How to Cite: Tyanakh, S., Baikenov, M.I., Gulmaliev, A.M., Ma, Feng-Yun, Musina, G., Khamitova, T.O., & Bolatbay, A.N. (2022) Kinetics of Thermolysis of a Low-Temperature Tar in the Presence of a Catalyzer Agent with Deposited Metals. *Bulletin of the University of Karaganda Chemistry*. https://doi.org/10.31489/2022Ch4/4-22-19

Article

Received: 01 September 2022 ǀ Revised: 21 October 2022 ǀ Accepted: 04 November 2022 ǀ Published online: 30 November 2022

UDC 541:665.94 https://doi.org/10.31489/2022Ch4/4-22-19

S. Tyanakh[1*], M.I. Baikenov[1], A.M. Gulmaliev[2], Feng-Yun Ma[3],
G. Musina[4], T.O. Khamitova[5], A.N. Bolatbay[1]

[1]*Karagandy University of the name of academician E.A. Buketov, Karaganda, Kazakhstan;*
[2]*Federal State-Funded Institution of Science, Topchiev University of Petrochemical Synthesis RAS, Moscow, Russia;*
[3]*Xinjiang University, Xinjiang, China;*
[4]*Karaganda Polytechnic University, Karaganda, Kazakhstan;*
[5]*Kazakh Agrotechnical University named after Saken Seifullin, Astana, Kazakhstan*
*(*Corresponding author's e-mail: saika_8989@mail.ru)*

Kinetics of Thermolysis of a Low-Temperature Tar in the Presence of a Catalyzer Agent with Deposited Metals

The thermal decomposition of low-temperature coal tar (LTCT) obtained from the coals of Shubarkol Komir JSC of the Republic of Qazaqstan in the presence of nanocatalysts with metal oxides (iron, cobalt and nickel) supported on microsilicate was studied for the first time. Microsilicate acts as a carrier and catalyst. Microsilicate is a product of the Karaganda silicon plant of "Tau-Ken.temir" LLP. The main chemical component of the original microsilicate is silicon oxide. The individual and chemical phase composition of the microsilicate was determined using X-ray spectral analysis. The particle size of the initial microsilicate and the mixture of microsilicate with metal oxide catalysts (nickel, cobalt, and iron) was determined using a nanosizer. Stages of thermal decomposition of LTCT and a mixture of LTCT with catalysts under conditions of programmed heating up to 640 °C in a nitrogen atmosphere have been established. On the basis of thermogravimetric analysis, the kinetic parameters (activation energy, mass loss rate, and pre-exponential factor) of LTCT pyrolysis and mixture with added catalysts were determined. The modeless integral isoconversion Ozawa–Flynn–Wall method was used to determine the kinetic parameters. The values of the activation energy for the thermal destruction of the LTCT in the absence and presence of the nanocatalyst ranged from 54.04 to 297.5 kJ/mol. A kinetic compensation effect was revealed, probably due to the multicomponent composition of the LTCT and the influence of added catalysts to the LTCT. The thermogravimetry method showed a high effect of the supported catalysts on the thermal degradation of LTCT. This method was used to determine the values of the activation energy and the pre-exponential degradation factor for the LTCT and the mixture with catalysts at different heating rates, which allows a detailed interpretation of the thermal analysis data. The obtained results of the kinetics of decomposition of LTCT can be used to create a database for mathematical modeling of the process of processing this type of raw material.

Keywords: kinetics, accelerant, microsilica, low-temperature coal tar, thermogravimetric analysis, iron, nickel, cobalt.

Introduction

At present, thermogravimetric analysis is widely used to study the kinetics of thermal decomposition of organic materials, such as LTCT, coal, and polymeric materials [1–5]. Due to the complex composition of LTCT, it is very important to obtain information about the kinetics of LTCT decomposition in the presence of various catalysts containing metal oxides of Group VIII of the Mendeleev Periodic Table. To determine the kinetic parameters of the thermal decomposition of LTCT in the presence of catalysts containing metal oxides (iron, nickel, cobalt), the integral method presented in [1] and the method for determining the thermokinetic parameters from the inflection point on the thermogravimetric curve [2] were used. Sources [6, 7] evidence that the mathematical models, which are used to determine the kinetic performance of polymer degradation, cause certain difficulties when applied to the thermal breakdown of low-temperature coal resin (LTCR) due to their complex structure, the variety of chemical bonds, and simultaneously occurring reactions. In this regard, one of the most important tasks facing the researchers is the designing of recommendations for the selection and development of an adequate kinetic model of LTCR thermal breakdown in the presence of a catalyst and the formation of a database of kinetic performance.

The organic mass of LTCT contains various aromatic, heterocyclic compounds. Due to the complex composition of the LTCT, it is difficult to select an efficient and selective catalyst for LTCT processing based on the kinetics of decomposition of the LTCT organic matter. When studying the kinetics of pyrolysis of organic substances, the thermogravimetric method of analysis (TGA) is widely used [6]. In the literature [8–10], various methods are known for determining the kinetic parameters of nonisothermal pyrolysis, which can be divided into model (model-fitting) and model-free (model-free) or isoconversion. One of them is the Ozawa-Flylin-Wall model-free method for calculating the kinetic parameters [11, 12], which requires the construction of kinetic curves at different heating rates.

The purpose of this work is to study the kinetics of thermal degradation of LTCT in the presence of catalysts with oxides of nickel, cobalt, and iron supported on microsilicate using thermogravimetric analysis methods.

Experimental

For the study of thermokinetic decomposition of low-temperature coal tar the raw material obtained during coal coking at the coking plant of JSC “Shubarkol komir” was used.

Physical and chemical characteristics of low-temperature coal tar JSC “Shubarkol Komir”» presented in the paper [13].

The used microsilica performs the role of carrier and catalyst — the product of Karaganda silicon plant LLP “Tau-Ken.temir”.

