UDC 543.5

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Thermogravimetric investigation and selection of catalyst of coal hydrogeneration

Abstract: Thermo gravimetric study of coal in the presence of polymers showed that availability of high asphalt-resinous components – asphaltenes and resins benzene within the temperature of 360 – 443^{0}C in the content was reduced. The optimum catalytics of coal hydrogenation is the compositions on the basis of Pd / C, at which there was the greatest absorption of hydrogen and Co / C, where the hydrogenation rate was maximum.

Key words: coal, polymers, hydrogenation, paste-head, Balkhash concentrate catalysts.

Introduction

The efficiency and effectiveness of performance of coal hydrogenation process at an industrial environment is carried out with great difficulties. Except the importance of features and structure of the original coal, a macro kineticchoice of pressure's modes, temperature and catalysts also has a great value.

The aim of majority processes of coal's chemical recycling (with the exception of the production of carbon materials) is its conversion into low molecular organic products, with a quite homogeneous composition. The conversion of coal into the more organic compounds can be achieved under the heat treatment and exposure to different reagents [1, 2]. During the heating process the weak aliphatic chains, which bind condensed aromatic structures, are usually disrupted primarily. The disruption of carbon-oxygen bonds has a decisive contribution during the process of depolymerization of brown coal.

Management of the reactions of disruption of certain bonds can be done by selective introduction of metal catalysts into the functional groups of the coal substance. For example, the temperature of aliphatic bond's disruption, which connects two aromatic fragments, reduces if a divalent metal cation replaces the protons of two neighbour phenolic groups.

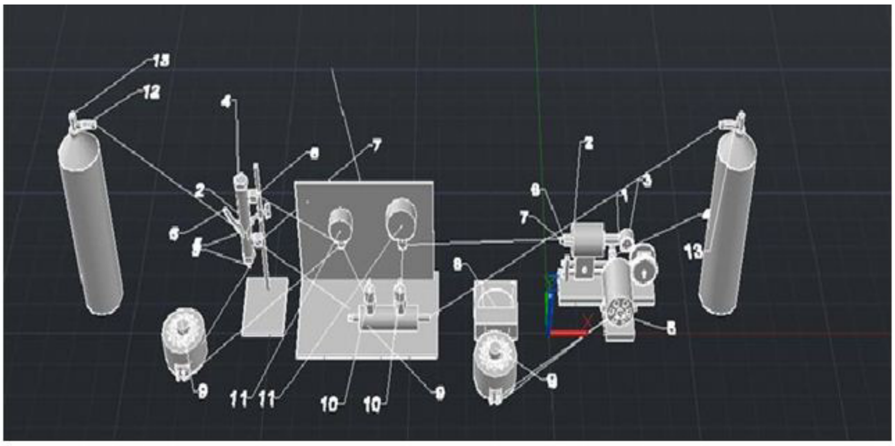
The main disadvantages of known techniques of chemical recycling of coal compared with the technologies of oil refining and petrochemical are a relatively low productivity and stringent conditions for their implementation (high temperature and pressure). To eliminate these shortcomings in the coal recycling, there is a wide spread usage of catalysts and new catalytic processes, which allows to obtain variety products from coal with a fuel and chemical features [3-8].

Experimental part

The experiment was conducted as following: 5 g of a mixture of dry brown coal from Karazhirskyi field was subjected to mechanical activation with a particle size of less than 0.1 mm, then a polyethylene with a particle size less than 0.5 mm, which was taken in an amount of from 10 to 70 wt.% by weight of a mixture of coal – polyethylene, were placed in a steel autoclave rotary with a volume of 0.5 l. The substances as Pd, Co, Mo and Fe were added as catalysts.

The autoclave was closed and the hydrogen was supplied until achieving a pressure of 5.0 MPa. The autoclave was heated to 430°C with continuous stirring, then it was kept at this temperature during 60 minutes, while the pressure in the autoclave was 6.0 MPa. After that, the autoclave was cooled and the gaseous products were separated. Then, the fraction, which was boiling up to 200°C, was separated from autoclave, and it was freezed out in a nitrogen trap. The solid product was separated and filtered.

Thermogravimetric studies were performed under the following experimental conditions: weight of the sample – (0.3 ± 0.03 g); analytical grinding;ceramic crucible with a lid, height of which is 15 mm and diameter 5 mm. Processing of the derivatograms included analysis of thermogram. The weight loss of the sample at a given temperature was determined according to the thermogravimetric curve. The rate of mass loss was determined in accordance with a differential thermogravimetry, temperature highs endo – or exo – effects – according to a differential thermogravimetric adsorption in line with standard procedures.



