 \cdot 10^3 L/(mol \cdot s))$ and significantly exceeds the rate constant of oxidation of the CH₂ group in alkyl substituents, as well as the rate constant of oxidation of aromatic hydrocarbons $(0.06-0.5 \text{ L/(mol \cdot s)})$. Appropriately, one can suggest that the reaction mainly proceeds at the sulphur atom. The major product of the first reaction stage is sulphoxide that further can be oxidized to sulphone but with a significantly (in 50-100 times) lower rate.

Based on the results of work [103], a reaction scheme, at the first stage of which an electron transfer from the sulphur atom to the ozone molecule occurs and an ion pair is formed, was proposed. An ion pair acts as a primary product in reactions of sulphides with hydroperoxides. The final products are sulphoxides and sulphones in a solution saturated with oxygen [103–105].

According to data of works [106–115], ozone reacts with substances of the dibenzothiophenes series by the principle of electrophilic addition. Sulphoxides, sulphones and other oxidation products formed resulting from oxidation, as noted earlier, can be isolated using extraction or thermal decomposition (due to low thermal stability) with the release of sulphur dioxide [116, 117].

Thus, the following major reactions characterizing ozone depletion potential can be distinguished:

1. Electrophilic reaction of ozone with C=C bonds of unsaturated compounds ($K = 5 \cdot 10^5$ L/(mol \cdot s)).

2. Electrophilic reaction of ozone with C=C bonds of benzene ($K = 0.06 \text{ L/(mol \cdot s)}$).

3. Radical oxidation reactions of alkyl substituents on aromatic rings ($K = 0.1-0.5 \text{ L/(mol \cdot s)}$).

4. Interaction of ozone with compounds containing **S** heteroatoms (thiophene, sulphide groups, $K = 1 \cdot 10^3 \text{ L/(mol \cdot s)}$).

5. Considering the presence in benzene of a mixture of saturated, aromatic, alkylated and

heteroaromatic hydrocarbons, as well as sulphur-containing compounds, one needs to select such oxidation conditions, at which the ozonolysis reaction will not affect the major component that is benzene.

Catalytic ozonolysis

Based on carried out analysis of existing methods for treatment coal crude benzene and the fact that the composition of undesirable impurities in target products of oil processing and by-product cake industries is approximately the same, ozonation may become one of the possible methods for treatment coal crude benzene.

In this regard, works [118, 119] studied the effect of ozonolysis for a change in component composition of coal crude benzene. Analysis of the composition of ozonation products suggests that reactions of ozone with crude benzene components (benzene, toluene, and xylene) mainly proceed without destruction of aromatic cycles. Radical reactions proceeding on the π -atom to the aromatic cycle without disturbing the cycle, moreover, their probability increases with a rise in the number of substituents. Unsaturated hydrocarbons react with ozone by the electrophilic addition mechanism to the C=C bond with the formation of mono- and dicarboxylic aliphatic acids and aldehydes or turn into polymer-like cross-linked structures. Sulphur compounds react with ozone forming SO2 and sulphoxides. The use of preliminary followed by adsorption refining even without additional distillation contributes to an increase of the content (approximately by 30 %) in crude benzene of the most valuable target component (benzene) and a decrease in the content of side products.

Works [120–122) demonstrated an opportunity to remove sulphur and unsaturated compounds by catalytic ozonolysis. Samples applied on Al_2O_3 containing separately magnesium chromite, platinum or palladium as active components were selected as catalysts. It was demonstrated that accumulation of carbon fragments happened during ozone catalytic desulphurization of benzene fractions that is due to adsorption of sulphur-containing molecules in the catalyst surface, as well as to the oxidation process of condensed hydrocarbon fragments of raw materials. Thermogravimetric analysis demonstrated that these products were removed from the catalyst surface in a temperature range of 200-400 °C. Herewith, according to X-ray structural analysis, the phase composition of catalysts during oxidation of benzene fractions with ozone-oxygen mixture did not change, therefore, a catalyst regeneration process allows restoring the catalyst activity and prolonging its operation time, which is especially relevant for processes with using catalysts based on expensive precious metals. The maximum removal degree of sulphur compounds is observed in the presence of applied magnesium chromite. The conversion level of sulphur compounds was 90 %. As a whole, the results demonstrated prospects for further studies.

CONCLUSION

Analysis of methods for treatment coal crude benzene from unsaturated and sulphur compounds proposed over recent years demonstrates that the improvement of existing sulphuric and catalytic hydrorefining technologies was the major research area.