The component chemical composition of the initial microsilica was determined by using X-ray and spectral analysis (Table. 1).

Table 1

Composition of initial microsilicate after leaching

Content of components, %									
SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	P_2O_5	K_2O	Na_2O
95.5	0.02	<0.95	<1.0	–0.5	0.4	0.04	0.06	<0.1	0.3

The initial microsilicate was preliminarily grinded, then samples with a particle size of 0.1 mm were taken by screen analysis. The initial microsilicate was leached using a 20 % hydrochloric acid solution to remove alkali and alkali earth metals.

The size of the particles of the original microsilica and the catalyst samples were determined by using the laser particle size detector Nano-S90 (Fig. 1).

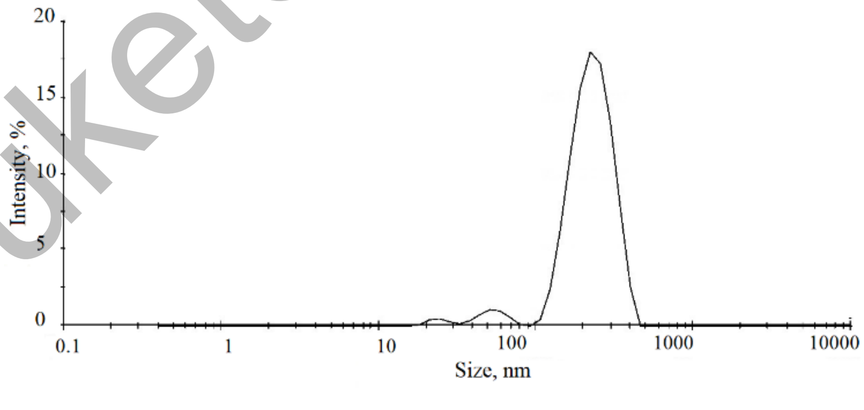


Figure 1. Particle size (sample 1) of the source microsilica

Figure 1 shows the particle size of the original microsilica — 232 nanometers. Size of metal-coated catalyst particles: sample 2 (microsilica+Ni) — 324.2 nanometers, sample 3 (microsilica + Co) — 139.4 nanometers, sample 4 (microsilica + Fe) — 196.3 nanometers.

The catalyst was obtained by wet impregnation of leached microsilica with a 1.5 % solution of $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$ salts. The salt-soaked microsilica was kept in the dryer for 2 hours, at 80–90 °C, and then dried at 105 °C also for 2 hours. Further, the catalyst samples obtained were calcified in the muffle oven at 550 °C for 2 hours (applied catalyst). The component chemical composition of the microsilicate after leaching was established using the X-ray spectral and gravimetric method and was presented in the (Table 2).

Table 2

Composition of initial microsilicate after leaching

Content of components, %									
SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	P_2O_5	K_2O	Na_2O
97.439	0.023	<0.95	<1.0	0.414	0.304	0.033	0.057	<0.1	0.276

As it can be seen from the data in Tables 1 and 2, the chemical composition of the initial microsilicate before and after leaching changed insignificantly.

Thermogravimetric study was performed using a *Labsys Evo TG-DTA/DSC* 1600 derivatograph (*Setaram*, France) in corundum crucibles in the temperature range from 30 to 600 °C in a nitrogen flow (flow rate of protective and purge gases was 20 and 50 ml/min^{-1} respectively). The sample weight for DTA analysis was 0.01 g. Kinetic parameters of thermal decomposition (rate constant, activation energy, and pre-exponential factor) of low-temperature coal tar (LTCT) with catalysts and microsilicate were calculated by the methods presented in works [11, 12]. Kinetic characteristics were determined on the basis of TGA — data at three different heating rates of 10, 20, and 30 deg/min^{-1}. Calculation and report of measurement results was performed using the software package “*OriginLab”* and the Python distribution *“Anaconda3”*.

The model-free Ozawa-Flynn-Wall (OFW) method was used [11, 12] when calculating the kinetic parameters of low-temperature coal resin (LTCR) thermal breakdown in the presence of a catalyst.

Results and Discussion

We previously used the integral method to determine the thermogravimetric parameters [1] and the method by the inflection point on the thermogravimetric curve [2].

The curves dependence of samples mass loss on temperature are shown in Figure1 at heating rates β — 10 °C/min, β — 20 °C/min, β — 30 °C/min at intervals of 140–480 °C using the Ozawa-Flynn-Wells (OFW) method. The reactivity of a substance can be described by the activation energy value.

The determination of the activation energy values was based on the generalized value expression (1) for the rate of the solid-phase reaction under nonisothermal conditions:

$$d\alpha / dT = A / \beta e^{(-Ea/RT)} f(\alpha), \tag{1}$$

where α is fractional conversion of raw material; β is the linear heating rate of samples, °C/min; A is the pre-exponential factor, c^{-1}; T is the absolute temperature, K; E is the activation energy, kJ/mol; R is the gas constant, kJ/mol K; $f(\alpha)$ is a mathematical model of the dimensionless kinetic function depending on the type and mechanism of the reaction.

The value α in equation (1) is the relative degree of oil sludge transformation, defined as $\alpha = m_s - m/m_s - m_f$ where m_s and m_f are the initial and final mass of the substance, m is the mass of the substance at the measurement point [14].

