Hydro-Liquefaction of Tile-Like Barzas Coals in the Presence of Some Transition Metal Additives

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Abstract. Using a laboratory micro-autoclave (of ~ 20 cm^3 volume), the effects of transition metal additives (MoO_3, Fe_2O_3 and commercial AlCoMo catalyst) on the thermal transformations of tile-like Barzas coals (sapromixites) in a hydrogen medium at T ~ 475°C and P ~ 6.0-7.5 MPa have been studied. It has been shown that catalytic additives under investigation somewhat suppress gas formation processes, facilitating the increase in H/C atomic ratios and in the amount of alkyl-containing structures in resin-like solid products of Barzas coal hydro-liquefaction. Maximal yields of "coal liquids" (maltenes + asphaltenes) (~ 35 wt.%, *daf* basis) were obtained during the heat treatment of sapromixites in the presence of ~ 1 wt.% MoO_3.

1 Introduction

Hydro-liquefaction processes to produce artificial liquid fuels are rather promising ways for utilization of low-metamorphised and low-rank coals [1-4]. It was previously established [5] that among various low-metamorphosed Kuzbass coals, Barzas sapromixites are the most promising raw materials for direct hydrogenation processes to produce liquid products, since this type of solid fuels contains large amounts of hydrogen (up to 9-10 wt.% from organic matter of coal) and is characterized by high yields of volatile products (50-60 wt.%). In particular, under non-isothermal conditions, sapromixites of Barzas coal field rather easily dissolve in a hydroaromatic solvent (tetralin) at already 425-450°C with the yield of liquefaction products (asphaltenes, resins and oils) of ~ 60-80% per organic matter of coal [6]. Moreover, during their hydrogenation (T ~ 400-430°C and P ~ 7 MPa) in the presence of an iron-containing catalyst and a petroleum residue (as a solvent), almost 94-97% of their organic matter is converted into gaseous and liquid products, with the yield of light liquid hydrocarbons (mainly C_6-C_9 paraffins, bp <200°C) up to 24-28 wt.% [7].

Thermal decomposition reactions of coals to smaller molecular fragments occurring in a hydrogen medium at high temperatures and pressures can be considered as an important stage in the process of their direct hydrogenation [4]. Therefore, a study of coal substance pyrolysis in various environments provides valuable information about basic regularities of

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the coal conversion product formations, depending on the technological parameters of the process of solid fuel heat treatment.

In our earlier works [8, 9], the experiments on thermal treatment of Barzas coals in hydrogen and carbon dioxide atmospheres within the temperature range of 400–550°C and pressures from 7 to 11.0 MPa have been carried out. The maximum yield of "coal liquids" (maltenes and asphaltenes) was obtained at T = 475°C for both media. At the same time, an antibate relationship was observed between the gas yields and H/C atomic ratios in solid tar containing products of coals heat treatment. Such behavior of Barzas coals during their thermal decompositions in various media was explained by the initial accumulation of alkyl-containing structures at T < 475°C and their subsequent transition into the gas phase at higher thermal treatment temperatures [5, 6]. It is well known that in the presence of various transition metal-containing catalytic additives, the reactions of hydrogenation, cracking and heteroatom removal from coals during their hydro-liquefaction process are considerably intensified [1-3]. Iron- and molybdenum-based catalytic systems are amongst the most active and widely used catalysts of coal hydrogenation [2, 3]. Therefore, in the given work, the effects of Fe- and Mo-containing additives (MoO_3, Fe_2O_3 and commercial AlCoMo catalyst) on the transformations of Barzas coals during their thermal treatment in a hydrogen medium have been investigated.

2 Experimental

2.1. Preparation of coal samples for hydroliquefaction

For this investigation, the most abundant, tile-like modification of Barzas coals was chosen as a raw material to study the processes of hydro-liquefaction.

Table 1. Characteristics of tiled Barzas sapromixite.

