

# KINETICS PRIMARY HYDROGENATION OF COAL TAR IN THE PRESENCE OF PSEUDO-HOMOGENEOUS IRON CATALYSTS

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Study of kinetic regularities destructive hydrogenation of primary coal tar (PKT) in the presence of pseudo-homogeneous iron catalysts (PHIC) is essential in the development of new, highly efficient hydrogenation processes, determine the optimal technical and economic conditions of the process, depending on the composition of the feedstock, the creation of new types of equipment and selection constructional materials [1-3].

The aim is to establish the kinetic parameters of the thermal degradation of the organic mass of primary coal tar (PKC) in the presence of pseudo-homogeneous iron catalysts (PGZHК).

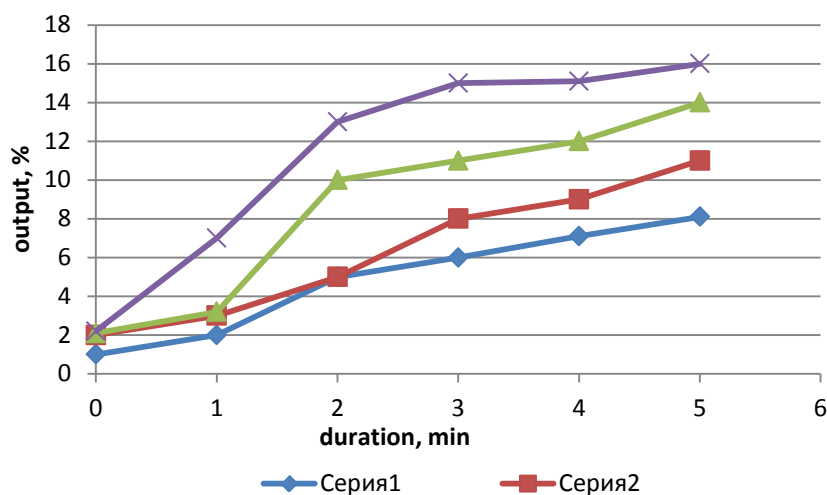
### Experimental part

Kinetic parameters of the primary hydrogenation of coal tar was carried out under autoclave conditions. Volume 0.05 liter autoclave previously was purged with hydrogen to remove air from

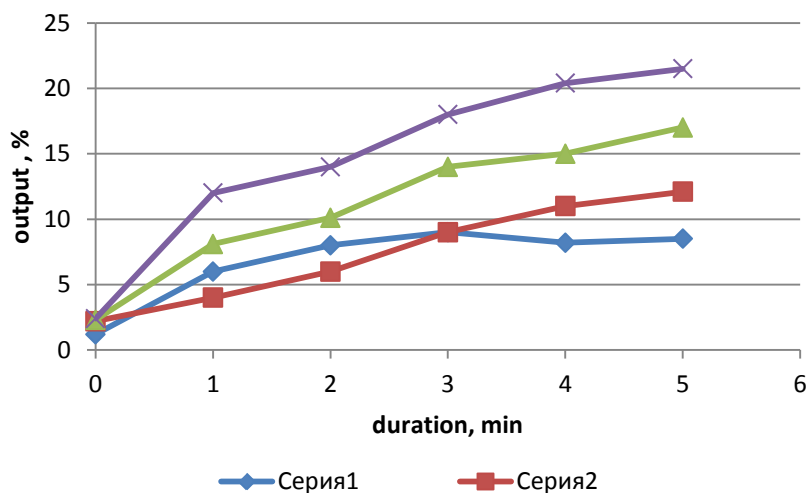
the autoclave, the initial hydrogen pressure was 2.0 MPa, the amount of added pseudo-homogeneous iron catalyst to organic primary weight coal tar was a 10% solution of ferrous sulfate and nickel.