There is active research in the area of the development of non-traditional desulphurization processes. Oxidation of impurities with ozone is one of the areas of petrochemistry. Since the composition of undesirable substances of oil and coal liquid products is similar, the regularities obtained should be considered when developing technologies for ozonolysis of coal crude benzene.

REFERENCES

- 1 URL: http://www.thyssenkrupp-industrial solutions, com/en/suche.html?query = aromatic + hydrocarbons + // (accessed April 20, 2017).
- 2 Obzor Rossiyskogo i Mirovogo Rynka Benzola. URL: http://www.rccgroup.ru (accessed April 20, 2017).
- 3 Obzor Rynka Benzola v SNG. URL: http:// www.marketing.rbc.ru// (accessed April 20, 2017).
- 4 Shelkov A. K. (Ed.), Spravochnik Koksokhimika, Metallurgiya, Moscow, vol. 3, 1966.
- 5 Titushkin V. A. and Frolovnin Yu. V., Koks Khim., 3 (2006) 43.
- 6 Rynok Benzola. Tekushchaya Situatsiya i Prognoz 2017–2021. URL: http://www.alto-group.ru (accessed April 20, 2017).
- 7 Kolyandr L. Ya., Ulavlivaniye i Pererabotka Khimicheskikh Produktov Koksovaniya, Metallurgizdat, Kharkov, 1962.

- 8 Kaufman A. A., Kharlampovich A. A., Tekhnologiya Koksokhimicheskogo Proizvodstva, VUKhIN-NKA, Yekaterinburg, 2005.
- 9 Korobchanskiy V. I., Koks Khim., 4 (1996) 33.
- 10 Zaretskiy M. I., Koks Khim., 9 (2002) 30.
- 11 Zaretskiy M. I., Koks Khim., 6 (2004) 20.
- 12 Rublevskiy V. N., Bylkov V. G., Ovchinnikova S. A., Chernyshev Yu. A., and Kovaleva N. I., Koks Khim., 2 (2004) 28.
- 13 RU Pat. No. 2119472 C1, 1998.
- 14 RU Pat. No. 7246412 C1/04, 1975.
- 15 Karlinskiy L. E., Levantovich I. A., Koks Khim., 5 (1956) 49.
- 16 USSR Inventor's Certificate No. 157675, 1963.
- 17 Yurkina L. P., Kern A. A., Pinchugov V. N., Akulov P. V., Vopr. Tekhnologii Ulavlivaniya i Pererabotki Produktov Koksovaniya (Treatises), Metallurgiya, Moscow, 1975, No. 4, p. 124.
- 18 Yanchitskiy V. V. and Mikhno S. I., Koks Khim., 7 (2002) 21.
- 19 Rubchevskiy V. N., Bylkov V. G., Ovchinnivova S. A., and Chernyshov Yu. A., Koks Khim., 3 (2004) 28.
- 20 Ma X. L., Sakanishi K. Y., Mochida I., Ind. Eng. Chem. Res., 33, 2 (1994) 218.
- 21 Sipovich S. Yu., Eru I. I., Orlov M. P., Koks Khim., 11 (1969) 26.
- 22 USSR Inventor's Certificate No. 1339696, 1983.
- 23 Karlinskiy L. E., El'bert E. I., Titushkin V. A., Smirnov V. K., Katsobashvili Ya. R., Koks Khim., 9 (1969) 29.
- 24 El'bert E. I., Titushkin V. A., Smirnov V. K., Koks Khim., 7 (1972) 35.
- 25 Dvinin V. A., Shakun A. N., Il'icheva L. F., Koks Khim., 3 (1987) 30.
- 26 Zamanov V. V., Krichko A. A., Ozerenko A. V., Frosin S. B., *Khim. Tv. Topl.*, 3 (2005) 67.
- 27 Kovalev E. T., Chernova P. A., Zhuravlev P. I., Koks Khim., 11 (2003) 21.
- 28 Houalla M., Broderick D. H., Sapre A. V., Nag N. K., Beer V. H. J. D., Gates B. C., Kwart H., J. Catal., 61, 2 (1980) 523.
- 29 Macaud M., Milenkovic A., Schulz E., Lemaire M., Vrinat M., J. Catal., 193, 2 (2000) 255.
- 30 Ma X. L., Sakanishi K., Mochida I., Ind. Eng. Chem. Res., 35, 8 (1996) 2487.
- 31 Sapre A.V., Broderick D.H., Fraenkel D., Gates B.C., Nag N.K., Aiche J., 26, 4 (1980) 690.
- 32 Ancheyta J., Morales P., Betancourt G., Centeno G., Marroquin G., Munoz J. A. D., Energy Fuels, 18, 4 (2004) 1001.
- 33 RU Pat. No. 2031904, 1995.
- 34 Podorozhanskiy M. N., Privalov V. E., Shustikov V. I., Privalov Z. G., Yavorskaya A. G., Khim. Tv. Topl., 4 (1975) 112.
- 35 Proizvodstvo Individual'nykh Aromaticheskikh Uglevodorodov (Benzola i Toluola).
- URL: http://www.e-him.ru (April 20, 2017).
- 36 Krichko A. A., Petrov Yu. I., Puchkov V. A., Artemova N. I., Bol'shakov D. A., Davydova M. K., Kambarov Yu. G., Aliev P. M., Koks Khim., 1 (1981) 22.
- 37 RU Pat. No. 2296618, 2005.
- 38 RU Pat. No. 2313389, 2006.
- 39 RU Pat. No. 2314154, 2008.
- 40 RU Pat. No. 2311959, 2007.
- 41 RU Pat. No. 2342994, 2009.
- 42 Ismagilov Z. R., Yashnik S. A., Startsev A. N., Boronin A. I., Stadnichenko A. I., Kriventsov V. V., Kasztelan S., Guillaume D., Makkee M., Moulijn J. A., Catal. Today, 144, 3–4 (2009) 235.