Ozawa-Flynn-Walls Method According to the Ozawa-Flynn-Walls method of non-isothermal kinetics, when integrating and then taking logarithm equation (1), we obtain expressions (2)

$$\ln G(\alpha) = \ln(AE / R) - \ln\beta + \ln p(z). \tag{2}$$

$G(\alpha)$ for a first-order reaction is equal to

$$\int_0^a d\alpha / f\alpha = \int_0^a da / 1 - a = -\ln(1 - a);$$

$$p(z) = e^{-z} / z - \int_{-\infty}^{z} e^{-z} / z\, dz; z = E / RT .$$

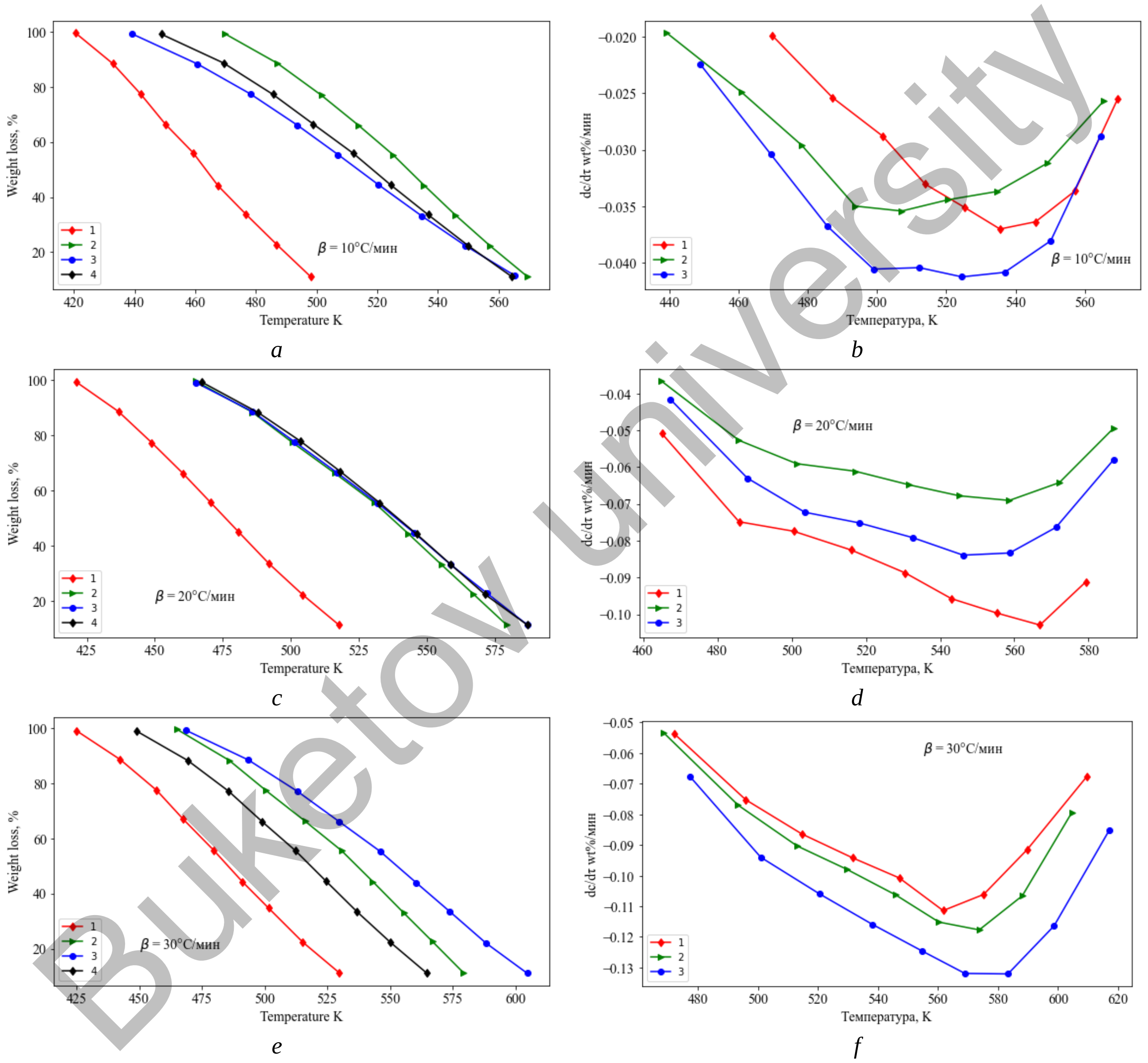
Using the Doyle approximation [15] we obtain equation (3) for substitution into expression (2):

$$\ln p(z) = -5.3305 - 1.052z. \tag{3}$$

The OFW method is based on the assumption that the reaction rate at a constant value of α depends only on temperature. When analyzing non-isothermal kinetics, the following equation is used:

$$\ln\beta_i = \ln\left[A_\alpha E_a / Rg(\alpha)\right] - 5.331 - 1.052 E_a / RT_{\alpha,i} . \tag{4}$$

Substitutions (2) and (3) provide the OFW equation (4) to calculate how thermal breakdown rate of catalyst mixtures with LTCR depends on inverse temperature calculated the activation energy and the pre-exponential multiplier [15]. Thermogravimetric (TG) curves (Fig. 2) were constructed by low-temperature coal tar to assess the influence of metal-coated microsilicate catalysts (iron, nickel, cobalt) on the thermal degradation rate. Thermogravimetric (TG) curves (Fig. 2) were constructed by low-temperature coal tar to assess the impact of metal-based microsilica catalysts (iron, nickel, cobalt) on thermal degradation rates. For this purpose, based on the thermogravimetry data of the low-temperature coal resin and the catalyst for their mixtures of a known composition, TG curves and mass loss rates were calculated at three heating speeds β — 10 °C/min, β — 20 °C/min, β — 30 °C/min, which described the thermolysis process of the low-temperature coal resin mixture and with the catalyst (Fig. 2 *a*–*f*).

