

Application of Iron Chloride to the Hydrogenation of Coal from the Shubarkol Deposit in a Mixture with Polyethylene

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Abstract—The results of the hydrogenation of Shubarkol coal with an applied catalytic additive of iron chloride and a polymer as a solvent and a source of hydrogen are described. The donor properties of the polymer in the process of hydrogenation were demonstrated by the reaction of anthracene as a model compound with polyethylene in the absence of external hydrogen, which leads to the formation of hydrogenated derivatives.

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Currently, a search for new hydrogen donors and new catalysts for the process of coal hydrogenation is actively conducted. The combined thermal transformations of fossil coals with synthetic polymers can be used for increasing the yield and quality of liquid products and also for utilizing plastic wastes. It is assumed that polymers with high H/C ratios, such as polyethylene, polypropylene, and polystyrene, are capable of serving as the sources of hydrogen in these processes [1, 2]. The use of polymer wastes as additives in the hydrogenation of coals can facilitate the stability of coal–oil mixtures supplied to a reactor and the enrichment of the reaction products in corresponding hydrocarbons [3]. The effects of polymer additives on the stability and rheological properties of coal–oil mixtures in the presence of molybdenum-containing catalysts were studied [4, 5]. However, the catalysts based on iron are economically more advantageous because they are highly active, inexpensive, and more environmentally sound in the case of the use of metallurgical wastes for these purposes.

It is well known [6] that coals with carbon contents lower than 80–85%, including coal from the Shubarkol deposit, are largely characterized by colloidal rather than crystalline nature. These coals swell under the action of organic solvents, which include liquid hydrocarbons formed upon the degradation of polyethylene, to result in an increase in the yield of liquid products.

To determine the effect of the thermal degradation products of polymers on the conversion of the organic matter of coal (OMC), we subjected the initial poly-

mer to thermal treatment under conditions analogous to those of a hydrogenation process, that is, in an autoclave at 400°C for 60 min.

A rotating 50-mL stainless steel autoclave was used in this study; it was loaded with a prepared coal sample and a polymer additive in a ratio of 70 : 30, closed, pumped with hydrogen, heated to a specified temperature, and kept for 60 min.

After cooling the autoclave, the gas was collected in a gas pipette for analysis. The contents were diluted with benzene and filtered. The solid residue was washed with benzene, dried at a temperature of 105°C, and weighed; the degree of conversion of the organic matter of coal was determined by difference.

We found that, under these conditions, polyethylene decomposed into a number of gaseous and liquid products. According to GLC analysis data, the gaseous products consisted of C₁–C₃ hydrocarbons (methane, ethylene, ethane, and propane) and hydrogen, whose content was not determined quantitatively for technical reasons (Table 1).

Liquid products were a multicomponent mixture, whose main components are shown in Table 2.

Table 1. Composition of the gaseous products of polyethylene degradation, vol %

CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₈
35.70	26.39	23.15	14.76

Table 2. Concentrations of the main products of the thermal degradation of polyethylene in a liquid phase

No.	Liquid products of polyethylene degradation	Concentration, %
1	Decane	8.61
2	Undecane	8.06
3	Dodecane	8.62
4	Tridecane	15.59
5	Tetradecane	9.58
6	Pentadecane	7.89
7	Hexadecane	5.54

Table 3. Dependence of the conversion of the organic matter of coal on the initial pressure of hydrogen (400°C; $\tau = 1$ h; coal : polyethylene = 70 : 30; $P_{\text{work H}_2} = 7.0\text{--}9.5$ MPa; catalyst, FeCl_3 ; autoclave)

Initial pressure of hydrogen, MPa	Working pressure of hydrogen, MPa	OMC conversion, %
0.5	7.0	28.42
1.0	8.2	41.05
1.5	9.1	48.42
2.0	9.0	47.89
2.5	9.5	51.58

The compositions of gaseous and liquid products were determined by GLC analysis on an LKhM-8MD chromatograph with columns packed with Polysorb 1 and zeolite CaA and a Kristallyuks 4000M chromatograph with a ZB-5 capillary column ($l = 30$ m), respectively.

For determining the donor properties of polymers in the process of coal hydrogenation, coal from the Shubarkol deposit (a fraction of 0.1 mm) with the following physicochemical characteristics (%) was used: A^d , 5.0; S^{daf} , 0.40; N^{daf} , 1.36; O^d , 15.85; V^{daf} , 43.4; C^{daf} , 76.99; and H^{daf} , 5.4. Iron chloride (FeCl_3) was used as a catalytic additive, which was supported on coal by

impregnation in an amount of 3% on a coal weight basis. High-pressure polyethylene (GOST [State Standard] 16337-77) from the Tomsk petroleum chemical plant was used as a polymer additive.