Proximate analysis (wt %)			Ultimate analysis (wt %, *daf* basis)					H/C atomic ratio
W^a	A^d	V^{daf}	C	H	N	S	O (by difference)	
1.7	25.8	50.1	84.78	8.91	0.56	1.24	4.51	1.26

Fig. 1. The most abundant, tile-like modification of Barzas coals.
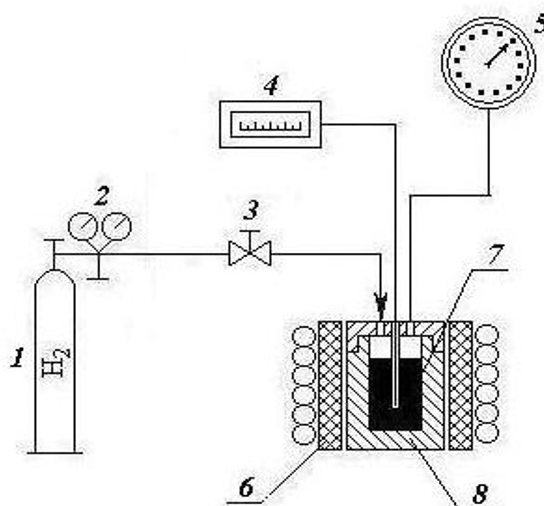
Fig. 2. Schematic view of a setup for coal hydro-liquefaction under high pressure: 1 – gas cylinder with hydrogen; 2 – gas 3edactor; 3 – valve; 4 – temperature regulator; 5 – manometer; 6 – electric furnace; 7 – coal sample; 8 – micro-autoclave.

The appearance of tile-like Barzas coal samples is shown in Fig. 1, and their basic characteristics are listed in Table 1. Proximate analysis of this coal was carried out using conventional methods [10], and its ultimate analysis, as well as elemental analyses of its thermal treatment products, were performed with a Flash 2000 elemental analyzer (Thermo Fisher Scientific, USA).

Several fractions of crushed and sieved Barzas coal particles sized of ~ 1-3 mm were used for hydro-liquefaction experiments. Some of these coal fractions were modified with various transition metal-containing catalytic additives: 1) 1 wt % MoO_3 (by impregnation with aqueous solutions of ammonium dimolybdate, followed by drying of impregnates at 120°C for 4 h); 2) 5 wt % Fe_2O_3 (by impregnation with aqueous solutions of iron (III) nitrate nonahydrate, followed by drying of impregnates at 120°C for 4 h) and 3) 11 wt % AlCoMo commercial hydrotreatment catalyst (by mixing of coal particles with the same size catalyst particles).

2.2. Hydro-liquefaction

Hydro-liquefaction of Barzas coal samples (with and without catalytic additives) were carried out using a specially constructed setup based on a microreactor-autoclave (of ~20 cm^3 volume) capable to operate at high pressures and temperatures (Fig. 2). The reactor loaded with coal samples was pre-pumped with H_2 up to P ~ 2.0 Mpa and then heated up to T ~ 475°C and to the ending pressures in the range from 6.0 to 7.0 MPa ; heating rate of coal samples in the reactor was of 10-12°C/min. The process temperature was controlled by a chromel-alumel thermocouple, and the pressure in the system was monitored by a manometer. The process duration at a given temperature was of 20 minutes, after which the reactor was cooled to room temperature.

Three main types of products are formed as a result of Barzas sapromixite thermal treatment in a hydrogen medium [9] : 1) gaseous products ; 2) resin-containing solid products and 3) small quantities (about 3-5 wt %) of liquid products representing aqueous solutions of organic substances (the latter ones were sometimes emerged only after sapromixite heat treatment at 475°C). The amount of gas formed after the reactor cooling

was measured using a drum counter; all the solid and resin-like products remaining after the reaction were selecting, weighing and sending for IR and elemental analyses. Also, the concentrations of "coal liquids" (maltenes and asphaltenes) present in resin-containing solid products were determined by their sequential extraction in a Soxhlet apparatus [8, 9]. Preliminarily it was established that no maltenes and asphaltenes were contained in as-received Barzas coal. For each experiment, a material balance of the solid, liquid and gaseous products formed was determined.

