THE STUDY OF PETROLEUM COKE THERMAL STABILITY AND ITS FURTHER MODIFICATION – EXPERIMENTAL APPROACH AND MODELING

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ABSTRACT

The methodology and results of thermal stability study for initial and modified commercial petroleum cokes are presented. TG/DSC technique was applied for an experimental study of the petroleum coke calcination and further characterization of the improved coke in an oxidation reaction. It was found that the commercial coke still contained residual volatiles in a noticeable amount. The high-temperature stability of this commercial "raw coke" to be used for electrodes formation (e.g., in silicone production furnaces) or in carbothermal processes can be further improved via its additional calcination in a tubular kiln or an electro-calcinator under specified conditions. Kinetic modeling of the calcination process was proposed and further simulation of the tubular kiln operation was done to determine the optimal conditions of its functioning. The ash quantity was estimated as close to zero that makes it especially valuable for metallurgical silicone production.

KEYWORDS: petroleum coke, coke analysis, TG/DSC technique, coke oxidation stability, kinetic modeling, tubular kiln simulation, process optimization.

1. INTRODUCTION

Calcination of various carboneous materials in an inert atmosphere is usually done to improve their properties and prepare them for further applications – formation of carbon or graphite electrodes, metal or silicone oxides reduction in carbo-metallurgical processes, etc. Some invaluable impurities (e.g., sulfur) can also be partly removed at calcination under specified conditions. The result is a porous material with a higher content of carbon, far less

content of volatiles and impurities, more active in solid state reactions and also with better electro-physical characteristics.[1,2] Further thermal treatment gives a less porous material with high conductivity that is resistant under oxidative conditions. Calcination is normally done in special furnaces of various kinds. There are generally three furnace kinds – rotary kilns, electric calcinators and retort furnaces. Rotary kilns are more common in industry and they also have a higher productivity.[2-4] Yet the product quality after electric calcinators is usually better. Anyway the initial raw material characteristics and peculiarities of its further calcination are the key parameters to select optimal conditions for an industrial apparatus functioning.

Anthracite was the main natural source of coke for metallurgy and various electrodes production for a long time. Nowadays petroleum coke is successfully competing with coal coke as it has several fundamental advantages (very small ash content first of all). Yet it is noticeably more expensive since the technology of its production is complicated and the quality of raw material is vital for final petroleum coke. In Russia there is a lack of high quality petroleum coke and coal coke is still widely used for various purposes, even for electrodes formation. Petroleum coke should be properly prepared and further modified if necessary in case if we want to get a proper specified product. This work is devoted to the procedure of a commercial petroleum coke characterization and its further modification to improve the properties for carbo-metallurgical applications and for electrodes production. It was found that a definite commercial petroleum coke could not be directly used for electrodes formation due to a noticeable amount of residual volatiles. TG/DSC technique is the best way to perform proximate analysis and characterize oxidation stability and volatiles content in coals and cokes.[5,6,16] The same technique can also be applied for the direct study of an industrial process kinetics together with the development of a corresponding mathematical model of this technological process. It is obviously a universal and powerful tool to provide necessary information on the reaction rate for the majority of chemical processes under investigation as they are usually accompanied with weight changing of a solid phase together with heat generation or consumption.[4,7-10,15,16] A TG or DSC curve is usually not specific, but a generalized response for the course of a complicated process. Yet these curves are highly informative, and one can select characteristic points to perform additional product analyses in the selected points. Modeling with applying formal kinetics approach makes it possible to present a complicated physico-chemical process as a system of differential equations and pass to developing mathematical model of an industrial apparatus.[7-8,11-12,15]

2. MATERIALS AND METHODS

TG/DSC technique and kinetic modeling were applied for the calcination reaction study and developing a mathematical model of the rotary kiln to specify the optimal calcination mode. Final product was additionally characterized for its oxidation stability.

3.1. Reagents. Initial petroleum coke was from the Volgograd oil refinery (Volgograd, Russia).

3.2. Thermal analysis. Kinetic measurements were performed using a Labsys evo thermal analyzer (SETARAM Instrumentation). Linear heating mode with the heating rate $\beta = 10.0°C \cdot min^{-1}$ was applied. N_2 dynamic atmosphere (flow rate 20 mL$\cdot$min^{-1}) was applied for calcination process study. Static air atmosphere was applied for oxidation stability study.