- 43 French K. H. V., The Gas World, Coking Sect., 130, 3381 (1949) 65.
- 44 US Pat. No. 2427988, 1974; US Pat. No. 2439777, 1948; US Pat. No. 2926134, 1960.
- 45 Molinari I. L. D., Coke and Gas, 23, 270 (1961) 453.
- 46 Haresnape D., Filder F. A., Laury R. A., Ind. Eng. Chem., 41, 12 (1949) 2691.
- 47 Volkov B. V., Koks Khim., 1 (1957) 53; USSR Inventor's Certificate No. 362799, 1973.
- 48 US Pat. No. 2462391, 1949; US Pat. No. 2464520, 1949; US Pat. No. 2563087, 1951.
- 49 Nechiporenko N. N., Koks Khim., 12 (1962) 43.
- 50 Molony O. W., Huges D., J. Appl. Chem., 8, 10 (1958) 10.
- 51 Kichkin G. I., Velikovskiy A. S., Khim. Tekhnol. Topliv Masel, 5 (1957) 59.
- 52 Nechiporenko N. N., and Manoylenko B. R., Koks Khim., 3 (1960) 37.
- 53 Graul R. J. and Karabinos J. V., Science, 2710 (1946) 557.
- 54 Belgium Pat. No. 538866, 1959.
- 55 Pol. Pat. No. 55804, 1968; FRG Pat. No. 1262252, 1968.
- 56 US Pat. No. 266794, 1954.
- 57 US Pat. No. 2960546, 1960; Wright O. L., Vanceri F. J., Ind. Eng. Chem., 53, 1 (1961) 15.
- 58 Kravchenko V. M., Zh. Prikl. Khim., 23, 3 (1950) 288.
- 59 Treybal R., Zhidkostnaya Ekstraktsiya, Khimiya, Moscow, 1966.
- 60 Kam'yanov V. F., Eliseev V. S., Kryazhev Yu. G., Neftekhim., 18, 1 (1978) 138.
- 61 Litvintsev I. Yu., Usp. Khim., 1 (2005) 14.
- 62 Kam'yanov V. F., Sivirilov P. P., Litvintsev I. Yu., Antonova T. V., Khim. Ust. Razv., 7 (1999) 33.
- 63 Kam'yanov V. F., Tekhnol. TEK, 1, 20 (2005) 32
- 64 Anisimov A. V., Tarakanova A. V., Zh. Ross. Khim. Obva im. D. I. Mendeleeva, LII, 4 (2008) 33.
- 65 Sharipov A. Kh., Nigmatullin V. R., Nigmatullin I. R., Zakirov R. V., Khim. Tekhnol. Topliv Masel, 6 (2006) 45.
- 66 Rao T. V., Sain B., Kafola S., Nautiyal B. R., Sharma Y. K., Nanoti S. M., Garg M. O., *Energy Fuels*, 21, 6 (2007) 3420.
- 67 Shiraishi Y., Hirai T., Energy Fuels, 18, 1 (2004) 37.
- 68 Ramirez-Verduzco L. F., Torrez-Garcia E., Gomez-Quintana R., Gonzalez-Pena V., Murrieta-Guevara F., Catal. Today, 98, 1–2 (2004) 289.
- 69 Caero L. C., Hernandez E., Pedraza F., Murrieta F., Catal. Today, 107–108 (2005) 564.
- 70 Omid Etemadi, Teh Fu Yen, Energy Fuels, 21, 4 (2007) 2250.
- 71 Samatov P. P., Sharipov A. Kh., Kolychev V. M., Dzhemilev U. M., Neftepererab. Neftekhim., 1 (2006) 27.
- 72 Eika W. Qian, Franck Dumeignil, Hiroshi Amano, Atsushi Ishihara, Prepr. Pap.-Am. Chem. Soc., Div. Pet. Chem., 5, 40 (2005) 430.
- 73 Ishihara A., Wang D., Dumeignil F., Amano H., Weihua Qian E., Kabe T., Appl. Catal. A: Gen, 279, 1–2 (2005) 279.
- 74 Nigmatullin V. R., *Neftepererab. Neftekhim.*, 4 (2012) 46. 75 Lu Liang, Cheng Shifu, Gao Jinbao, Gao Guohua, He
- Mingyuan, Energy Fuels, 21, 1 (2007) 383.
- 76 RU Pat. No. 2232789, 2004.
- 77 RU Pat. No. 2289607, 2006.
- 78 RU Pat. No. 2335525, 2008.
- 79 RU Pat. No. 2455967, 2008.
 80 Khanikyan V. L., Okislitel'noye Initsiirovaniye Nizkotemperaturnoy Pererabotki Ostatochnykh Neftyanykh Fraktsiy (Candidate's Dissertation in
- Chrmistry), Moscow, 2007.
 81 Galiev R. G., Luganskiy A. I., Tret'yakov V. F., Moroz I. V., Ermakov A. N., *Mir Nefteproduktov*, 8 (2007) 16.

