Physicochemical characteristics of the wide fraction of the coal tar from ArselorMittal Temirtau, JSC

A T Ordabayeva, M G Meiramov and A M Gazaliev
Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, Kazakhstan, Karaganda, 1, Alikhanov Str., 100008

E-mail: aigul_serik_kz@mail.ru

Abstract. Gas-liquid chromatography was used to establish the composition of the wide fraction with a final boiling point of up to 410 °C that includes high-boiling—primarily polyaromatic—compounds. Binary composite iron- and cobalt-based catalysts were synthesized on the substrate from synthetic zeolites and carbon carrier for hydrocatalytic processing of the wide fraction of the tar. The paper elucidates the conversion degree and quantitative composition of the forming products to be different and dependent on the activity and selectivity of the catalysts that, in their turn, are connected with the surface area, dimension and porous structure. When hydrogenating the tar wide fraction in the presence of composite catalysts, such as Fe-Co/CaA, Fe-Co/C and Fe-Co/ZSM, the content of naphthalene derivatives reduces as compared to their initial content in the fraction. This is due to the hydrogenation of naphthalene during the hydrocatalytic processing of the tar fraction, which yields tetrathine. It was established that the iron-containing binary composite catalyst on the carbon carrier manifests higher catalytic activity and selectivity as compared to the catalysts based on synthetic zeolites.

1. Introduction
Currently, in coal and metallurgical industries of the Republic of Kazakhstan, there are factories for producing coke and special coke when the side products and waste are not recycled, but accumulated in settling pits and burial sites. Their processing into useful products of oil and coal chemistry is an urgent problem of deeper conversion of hydrocarbon commodities and enhanced environment control. The issues on creation of effective and green technologies for deep processing of coal and production of new beneficial import-substituting chemicals competitive on the world market are especially severe and high on the agenda [1].

The Karaganda Metallurgical Combine together with Chemical and Metallurgical Plant of TEMC Company (Temirtau Electro-Metallurgical Combine) are the primary pollution sources in Temirtau city. In Karaganda Oblast, the combined pollution share of ArselorMittal Temirtau Company and Kazakhmys reaches 70% of total pollution amount. The coke and by-product process of ArselorMittal Temirtau metallurgical company yields the main product—coke and by-products—gas and tar. In Soviet Union, the coal tar after coke production was send to Nizhniy Tagil for deep processing. Today, due to health detrimental effects, the waste is stored under water, which is dangerous in terms of pollution of water bodies, poisoning and killing of fish. Noteworthily, ArselorMittal Temirtau, JSC has two chemical dumps with approx. 100K tons of coal tar. In addition, huge amounts of tar are discharged into unlicensed settling
pits outside the company territory. The coke and by-product production should be accompanied by obligatory comprehensive processing of pyrolysis tars and production of components of motor and burner oils, deficit chemical products, organic binders for patent-fuel manufacturing and road construction, electrode materials [2, 3].

The crucial processes in oil processing are hydrocracking, hydrodesulfurization, hydroaromatization, hydroisomerization, alkylation, dehydrogenation and catalytic reforming. Therefore, the creation of novel catalysts for directed hydroprocessing of oil and its fractions into high-quality fuel will remain high on the agenda in the foreseeable future [4].

This work is aimed at studying the physicochemical characteristics of the wide fraction of the coal tar from ArselorMittal Temirtau, JSC and its hydrocatalytic processing into beneficial products.

2. Experimental

The starting material was coal tar from ArselorMittal Temirtau company separated by distillation fractionation. The tar yield after coke production is 6–8% of dry coal. Hence, the produced tar, in terms of structure and type of functional groups and structure fragments, is very similar to those of organic mass of the initial coal. The wide fraction was produced by vacuum fractioning from coal tar of ArselorMittal Temirtau, JSC. The wide fraction of the tar and its hydrogenation products were analyzed by gas chromatography (GC).

Highly dispersed distribution of active metals can be achieved by impregnation of the carrier (artificial zeolite CaA) by solutions of their salts and complex compound with consequent conversion into required form using various chemical and physical processing methods.

The active additives were applied by impregnating the carrier by water-soluble salts with consequent moist removal. The product was thermally treated which destroys metal salts adsorbed in the carrier pores due to high temperature effects. The atoms and clusters of metals forming in the process modify the active centers in certain locations of zeolite, which stabilizes them in the nano- and meso-pores of the carrier and assures their fixation on its surface.