3.3. Data acquisition and primary processing. *Calisto* program package (v 1.086, AKTS AG) was applied for running the experiment, data collection, and initial processing. *Experiment* program package (v 4.31, CISP Ltd) was applied for data preparation for kinetic analysis.

3.4. Kinetic analysis of the experimental data and modeling. *ReactOp Cascade* program package (v 3.20, CISP Ltd) was applied for data kinetic analysis, synthesis of the tubular kiln mathematical model and searching the calcination process optimal conditions.

3. LITERATURE OVERVIEW

Rotary kilns are widely used in industry for such processes as coke production, cement clinker production,[2-4] alumina production and others. Basic equations concerning solid material behavior and gas phase behavior inside the kiln were studied and discussed in detail in many papers, e.g.,[3-4,8] Yet the basic equations need to be emphasized to explain the possibility of applying a plug flow model to both the solid and the gas phase movement at petroleum coke calcination.

Movement of a solid material in the rotary kiln – basic equations

Peculiarities of a solid powder material transportation in the rotary kiln affect all important physical and chemical processes inside the drum. Movement of an interspersed layer is usually assumed for the initial raw material. Two force moments appear in the result of a drum rotation around its axis under the gravity force. These moments take part in the formation of this interspersed layer. Hence it is possible to assume a perfect mixing model in

the radial direction as remixing of particles along the drum axis takes place only in the interspersed layer. It depends upon the length of the chord cross-sectional layer and the special function f of angle β_c, kiln slope α_p and the free surface slope of the material to kiln axis α_M. This function f for a kiln with uniform layer l (that has the same height $\alpha_M = 0$) is approximately equal to (1):

$$f(\alpha_p, \alpha_M, \beta_c) \approx \frac{\sin \alpha_p}{\sin \beta_c} \qquad (1)$$

The particles movement equations based upon average values characterizing the motion of a solid material were proposed in.[3,13] Analytical solution of the equations system is not possible as the angle β_c value should be found experimentally. To complete the equations system discussed in[8] it was proposed to introduce an analytical expression for the main parameter of interspersed layer movement - bed height h, m[3]:

$$h_{м.р.} = \frac{\pi D n (1 - \cos F/2)[D(1 + \cos F/2) + 2h_{м.р.}]}{138{,}6 g^{0,5} \left(\dfrac{h_{м.р.}}{\cos \beta_c}\right)^{0,5} + 2\pi n [D(1 + \cos F/2) + 2h_{м.р.}]} \qquad (2)$$

Average speed of the material movement along the axis of the furnace W, m s^{-1}

$$W_M = \frac{4{,}62 g^{0,5} h_{м.н.}^{1,5}[D^2 - (D\cos F/2 + h_{м.р.})^2]^{0,5}}{D^2 \left(\dfrac{\pi F}{180} - \sin F\right)\cos^{0,5}\beta_c} \cdot f(\alpha_p, \alpha_M, \beta_c) \qquad (3)$$

Volumetric flow rate of the material, m^3 s^{-1}

$$W_M = \frac{0{,}577}{\cos^{0,5}\beta_c} g^{0,5} h_{м.р.}^{1,5}[D^2 - (D\cos F/2 + h_{м.р.})^2]^{0,5} \cdot f(\alpha_p, \alpha_M, \beta_c) \qquad (4)$$

Average rate of pouring, m s^{-1}

$$W_{м.р.} = \left(\frac{g h_{м.р.}}{3\cos \beta_c}\right)^{0,5} \qquad (5)$$

An important conclusion is that plug flow model may be used for describing mass transfer processes in a solid material inside the kiln and also for describing the gas phase motion as it is moved in a turbulent mode. Finally one should add a mass transfer equation inside the charge via the equation of mass transfer between the solid and gas phases and also a heat transfer equation between the charge, gas phase and surrounding medium. The source of heat for the process is natural gas burning inside the kiln.

