ON THE KINETICS OF THE PRIMARY COAL TAR HYDROGENATION PROCESS

This paper presents the study of the kinetics of the primary destructive coal tar hydrogenation at coking factories of Kazakhstan. Under laboratory conditions, the dependence of fraction yield on the temperature and processing time duration was determined. As catalytic agents were used pseudohomogeneous ferriferous catalytic agents. Based on the studies, a mathematical model, describing the kinetics of the process, was developed. The results will be used in the development of tar processing equipment operating modes at coking factories.

Key words: kinetics, coal, fraction, yield, temperature.

INTRODUCTION

Destructive hydrogenation is a step process of catalytic addition of hydrogen under high pressure, followed by the cleavage of high molecular weight components of raw materials and the formation of low molecular weight hydrocarbons.

Recently, due to the reduction of oil reserves, significant fluctuations in its prices and high cost of exploring new deposits, scientific research and industrial experiment works on the upgrading and improving of performance of particular process steps of hydrogenation processing of solid fossil fuels became relevant again.

As raw material for hydrogenation can be used brown and hardcoal, distillation residues from coal, producer and primary tar, resin from light tight oil processing, dead oil (axle oil, oil tar, cracked residues), etc [1].

Another kind of raw material for destructive hydrogenation is primary coal tar, obtained in the process of semi-coking at the coking factories of Kazakhstan. It is very similar to the organic matter of initial coal in the structure, functional groups and structural fragments type. Is characteristic of primary coal tar to contain organic materials with a wide range of molecular weights [2-6]. It can be obtained in the conditions without high-temperature pyrolysis of these substances, allowing to use resin as a raw material for industrial organic synthesis.

In addition, the composition of primary coal tar differs from traditional coking factories resin, so it cannot be processed by the technology of high-temperature coal tar to produce certain market products [7-8].

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METHODS

The kinetic relationships were studied in an autoclave, pre-airated for the air drive. For the experiment was used technical hydrogen in cylinders with a purification rate of 99,98 %. The initial pressure in the autoclave was at the level of about 2,0 MPa. The amount of the added pseudohomogeneous ferriferous catalytic agent (ferric and nickel sulfate solution) was equal to 10 % of the organic matter of primary coal tar. The size of the catalytic agent particles ranged from 0,01 to 0,1 microns.

Resin with a catalytic agent was placed into an autoclave room with the volume of 0,05 litres, filled with hydrogen at the pressure of 2,0 MPa and heated at 400° C, 417° C, 423° C and 450° C for a certain time (see Figure 1).

DATA, ANALYSIS & RESULTS

After cooling the autoclave, liquid products were drained, separated from pyrolysis water, dried over anhydrous sodium sulfate and distilled the fractions having a boiling of under 180° C, 180 - 230° C, 230 - 270° C, 270 - 300° C, and over 300° C.

Figures 1a-1e show the dependence of coal tar fractions yield from the primary temperature and processing time duration.

