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## The calculation of the thermodynamic functions of the hydrocarbon composition of the light fraction of primary coal tar with the boiling point 175 °C

The calculation of the thermodynamic functions of the hydrocarbon composition of primary coal tar fractions with the boiling point 175 °C is given in this article. Quantitative data of the elemental composition of primary coal tar fractions were used. The presence of hydroxyl and carboxyl groups (COOH, OH) in the primary coal tar fractions has been determined by means of acetate method and neutralization with alkalis. It is shown that dephenolized fraction obtained from hydrogenation product of primary coal tar fractions with boiling point 175 °C is an effective donor and a hydrogen carrier. This fraction also is capable to inhibit polymerization processes, stabilizing the radicals formed as a result of hydrogenation processes.

*Key words:* primary coal tar, thermodynamic calculation, hydrogenation, heavy hydrocarbon feedstock, nanocatalysts, Gibbs energy, coal chemical process, thermodynamic functions.

In the hydrogenation process of heavy hydrocarbon feedstock (HHF) the most important task is to increase the yield of liquid products by transferring hydrogen compounds, which give partially their hydrogen atoms to the reaction mixture [1]. Such compounds are called hydrogen donor. As it is known as hydrogen donor can be different solvents, fractions of coal tar, petroleum, heavy oil and its fractions. Thermodynamic calculations allow to establish the optimal degree of saturation with hydrogen donor molecules [2].

It was shown that the hydrogen content in composition of the donor strongly influences on the values of its thermodynamic functions and authors concluded that the effectiveness of H-donor is not determined by the amount of hydrogen in its composition, but by the values of thermodynamic functions [3].

For thermodynamic studies of coal chemical processes, in particular, for the hydrogenation processing of coal, primary coal tar and its fractions over a wide temperature interval, it is necessary to have data on the value of the thermodynamic functions such as heat capacity, enthalpy, entropy, Gibbs free energy. At present, there are no corresponding experimental data on the thermodynamic functions of the hydrocarbon composition of primary coal tar and its fractions, so in the literature, researchers pay more attention to the development of theoretical and practical methods of calculation [4].

It should be noted that the basis of the thermodynamic functions calculation of the hydrocarbon composition is the additive scheme for the study of model compounds' reactivity. Additive method for calculating of the thermodynamic functions of model compounds included in the fragmented structure of primary coal tar and its fractions was developed by Professor A.M.Gyulmaliev [5]. The proposed method is based on the additive system where for the calculation of the temperature dependence of the thermodynamic function in the temperature range from 298 to 1000 K of hydrocarbons of arbitrary structure is defined a set of parameters. According to the additive scheme thermodynamic function is:

$$\Phi_M = \sum_{\mu} f_{\mu},$$

where  $f_{\mu}$  is the value of the properties  $F$  attributable to  $\mu$ -th type of structure group.

The list of atomic groups used to calculate of hydrocarbons' thermodynamic functions and other organic molecules is given in [5]. For each group of atoms the values of  $C_p(T)$ ,  $\Delta H_{298}$  and  $\Delta S_{298}$ , are determined from the corresponding data for the known models. The calculation of the temperature dependence of fragments was carried out by a quadratic function:

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

where  $a, b, c$  — coefficients.

The changes of enthalpy and entropy of the molecule as a function of temperature is calculated as follows:

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

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

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

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

where,  $\alpha = \sum_{\mu} a_{\mu}$ ;  $\beta = \sum_{\mu} b_{\mu}$ ;  $\gamma = \sum_{\mu} c_{\mu}$ .

Gibbs free energy was calculated by the formula:

$$\Delta G(T) = \Delta H(T) - T\Delta S(T) .$$

The data of elemental composition of primary coal tar fraction have been used to calculate of thermodynamic functions of hydrocarbon composition of primary coal tar (PCT) fraction with boiling point 175 °C. The presence of hydroxyl and carboxyl groups (COOH, OH) in the fractions is determined by acetate method and neutralization with alkalis. The values of thermodynamic functions of the hydrocarbon composition of the initial fraction with boiling point 175 °C are given in Table 1.