Gas combustion and movement of gas phase in the rotary kiln - basic equations

Gas combustion for natural gas that moves in a turbulent mode inside the kiln is generally described with a complex system of equations. This system includes the equations of flow and continuity for the stream of a viscous compressible gas, the equations of energy and diffusion for the components of the combustible mixture followed by the equations for reaction products with nonlinear sources of heat and mass.

The intensity of these sources is a function of the chemical kinetics equations of gas burning. Generally, changes in the molecular mass of the reagents, the difference between heat capacity of initial products and combustion products, heat losses due to flame emission, dissociation and ionization phenomena – should be taken into account. The effects of heat and pressure diffusion, thermal conductivity diffusion should also be considered if possible.

Calculations related to gas combustion in a turbulent mode are generally complicated with the traditional hydrodynamic difficulties associated with an open system of equations for the Reynolds average turbulent motion. To complete the system of equations one should use some phenomenological models of the average flow and the equations that connect the effective (turbulent) transfer coefficients with the mean values of variables and their derivatives. Thus, analytical presentation of gas combustion in a turbulent flow needs to introduce some empirical coefficients and functions.[3,8]

A considerable simplification of the problem mathematical formulation is absolutely necessary. The full system of Navier-Stokes equations regarding the boundary layer should be replaced. It is also possible to neglect the pressure change in the flow field of a free jet. Heat transfer between gas phase, solid material and the kiln drum is provided due to radiation according to Stephen-Boltzmann equation. Heat transfer passes to the case of gas laminar flow,[8] after reducing the gas phase temperature.

Flame length is considered to be the main parameter of the burning gas jet. This parameter directly affects the whole process efficiency in a rotary kiln. The procedure of estimating flame length of a burning gas is discussed in a number of articles (see, e.g.,[14]).

Dust priming and dust returning - basic equation

At the very beginning of grinded coke calcination the charge undergoes a series of changes as a result of water and volatiles evaporation. At first the charge may even lose its initial

mobility, but after that there appears some other mobility in a new granular state. Since we deal with already pre-heated petroleum coke - this stage might be of less importance, yet it should not be totally neglected.

In the result of removing fine particles in course of a solid material movement the coke charge composition is changed. Coke dust that passed to a suspended state is almost totally burnt and due to this fact one can reduce the natural gas consumption. An empirical formula to calculate the weight concentration **μ** (kg/kg) of dust to be burnt in the gas stream inside a rotary kiln is as follows,[14]

$$\mu = 2 \cdot 10^{-11} \cdot \left(W_g \sqrt[3]{\frac{\rho_g}{\rho_M}} \right)^m \cdot \frac{D^{3/2}}{(\bar{d} r^3)} \cdot \left(\frac{n}{\psi} \right)^{2/3} \qquad (11)$$

where

W_g - gas flow rate, m/s;

ρ_g and ρ_M - densities of gases and material (coke), kg/m^3;

D - diameter of the furnace, m;

v - kinematic viscosity of gases m^2 sec^{-1},

$\bar{d}$ - average particle size of the material , m;

r - criterion of multi-fractional material characterization;

n − rate of kiln rotation, rpm;

ψ - degree of filling the kiln with solid material.

4. RESULTS AND DISCUSSION

Kinetic study details

Petroleum cokes are usually produced from highly aromatic secondary gasoils of catalytic cracking or gasoil stocks and pyrolysis heavy stocks in a semi-batch mode in special big reactors. After that green petroleum coke is calcinated at high temperature (over 1000°C) in tubular kilns, electric calcinators or retort furnaces. Electric calcinators and retort furnaces are less common yet the coke quality after them is usually higher. One may conclude that a proper calcination mode is the key parameter that is responsible for the coke final characteristics. It is not easy to select an optimal temperature mode for the definite green coke and provide its uniform calcination in an industrial rotary kiln. The problem was to

study the commercial petroleum coke (an already calcinated one) and propose a procedure to test and improve its specific characteristics if necessary.

At first the commercial coke sample was tested for its oxidative stability in air under comparable conditions with applying TG/DTG/DSC technique. Temperature intervals of oxidation were found and ash quantity was estimated. It was proved that ash quantity was close to zero (0±0.25%) within the determination error. Experimental data are given in Fig. 1.