According to the data, presented on Fig. 1a-1e, with the increase of temperature within the range of 400 - 450° C and the increase of contact time, the yield of fraction under 180° C increases from 2 to 16 % (Figure 1a), and the yield of fraction 180-230°C – from 2 to 21 % (Figure 1b). The maximum yield of the fraction 230-270° C was 25 % at the temperature of 423° C and processing time duration of 4 minutes (Figure 1c). The yield of fraction 270 - 300° C and fraction over 300° C reduces with the increase of processing time duration.
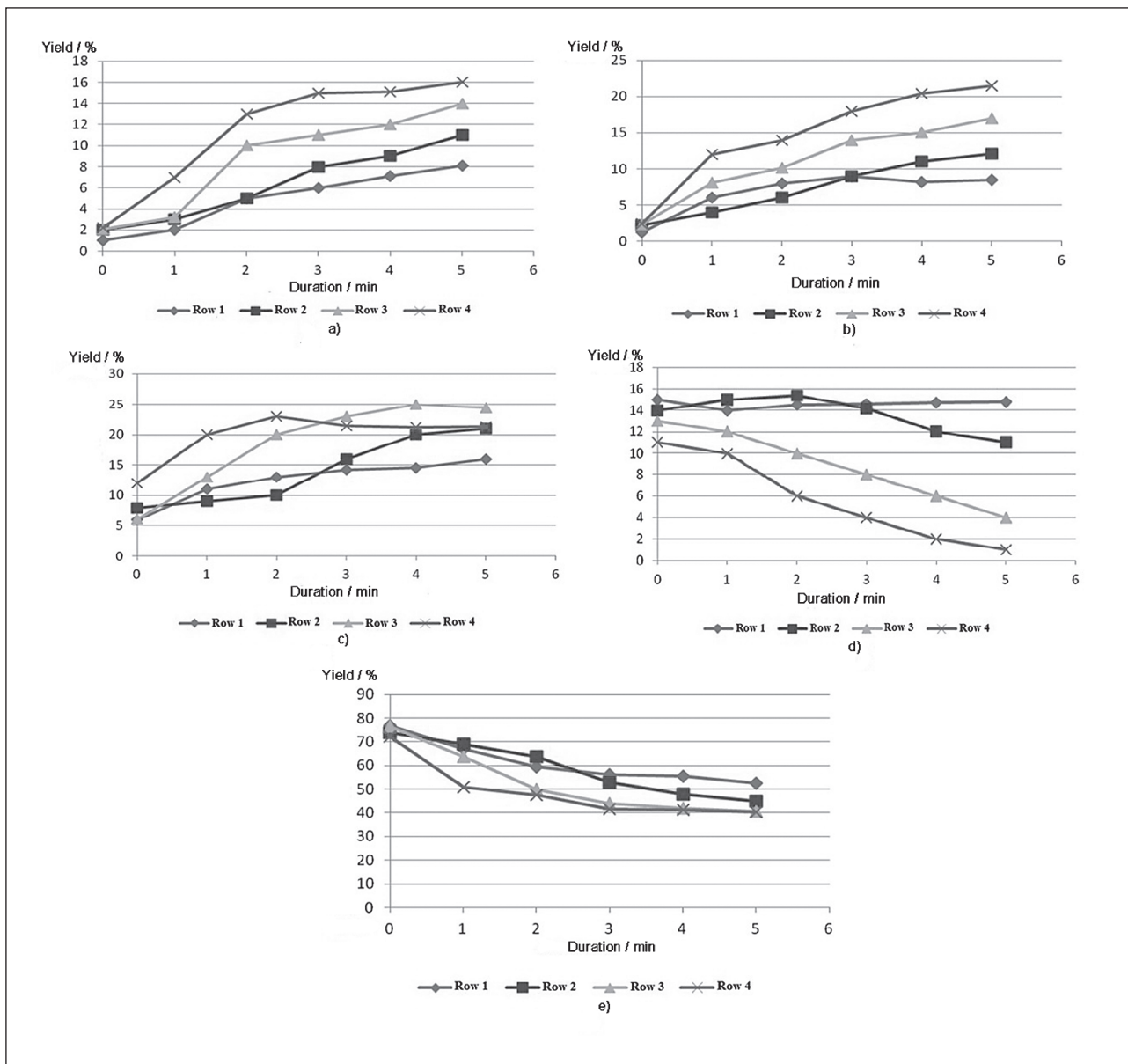
Figure 1 The dependence of fraction yield from duration and hydrogenation process temperature: a) fraction under 180° C; b) fraction of 180 - 230° C; c) fraction of 230 - 270° C; d) fraction of 270 - 300° C; e) over 300° C: where: Row 1 - processing temperature of 400° C; Row 2 - processing temperature of 417° C; Row 3 - processing temperature of 423° C; Row 4 - processing temperature of 450° C.
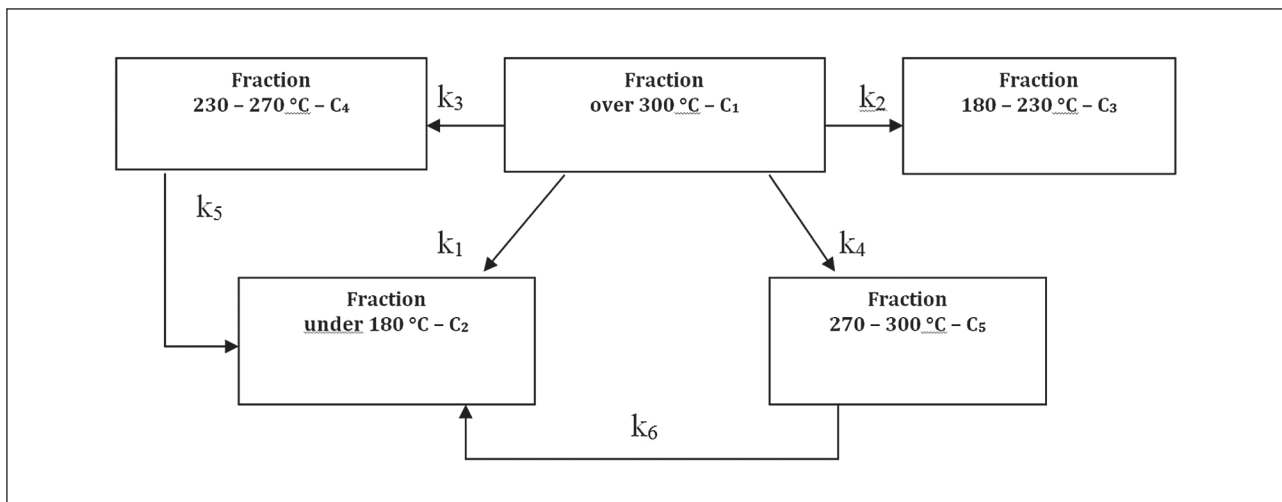
Figure 2 The conversion scheme of PCT organic matter into various fractions