### Results and discussion

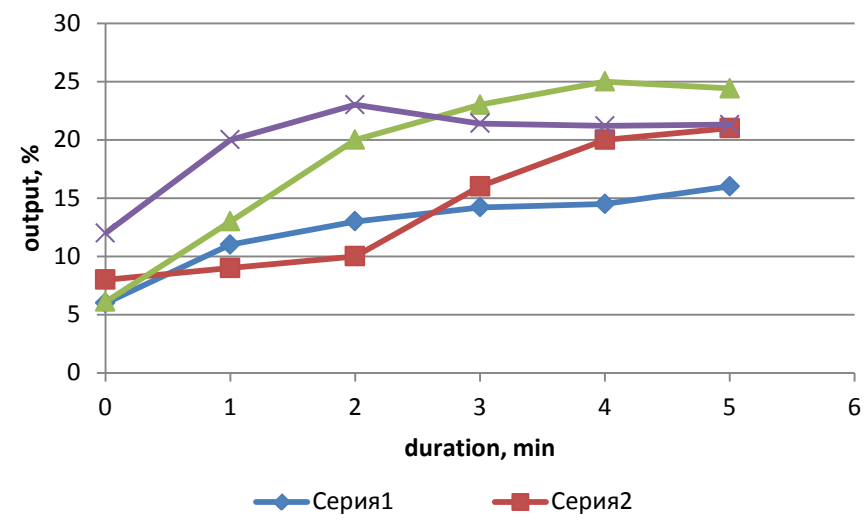
Figure 1 (a - d) shows the dependence of the output fractions hydrogenation process of PKT in the presence of PHIC, from which it follows that an increase in temperature and increase in contact time increases the output fraction to 453 K (Figure 1 a) in the temperature range 673 - 723 K 2 to 16%, as output fractions 453 - 503 K with 2 to 21% (Figure 1b). The maximum yield of the fraction 453 - 543 K is 25% (treatment time 4 min. at 707 K) (Figure 1). Output fractions 543 - 573 K with increasing duration of treatment time decreases monotonically.



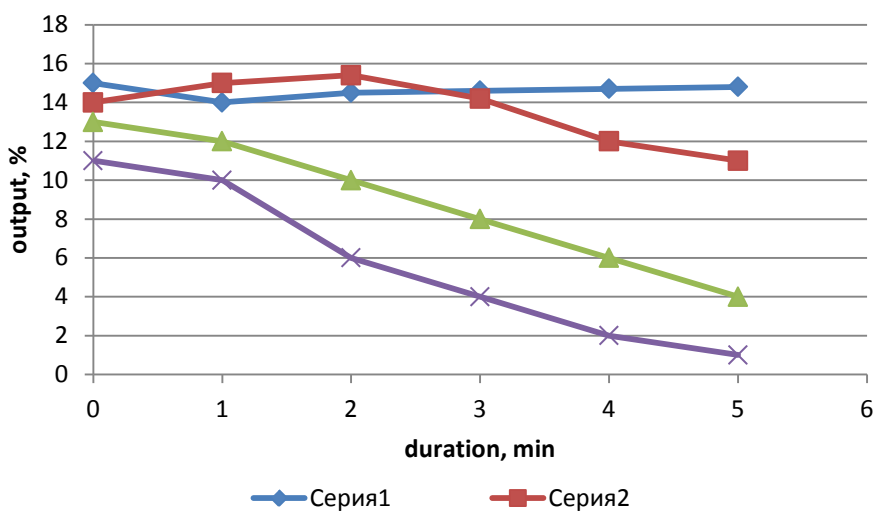
a)