Yields of Barzas coal conversion products were calculated as follows:

$$Y_g = [(m_c - m_s - m_w)/m_c] \times 100/[100 - W^a - C_{cat} - (100 - C_{cat})A^d/100] \quad (1)$$

$$Y_w = [m_w/m_c] \times 100/[100 - W^a - C_{cat} - (100 - C_{cat})A^d/100] \quad (2)$$

$$Y_m = [m_m/m_c] \times 100/[100 - W^a - C_{cat} - (100 - C_{cat})A^d/100] \quad (3)$$

$$Y_a = [m_a/m_c] \times 100/[100 - W^a - C_{cat} - (100 - C_{cat})A^d/100] \quad (4)$$

where Y_g, Y_w, Y_m and Y_a are the yields of gases, aqueous phase products, maltenes (*n*-hexane 4oluble) and asphaltenes (benzene 4oluble but *n*-hexane insolubles), calculated on the dry ash-free (*daf*) basis, wt %, respectively; A^d and W^a are the ash and moisture contents in feed coal, wt %, respectively; C_{cat} is the concentration of a catalytic additive, wt %; m_c, m_w, m_s, m_m and m_a are the weights of feed coal, aqueous phase products, solid resin-containing products, maltenes and asphaltenes, g, respectively. The efficiency of coal liquefaction process (yield of "coal liquids") was calculated as a sum of the yields of maltenes and asphaltenes, wt % (*daf*).

2.3. FTIR analysis of hydroliquefaction products

A Fourier transform IR (FTIR) spectroscopy method was used to study the functional composition of solid products obtained after hydroliquefaction of Barzas coal samples with and without catalytic additives; FTIR spectra of the samples studied were recorded with an Infralum FT-801 instrument (Lumex-Siberia, Russia) in the 500-4000 cm^{-1} spectral range using a KBr disk pressing technique.
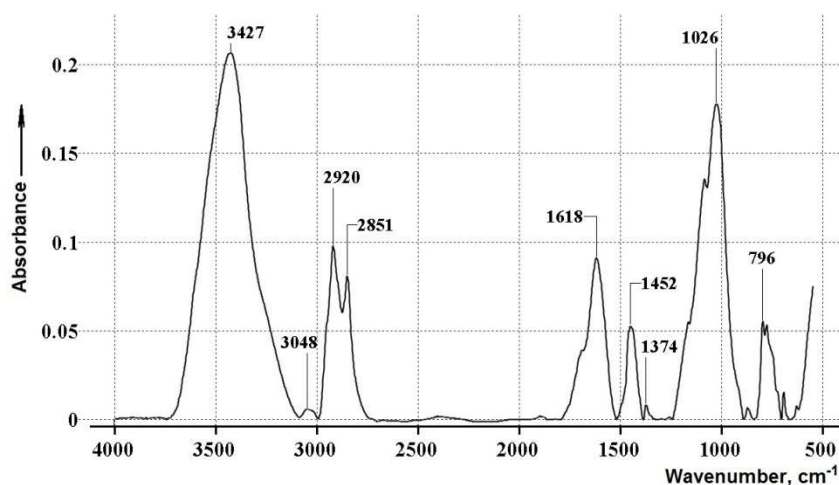

Fig. 3. A typical FTIR spectrum of as-received tile-like Barzas coal.

Typical FTIR spectra of as-received tile-like Barzas coal and solid products of its hydro-liquefaction in the presence or absence of catalytic additives are presented in Figs. 3-5.
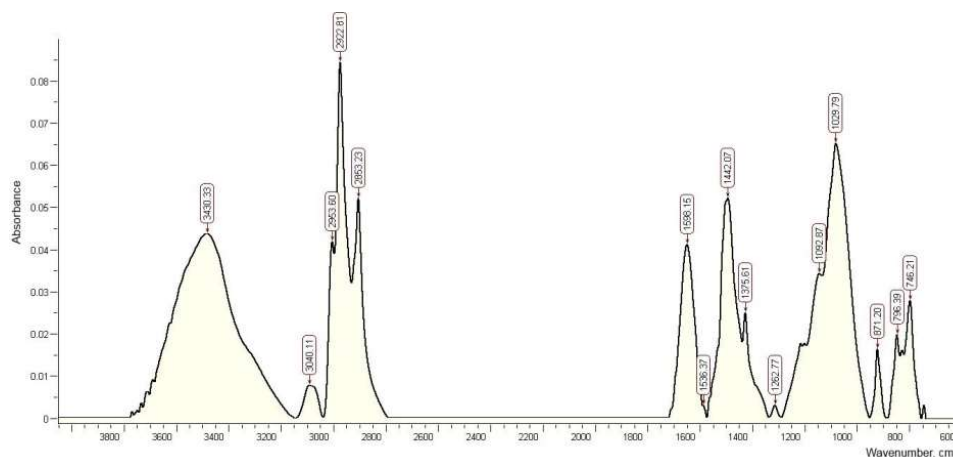

Fig. 4. A typical FTIR spectrum of catalytic additive-free Barzas coal after its thermal treatment in a hydrogen medium at 475°C.