1 – reactor with a rotating autoclave, 2 – oven, 3 – manometer measuring the pressure at the outlet
4 – tap to collect gases, 5 – stationary reactor, 6 – bush for measuring the temperature in the stationary reactor, 7 – thermocouple for temperature control in a rotating reactor,
8 – manometers for temperature control, 9 – LATRS, 10-taps for establishing pressure in the reactor,
11 – manometer for controlling the pressure in the reactors, 12 – reducers to control the gas flow,
13 – cylinders of compressed argon and helium gases.

Figure 1 – Installation for hydrogenation in a stationary reactor and in a rotating autoclave

Results and their discussion

Thermogravimetric analysis was performed for the samples of original materials: solid polymeric products and coal material. A measurable weight loss curves (TG curves), and mass loss rate (DTG curves) were calculated on the basis of 1 g of the original sample and manifested as the temperature dependence, the nature of which is illustrated by the given thermograms (Figure 2.3). On the basis of DTG curves, the temperature (T_{max}) was determined in correspondence to the maximum rate of weight loss. In this paper, the weight loss is identical to the output of volatile products and the rate of mass loss is equivalent to the rate of release of volatile products during the heating.

When grinding coal from Karazhyr field, there were identified some general patterns, which are well observed by differential thermogravimetric curves after mechanical processing of coal in the mill.

Thermogravimetric curves (Figure 2.4) have a one minimum indicating to dehydration at the temperatures 109–116°C.

During the mechanical impact on coal, along with a change in the total amount of soluble fractions, their composition and structure are also changes, compared with the factions of the original coal.

The following stages of the transformation of coal from «Karazhir» field, after mechanical activation in the presence of a catalyst based on Fe and hydrogen-donor solvent tetralin have been established by the method of gravimetrical study: 1) Dehydration at temperatures 109°C; 2) thermal decomposition of a macro molecular structure of coal with formation of the radical fragments of 272–385°C; 3) recombination of these radicals with formation of high molecular products, saturation of radicals as a result of hydrogenation reactions by molecular hydrogen or by a hydrogen of hydrogen-donor solvent with formation of a low molecular products at the temperature range of 559–619°C.

Thermogravimetric study of coal in the presence of polymers (Figure 4) showed that the presence of high asphalt-resinous components – asphaltenes and benzene resins at the range 360–443°C was reduced in their content.