Thus, in the process of catalytic hydrogenation of primary coal tar, the increase of processing time duration increases the yield of its intermediate and floating fractions.

Based on the data on hydrogenation kinetics of coal, heavy oil residue and semi-coking tar [9], the following scheme of the primary catalytic hydrogenation route of coal tar was proposed (Figure 2):

According to the introduced scheme, the process can be described in the following system of differential equations (1):

$$\left.\begin{aligned}
\frac{dC_1}{d\tau} &= -\left(k_1 + k_2 + k_3 + k_4\right) \\
\frac{dC_2}{d\tau} &= k_1 C_1 + k_5 C_4 + k_6 C_5 \\
\frac{dC_3}{d\tau} &= k_2 C_1 \\
\frac{dC_4}{d\tau} &= k_3 C_1 - k_5 C_4 \\
\frac{dC_5}{d\tau} &= k_4 C_1 - k_6 C_5
\end{aligned}\right\} \quad (1)$$

where (C_1) – total mass fraction over 300º C at a moment of time τ;

(C_2) – total mass fraction under 180º C at a moment of time τ;

(C_3) – total mass fraction 180 – 230º C at a moment of time τ;

(C_4) – total mass fraction 230 – 270º C at a moment of time τ;

(C_5) – total mass fraction 270 – 300º C at a moment of time τ;

k_1 – conversion speed constant of fraction under 180º C min^{-1};

k_2 – conversion speed constant of fraction 180 – 230º C min^{-1};

k_3 – conversion speed constant of fraction 230 – 270º C min^{-1};

k_4 – conversion speed constant of fraction 270 – 300º C min^{-1};

k_5 – conversion speed constant of fraction 180 – 270º C into fraction under 180º C min^{-1};

k_6 – conversion speed constant of fraction 270 – 300º C into fraction under 180º C min^{-1}.

The calculation of equations (1) was performed using the program "Poisk". This program was specifically designed for the calculation of speed constants; it allows to determine the kinetic dependencies with given initial conditions and to conduct an automatic optimum value gradient method fitting of a speed constants k_1-k_6. The optimization of speed constants was conducted through the condition of square deviation minimum between the experimental and calculated values of total mass fractions of the products of PCT hydrogenation.