Table 1

**Thermodynamic functions of the hydrocarbon composition of the organic mass of initial fraction of primary coal tar with boiling point 175 °C**

T, K	C <sub>p</sub> , J·mol <sup>-1</sup> ·K <sup>-1</sup>	ΔH, kJ/mol·K	S, J·mol <sup>-1</sup> ·K <sup>-1</sup>	ΔG, J·mol <sup>-1</sup> ·K <sup>-1</sup>	ΔΦ <sup>II</sup> , J·mol <sup>-1</sup> ·K <sup>-1</sup>
298	386.390	-437.579	453.635	-421.181	453.635
300	388.709	-437.279	456.228	-421.074	453.644
400	496.698	-419.793	583.214	-418.202	470.276
500	589.116	-397.916	704.266	-420.127	505.075
600	665.962	-372.369	818.703	-426.674	547.905
700	727.237	-343.878	926.163	-437.619	594.350
800	772.940	-313.163	1026.429	-452.707	642.169
900	803.072	-280.950	1119.361	-471.667	690.096
1000	817.633	-247.961	1204.863	-494.218	737.360

$$C(p) = -3.55139E+01*(T - 298) + 7.28480E-01*(T^2 - 298^2)/2 - 3.61606E-04*(T^3 - 298^3)/3.$$

The values of thermodynamic functions (heat capacity of the process, enthalpy, entropy, Gibbs energy) of the hydrocarbon fraction of PCT at 270 °C obtained from the hydrogenation of PCT fraction in the presence of nanocatalysts β-FeOOH, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> in the temperature range from 298 K to 1000 K, are shown in Tables 2–4. The conditions of hydrogenation PCT fraction at 175 °C are given as well.

Table 2

**Thermodynamic functions of the hydrocarbon composition of the organic mass of PCT fraction at 270 °C by the addition of nanocatalysts β-FeOOH**

T, K	C <sub>p</sub> , J·mol <sup>-1</sup> ·K <sup>-1</sup>	ΔH, kJ/mol·K	S, J·mol <sup>-1</sup> ·K <sup>-1</sup>	ΔG, J·mol <sup>-1</sup> ·K <sup>-1</sup>	ΔΦ <sup>II</sup> , J·mol <sup>-1</sup> ·K <sup>-1</sup>
298	351.083	-1049.861	761.207	-1125.120	761.207
300	352.735	-1049.633	763.561	-1125.628	761.215
400	429.355	-1037.344	875.812	-1152.792	776.045
500	494.186	-1023.612	978.803	-1183.092	806.439
600	547.227	-1008.780	1073.771	-1216.126	843.186
700	588.481	-993.195	1161.376	-1251.585	882.469
800	617.945	-977.200	1242.011	-1289.209	922.443
900	635.620	-961.140	1315.930	-1328.770	962.119
1000	641.507	-945.362	1383.308	-1370.063	1000.923

Table 3

**Thermodynamic functions of the hydrocarbon composition of the organic mass  
of PCT fraction at 270 °C by the addition of nanocatalysts  $\beta$ -Fe<sub>2</sub>O<sub>3</sub>**

$T, K$	$C_p, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta H, kJ / mol \cdot K$	$S, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta G, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta \Phi'', J \cdot mol^{-1} \cdot K^{-1}$
298	348.229	-1142.471	797.127	-1228.434	797.127
300	349.868	-1142.248	799.462	-1229.014	797.135
400	425.754	-1130.283	910.790	-1259.721	811.844
500	489.750	-1116.951	1012.890	-1293.474	841.984
600	541.857	-1102.609	1106.968	-1329.873	878.415
700	582.074	-1087.611	1193.668	-1368.606	917.343
800	610.402	-1072.313	1273.375	-1409.413	956.937
900	626.840	-1057.069	1346.336	-1452.064	996.211
1000	631.389	-1042.234	1412.720	-1496.348	1034.597

Table 4

**Thermodynamic functions of the hydrocarbon composition of the organic mass  
of PCT fraction at 270 °C by the addition of nanocatalysts  $\beta$ -Fe<sub>3</sub>O<sub>4</sub>**

$T, K$	$C_p, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta H, kJ / mol \cdot K$	$S, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta G, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta \Phi'', J \cdot mol^{-1} \cdot K^{-1}$
298	362.176	-784.806	648.989	-826.624	648.989
300	364.041	-784.555	651.418	-826.908	648.997
400	450.746	-770.624	768.326	-843.077	664.396
500	524.691	-754.289	877.087	-862.910	696.187
600	585.876	-735.991	978.352	-886.085	734.877
700	634.300	-716.174	1072.465	-912.327	776.465
800	669.963	-695.279	1159.634	-941.387	818.985
900	692.866	-673.749	1239.992	-973.034	861.361
1000	703.008	-652.024	1313.629	-1007.047	902.962