Then a series of kinetic experiments on calcination reaction study in an inert atmosphere was performed and weight loss value was estimated as well as weight loss kinetics. It was found that at heating up to 1100°C total weight loss was around 15%, that is rather noticeable for an already calcinated petroleum coke. We may conclude that the commercial petroleum coke can be further improved through an additional calcination. Two additionally calcinated coke samples were prepared. Oxidation behaviour of the initial and these two additionally modified cokes (up to weight loss 10 and 15%, respectively) is presented in Fig. 3.
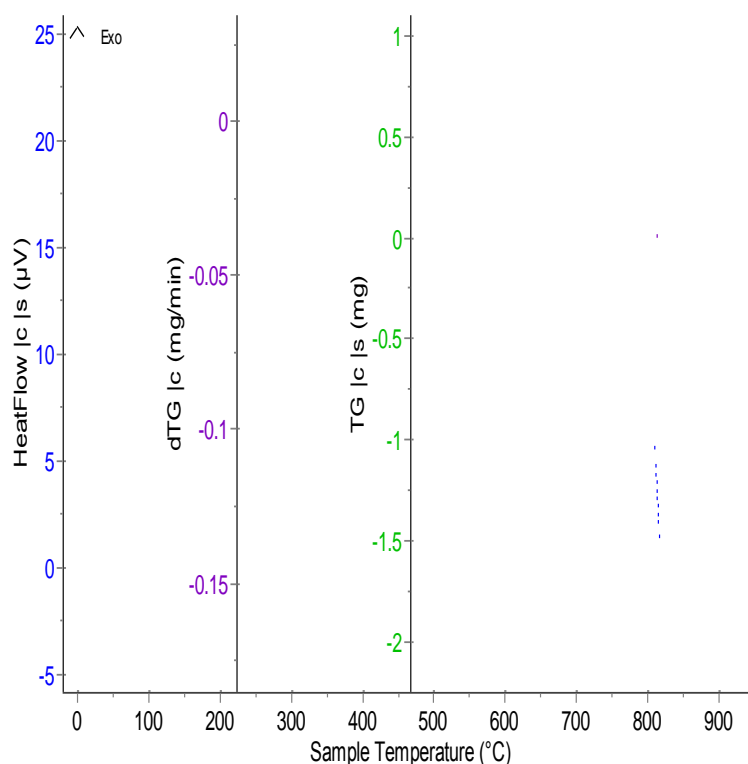

Fig. 1: Oxidation in air. Thermal analysis results for the commercial petroleum coke.

Linear heating, $\beta = 10°C \cdot min^{-1}$, static air, 20-900°C.

Apparatus: Labsys Evo

Initial Mass: 3.09 (mg) Wt. loss: 100.0±0.25%

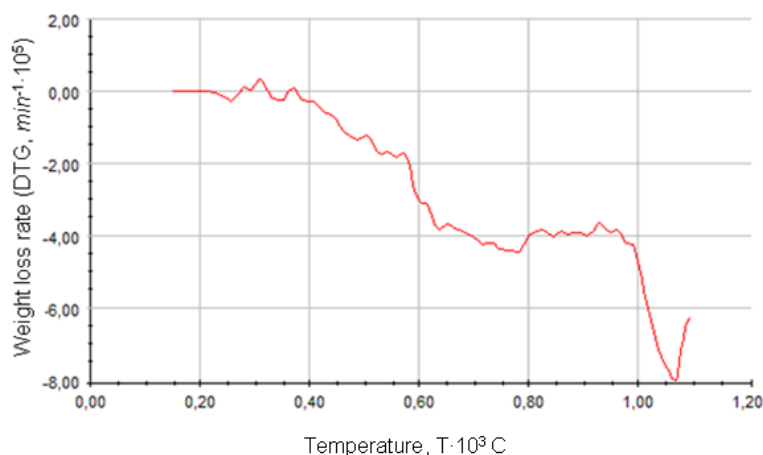**Fig. 2: Calcination in an inert atmosphere. Weight loss rate (DTG, $min^{-1} \cdot 10^5$) as a function of T (°C) for the commercial petroleum coke.**

Linear heating, β = 10°$C \cdot min^{-1}$, N_2 flow (20 $mL \cdot min^{-1}$).