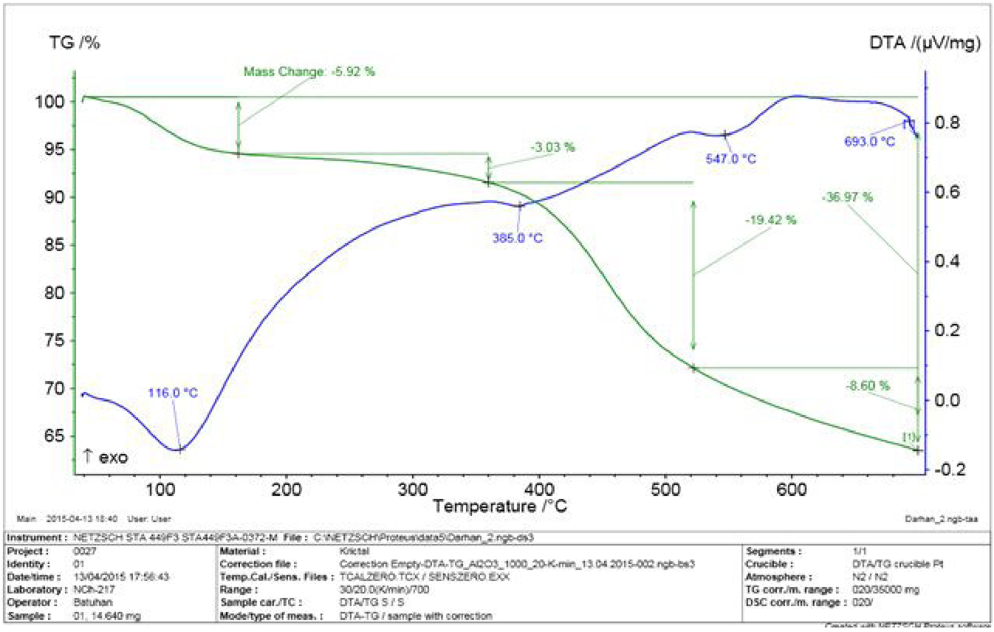


Figure 2 – Thermogravimetric study of the original coal

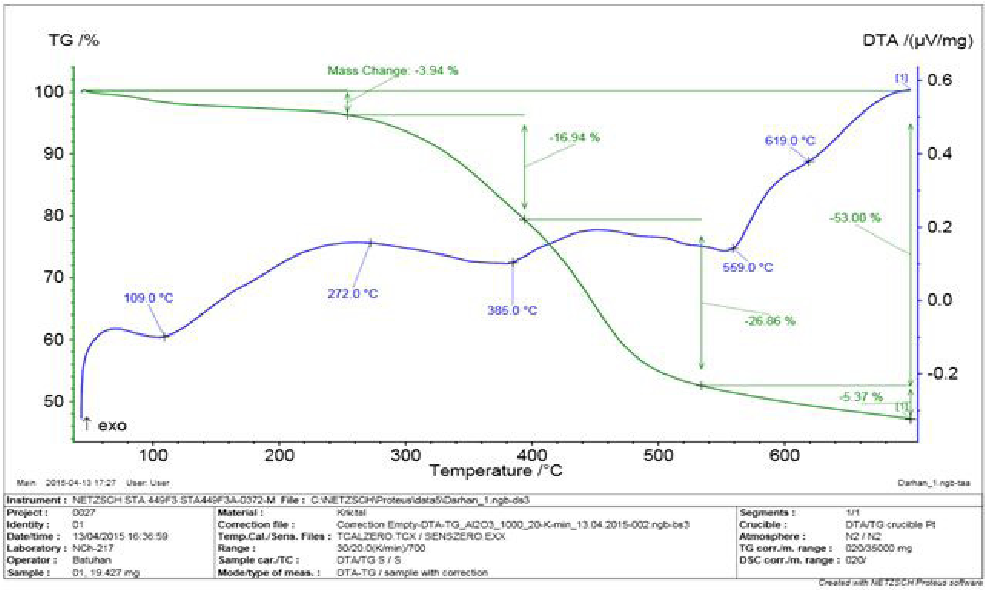
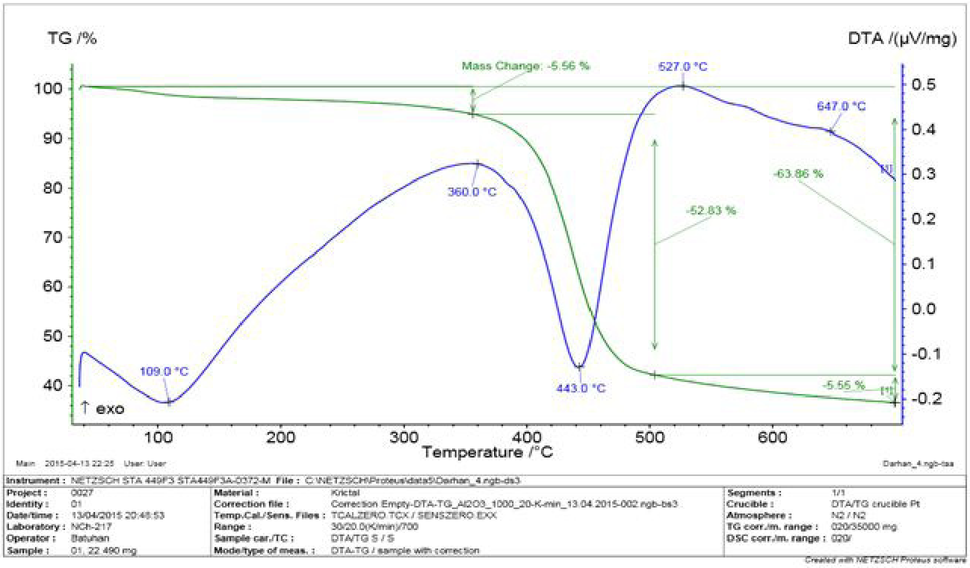


Figure 3 – Thermogravimetric studies of coal conversion after mechanical activation in the presence of a catalyst BC

Role of the components with lower molecular weight – benzene resins and oils was increased as a result of thermal effects in the bitumen. The presence of light petroleum-ether resins and aromatic hydrocarbons within the range of 443–527°C was increased in the content of the oil fraction.



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Operator : Batuhan
Sample : 01, 22.490 mg

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Range : 30/20.0(K/min)/700
Sample car./TC : DTA/TG S / S
Mode/type of meas. : DTA-TG / sample with correction

Segments : 1/1
Crucible : DTA/TG crucible Pt
Atmosphere : N2 / N2
TG corr./m. range : 020/35000 mg
DSC corr./m. range : 020/

