

DETERMINATION OF THE THERMODYNAMIC FUNCTIONS OF HEAVY HYDROCARBON CRUDE (COAL TAR) AND HYDROGENATION PRODUCT BY ADDITIVE PROCESS

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For the thermodynamic research of the coal-chemical process, in particular, the hydrogenation of coal processing of primary coal tar (PCT) in a wide temperature range it is necessary to have data on the value of the thermodynamic functions such as heat capacity, enthalpy, entropy, Gibbs free energy and the specified thermodynamic potential [1,2].

The purpose of the work is to determine the thermodynamic functions of: heat capacity (ΔC_p), enthalpy (ΔH), entropy (ΔS), Gibbs free energy (ΔG) and the specified thermodynamic potentials ($\Delta \Phi^{**}$) of the organic mass of coal (OMC) and the organic mass of the primary coal tar (PCT) obtained in the process of hydrogenation.

With the aim of determining the thermodynamic function (ΔC_p , ΔH , ΔS , ΔG , $\Delta \Phi^{**}$) of original OMC and a fragment of OMC after the hydrogenation processing, and of original PCT and hydrogenates obtained in the processing of hydrogenation of PCT with pseudohomogeneous ferrous catalysts (PHFC) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ an additive method of professor A.M. Gyulmaliev was used [2]. The offered method is based on the additive scheme wherein for calculation of temperature dependence of thermodynamic functions in the range of temperatures from 298 to 1000 K hydrocarbons of free structure defines a set of parameters from the hybrid states of carbon atoms and hydrogen atoms combined within by a chemical bond. According to the additive scheme thermodynamic function is:

$$\Phi_M = \sum_{\mu} f_{\mu}, (1)$$

Here f_{μ} is the value of the property F going over μ the type of the structural group.

For each group of atoms of the marks of value $C_p(T)$, ΔH and ΔS were defined from the relevant data for known models. The calculation of temperature dependence of C_p fragments was held by the quadratic function:

$$C_p(C_i^j) = a + bT + cT^2, (2)$$

Here a, b, c – coefficients.

Changes of an enthalpy and entropy of a molecule according to the temperature were calculated by the following formulas:

$$\Delta H_M(T) = \Delta H_{298} + \int_{298}^T \Delta C_{p,M}(T) dT, (3)$$

$$\Delta S_M(T) = \Delta S_{298} + \Delta T_{298} + \int_{298}^T \Delta C_{p,M}(T) d(\ln T), (4)$$

With due to (3) from the formula (4) here we have:

$$\Delta H(T) = \Delta H_{298} + \alpha(T-298) + \frac{\beta}{2}(T^2-298^2) + \frac{\gamma}{3}(T^3-298^3), (5)$$

$$\Delta S(T) = \Delta S_{298} + \alpha \ln \frac{T}{298} + \beta(T-298) + \frac{\gamma}{2}(T^2-298^2), (6)$$

где

$$\alpha = \sum_{\mu} a_{\mu};$$

$$\beta = \sum_{\mu} b_{\mu};$$

$$\gamma = \sum_{\mu} c_{\mu}.$$

Gibbs free energy ΔG was calculated by formula:

$$\Delta G(T) = \Delta H(T) - T\Delta S(T), (7)$$

With the aim of calculating the thermodynamic functions of the original OMC quantitative data of ultimate composition of Shubarkol coal deposit were used, the number of fragments of functional groups for ligneous (brown) coal were taken from [3]. Calculated values of thermodynamic functions of the original OMC are given in table 1.