It follows that additional calcination up to weight loss 10% (curve 2 in Fig. 3) makes the coke more active in chemical reactions (e.g., for pyrometallurgical processes) due to improving its porous structure and the deeper calcination makes coke more oxidation-resistant compared to the initial coke (see curve 3). Hence the basic properties of commercial coke may be effectively improved depending on its definite application. The next task is to find an optimal technological mode of the chosen rotary kiln to perform the additional coke calcination.
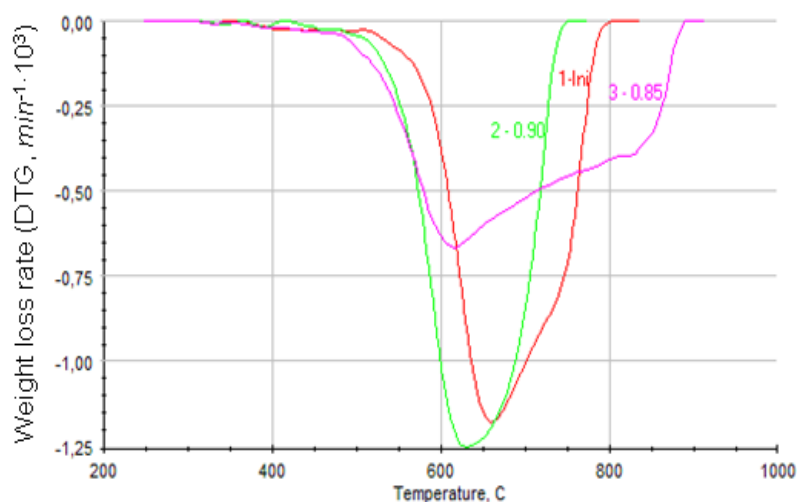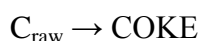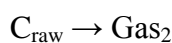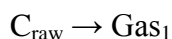

Fig. 3: Oxidation in air. Weight loss rate (DTG, $min^{-1} \cdot 10^3$) as a function of T (°C) for the initial petroleum coke (1), initial coke calcinated to weight loss 10% (2) and initial coke

calcinated to weight loss 15% (3) under similar conditions. Linear heating, β = $10°C \cdot min^{-1}$, static air.

Maximum value of oxidation rate for the modified petroleum coke (**3**) is only 55% of that for the initial petroleum coke (**1**).

ReactOp Cascade program package was used for developing the kinetic model and solving the inverse kinetic task on the base of the experimental weight loss data. LSODA solver of stiff and non-stiff systems of differential equations was implemented. A formal 3-stage N-order model was applied for the calcination reaction kinetic modeling. It looks as follows:

$C_{raw} \rightarrow Gas_1$

$C_{raw} \rightarrow Gas_2$

$C_{raw} \rightarrow COKE$

Where:

- C_{raw} – initial commercial ("raw") Coke to be modified;
- Gas_1 – coking Gas (1) containing mainly hydrogen (H_2);
- Gas_2 – coking Gas (2) containing methane and other light hydrocarbons.
- COKE – modified coke with better characteristics.

Initial coke gives two kinds of coking gas at calcination and the residual solid phase is transformed in the result to a modified coke ('COKE").