Analysis of the results of thermodynamic functions calculation given in Tables 5–8 showed that the addition of nanocatalysts  $\beta$ -FeOOH to the process of PCT fraction hydrogenation with boiling point 175 °C increases the value of the specific heat from 351 to 641.5 J/mol<sup>1</sup> K<sup>-1</sup>. When using the nanocatalysts Fe<sub>2</sub>O<sub>3</sub>, the value of the specific heat rises from 348.2 to 631.3 J/mol<sup>1</sup>K<sup>-1</sup>, in the process with the participation of Fe<sub>3</sub>O<sub>4</sub> is observed the same situation. The value of the heat capacity range from 362 to 703 J/mol<sup>1</sup>K<sup>-1</sup>, the values of entropy and chemical potential increase, while negative values of Gibbs energy rises. In the temperature range from 298 to 1000 K, the heat capacity, entropy and Gibbs energy are increasing in absolute value, and the enthalpy of the selected temperature range is increased to the positive side. The increase of entropy and rise of the negative value of enthalpy to positive side in the studied temperature range allows to draw a conclusion about the positive impact of nanocatalysts on the hydrocarbon composition of broad fraction 270 °C toward the increasing of low-molecular substances' yield.

Table 5

**Thermodynamic functions of the hydrocarbon composition  
of the dephenolized organic mass of PCT fraction at 175 °C**

$T, K$	$C_p, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta H, kJ / mol \cdot K$	$S, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta G, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta \Phi'', J \cdot mol^{-1} \cdot K^{-1}$
298	386.390	-437.579	453.635	-421.181	453.635
300	388.709	-437.279	456.228	-421.074	453.644
400	496.698	-419.793	583.214	-418.202	470.276
500	589.116	-397.916	704.266	-420.127	505.075
600	665.962	-372.369	818.703	-426.674	547.905
700	727.237	-343.878	926.163	-437.619	594.350
800	772.940	-313.163	1026.429	-452.707	642.169
900	803.072	-280.950	1119.361	-471.667	690.096
1000	817.633	-247.961	1204.863	-494.218	737.360

The values of the thermodynamic functions of the dephenolized hydrocarbon composition of initial fraction at 175 °C and dephenolized distillate fraction at 270 °C obtained from hydrogenate in the presence of nanocatalysts are shown in Tables 6–8.

Table 6

**Thermodynamic functions of the hydrocarbon composition of the organic mass of dephenolised fraction at 270 °C by the addition of nanocatalysts  $\beta$ -FeOOH**

$T, K$	$C_p, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta H, kJ / mol \cdot K$	$S, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta G, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta \Phi'', J \cdot mol^{-1} \cdot K^{-1}$
298	361.377	-285.803	258.580	-211.279	258.580
300	363.430	-285.553	261.004	-210.782	258.588
400	458.966	-271.232	378.973	-187.944	274.072
500	540.608	-253.681	490.416	-168.967	306.307
600	608.356	-233.454	595.180	-153.645	345.816
700	662.211	-211.108	693.181	-141.762	388.520
800	702.172	-187.197	784.371	-133.094	432.373
900	728.239	-162.278	868.716	-127.415	476.233
1000	740.413	-136.906	946.195	-124.495	519.413

Table 7

**Thermodynamic functions of the hydrocarbon composition of the organic mass of dephenolised fraction at 270 °C by the addition of nanocatalysts  $\beta$ -Fe<sub>2</sub>O<sub>3</sub>**

$T, K$	$C_p, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta H, kJ / mol \cdot K$	$S, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta G, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta \Phi'', J \cdot mol^{-1} \cdot K^{-1}$
298	356.919	-357.815	300.241	-295.707	300.241
300	358.966	-357.575	302.636	-295.292	300.249
400	454.237	-343.713	419.285	-276.550	315.554
500	535.546	-326.650	529.639	-261.548	347.443
600	602.895	-306.949	633.446	-250.099	386.552
700	656.284	-285.172	730.571	-241.998	428.840
800	695.711	-261.880	820.934	-237.028	472.275
900	721.179	-237.636	904.485	-234.965	515.720
1000	732.685	-213.003	981.187	-235.583	558.489

Table 8

**Thermodynamic functions of the hydrocarbon composition of the organic mass of dephenolised fraction at 270 °C by the addition of nanocatalysts  $\beta$ -Fe<sub>3</sub>O<sub>4</sub>**