The process of coal hydrogenation was conducted in the following two directions: with a change in the initial pressure of hydrogen and with a change in the process temperature.

It was established that the degree of conversion of the organic matter of coal increased from 28.42 to 51.58% as the initial pressure of hydrogen was increased from 0.5 to 2.5 MPa (Table 3). It is likely that the decrease in the operating pressure of hydrogen at an initial pressure of 2.5 MPa was due to both its absorption and the partial decompression of the autoclave.

The experimental results indicate that, in the hydrogenation of Shubarkol coal in a mixture with polyethylene, the performance characteristics of the process were improved with increasing the initial pressure of hydrogen toward increasing the degree of degradation of the organic matter of coal.

Upon the determination of the effect of temperature on the process of the hydrogenation of Shubarkol coal with supported iron chloride in the presence of polyethylene, we found that the conversion of the organic matter of coal did not increase considerably with increasing process temperature, and this increase varied from 38.95 to 45.26% (Table 4).

The addition of 3% sulfur on an OMC basis does not increase the catalytic properties of supported iron chloride.

Earlier, we studied the process of the hydrogenation of anthracene and phenanthrene as model coal substances in an atmosphere of hydrogen and the $\text{CO}/\text{H}_2\text{O}$ system in the presence of an STK-1 iron–chromium catalyst, iron pentacarbonyl, and a pyrite concentrate. In all cases, considerable amounts of 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene were present in the reaction mixture together with other hydrogenation and hydrogenolysis products [7, 8].

Table 4. Dependence of the conversion of the organic matter of coal on the process temperature of the hydrogenation of Shubarkol coal (400°C; $\tau = 1$ h; coal : polyethylene = 70 : 30; $P_{\text{work H}_2} = 7.2\text{--}13.0$ MPa; catalyst, FeCl_3 ; autoclave)

Temperature, °C	Working pressure of hydrogen, MPa	OMC conversion, %	Gas composition, vol %			
			CH_4	C_2H_4	C_2H_6	C_3H_8
350	7.2	38.95	30.72	31.95	18.21	18.09
400	10.2	39.47	35.70	26.39	23.15	14.76
425	10.0	41.75	41.03	21.09	20.74	17.15
450	13.0	45.26	30.72	31.95	18.21	18.09

Table 5. Effect of the polymer additive amount on the process of hydrogenation of the model compound anthracene, %

No.	Ratio between anthracene and polyethylene	Anthracene hydrogenation products		Anthracene	Anthracene conversion
		DHA	THA		
1	30 : 70	27.56	18.20	54.24	45.76
2	50 : 50	19.70	17.55	63.28	36.76
3	60 : 40	14.82	17.12	68.06	31.94
4	70 : 30	22.09	14.60	63.85	36.15

The participation of polymers as the donors of hydrogen in the process of coal hydrogenation was supported by the interaction of a model compound (anthracene) with the supported iron chloride additive with polyethylene degradation products under analogous conditions without the introduction of external hydrogen into the reactor.

The experiment was carried out in a rotating 50-mL autoclave, which was loaded with 3 g of anthracene with supported iron chloride (3% on an anthracene weight basis) and ground polyethylene. The autoclave was purged with argon, heated to 400°C, and kept at this temperature for 60 min.

The gas composition was determined by GLC analysis on LKhM-8MD chromatograph with columns packed with Polysorb 1 and zeolite CaA, and the composition of anthracene reaction products was determined on a Kristallyuks 4000M chromatograph with a column (1–2 m) packed with 5% SKTFT-50 on Inerton AW in the temperature range of 100–180°C at a heating rate of 6 K/min.

The chromatographic analysis of gaseous and liquid products showed the presence of hydrogen (whose content was not determined quantitative), 38.59% methane, 32.88% ethylene, 30.37% ethane, and 8.16% propane.

The main conversion products of anthracene (with concentrations higher than 1%) were its hydrogenated derivatives 9,10-dihydroanthracene (DHA) and 1,2,3,4-tetrahydroanthracene (THA). Table 5 summarizes the composition of the reaction products at different anthracene : polyethylene ratios.

Upon performing the process of the hydrogenation of the model compound, considerable variations in anthracene conversion were not observed. However, the formation of the hydrogenation products 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene

unambiguously confirms the participation of the polymer as a donor of hydrogen.

The results described in this work demonstrate the participation of the polymer as the donor of hydrogen because 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene are the main products found by the analysis of the products of the reaction of the model compound anthracene with polyethylene without the participation of external hydrogen under the conditions analogous to hydrogenation conditions. The effects of hydrogen pressure and temperature on the hydrogenation process of Shubarkol coal in the presence of a supported catalytic additive of iron chloride and the polymer as a solvent and donor of hydrogen were found.

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