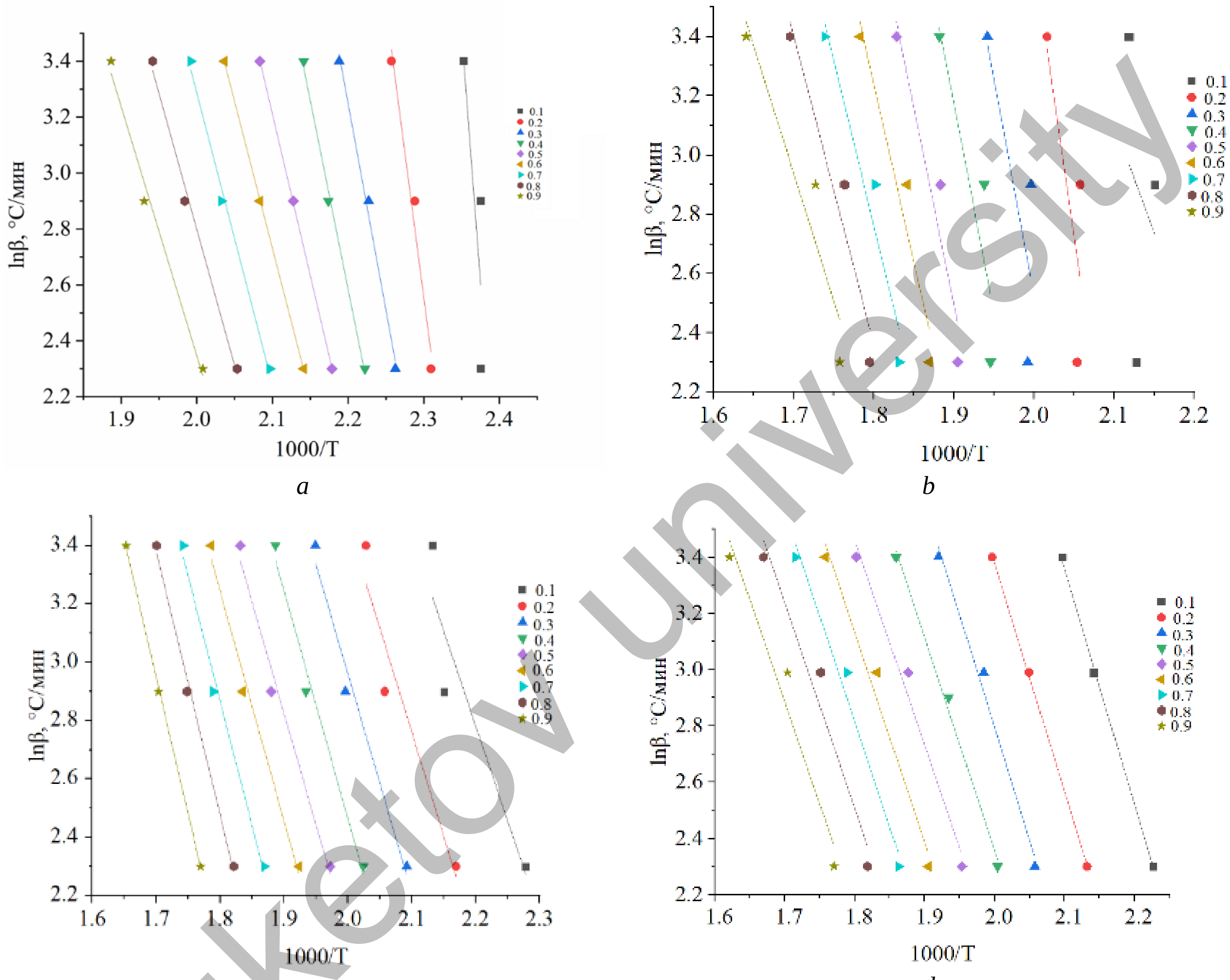


1 — low-temperature coal tar; *2* — low-temperature coal tar with applied nickel;
3 — low-temperature coal tar with cobalt applied; *4* — low-temperature coal tar with iron applied

Figure 2. Thermogravimetric mass loss curves (*a*), (*c*), (*e*) and mass loss rate (*b*), (*d*), (*f*) of tested NCC samples in the presence of microsilica with applied catalyst

On the curves, the mass loss rate at three heating speeds β is one maximum (Fig. 2 *b*, *d*, *f*), due to the decomposition of the organic mass of low-temperature coal tar in the presence of nickel, cobalt and iron to the formation of volatile substances. It has been established that, when iron is applied to microsilica (Fig. 2 *b*), the maximum decomposition of the organic mass of low-temperature coal tar is achieved at a temperature of 525 K. When the nickel applied to microsilica, the maximum decomposition rate of the organic mass of low-temperature coal tar is reached at a temperature of 537 K (Fig. 2 *d*) and when iron is added, there is a maximum decomposition of the organic mass of low-temperature coal tar at 579 K (Fig. 2 *f*).

Equation (4) implies that for a series of temperature measurements of thermal degradation of low-temperature coal tar catalyst mixtures obtained at different β heating speeds of samples and fixed values of their transformation degree α, the graph of the function $\ln\beta = f(1/T)$ gives straight lines (isoconversion lines) the tangent of the inclination of which — $1.052E/R$ is directly proportional to the activation energy [15] (Fig. 3 *a*–*d*).



a

b

c

d

a — low-temperature coal tar; *b* — low-temperature coal tar with nickel applied to microsilica,
c — low-temperature coal tar with cobalt applied to microsilica;
d — low-temperature coal tar with iron applied to microsilica

Figure 3. Heating rate logarithm dependence β — 10 °C/min, β — 20 °C/min, β — 30 °C/min low-temperature coal tar mixture samples

The experimental points lie adequately on straight lines in the entire range of conversion degrees, indicating the correct Doyle approximation used in the mathematical treatment of thermogravimetric data. The calculated activation energy values and preexponential multiplier shows a high correlation coefficient ($R^2 \geq 0.997$) of Table 3.