$T, K$	$C_p, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta H, kJ / mol \cdot K$	$S, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta G, J \cdot mol^{-1} \cdot K^{-1}$	$\Delta \Phi'', J \cdot mol^{-1} \cdot K^{-1}$
298	362.231	-290.791	69.202	-159.832	69.202
300	364.388	-290.540	71.632	-158.956	69.210
400	464.575	-275.881	190.538	-117.219	84.790
500	549.803	-257.581	303.639	-79.478	117.353
600	620.071	-236.300	410.318	-45.573	157.382
700	675.381	-212.700	510.248	-15.301	200.735
800	715.731	-187.444	603.233	11.569	245.309
900	741.122	-161.194	689.146	35.281	289.917
1000	751.554	-134.612	767.903	56.092	333.838

It was shown that the increase of the Gibbs energy's negativity and enthalpy leads to rise of the donor ability of paste former [6, 7]. Analysis of the results presented in Table 8 shows that the calculated thermodynamic functions Gibbs free energy and enthalpy of the selected fraction as a hydrogen donor, are correlated with the calculated thermodynamic functions for individual substances such as tetralin, decalin. Analysis of the results presented in Table 8 shows that the calculated thermodynamic functions Gibbs free energy and enthalpy of the selected fraction as a hydrogen donor, correlates with the calculated thermodynamic func-

tions for individual substances such as tetralin, decalin. However, the values of enthalpy and Gibbs energy presented in the Table 8 do not correlate, as this figure is reduced for the individual substances and, in the case of the dephenolised PCT fraction with boiling point 270 °C increases (from negative value tends to the positive) in the chosen temperature range. Previously, the individual chemical composition of dephenolised PCT fractions at 175 °C was investigated [8], and established that there are various types of organic compounds such as cycloalkanes, aromatic and polyaromatic hydrocarbons in its structure. The presence of the alkyl substituents in the cycloalkane increases the donor ability and aromatic and polyaromatic hydrocarbons without alkyl substituents will serve as a hydrogen carrier better than the alkyl-substituted ones. In addition, the calculated values of the Gibbs energy presented in the Table 8 indicate that the transmission of hydrogen from a hydrogen donor to the carbon radicals is realized thermodynamically effectively when  $\Delta G < 0$ , that is, the donor must give hydrogen easily and to accept difficultly.

Thus, the thermodynamic functions of model organic compounds included in composition of the PCT fractions with boiling point 270 °C obtained from the hydrogenation of fraction with boiling point 175 °C before and after dephenolisation in presence of nanocatalysts  $\beta$ -FeOOH, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> have been calculated. According to the presented results of thermodynamic calculations, dephenolized broad fraction obtained from the hydrogenation PCT fraction with boiling point 175 °C is an effective donor and a carrier of hydrogen, i.e., capable to inhabit polymerization processes, stabilizing the radicals which are formed as a result of hydrogenation processes.

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### Соңғы қайнау температурасы 175 °C біріншілік тас көмір шайыр жеңіл фракциясының көмірсутектік құрамының термодинамикалық функцияларының есебі

Мақалада соңғы қайнау температурасы 175 °C біріншілік тас көмір шайыр фракциясының көмір-сутектік құрамының термодинамикалық функцияларының есебі қарастырылған. Біріншілік тас көмір шайыр (БТШ) фракциясының элементтік құрамының сандық деректері және сілтілерді бейтараптау, ацетатты әдістің көмегімен анықталған БТШ фракциясында карбоксилді және гидроксилді топты (COOH, OH) сандық анықтау нәтижелері қолданылған. Соңғы қайнау температурасы 175 °C фенолсыздандырылған БТШ фракция гидрогенизатынан алынған фенолсыздандырылған кең фракция тиімді донор және сутек тасымалдаушы, яғни гидрогенизация процесі нәтижесінде, түзілетін радикалдарды тұрақтандыра отырып, полимерлену процесі жылдамдығын төмендете алатыны анықталды.

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**Расчет термодинамических функций углеводородного состава  
легкой фракции первичной каменноугольной смолы  
с концом кипения 175 °С**

В статье проведен расчет термодинамических функций углеводородного состава фракции первичной каменноугольной смолы с концом кипения 175 °С. Для расчета были использованы количественные данные элементного состава фракции ПКС и результаты количественного определения карбоксильных и гидроксильных групп (СООН, ОН) во фракции ПКС, установленные с помощью ацетатного метода и нейтрализации щелочами. Показано, что обесфеноленая широкая фракция, полученная из гидрогенизата обесфеноленной фракции ПКС с концом кипения 175 °С, является эффективным донором и переносчиком водорода, т.е. способна ингибировать процессы полимеризации, стабилизируя радикалы, которые образуются в результате гидрогенизационных процессов.