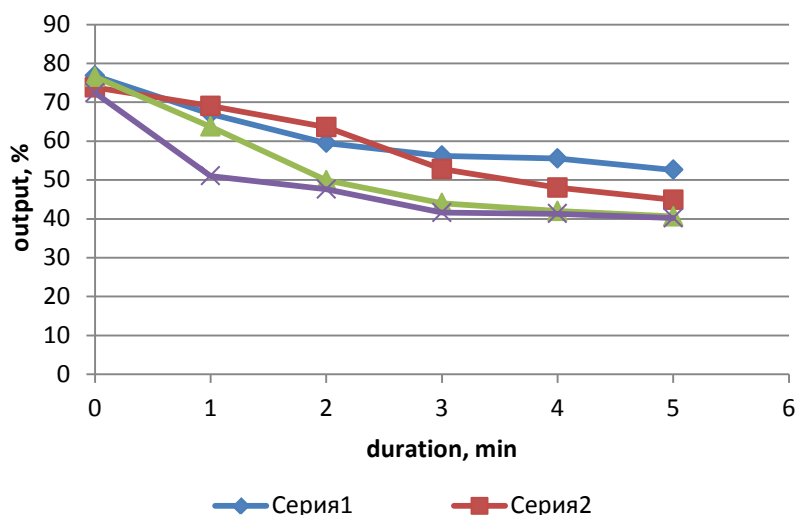
б)



в)



г)



д)

Figure 1. The dependence of the output fractions:

а) fraction to 453 K; б) 453 – 503 K; в) 453 – 543 K; г) 543 – 573 K;  
 д) above 573 K of PKC on the duration and temperature of hydrogenation treatment in the presence PH IK

where

- series 1 – processing temperature 673 K ;
- series 2 – processing temperature 690 K;
- series 3 – processing temperature 707 K;
- series 4 – processing temperature 723 K.

Under conditions of catalytic hydrogenation PKT high degree converting is provided it into light and middle fractions by high activity PHIK, particle size of 0.01 - 0.1 microns. Moreover, from the References [4] that hydrocarbons (such as PKS) have conjugated bonds are complexing agents with respect to transition metals. In [5], the authors found that clusters of nickel and iron with naphthalene(one of the model compounds form the basis of the PKT) to form the intermediate  $\pi$ -complexes, it is possible that in our case takes the selective hydrogenation of the hydrogen atom of one

ring of naphthalene takes place. Subsequently, the resulting  $\pi$ -complex is decomposed and forms a hydrogen donor - tetralin which further participates in the hydrogenation reaction, a high molecular weight part of PKT, thereby increasing the conversion yield of PKT and output of middle and light fractions.

Given the literature data on the kinetics of the hydrogenation of coal, heavy oil residue and semicarbonization tar, the following scheme of the route PKC catalytic hydrogenation is offered. (Figure 2) [6]:

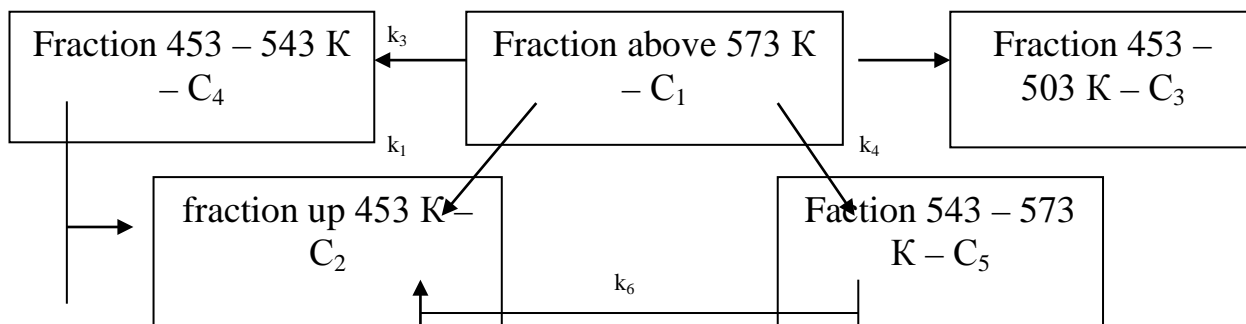


Figure 2. The kinetic scheme of transformation of the organic mass of the PKT in various fractions

Under the proposed scheme, the process can be described by the following system of differential equations (1):

$$\left. \begin{aligned} \frac{dC_1}{d\tau} &= -(k_1+k_2+k_3+k_4) C_1 \\ \frac{dC_2}{d\tau} &= k_1C_1+k_5C_4+k_6C_5 \\ \frac{dC_3}{d\tau} &= k_2C_1 \\ \frac{dC_4}{d\tau} &= k_3C_1-k_5C_4 \\ \frac{dC_5}{d\tau} &= k_4C_1-k_6C_5 \end{aligned} \right\} \quad (1)$$