The procedure of solving the inverse kinetic task was to determine the kinetic parameters from experimental data in the result of minimizing the sum of squared deviations between experimental and calculated (i.e., generated due to a selected model) data. This value is a complex function of the kinetic parameter set; hence, the task of its determination is to find a minimum value of the many variables function.[11,12] A good correlation between experimental and calculated kinetic curves was reached in the result (see Fig. 4).
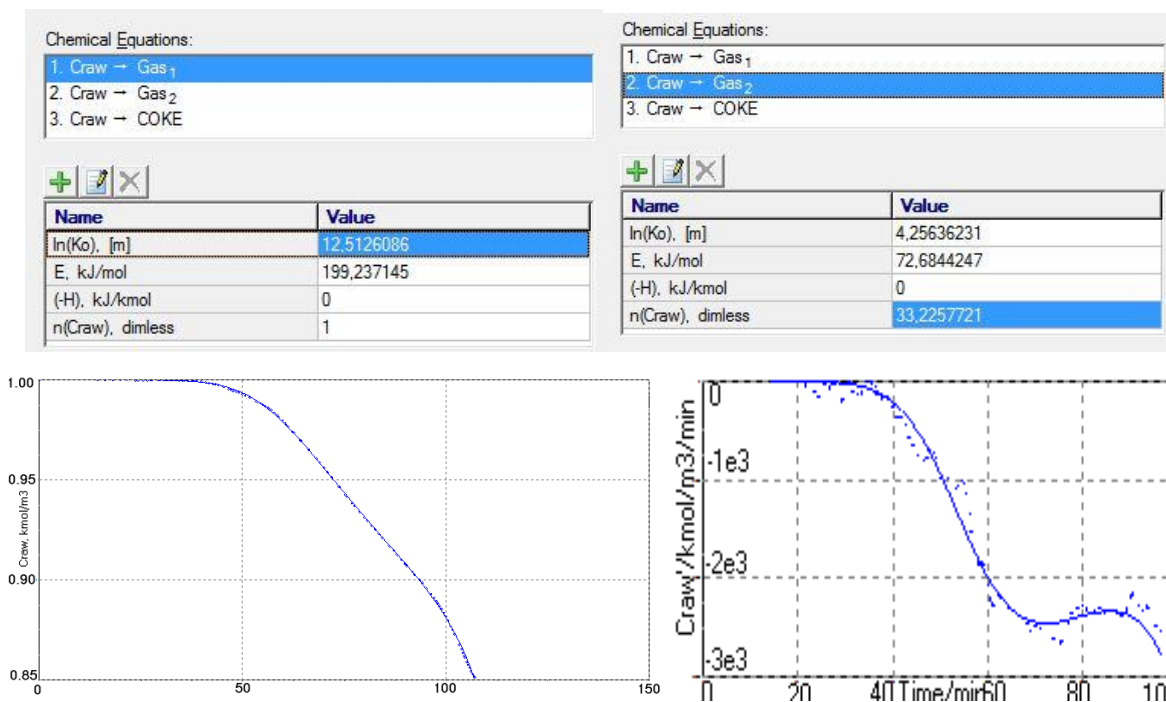
Fig. 4: The results of kinetic analysis for the reaction of commercial petroleum coke additional calcination in an inert atmosphere. Experimental (points) and calculated (lines) weight loss response (TG, left) and weight loss rate response (DTG, right). 3-stage N-order formal model.

Searching an optimal temperature profile inside the tubular rotary kiln

Temperature difference between gas burning flame and solid material is the main route of heat transfer in a tubular furnace. In the calcination zone the temperature should be strictly definite. Any excessive overheating may cause an invaluable aggregation of small particles of the charge. Analysis of simulation results indicates that the behavior of temperature profiles for gas phase and solid material in the process of calcinating the coke corresponds to these basic restrictions described in the literature.

A mathematical model of the calcination process makes it possible to define an optimal temperature profile through solving the corresponding optimization problem. Weight loss of the initial commercial petroleum coke ("raw coke") at the exit of the rotary kiln can be chosen as an optimization criterion for the calcination process. Its value was defined in course of the thermoanalytical study. It is 10% if we need an active material for carbothermal processes or 15% if we need a material for electrodes formation. Temperature profile control along the length of the kiln is as follows:

$$u = T(l) \qquad (12)$$

Optimization criterion is expressed through the solid charge weight loss along the kiln. Thus the control variable is the control function $T(l)$. Generally it is a variational calculation task. If we represent the desired optimal temperature profile as a piecewise linear approximation of the control function along the kiln length, we can pass from the variational problem to the normal problem of searching the extremum of a function of several variables:

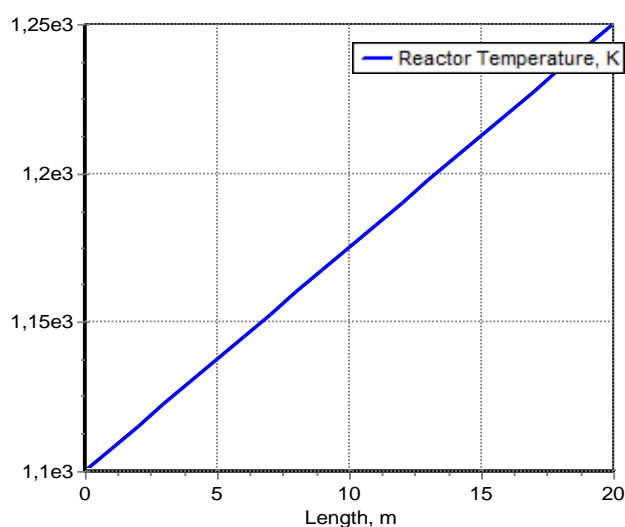$$T_{i\min} \leq T_i \leq T_{i\max} \tag{13}$$

The control values (i.e., temperature at certain points) should be found from a given control field. For each step the temperature profile restrictions are set separately. It is a typical problem of searching an extremum with constraints given in the form of inequalities. The method of nonlinear programming may be used to solve this kind of a problem. It is implemented in the program package *ReactOp*. Temperature profile of the solid phase is the control variable that we need to find through solving the optimization problem. The reaction kinetic model was introduced to a tubular kiln model and optimal conditions of petroleum coke calcination process were established. Two models of rotary kiln were consecutively applied:

1) Standard Plug flow reactor model (no heat exchange, T given) to estimate kiln length, rate of material movement, thickness of layer and heating mode range.

2) Modified Plug flow reactor model with heat exchange to determine a precise temperature mode, weight loss of initial coke and output of the improved coke.
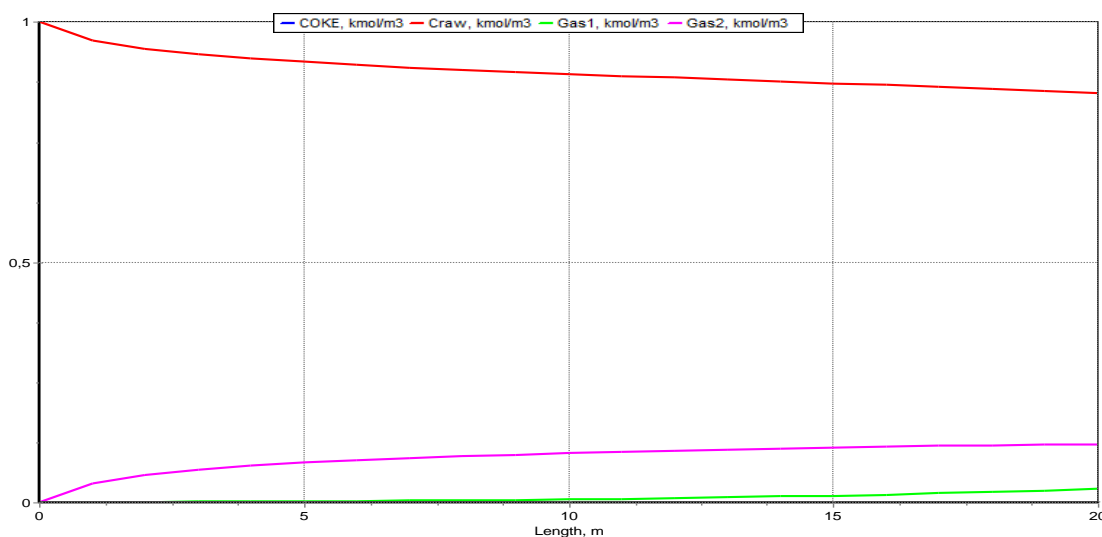
The task of searching the optimal temperature profile $T(l)$ has been successfully solved. This optimal temperature profile $T(l)$ was introduced into the process mathematical model and the consumptions of natural gas and air to support this regime were found. This procedure allowed us to find the necessary control variable values for an industrial rotary kiln of the given characteristics (length 20 *m*, diameter 1 *m*, effective diameter of solid charge 0.2 *m*, linear velocity of charge movement 0.2…0.5 *m min*$^{-1}$). Solution results of the optimization task are given in Table 1 and Figures 5-6.

Table 1: Basic technological parameters of petroleum coke calcination.