According to literature data on the IR spectra of various coals [11, 12], the main groups of Barzas sapromixite sample IR absorption bands are manifested in the following frequency ranges : 3700-3200 cm^{-1} with a maximum at ~ 3480 cm^{-1} – stretching vibrations of hydrogen-bonded OH groups ; 3080-3020 cm^{-1} – stretching vibrations of aromatic C-H groups; 2920-2960 cm^{-1} with a maximum about 2947 cm^{-1} – stretching vibrations of methylene $>CH_2$ groups and asymmetric stretching vibrations of CH_3 groups; 2860-2880 cm^{-1} – symmetric stretching vibrations of CH_3 groups; an intensive absorption band at ~ 1600 cm^{-1} – stretching vibrations of aromatic C=C groups, which is partially overlapping with an absorption band of water deformation (bending) vibrations (δ_{H-O-H}), manifested in the ~ 1630-1650 cm^{-1} region ; an absorption band at ~ 1700 cm^{-1} – stretching vibrations of carbonyl C=O groups; absorption bands in the 1450-1430 cm^{-1} – bending vibrations of CH_2 groups and asymmetric deformation vibrations of CH_3 groups; an absorption band at ~ 1380 cm^{-1} – symmetric deformation vibrations of CH_3 groups.
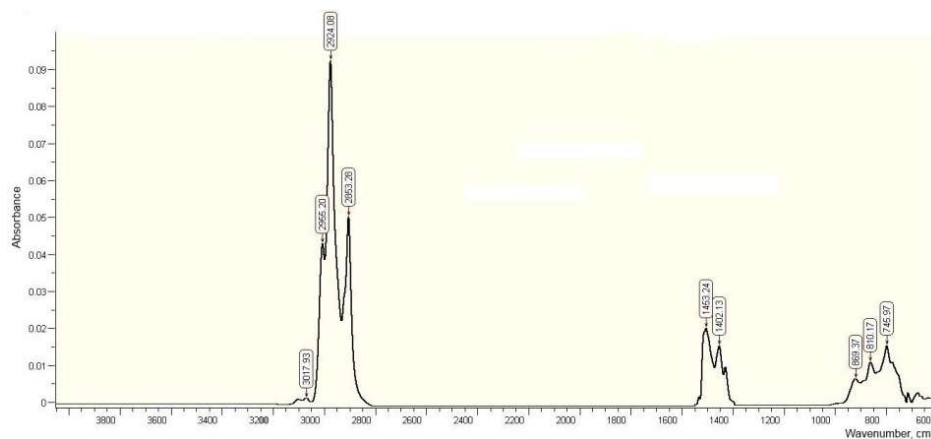

Fig. 5. A typical FTIR spectrum of Barzas coal modified with 11 wt.% AlCoMo catalyst and then thermally treated in a hydrogen medium at 475°C.

Besides that, the following absorption bands are also observed in these spectra : an absorption band in the 1200-1100 cm^{-1} region – stretching vibrations of C-O-H groups.

A group of absorption bands in the 1080-1020 cm^{-1} interval with a maximum at ~ 1050 cm^{-1} – stretching vibrations of bridging ether C-O-C groups; a group of absorption bands in the 700-900 cm^{-1} range that are associated with out-of-plane vibrations of aromatic ring C-H bondings.

A semi-quantitative assessment of changes occurring in the solid samples of Barzas coals after their hydro-liquefaction in the absence and in the presence of catalytic additives was made from variations in relative intensities of the absorption bands belonging to alkyl groups (CH_3 and CH_2 groups), defined as the areas of infrared absorption bands in the 2800-2970 cm^{-1} range, normalized to the total area of all the absorption bands in the FTIR spectrum of the sample studied, i. e., from $(A_{CH_3}+A_{CH_2})/\Sigma A_n$ ratios.