As a result of determining the differential equations system (1), the authors proved the satisfactory correspondence between the experimental evidence and the calculated figures of the stated fractions. The calculated speed constants are given in Table 1, in which it is demonstrated that the limiting speed of PCT catalytic hydrogenation is the conversion case of fraction over 300ºC,

Table 1 **Fractions conversion speed constants and activation energy of PCT catalytic hydrogenation**

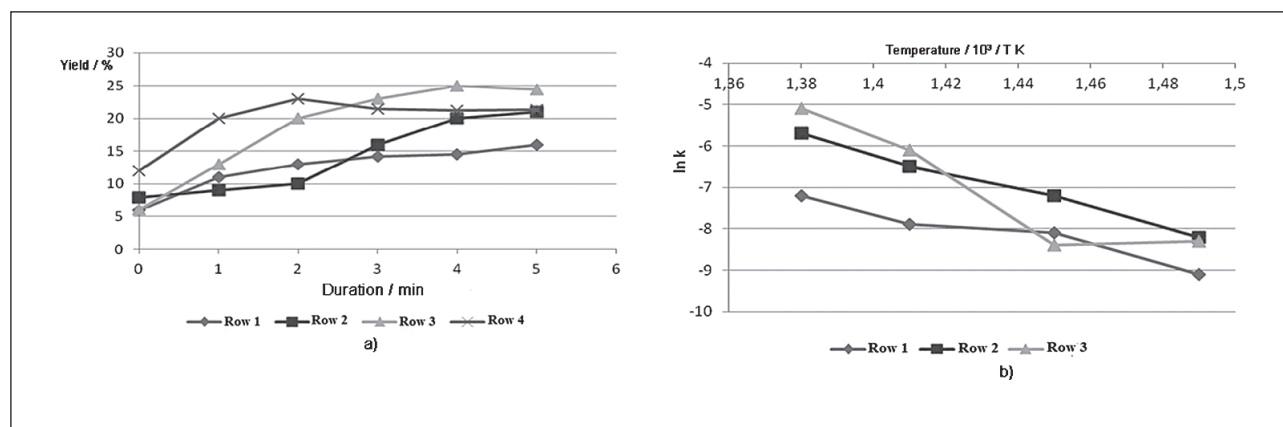| Tº C	$k_1 \cdot 10^{-3}$ min^{-1}	$k_2 \cdot 10^{-3}$ min^{-1}	$k_3 \cdot 10^{-3}$ min^{-1}	$k_4 \cdot 10^{-4}$ min^{-1}	$k_5 \cdot 10^{-4}$ min^{-1}	$k_6 \cdot 10^{-3}$ min^{-1}
400	0,36967	2,1333	1,3508	1,0783	2,7367	0,25017
417	1,2715	4,8733	2,5183	2,8950	7,2667	0,23568
423	7,9033	13,936	5,42	3,8067	15,005	2,1833
450	22,395	35,763	11,763	7,1917	33,350	5,965
E kilojoule/mole	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

Figure 3 The dependency of speed constant of tar hydrogenation process on the reciprocal temperature: a) row 1 – k_1 speed constant; row 2 – k_2; row 3 – k_3; b) row 1 – k_4 speed constant; row 2 – k_5; row 3 – k_6

as well as 270-300ºC into fraction under 180ºC (k_4 and k_6) (see Table 1).

The activation energy values were determined by approximation of Arrhenius equation, described by linear function ln k = f(1/T) (Figure 3).

CONCLUSION

The apparent activation energy in the process of PCT conversion into floating and intermediate fractions increases from 54,9 to 132,1 kilojoule/mole. The value of the apparent activation of total fraction conversion over 300º C into floating and intermediate fractions ranges from 54,9 - 132,1 kilojoule/mole (Table 1), which is characteristic of heterogeneous catalytic process. The activation energy of 132,1 kilojoule/mole is characteristic of the conversion case of fraction over 300º C into 180º C, which corresponds with diffusion region.

Therefore, in the conditions of PCT hydrogenation with pseudohomogeneous ferriferous catalytic agent present, within the range of temperatures between 400-450ºC, the creation speed constants of fractions under 180º C, 180 - 230º C, 230 - 270º C, 270 - 300º C and over 300º C, as well as the activation energy, were determined. The obtained data allow to predict the yield of various fractions in a production environment and can be used in determining the operating procedure of tar processing equipment at the coking factories of Kazakhstan.

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Note: The responsibile for english language is the Lector in from University