Table 1. Thermodynamic functions of the original OMC

T, K	C_p , J/mole·K	ΔH , kJ/mole	S, J/mole·K	ΔG , kJ/mole	$F^{**}(T)$, kJ/mole·K
298	1964,6	-2391,5	1118,7	462,4	1118,7
300	1976,9	-2393,7	1131,9	480,9	1118,8
400	2550,8	-2488,2	1781,2	1428,4	1203,7
500	3043,2	-2559,5	2404,8	2417,7	1382,0
600	3454,3	-2611,3	2997,2	3433,7	1602,3
700	3784,0	-2647,8	3555,5	4462,0	1841,9
800	4032,3	-2672,7	4077,9	5488,5	2089,1
900	4199,2	-2690,2	4563,2	6499,1	2337,4
1000	4284,7	-2704,1	5010,8	7479,8	2582,7

Raise of temperature brings to a decrease of the enthalpy, and in the case of entropy temperature dependence has opposite character that shows the complication of structure of the obtained products.

Thus the temperature increase leads to the destruction of supramolecular ordering of macromolecules which formulates OMC.

With the aim of calculating thermodynamic functions of OMC after hydrogenation processing the fragment of OMC was used [4] (appendix 1). Calculated values of thermodynamic functions of the OMC fragment after hydrogenation processing is presented in Table 2.

Table 2. Thermodynamic functions of the OMC fragment after hydrogenation processing

T, K	C _p , J/mole·K	ΔH, kJ/mole	S, J/mole·K	ΔG, kJ/mole	F ^{**} (T), kJ/mole·K
298	188,5	-193,3	469,6	35,2	469,6
300	189,5	-193,7	470,9	36,6	469,6
400	234,9	-216,5	531,7	114,5	477,6
500	274,9	-240,9	588,5	200,3	494,2
600	309,4	-266,7	641,8	292,3	514,4
700	338,4	-293,5	691,7	389,2	536,2
800	361,9	-321,1	738,5	489,3	558,6
900	379,9	-349,1	782,2	591,2	581,0
1000	392,4	-377,3	822,9	693,3	603,2

It is known [5] that general characteristics of organic mass of PCT can be presented as the sum of characteristics of its components (fragments). Therefore studying of thermodynamics of hydrogenation process of PCT was carried out with the use of model compounds.

To calculate the thermodynamic functions of the organic mass of PCT before and after the hydrogenation processing with PHFC quantitative data of individual chemical composition of the original PCT and the products received after its hydrogenation within PHFC were used.

The individual chemical composition of the original PCT as well as the structure of hydrogenation products is given in the research [5] and presented by the following connections (concentration of compounds more than 1%): of 1,3-dimethylcyclohexane, ethylbenzene, octahydro-1H-indene, 1,2,3-trimethylbenzene, isoquinoline, 1,2-dimethylnaphthalene, 4-metildifenil, isopropylnaphthalene, fluorene, anthracene, phenanthrene.

With each catalyst on reactionary activity the number of compounds is formed. The chemical composition of the hydrogenation product which was obtained after the hydrogenation process of PCT with PHC - FeSO₄ · 7H₂O in an amount of 3% on the original weight of the tar is represented by the following compounds: 1,3-dimethylcyclohexane, ethylbenzene, octahydro-1H-indene, 1,2,3-trimethylbenzene, isoquinoline, 1,2-dimethylnaphthalene, 4-metildifenil, isopropylnaphthalene, fluorene. The chemical composition of the hydrogenation product obtained after the hydrogenation processing of PCT with PHF K - NiSO₄ · 6H₂O in an amount of 3% on the original weight of the tar is represented by the following compounds: naphthalene, 1-methylnaphthalene, biphenyl, 2-ethylnaphthalene, 2,6-dimethylnaphthalene, acenaphthene, dibenzofuran, fluorene.

The calculated values of thermodynamic functions of organic mass of the original PCT are given in Table 3, and the calculated values of hydrogenates of PCT with PHFC are given in Table 4.