To obtain composite iron-containing catalysts, iron sulphate (FeSO$_4$·7H$_2$O) was dissolved in deionized water; and the solution was added to synthetic zeolite [4]. The mixture was stirred at room temperature and evaporated on a rotary evaporator. The produced specimen was thermally modified (at a temperature of 750 °C during 30 minutes) to convert the metal into oxide, which leads to the formation of catalytically active centers with formation of iron oxide (hematite). The iron and cobalt-based composite catalysts were similarly obtained on ZSM zeolite.

The application of carriers prevents adherence of catalyst particles, increases its thermal and chemical stability, enhances the resistance of the catalysts to poisoning and coking, sharply reduces the density of catalytic active phase, increases efficiency and mechanical strength of the catalysts, promotes the life of the catalytic systems. It should be taken into account that the impregnating metal into zeolite along its whole volume is not always beneficial. The formation of the particles on the surface sometimes yields a more active catalyst [5].

More effectively highly molecular hydrocarbon commodities are processed by catalysts introduced as highly dispersed particles uniformly distributed in the volume. To provide maximum stability of the catalytic system, the catalyst particles dimensions should be very small, i.e. approach the diameter of the particles in molecular or colloid solutions. In this connection, such catalytic systems can be regarded as composite ones.

The application of catalysts on carriers with uniform volumetric distribution of active phase in the sorbent reduces the consumption of active component and raises the catalyst’s
activity [6]. One of the conditions for producing a catalyst with stable chemical composition of the active center is displacement of activating additives from the solution onto the surface of hardly soluble oxides and their uniform distribution on it.

The experiment on hydrocatalytic processing of the tar wide fraction was conducted in an CJF-0.05 high-pressure autoclave from heat-proof stainless steel with the volume of 0.05 l. The preliminarily mixed starting materials were put into the reactor, sealed, pumped with hydrogen, pressurized with hydrogen up to 8.0 MPa, heated up to 420 °C at a rate of 10 deg/s. The process duration was 120 minutes after autoclave was reaching the working temperature. After the experiment, the reactor was cooled down to room temperature. The reaction mixture composition was determined by gas chromatography (GC).

The product of hydrocatalytic processing of anthracene oil was analyzed on a Kristalluks 4000 M chromatograph with flame ionization detector (FID) using ZB-5 column (30 m x 0.53 mm x 1.50 μm) with programmable thermostat temperature from 60 to 250 °C at the heating rate of 6 deg/s. The gaseous products were analyzed on a Kristalluks 4000 M chromatograph with a detector module including thermal conductivity detector and FID using CaA column (1 = 3 m, d = 3 mm) for permanent gases and Porapak R column (1 = 3 m, d = 3 mm) for hydrocarbon gases. The liquid products were analyzed on a Kristalluks 4000 M chromatograph with FID using DB-5ms column (30 mm x 0.250 mm x 0.50 μm). The data were processed in NetChrom V2.1 software.

### 3. Results and Discussion

The GC analysis of the tar wide fraction the composition of the main component was identified: phenanthrene (9.77%), anthracene (1.54%), naphthalene derivatives (>50%), aromatics (>3%), phenol derivatives (>1%), biphenylene (<6%), fluorene (<6%), indene (3.02%). The tar fractional composition is presented in Table 1. The mass of the identified components amounts to almost 92% of the total tar mass. Unidentified compositions that amount to 8% of the total mass at current stage are out of practical interest, because each of them amounts to less than 0.01%.

**Table 1. Composition of coal tar wide fraction.**

| No. | Component                  | Concentration [%] | No. | Component            | Concentration [%] |
|-----|----------------------------|-------------------|-----|----------------------|-------------------|
| 1   | toluene                    | 0.14              | 11  | biphenylene          | 5.44              |
| 2   | o-xylene                   | 0.09              | 12  | acenaphthene         | 1.25              |
| 3   | phenol                     | 0.42              | 13  | dibenzofuran         | 4.28              |
| 4   | indan                      | 0.26              | 14  | fluorene             | 5.35              |
| 5   | indene                     | 3.02              | 15  | dihydrophenanthrene  | 0.20              |
| 6   | naphtalene                 | 46.58             | 16  | tetanthrene          | 0.58              |
| 7   | 2-benzothiophene           | 0.67              | 17  | phenanthrene         | 9.77              |
| 8   | 1-methylnaphthalene        | 5.07              | 18  | anthracene           | 1.54              |
| 9   | 2-methylnaphthalene        | 1.95              | 19  | fluoranthene         | 2.29              |
| 10  | diphenyl                   | 1.67              | 20  | pyrene               | 0.92              |
|     | Total:                     |                   |     |                      | 91.77             |
The catalytic properties of synthesized binary catalysts were scrutinized during hydrocatalytic processing of the tar wide fraction from ArselorMittal Temirtau, JSC. The composition of the products of tar fraction hydrogenation in the presence of various binary composite catalysts is presented in Table 2.