Parameter	10% weight loss	15% weight loss
Temperature interval, K	1000-1150	1100-1250
Rate of coke movement, $m \cdot min^{-1}$	0.52	0.30
Mass fractions of the products at output:		
- Coke	0.90	0.851
- Gas1	0.003	0.028
- Gas2	0.097	0.121

Fig. 5: Temperature profile of the solid phase for the process of initial coke calcination to reach final weight loss of the charge 15% from the initial value.

Kiln length – 20 *m*; estimated linear velocity value of the charge – 0.30 $m \cdot min^{-1}$.

Fig. 6: Conversion profiles of the components along the kiln for the process of initial coke calcination to reach final weight loss of the charge 15% from the initial value. Estimated linear velocity value of the charge – 0.30 $m \cdot min^{-1}$.

CONCLUSION

The results obtained in course of the study indicate of the effectiveness of applying thermal analysis technique together with mathematical modeling to the task of petroleum cokes characterization and further modification in tubular rotary kilns. To develop a mathematical model of the industrial kiln with the known chemical transformation we need to study kinetics of the corresponding chemical reaction with the use of TG-DTG or TG-DSC technique. In course of the kinetic modeling a formal model has been effectively used for describing a definitely heterogeneous process in an industrial apparatus. It should be emphasized that numerical values of the kinetic parameters found are a function of the solid phase dispersion and the method of charge preparation.

The developed mathematical model of petroleum coke calcination for improved coke production describes chemical transformations through weight loss of the charge in the chosen rotary tubular kiln with an appropriate adequacy. It can be used for optimization of an industrial process with the use of nonlinear programming mathematical methods.

ACKNOWLEDGMENT

REFERENCES

1. A. Rohani, K.Sharifi, R.Golpasha. Calcinations of Petroleum Coke // 3rd International Conference on Chemical, Ecology and Environmental Sciences, 2014; 3.

2. M.A. Martins, L.S. Oliveira, A.S. Franca. / Modeling and simulation of coke calcination in rotary kilns // Fuel, 2001; 80: 1611-1622.

3. Sribner N.G. / Analysis of the bulk materials movement in rotating drums // Chemical Industry, 1979; 232-235.

4. Borisov I.N. / Routes to increase the efficiency of chain curtains in rotary kilns. // Cement and its application, 2003; 3: 17-20.

5. ASTM E1131 Standard Test Method for Compositional Analysis by Thermogravimetry.

6. ASTM D3172 Standard Practice for Proximate Analysis of Coal and Coke.

7. Peter J. Haines / Principles of thermal analysis and calorimetry // The Royal Society of chemistry, 2002; 55-92.

8. Sharikov Y.V., Sharikov F.Y., Titov O.V. / Optimization of process conditions in a tubular rotary kiln with applying TG/DSC technique and mathematical modeling // J Therm Anal Calorim, 2015; 122: 1029–1040.

9. Navrotsky A. / Progress and New Directions in High Temperature Calorimetry // Phys. Chem. Miner, 1997; 24: 222.

10. Wilthan B. / Uncertainty budget for high temperature heat flux DSCs // J Therm Anal Calorim, 2014; doi:10.1007/s10973-014-3671-0.

11. Sharikov Y.V., Beloglazov I.N. / Modeling of Systems. Part 1 // Saint-Petersburg State Mining University. SPb., 2011; 89-43.

12. Y.V. Sharikov, I.N. Beloglazov. / Modeling of Systems. Part 2 // Saint-Petersburg State Mining University. SPb., 2012; 74-27.

13. Borisov I.N. / Some features of the behavior of sludge on the drying circuit // Cement and its application, 2002; 5: 26-28.

14. Khodorov E.I., Ekimov V.A., Limonov B.S. / A study of the material behaviour in the open surface layer in a rotary kiln // Alumina proceedings YOU. - L: YOU, 1974; 88: 48-57.

15. Sharikov F.Yu., Sharikov Yu.V., Titov O.V. / Application of heat-flow calorimetry for developing mathematical models of reactor processes // Theoretical Foundations of Chemical Engineering, 2016; 50(2): 225-230.

16. Sharikov F.Yu., Bazhin V.Yu. / The study and modeling of coals and cokes behaviour with applying thermal analysis technique // Proceedings of XIX International Coal Preparation Congress. New Dehli, 2019; I: 105-114.