Table 3. Thermodynamic functions of organic mass of the original PCT

T, K	C _p , J/mole·K	ΔH, kJ/mole	S, J/mole·K	ΔG, kJ/mole	F ^{**} (T), kJ/mole·K
298	1148,4	116,1	2659,9	2097,2	2659,9
300	1155,5	112,4	2667,6	2109,9	2659,9
400	1488,4	-71,6	3046,6	2782,6	2709,5
500	1782,5	-260,1	3411,0	3519,2	2813,6
600	2037,7	-451,9	3759,1	4305,7	2942,4
700	2254,0	-645,8	4090,0	5128,3	3082,9
800	2431,4	-840,5	4403,0	5973,3	3228,6
900	2569,8	-1034,9	4697,7	6826,9	3375,6
1000	2669,4	-1227,7	4974,0	7675,5	3521,8

In a temperature range from 298 to 1000 K ΔC_p, ΔS, ΔG, ΔF^{**} increase in absolute value and ΔH in the chosen temperature range decreases.

Table 4

Thermodynamic functions of hydrogenates of PCT with PHC

T, K	C _p , J/mole·K	ΔH, kJ/mole	S, J/mole·K	ΔG, kJ/mole	F ^{**} (T), kJ/mole·K
the hydrogenate obtained at hydrogenation processing of PCT with FeSO ₄ · 7H ₂ O					
298	963,0	-103,0	2248,2	1563,1	2248,2
300	968,8	-105,9	2254,7	1573,7	2248,2
400	1243,7	-253,5	2571,8	2137,8	2289,7
500	1487,0	-402,9	2876,0	2753,9	2376,8
600	1698,7	-553,3	3166,4	3410,3	2484,4
700	1878,7	-703,9	3442,1	4095,2	2601,7

800	2027,2	-854,0	3703,0	4797,0	2723,2
900	2144,0	-1002,9	3948,9	5503,9	2845,9
1000	2229,1	-1149,8	4179,4	6204,4	2967,8
the hydrogenate obtained at hydrogenation processing of PCT with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$					
298	777,3	326,6	1901,3	1511,7	1901,3
300	782,2	324,2	1906,5	1519,3	1901,3
400	1011,9	199,1	2163,7	1924,4	1934,9
500	1214,2	68,1	2411,7	2371,7	2005,7
600	1389,2	-67,7	2649,0	2852,6	2093,3
700	1536,8	-206,9	2874,5	3358,6	2188,9
800	1657,0	-348,4	3087,9	3881,5	2288,1
900	1750,0	-490,9	3288,7	4413,1	2388,2
1000	1815,5	-633,3	3476,7	4945,0	2487,8

Entropy increment allows to make the conclusion about the positive impact of PHC at hydrogenation processing towards the increasing yield of the light and medium fractions.

The equations of temperature dependence of the heat capacities of the original OMC, OMC fragment after the hydrogenation processing, the original PCT and hydrogenates obtained after PCT hydrogenation with PHC are given in Table 5.

Table 5

The equations of temperature dependence of the heat capacities of original raw materials and products of a hydrogenation

Compounds	Coefficients of equations $C_p = a + bT + cT^2 \text{ J/(mole} \cdot \text{K)}$			$\Delta T, \text{ K}$
	A	$b \cdot 10^{-2}$	$c \cdot 10^{-5}$	
OMC	-232,9	858,7	-406,9	298-1000
OMC fragment after the hydrogenation processing	-20,2	64,7	-27,4	298-1000
The original PCT	-76,8	469,1	-194,5	298-1000
Hydrogenate obtained with the adding $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	-45,7	385,6	-158,1	298-1000
Hydrogenate obtained with the adding $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	-70,8	325,4	-136,7	298-1000

Thus, using an additive method in the range of temperatures 298 – 1000 K the values of a heat capacity, an enthalpy, entropy, Gibbs free energy and the specified thermodynamic potential of the original OMC, OMC fragment after the hydrogenation processing, the original PCT and hydrogenates obtained in the process of PCT hydrogenation with PHFC were calculated. And also the equations of temperature dependence of heat capacities are calculated.

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Appendix 1

A fragment of organic mass of coal after hydrogenation processing