Where:

- [C<sub>i</sub>] – mass part of fractions at time  $\tau$ ;
- [C<sub>1</sub>] fraction above 573 K; [C<sub>2</sub>] – fraction to 453 K,
- [C<sub>3</sub>] – fraction 453 – 503 K; [C<sub>4</sub>] – fraction 453 – 543 K;
- [C<sub>5</sub>] – fraction 543 – 573 K. [C<sub>1</sub>] = 1;
- k<sub>1</sub> – rate constant of hydrogenation, min<sup>-1</sup>;
- k<sub>1</sub> – the rate constant for the conversion of fractions до 453 K;
- k<sub>2</sub> – the rate constant for conversion 453 – 503 K;
- k<sub>3</sub> – the rate constant for the conversion of the fraction of PKT 453 – 543 K;
- k<sub>4</sub> – the rate constant for the conversion of the fraction of PKT 543 – 573 K;
- k<sub>5</sub> – the rate constant for the conversion of fractions 453 - 543 K in the fraction to 453 K;
- k<sub>6</sub> – the rate constant for the conversion of fractions 543 - 573 K in the fraction to 453 K.

The calculation of the system of equations (1) was carried out using a special program called "Search". The program developed for the calculation of the rate constants allows the calculation of the kinetic dependence for given initial conditions and to conduct automated selection of optimal gradient method of rate constants k1 - k6. Optimization of the rate constants was carried out by minimizing the squared deviations between the experimental and calculated values of the mass fractions of hydrogenation products of PKT.

As a result of the calculation system of differential equations (1) a satisfactory agreement between the experimental data and the calculated values of these fractions is given. The calculated rate constants are shown in Table 1, which shows that the rate-limiting catalytic hydrogenation of PKT is the step of converting fractions above 573 K in the fraction of 543 - 573 K, and the fractions 543 - 573 K in the fraction to 453 K (k4 and k6).

Table 1. The calculated rate constant and the activation energy of catalytic hydrogenation of PKT in the presence of PHIK

T, K	k <sub>1</sub> ·10 <sup>-3</sup> , min <sup>-1</sup>	k <sub>2</sub> ·10 <sup>-3</sup> , min <sup>-1</sup>	k <sub>3</sub> ·10 <sup>-3</sup> , min <sup>-1</sup>	k <sub>4</sub> ·10 <sup>-4</sup> , min <sup>-1</sup>	k <sub>5</sub> ·10 <sup>-4</sup> , min <sup>-1</sup>	k <sub>6</sub> ·10 <sup>-3</sup> , min <sup>-1</sup>
673	0,36967	2,1333	1,3508	1,0783	2,7367	0,25017
690	1,2715	4,8733	2,5183	2,8950	7,2667	0,23568
707	7,9033	13,936	5,42	3,8067	15,005	2,1833
723	22,395	35,763	11,763	7,1917	33,350	5,965
E, kJ / mol	132,1	88,34	66,1	54,9	77,95	93,6
R	0,9952	0,9983	0,9976	0,9783	0,9988	0,9965

The values of activation energy were obtained by fitting the Arrhenius equation described by a linear function  $\ln k = f(1/T)$  (Figure 2 a, b).