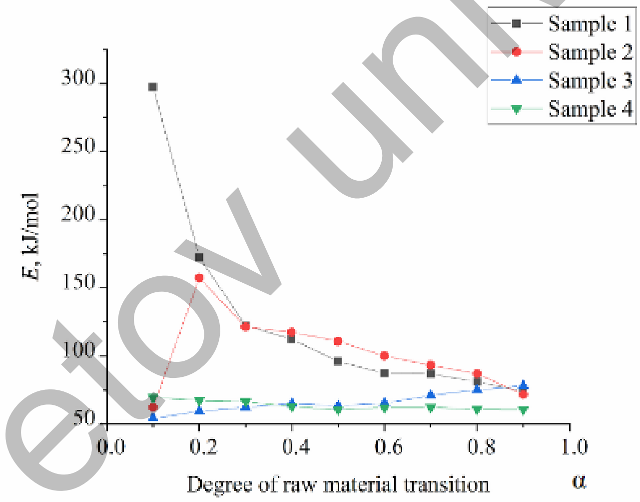
Energy Activation of Thermal Destruction of Low-temperature Coal Tar Blend and Microsilica with Applied Catalysts (Table 3).

Table 3

Energy Activaition of Thermal Destruction of Low-temperature Coal Tar Blend and Microsilica with Applied Catalysts

Relative degree of conversion, α	Sample 1 (low-temperature coal tar without catalyst)		Sample 2 (microsilica + Ni 1.5 % + low-temperature coal tar, particle size 0.1 mm)		Sample 3 (microsilica + Co 1.5 % + low-temperature coal tar, particle size 0.1 mm)		Sample 4 (microsilica + Fe 1.5 % + low-temperature coal tar, particle size 0.1 mm)	
	E_a, KJ/mol	$\ln Ac^{-1}$	E_a, KJ/mol	$\ln Ac^{-1}$	E_a, KJ/mol	$\ln Ac^{-1}$	E_a, KJ/mol	$\ln Ac^{-1}$
0.1	297.5	87.6	62.18	18.8	54.04	17.09	69.53	20.92
0.2	172.3	50.2	157.3	41.5	59.27	17.74	67.32	19.57
0.3	122.3	35.7	121.2	31.6	62.18	17.93	66.42	18.77
0.4	112.3	32.3	117.4	30.01	65.01	18.11	62.84	17.47
0.5	95.9	27.4	110.7	27.79	63.35	17.31	60.51	16.55
0.6	87.3	24.7	99.9	24.88	65.34	17.40	62.06	16.56
0.7	86.7	24.1	93.2	22.94	70.91	18.22	62.22	16.28
0.8	80.9	22.2	86.8	21.15	74.99	18.72	60.75	15.65
0.9	74.1	20.1	71.6	17.59	77.98	18.89	60.48	15.25

On the Figure 4 activation energy dependence on conversion rate (α) of low-temperature coal tar without catalyst and sample mixture of low-temperature coal tar with catalyst. Ozawa – Flynn – Wells Curve — $E = f(\alpha)$) (Fig. 4) shows the complex process of thermal destruction of the low-temperature coal tar mixture with the catalyst.



1 — low-temperature coal tar; *2* — low-temperature coal tar with nickel applied to microsilica;
3 — low-temperature coal tar with cobalt applied to microsilica;
4 — low-temperature coal tar with iron applied to microsilica

Figure 4. Dependence of activation energy E on the level of conversion of α samples (Ozawa – Flynn – Wells analysis)

Figure 4 shows the calculated activation energy values represented by the thermal breakdown degree α of low-temperature coal resin and the sample mixture of the low-temperature coal resin with catalyst. It is shown that for Sample 1 activation energy with increased conversion decreases from 297.5 to 74.1 kJ/mol. Sample 2 with the conversion degree from 0.1 to 0.2 the activation energy increases from 62.18 to 157.3 kJ/mol, and further conversion increase rate leads to a reduction in activation energy from 121.2 to 71.6 kJ/mol. For Sample 3 with increased conversion rate, there is a significant change in activation energy from 54.04 to 77.98 kJ/mol. Slight activation energy change with conversion degree obsession is observed for sample 4 from 69.53 to 60.48 kJ/mol.

Figure 4 shows that for the sample, the first stage of thermal decomposition is flowing with a high amount of activation energy, which may be due to a low degradation of high molecular weight asphaltene and tar compounds. Thermal decomposition of the low-temperature coal tar mixture with nickel, cobalt and iron applied to microsilica is described by more complex kinetic curves. The initial stages of the activation energy of sample 2, sample 3 and sample 4 proceed with a lower activation energy than for sample 1. It seems to be due to the fact that an organo structure with added metals is formed, the latter act as a catalyst, that is, they accelerate the reaction of the destruction of the organic mass of the low-temperature coal tar and thus lead to a decrease in the activation energy (Table 3 and Fig. 4.). Among the number of metals added to the microsilica, cobalt and iron were the most influential, and the addition of nickel with an increased conversion rate of 0.1–0.2 leads to an increase in activation energy and a pre exponential factor, and further increasing the conversion rate from 0.3 to 0.9 significantly reducing the activation energy. Low activation energy appears to be associated with the splitting of the weakest oxygen-containing, nitrogen-containing bonds and the influence of catalytic additives on the thermal degradation of low-temperature coal tar. High activation energy values are associated with low volatility of condensed aromatic hydrocarbons contained in the original low-temperature coal tar. Solid semi-coke is formed by condensation of solids that do not degrade.

Conclusions

The information above about the influence of catalysts on the destruction of low-temperature coal resin shows that the method of thermogravimetry makes it possible to determine sufficiently the influence of the applied catalysts on the thermal breakdown of low-temperature coal resin. On the basis of TG-analysis, the kinetic parameters (activation energy and pre-exponential factor) were determined using the model-free OFW method. The obtained experimental data on the kinetics of LTCT destruction were verified by correlation coefficients ($R^2 \geq 0.997$).

By changing the organometallic structure of low-temperature coal tar with applied catalyst due to metabolic reaction with metal, it is possible to control the process of thermal destruction, changing its speed and kinetic parameters, and to test selected catalysts for thermal destruction of low-temperature coal tar.