Table 2. Comparison of hydrogenate concentration in presence of binary catalysts.

| No | Component        | Concentration [%] on Fe-Co/C | Concentration [%] on Fe-Co/CaA | Concentration [%] on Fe-Co/ZSM |
|----|------------------|------------------------------|---------------------------------|-------------------------------|
| 1  | toluene          | 11.58                        | 0.60                            | 1.85                          |
| 2  | p-xylene         | 14.08                        | 0.78                            | 0.85                          |
| 3  | m-xylene         | 1.02                         | -                               | 0.89                          |
| 4  | o-xylene         | 0.20                         | 0.14                            | 0.20                          |
| 5  | phenol           | 0.35                         | 0.38                            | -                             |
| 6  | indan            | 2.04                         | 2.53                            | 2.48                          |
| 7  | indene           | 0.18                         | 0.30                            | 0.27                          |
| 8  | tetraline        | 9.08                         | 6.89                            | 4.01                          |
| 9  | naphthalene      | 37.71                        | 43.30                           | 43.8                          |
| 10 | 1-methylnaphthalene | 1.81                      | 4.36                            | 4.53                          |
| 11 | 2-methylnaphthalene | 0.49                      | 1.70                            | 1.67                          |
| 12 | diphenyl         | 4.06                         | 3.14                            | 2.74                          |
| 13 | acenaphthene     | 0.61                         | 4.48                            | 4.26                          |
| 14 | dibenzofuran     | 0.96                         | 4.41                            | 4.03                          |
| 15 | fluorene         | 2.08                         | 5.95                            | 5.34                          |
| 16 | dihydrophenanthrene | 0.83                      | 1.91                            | 0.18                          |
| 17 | tetanthrene      | 0.36                         | 0.95                            | 0.48                          |
| 18 | phenanthrene     | 3.06                         | 9.89                            | 9.68                          |
| 19 | anthracene       | 0.24                         | 0.69                            | 0.12                          |
| 20 | fluoranthen     | -                            | 1.53                            | 1.78                          |
| 21 | pyrene           | -                            | 0.90                            | 1.09                          |

In terms of the conversion degree of the hydrogenation products of the coal tar fraction, a number of activities in the catalytic systems was revealed: Fe-Co / C > Fe-Co / CaA > Fe-Co / ZSM. It was established that in the presence of Fe-Co/C catalyst, naphthalene is hydrogenated to tetraline (9.08%), indene to indan (2.04%), initial naphthalene amounts to 37.71%; there are derivatives of aromatics hydrocarbons (15.3% of methylbenzenes). Plus, there is 4.06% of diphenyl. The toluene content reached its extremum as compared to the initial fraction under study.

We also noted that during high-temperature hydrogenation of the anthracene oil using synthesized iron-containing catalysts on carbon and zeolite carriers, indene and biphenylene easily accept hydrogen yielding indan and diphenyl.
The hydrogenation of naphthalene proceeds with formation of tetraline.

4. Conclusions
The component composition of the long fraction of the coal tar from ArselorMittal Temirtau, JSC was established. Binary iron- and cobalt-based composite catalysts were synthesized on the substrate from synthetic zeolites and carbon. It was shown that the iron-containing binary composite catalyst on carbon carrier exhibits high activity and selectivity.

References
[1] Lozbin V I, Mochalnikov S V, Solodo G A, Nevedrov A V and Papin A V 2007 Bulletin of the Tomsk Polytechnic University 310 2 149 – 151
[2] Chistyakov A N 1990 Chemistry and technology for processing coal tar Chelyabinsk: Metallurgia 10
[3] Kostyuk V A and Slavinskaya I I 1987 Phenol removal from hydrogenated brown coal in continuous countercurrent Chemistry of solid fuel 2 78 – 82
[4] Krylov O V 2004 Heterogeneous catalysis Akademkniga 258 p
[5] Kubasov A A 2000 Zeolites in catalysis: today and Sorov educational journal 6 44-51
[6] Meiramov M G 2017 Angular-linear isomerization during the hydrogenation of phenanthrene in the presence of iron-containing catalysts (in Russian) Solid Fuel Chemistry 2 42-45