- 82 Likhterova N. M., Lunin V. V., Torkhovskiy V. N., Sazonov D. S., Vasil'yeva E. S., Kirillova O. I., Khim. Tekhnol. Topliv Masel, 4 (2006) 47.
- 83 Kam'yanov V. F., Lebedev A. K., Sivirilov P. P., Ozonoliz Neftyanogo Syr'ya, MGP "Rasko", Tomsk, 1997.
- 84 Lebedev A. K., Tsoy L. A., Sagachenko T. A., Kam'yanov V. F., *Neftekhim.*, 21, 2 (1981) 278.
- 85 Lunin V. V., Frantsuzov V. K., Likhterova N. M., Neftekhim., 42, 3 (2002) 195.
- 86 Lunin V. V., Popovich M. P., Tkachenko S. N., Fizicheskaya Khimiya Ozona, Izd-vo MGU, Moscow, 1998.
- 87 Likhterova N. M., Lunin V. V., Torkhovskiy V. N., Sazonov D. S., Vasilieva E. S., Kirillova O. I., Khim. Tekhnol. Topliv Masel, 4 (2006) 18.
- 88 Kam'yanov V. F., Tekhnol. TEK, 2 (2005) 62.
- 89 RU Pat. No. 2123026, 1998.
- 90 Sazonov D. S., Polucheniye Komponentov Syr'ya Ekologicheski Chistogo Dizel'nogo Topliva Metodom Ozonoliza Srednedistillatnykh Fraktsiy Nefti (Candidate's Dissertation in Chemistry), Moscow, 2010.
- 91 Kam'yanov V. F., Eliseev V. S., Kryazhev Yu. G., Tuychiev Sh., Numanov I. U., *Neftekhim.*, 18, 1 (1978) 138.
- 92 Kam'yanov V. F., Lebedev A. K., Sivirilov P. P., Osnovnye Napravleniya Reaktsiy i Produkty Ozonoliza Neftyanogo Syr'ya, Tomsk Scientific Center SB RAS, Tomsk, Prepr. No. 2, 1996.
- 93 Kam'yanov V. F., Lebedev A. K., Sivirilov P. P., Prevrashcheniya Neftyanykh Komponentov pri Ozonolize, IPF TPU, Tomsk, 1997.
- 94 Kam'yanov V. F., Lebedev A. K., Sivirilov P. P., Ozonoliz v Pererabotke Prirodnogo Uglevodorodnogo Syr'ya, IPF TPU, Tomsk, 1997.
- 95 Baltimor Md., Grace W. R., Ozone Generation and Commercial Ozone Generation, Am. Chem. Soc., Washington D. C., 2001, Ser. 21, p. 3031.
- 96 Kam'yanov V. F., Frenkel' V. Ya., Sovremennaya Neftepererabotka, Spetsifika Yeye Osushchestvleniya na Malotonnazhnykh Predpriyatiyakh i Novye Perspektivy, Scientific Center SB RAS, Tomsk, Prepr. No 3, 1994.
- 97 Baltimor Md., Grace W.R., Ozone Generation and Commercial Ozone Generation, Am. Chem. Soc., Washington D.C., 2001, Ser. 21, p. 3096.
- 98 Eliseev V. S., Kam'yanov V. F., Numanov I. U., Neftekhim., 20, 2 (1980) 277.
- 99 Odinokov V. N., Zhemayduk L. P., Tolstikov G. A., Zh. Org. Khim., 14, 1 (1978) 54.
- 100 Galstyan A. G., Galstyan S. G., Tyupalo N. F., Zh. Prikl. Khim., 83, 2 (2010) 268.
- 101 Razumovskiy S. D., Kislorod Elementarnye Formy i Svoystva, Khimiya, Moscow, 1979.
- 102 Razumovskiy S. D. and Zaikov G. E., Izv. Akad. Nauk SSSR. Ser. Khim, (1971) 2657.
- 103 Razumovskiy S. D. and Zaikov G. E., Ozon i Yego Reaktsii s Organicheskimi Soyedineniyami, Nauka, Moscow, 1974.
- 104 Bailey P. S., Chem. Revs., 58, 7 (1958) 925.
- 105 Emanuel' N. M., Denisov E. T., Mayzus Z. K., Tsepnye Reaktsii Okisleniya Uglevodorodov v Zhidkoy Faze, Nauka, Moscow, 1965.
- 106 Krivtsov E. B., Prevrashcheniye Sernistykh Soyedineniy i Aromaticheskikh Uglevodorodov Dizel'nykh Fraktsiy Neftey v Protsessakh Okislitel'nogo Obesserivaniya (Abstract of Candidate's Dissertation in Chemistry), Tomsk, 2011.