3 Results and Discussion

Analysis of FTIR spectra presented in Fig. 3-5 shows that heat treatment of Barzas coals under pressure in a hydrogen atmosphere leads to a sharp decrease in the intensity of IR absorption bands related with oxygen-containing groups, especially the absorption bands of OH groups (~ 3430 cm^{-1}), C = O groups (~ 1700 cm^{-1}) and C-O-C/C-O-H groups (1000-1100 cm-1). In addition, the fall in intensity of IR absorption bands associated with aromatic structures (~ 3030 cm^{-1} and ~ 1600 cm^{-1}) is also observed. On the other hand, the IR absorption bands intensities of alkyl groups (peaks at 1800-1970 cm^{-1}, ~ 1450 cm^{-1} and ~ 1380 cm^{-1}) markedly increase. These changes point to the O-containing functional groups removal and the occurrence of coal hydrogenation reactions. In the presence of catalytic additives, these processes become much more intensive; thus, solid products of Barzas coal hydro-liquefaction obtained in the presence of an AlCoMo catalyst additive practically do not contain any oxygen-containing and aromatic structures (see Fig. 5).
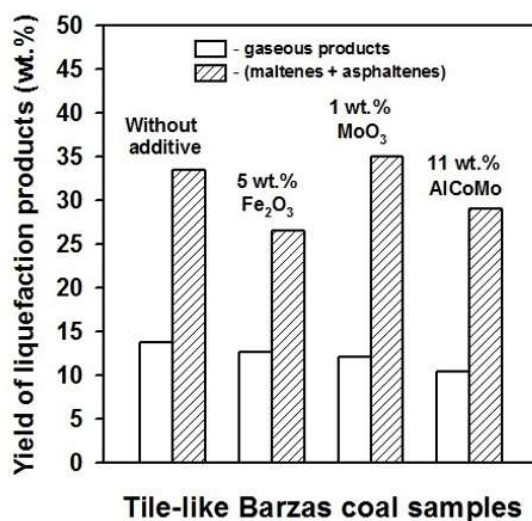

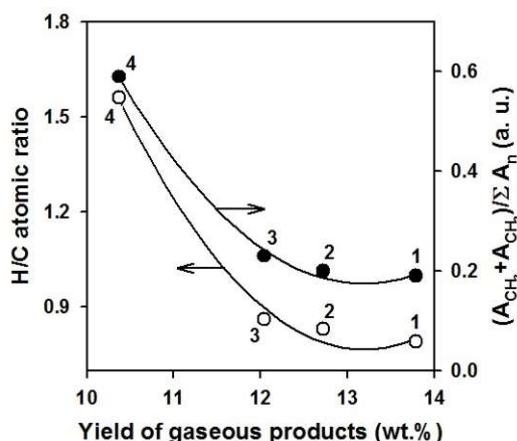**Fig. 6.** Effects of catalytic additives on the yields of Barzas coal hydro-liquefaction products.

Fig. 7. Dependences of H/C atomic ratios and relative IR absorption band intensities of alkyl groups in solid products of Barzas coal hydro-liquefaction on the yields of gaseous products: coal samples without catalytic additive (1), with 5 wt.% Fe_2O_3 (2), with 1 wt.% MoO_3 (3) and with 11 wt.% AlCoMo catalyst (4).

Effects of catalytic additives on the yields of "coal liquids" during Barzas coal hydro-liquefaction are plotted as hystograms in Fig. 6. As it can be seen from this figure, in the presence of catalytic additives, the yield of gaseous products somewhat decreases, and, besides that, in case of the Mo-containing additive, the yield of liquid (resin-like) products slightly increases, as compared to that for a coal sample without catalyst. Maximal yields of "coal liquids" (maltenes + asphaltenes) (~ 35 wt.%, *daf* basis) were obtained during the heat treatment of sapromixites in the presence of ~ 1 wt.% MoO_3. Figure 7 demonstrates relationships between yields of gaseous products and H/C atomic ratios and also relative IR absorption band intensities of alkyl groups in solid products of Barzas coal hydro-liquefaction in the presence or absence of catalytic additives. The data presented here clearly indicate a close relationship between the amount of hydrogen-rich structures in resin-like products of Barzas coal transformations and gas formation processes during its thermal treatment: the higher the gas yield during coal hydro-liquefaction, the lower the H/C atomic ratio and the lower the concentration of alkyl groups in resin-like solid products of coal transformations. Similar regularities were also observed in the studies of temperature dependences of Barzas coal thermal decompositions in various media [8, 9].

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