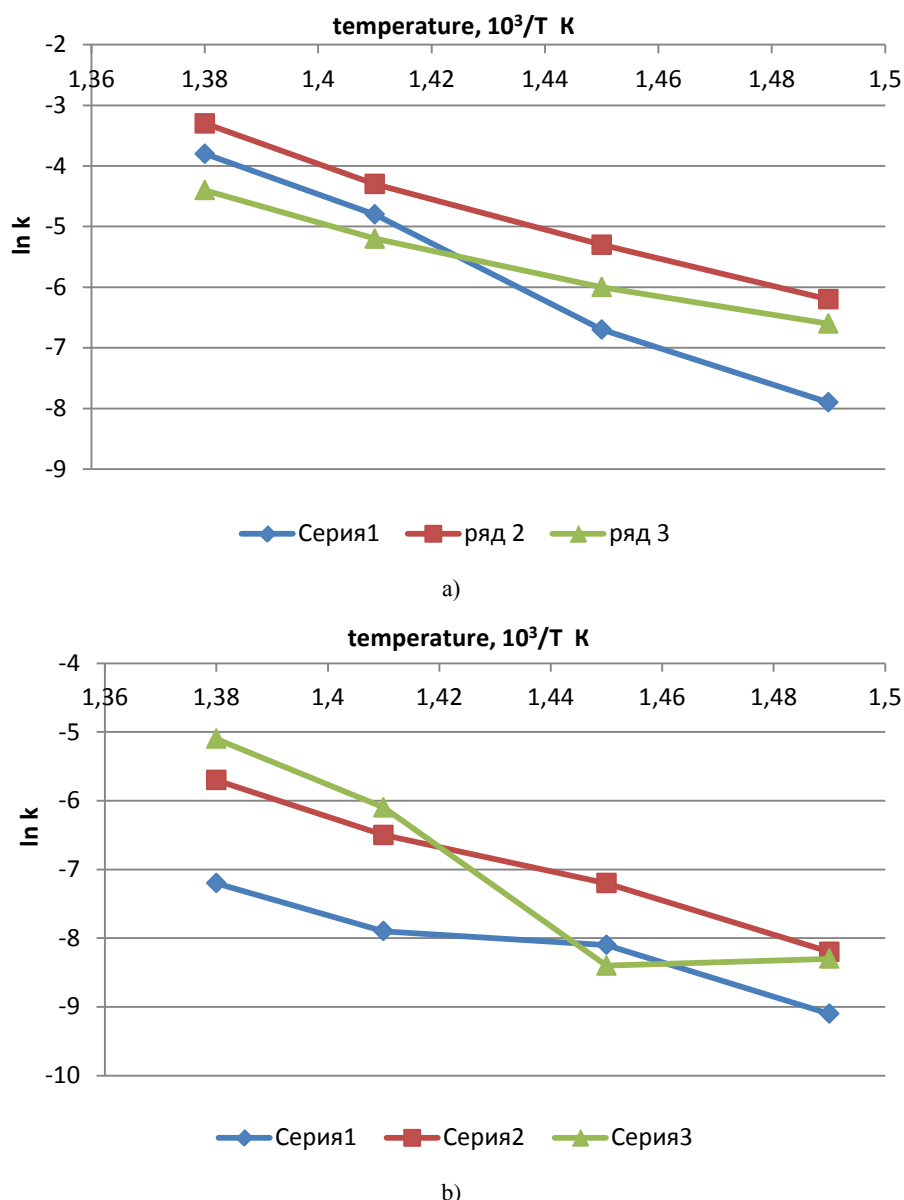


Figure 2. The dependence of the rate constant for the hydrogenation process of PKT from the return temperature : a) series 1 – rate  $k_1$ ; series 2 –  $k_2$ ; series 3 –  $k_3$ ; б) series 1 – rate constant  $k_4$ ; series 2 –  $k_5$ ; series 3 –  $k_6$

The apparent activation energy for the conversion process to the PCT in light and medium fraction is increased from 54.9 to 132.1 kJ / mol. The value of the apparent activation energy of the total transformation of the fraction above 573 K in the light and medium fraction is 54.9; 66.1; 77.95; 88.34 and 93.6 kJ / mol (see Table 1), which is characteristic of heterogeneous catalytic process, and the activation energy with the value of 132.1 kJ / mol - stage transformation fraction above 573 K to 453 K fraction corresponds to the diffusion region.

Thus, in a hydrogenating treatment of PKC in the presence PGZHK in the temperature range 673 - 723 K constants of rate of formation of fractions up to 453 K, 453 - 503 K, 453 - 543 K and 543 - 573 K, activation energy is calculated, and it is found that PHIK accelerates the degradation reactions and hydrogenation.

## References

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