References

1 Букварева О.Ф. Кинетика и термохимия процессов термодеструкции углеродсодержащих веществ / О.Ф. Букварева, Т.В. Бухаркина. — М.: РХТУ им. Д.И. Менделеева, 2001. — 28 с.

2 Гюльмалиев А.М. Теоретические основы химии угля / А.М. Гюльмалиев, Г.С. Головин, Т.Г. Гладун. — М.: Изд-во Моск. гос. гор. ун-та, 2003. — 556 с.

3 Тянах С. Кинетическое изучение термического разложения первичной каменноугольной смолы в присутствии катализаторов с нанесенными на микросиликат оксидами никеля, кобальта и железа / С. Тянах, А. Тусипхан, А.М. Гюльмалиев, Ма Фэн-Юнь, Г.Г. Байкенов, Д.А. Кайкенов, А.И. Халитова, М.И. Байкенов // Химия твердого топлива. — 2022. — № 1. — С. 19–27. https://doi.org/10.31857/S002311772201008X

4 Burkeev M. Kinetic parameters of thermal destruction of the copolymer of polyethylene glycol fumarate with acrylic acid in inert medium / M. Burkeev, A. Bolatbay, D. Havlicek, Y. Tazhbayev, S. Davrenbekov, L. Zhaparova // Chemical Bulletin of Kazakh National University. — 2022 — Vol. 105, No. 2. — P. 26–33. https://doi.org/10.15328/cb1260

5 Фетисова Ю.О. Кинетическое изучение стадийности термического разложения различных углей Монголии / Ю.О. Фетисова, П.Н. Кузнецов, Б. Пуревсурен, Б. Авид // Химия твердого топлива. — 2021. — № 1. — С. 3. https://doi.org/10.31857/S0023117721010035

6 Du Z. Activation energy in temperature-programmed desorption: Modeling and application to the soot-oxygen system / Z. Du, A.F. Sarofim, J.P. Longwell // Energy and Fuels. — 1990. — Vol. 4. — P. 296.

7 Бодыков Д.У. Переработка нефтешлама с использованием электрогидравлического эффекта / Д.У. Бодыков, М.С. Абдикаримов, М.А. Сейтжанова, Ж.К. Елемесова // Горение и плазмохимия. — 2017. — Т. 15, № 2. — С. 140–147.

8 Li Y. Effects of different ionizable groups on the thermal properties of waterborne polyurethanes used in bulletproof composites / Y. Li, J. Zheng, Y. Luo, H. Zhou, and Q. Wang // J. Appl. Polym. Sci. — 2015. — Vol. 132. — P. 42374, https://doi.org/10.1002/app.42374

9 Hui K. Status and prospect of oil recovery from oily sludge: A review / K. Hui, Ju. Tang, H. Lu, B. Xi, Ch. Qu, J. Li // Arab. J. Chem. — 2020. — Vol. 13, No. 8. — P. 6523. https://doi.org/10.1016/j.arabjc.2020.06.009

10 Flynn J.A Quick, Direct Method for the Determination of Activation Energy from Thermogravimetric Data / J. Flynn, L. Wall // J. Polym. Sci. Part B: Polym. Phys. — 1966. — Vol. 4. — P. 296.

11 Ozawa T.A New Method of Analyzing Thermogravimetric Data / T. Ozawa // Bulletin of the Chemical Society of Japan. — 1965. — Vol. 38. — P. 1881–1886.

12 Aitbekova D.E. Hydrogen distribution in primary coke oven tar and its fractions / D.E. Aitbekova, D.K. Makenov, E.I. Andreikov, A.G. Tsaur, Ma Feng Yung, G.G. Baikenova, A. Tusipkhan, A.A. Muratbekova, M.I. Baikenov // Bull. University Karaganda. Chemistry. — 2021. — Vol. 101, No. 1. — P. 82. https://doi.org/10.31489/2021Ch1/82-90

13 Doyle C.D. Kinetic Analysis of Thermogravimetric Data / C.D. Doyle // Appl. Polymer Science. — 1961. — Vol. 15, № 5. — P. 285.

14 Стрижаков Д.А. Кинетика термолиза смеси гудрона и сосновых опилок / Д.А. Стрижаков, А.И. Юсевич, В.В. Юрачка, Х.М. Кадиев, В.Е. Агабеков, С.Н. Хаджиев // Нефтехимия. — 2016 — Т. 56, № 5. — С. 475–482 https://doi.org/10.1134/S0965544116080168

15 Balpanova N.Zh. Thermokinetic parameters of the primary coal tars destruction in the presence of catalysts and polymeric materials / N.Zh. Balpanova, M.I. Baikenov, A.M. Gyulmaliev, Z.B Absat, Zh. Batkhan, F. Ma, K. Su, S.V. Kim, G.G. Baikenova, D.E. Aitbekova, A. Tusipkhan // Bulletin of University of Karaganda. Series «Chemistry». — 2021. — № 2 (102). — P. 86–95. https://doi.org/10.31489/2021Ch2/86-95

С. Тянах, М.И. Байкенов, А.М. Гюльмалиев, Ма Фэн-Юн,
Г. Мусина, Т.О. Хамитова, А.Н. Болатбай

Металдармен байытылған катализдік қоспа қатысындағы төментемпературалы шайыр термолизінің кинетикасы