Figure 4 – Thermogravimetric studies of coal and polymers convertion

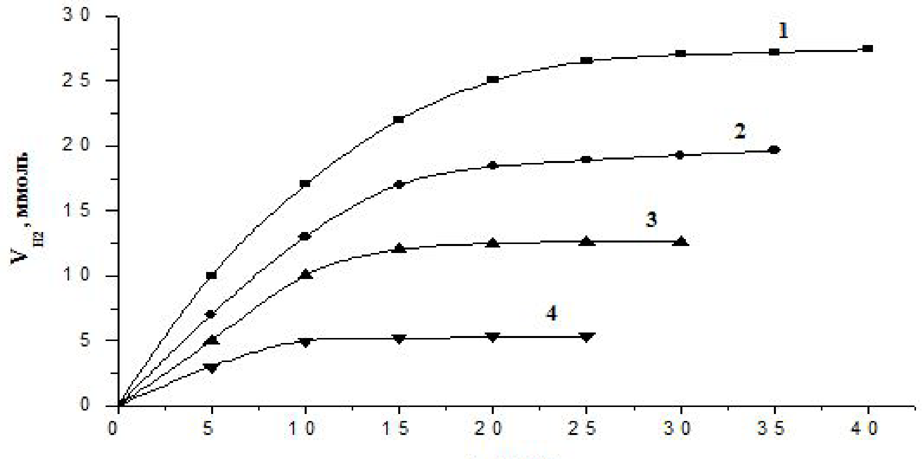
Thus, it was found that the iron catalysts promoted thermal decomposition of organic mass of coal.

Series of experiments was performed with the aim to select the optimum composition of the catalyst. Al_2O_3 and carbon were used as the carriers, while Pd, Co, Mo and Fe were used as an active phase. The percentage of metal in all of the catalyst was 5%. The experiment was conducted at a temperature of 325°C and a pressure of 5 MPa.

During the hydrogenation of the original material at all catalysts, there is a direct relationship between the hydrogen absorption and duration of the experiment. The maximum result was observed at the catalyst containingPd and was VH2 = 27.4 mmol (Figure 5).

In terms of swallowed hydrogen, catalysts are arranged in the following order:

Pd/C (27.4 mmol) > Co/C (19.6 mmol) > Mo/C (12.6 mmol) > Fe/C (5.3mmol)

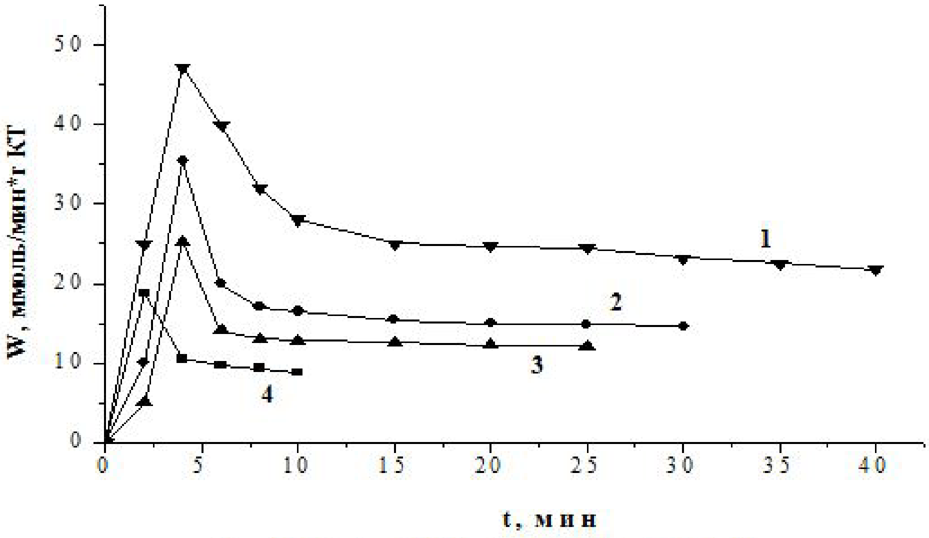


1 – Pd/C; 2 – Co/C; 3 – Mo/C; 4 – Fe/C

Figure 5 – The dependence of the absorption of hydrogen from the duration of the experiment at different catalysts with 5% metal content

Characteristically, with the duration of the experiment the catalysts arrange in the same sequence. In contrast to hydrogen absorption, the maximum rate of hydrogenation is observed on Co-containing catalyst and is 47.2 mmol/min*g CT (Figure 6).

Figure 6 shows that the maximum hydrogenation speed of the first three catalysts are observed on the 4th minute of hydrogenation, after that the rate is sharply fell and in the range of 15–40 min is almost unchanged. On the catalyst of Fe/C hydrogenation takes place at the lowest rate, the maximum of which is observed at the 2-nd minute of hydrogenation and it is 18.7mmol/min*g CT, which is ~ 2.5 times lower than the maximum speed observed on the most active Co-containing catalyst.



1 – Co/C; 2 – Pd/C; 3 – Mo/C;, 4 – Fe/C

Figure 6 – The dependence of the rate of hydrogen uptake from the experiment time on the different catalysts

Conclusion

Thus, based on the results of experiments, the highest activity still have catalysts on the basis of Pd/C, at which there was the greatest absorption of hydrogen and Co/C, in which the hydrogenation rate was the highest.

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