- 107 Antonova T. V., Prevrashcheniya Neftyanykh Komponentov pri Ozonolize (Abstract of Candidate's Dissertation in Chemistry), Tomsk, 1999.
- 108 Krivtsov E. B. and Golovko A. K., VI Vseros. Nauch-Prakt. Konf. "Dobycha, Podgotovka, Transport Nefti i Gaza" (Proceedings), Tomsk, 2007, pp. 156–159.
- 109 Krivtsov E. B. and Golovko A. K., Neftepererab. Neftekhim., 1 (2011) 3.
- 110 Krivtsova K. B., Krivtsov E. B., Golovko A. K., VI Mezhdunar. Konf. Studentov i Molodykh Uchenykh "Perspektivy Razvitiya Fundamental'nykh Nauk" (Proceedings), Tomsk, 2009, pp. 402–405.
- 111 Krivtsov E. B., and Golovko A. K., Chem. Sust. Dev., 17, 1 (2009) 89.

URL: http://www.sibran.ru/en/jornals/KhUR

- 112 Krivtsov E. B., Golovko A. K., Lutchenko I. V., IV Vseros. Nauch. Molodezhnaya Konf. "Pod Znakom Sigma" (Proceedings), Omsk, 2007, pp. 107–108.
- 113 Krivtsov E. B. and Golovko A. K., VI Mezhdunar. Konf. "Khimiya Nefti i Gaza" (Proceedings), Tomsk, 2006, pp. 461–465.

- 114 Krivtsov E B and Golovko A K, VII Mezhdunar. Konf. "Khimiya Nefti i Gaza" (Proceedings), Tomsk, 2009, pp. 592–595.
- 115 Krivtsov E. B. and Golovko A. K., V Vseros. Nauch-Prakt. Konf. "Dobycha, Podgotovka, Transport Nefti i Gaza" (Proceedings), Tomsk, 2010, pp. 69?72.
- 116 Budnik V. A., Gariffulin T. M., Zol'nikov V. V., Neftepererab. Neftekhim., 112 (2010) 19.
- 117 Sigaru Oae, Chemistry of Sulfur Organic Compounds [in Russian], Khimiya, Moscow, 1975.
- 118 Semenova S. A., Mikhaylova E. S., Ismagilov Z. R., Koks Khim., 1 (2013) 40.
- 119 Semenova S. A., Mikhaylova E. S., Ismagilov Z. R., Lyrshchikov S. Yu., Koks Khim., 6 (2013) 36.
- 120 Mikhaylova E. S., Ismagilov Z. R., Zakharov Yu. A., Vestn. Kuzbas. Gos. Tekhn. Un-ta, 5 (2013) 66.
- 121 Mikhaylova E. S., Lyrshchikov S. Yu., Ismagilov Z. R., Chem. Sust. Dev., 22, 3 (2014) 313.

URL: http://www.sibran.ru/en/jornals/KhUR

122 Mikhaylova E. S., Ismagilov Z. R., Shikina N. V., Khim. Ust. Razv., 24, 3 (2016) 369.