Алғаш рет металл оксидтері (темір, кобальт және никель) бар микросиликатқа енгізілген нанокатализаторлардың қатысуымен Қазақстан Республикасы «Шұбаркөл Көмір» АҚ көмірлерінен алынған төментемпературалы таскөмір шайырының (ТТТШ) термиялықыдырауы зерттелді. Микросиликат тасымалдаушы және катализатор қызметін атқарады. Микросиликат — «Tau-Ken.temir» ЖШС Қарағанды кремний зауытының өнімі. Бастапқы микросиликаттың негізгі компоненті кремний оксиді. Микросиликаттың жеке және химиялық фазалық құрамы рентгендік спектрлік талдау арқылы анықталды. Бастапқы микросиликаттың бөлшектерінің өлшемі және микросиликаттың металл оксиді катализаторларымен қоспасы (никель, кобальт және темір) наносайзердің көмегімен табылды. Азот атмосферасында 640 °C дейін бағдарламаланған қыздыру жағдайында ТТТШ термиялықыдырау сатысы және катализаторлармен ТТТШ қоспасы дәлелденген. Термогравиметриялық талдау негізінде ТТТШ пиролизі және катализаторлар қосылған ТТТШ қоспасының кинетикалық параметрлері (активтендіру энергиясы, массаның жоғалу жылдамдығы және алдындағы экспоненциалды көбейткіш) анықталды. Кинетикалық параметрлерді анықтау үшін Озава – Флинн – Уоллдың модельсіз интегралды изоконверсиялық әдісі қолданылды. Нанокатализатор бар болған және болмаған кезде төментемпературалы таскөмір шайырының термиялықыдырау активтендіру энергиясының мәндері 54,04-тен 297,5 кДж/мольге дейін ауытқиды. Кинетикалық компенсация әсері анықталды, бұл төментемпературалы таскөмір шайырының көпкомпонентті құрамына және төментемпературалы таскөмір шайырына қосылған катализаторлардың әсеріне байланысты болуы мүмкін. Төментемпературалы таскөмір шайырының ыдырау кинетикасынан алынған нәтижелерді көрсетілген шикізаттың түрін қайта өңдеу процесінде математикалық модельдеуді жүргізу үшін деректер базасын құру кезінде пайдалануға болады.

Кілт сөздер: кинетика, катализатор, микросиликат, төментемпературалы таскөмір шайыры, темір, никель, кобальт.

С. Тянах, М.И. Байкенов, А.М. Гюльмалиев, Ма Фэн-Юн,
Г. Мусина, Т.О. Хамитова, А.Н. Болатбай

Кинетика термолиза низкотемпературной смолы в присутствии каталитической добавки с нанесенными металлами

Впервые изучено термическое разложение низкотемпературной каменноугольной смолы (НКС), полученной из углей АО «Шубарколь комир» Республики Казахстан, в присутствии нанокатализаторов с нанесенными на микросиликат оксиды металлов (железо, кобальт и никель). Микросиликат выполняет роль носителя и катализатора. Микросиликат — продукт Карагандинского кремниевого завода ТОО «Tau-Ken.temir». Основным химическим компонентом исходного микросиликата является оксид кремния. Индивидуальный и химический фазовый состав микросиликата определяли с помощью рентгеноспектрального анализа. Размер частиц исходного микросиликата и смеси микросиликата с катализаторами оксида металлов (никель, кобальт и железо) определяли с помощью наносайзера. Установлены стадийность терморазложения НКС и смесь НКС с катализаторами в условиях программируемого нагрева до 640 °C в атмосфере азота. На основе термогравиметрического анализа определены кинетические параметры (энергия активации, скорость потерии массы и предэкспоненциальный множитель) пиролиза НКС и смеси НКС с добавленными катализаторами. Для определения кинетических параметров использован безмодельный интегральный изоконверсионный метод Озава–

Флинн–Уолла. Значения энергии активации термодеструкции НКС в отсутствии и в присутствии нанокатализатора находились в диапазоне 54,04–297,5 кДж/моль. Выявлен кинетический компенсационный эффект, вероятно, обусловленный многокомпонентным составом НКС и влиянием добавленных катализаторов к НКС. Метод термогравиметрии показал высокое влияние нанесенных катализаторов на термодеструкцию НКС. С помощью данного метода определены значения энергии активации и предэкспоненциальный множитель деструкции НКС и смеси НКС с катализаторами при различных скоростях нагрева, что позволяет подробно интерпретировать данные термического анализа. Полученные результаты кинетики разложения НКС могут быть использованы при создании базы данных для проведения математического моделирования процесса переработки указанного вида сырья.

Ключевые слова: кинетика, катализатор, микросиликат, низкотемпературная каменноугольная смола, железо, никель, кобальт.

References

1 Bukvareva, O.F., & Bukharkina, T.V. (2001). Kinetika i termokhimiia protsessov termodestruktsii uglerodsoderzhashchikh veshchestv [Kinetics and Thermochemistry of the Thermal Destruction of Carbon-Containing Substances]. Moscow: RKhTU imeni D.I. Mendeleeva [in Russian].

2 Gyulmaliev, A.M., Golovin, G.S., & Gladun, T.G. (2003). Teoreticheskie osnovy khimii uglia [Theoretical foundations of coal chemistry]. Moscow: Izdatelstvo Moskovskogo gosudarstvennogo univtrsiteta [in Russian].

3 Tyanakh, S., Tusipkhan, A., Gyulmaliev, A.M., Ma, Feng Yung, Baikenova, G.G., Kaikenov, D.A., Khalitova, A.I., & Baikenov, M.I. (2022). Kineticheskoie izuchenie termicheskogo razlozheniia pervichnoi kamennougolnoi smoly v prisutstvii katalizatorov s nanesennymi na mikrosilikat oksidami nikelia, kobolta i zheleza [A Kinetic Study of the Thermal Decomposition of Primary Coal Tar in the Presence of Catalysts with Nickel, Cobalt, and Iron Oxides Supported onto Microsilicate]. *Khimiia tverdogo topliva — Solid fuel chemistry, 56*, 1, 29–36 [in Russian]. https://doi.org/10.3103/S0361521922010086 .

4 Burkeev, M., Bolatbay, A., Havlicek, D., Tazhbayev, Y., Davrenbekov, S., & Zhaparova, L. (2022). Kinetic parameters of thermal destruction of the copolymer of polyethylene glycol fumarate with acrylic acid in inert medium. *Chemical Bulletin of Kazakh National University, 105*(2), 26–33. https://doi.org/10.15328/cb1260

5 Fetisova,.Yu.O, Kuznetsov, P.N., Purevsuren, B., & Avid, B. (2021). Kineticheskoe izuchenie stadiinosti termicheskogo razlozheniia razlichnykh uglei Mongolii [A Kinetic Study of the Stepwise Thermal Decomposition of Various Coals from Mongolia] *Khimia tverdogo topliva — Solid fuel chemistry, 55*, 1, 1. https://doi.org/10.31857/S0023117721010035 [in Russian].

6 Du, Z., Sarofim, A.F., & Longwell, J.P. (1990). Activation energy distribution in temperature-programmed desorption: modeling and application to the soot oxygen system. *Energy & Fuels, 4*(3), 296–302. https://doi.org/10.1021/ef00021a014

7 Bodykov, D.U., Abdikarimov, M.S., Seitzhanova, M.A., Yelemesova, Zh.K. (2017) Pererabotka nefteshlama s ispolzovaniem electrogidravlicheskogo effecta [Processing of oil sludge using electro-hydraulic effect]. *Combustion and plasma chemistry, 15*, 2, 140–147 [in Russian].

8 Li, Y., Zheng, J., Luo, Y., Zhou, H., & Wang, Q. (2015). Effects of different ionizable groups on the thermal properties of waterborne polyurethanes used in bulletproof composites. *J. Appl. Polym. Sci., 132*, 42374. https://doi.org/10.1002/app.42374

9 Hui K., Tang Ju., Lu H., Xi B., Qu Ch., Li J. (2020). Status and prospect of oil recovery from oily sludge: A review. *Arab. J. Chem., 13*, 8, 6523. https://doi.org/10.1016/j.arabjc.2020.06.009

10 Flynn, J. Wall, L. (1966). A Quick, Direct Method for the Determination of Activation Energy from Thermogravimetric Data. *Polym. Sci. Part B: Polym. Phys. 4*, 296.

11 Ozawa T. (1965) A New Method of Analyzing Thermogravimetric Data. *Bulletin of the Chemical Society of Japan. 38*, 1881–1886.

12 Aitbekova, D.E., Makenov, D.K., Andreikov, E.I., Tsaur, A.G., Ma Feng Yung, Baikenova, G.G., Tusipkhan, A., Muratbekova, A.A., & Baikenov, M.I. (2021). Hydrogen distribution in primary coke oven tar and its fractions. *Bulletin of the University of Karaganda — Chemistry, 1*(101), 82–90. https://doi.org/10.31489/2021Ch1/82-90

13 Doyle, C.D. (1961). Kinetic Analysis of Thermogravimetric Data. *Appl. Polymer Science, 15*, 5, 285.

14 Strizhakov, D.A., Yusevich, A.I., & Yurachka, V.V. et al. (2016). Kinetika termoliza smesi gudrona i sosnovykh opilok [Kinetics of thermolysis of vacuum tower bottoms mixed with pine sawdust]. *Pet. Chem., 56*, 703–710 [in Russian]. https://doi.org/10.1134/S0965544116080168

15 Balpanova, N.Zh., Baikenov, M.I., Gyulmaliev, A.M., Absat, Z.B., Batkhan, Zh., Ma F., Su K., Kim, S.V., Baikenova, G.G., Aitbekova, D.E., Tusipkhan, A. (2021). Thermokinetic parameters of the primary coal tars destruction in the presence of catalysts and polymeric materials. *Bulletin of the University of Karaganda Chemistry, 2*(102), 86–95. https://doi.org/10.31489/2021Ch2/86-95

Information about authors[*]

Tyanakh, Sairagul (*corresponding author*) — master, doctoral student Karagandy University of the name of academician E.A. Buketov, Universitetskaya street, 28, 100024, Karaganda, Kazakhstan; e-mail: saika_8989@mail.ru; https://orcid.org/0000-0001-5343-4695

Baikenov, Murzabek Ispolovich — professor, Karagandy University of the name of academician E.A. Buketov, Universitetskaya street, 28, 100024, Karaganda, Kazakhstan; e-mail: murzabek_b@mail.ru; https://orcid.org/0000-0002-8703-0397

Gyulmaliyev, Agadzhan Mirzoevich — chief researcher, A.V. Topchiev Institute of Petrochemical Synthesis, RAS, Leninsky prospect, 29, 119991, Moscow, Russia; e-mail: gyulmaliev@ips.ac.ru; https://orcid.org/0000-0003-2458-6686

Ma, Feng-Yun — PhD, Professor, Xinjiang University, Urumqi, Nan Min Lu street, 666, Xinjiang Uygur Autonomous Region (XUAR) People's Republic of China (PCR); e-mail: ma_fy@126.com;

Musina, Gulnaz Nurgaliyevna — candidate of chemical Sciences, Karaganda technical University, Ave. Nursultan Nazarbayev, 56, 100027, Karaganda, Kazakhstan; e-mail: kargtu@kstu.kz; https://orcid.org/0000-0003-4683-2868

Khamitova, Tolkyn Ondirisovna — PhD, Agronomic Faculty, S. Seifullin Kazakh Agro Technical University, Zhenis avenue, 62, 010011, Astana, Kazakhstan; e-mail: khamitova.t@inbox.ru; https://orcid.org/0000-0002-4691-3732

Bolatbay, Abylaikhan Nurlanuly — master, doctoral student, Karagandy University of the name of academician E.A. Buketov, Universitetskaya street, 28, 100024, Karaganda, Kazakhstan; e-mail: abylai_bolatabai@mail.ru; https://orcid.org/0000-0001-5047-3066

---

*The author's name is presented in the order: *Last Name, First and Middle Names*