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The Use of the Catalysts Based on Coal Ash Microsphere and Chrysotile in the Thermal Destruction of Primary Coal Tar

In order to evaluate the possibility of using different catalysts prepared for the hydrogenation process of primary coal tar, the method of differential thermal analysis was used, which allows to determine the kinetic parameters of thermal destruction, such as the rate constant, activation energy, and pre-exponential multiplier. The effect of catalysts on characteristics of mass loss during heating of “Shubarkol Komir” JSC primary coal tar at a constant speed (20 K/min) in a nitrogen medium has been considered. Microsphere, NiO/microsphere, CoO/microsphere, chrysotile and NiCo/chrysotile have been taken as catalytic additives. In the presence of the catalysts, the rate of thermal destruction of primary coal tar increases in the following order: CoO/microsphere < NiO/microsphere < NiCo/chrysotile. While microsphere catalysts extend the range of thermal destruction, chrysotile catalysts lead to the rapid completion of the destruction process. This fact is characterized by the formation of bonds between catalytic additives and primary coal tar. It is important to determine such parameters that affect on the activation energy and macrokinetics of the thermal decomposition process for prediction of catalyst activity during hydrogenation of heavy hydrocarbon raw materials.

Keywords: primary coal tar, differential thermal analysis, catalyst, hydrogenation, microsphere, chrysotile, nickel, cobalt.

Introduction

The exploration of catalyst-assisted thermal processes for hydrocarbon raw materials has garnered significant attention due to its relevance in industrial applications, including pyrolysis and hydrogenation. Thermogravimetric analysis (TGA), complemented by advanced analytical tools, has become a cornerstone in unraveling the complex interactions between hydrocarbons and catalysts. The thermal decomposition approach proves advantageous for forecasting the efficacy of catalysts in the catalytic processing of dense hydrocarbon feedstock, including high-viscosity oil, residual heavy oil, and coal tars [1].

Ibrahim and co-authors asserted that a key metric for assessing the hydrogenation of dense hydrocarbon feedstock lies in the thermal decomposition of their organic mass within an inert medium, specifically, the peak rate of mass loss [2].

The thermal degradation of dense hydrocarbon feedstock involves the cleavage of donor-acceptor and valence bonds, accompanied by the liberation of moisture. This process results in the generation and segregation of gaseous and volatile liquid compounds, as well as non-volatile liquid and solid substances. Furthermore, it entails the polycondensation of decomposition by-products, leading to the formation of semi-coke and coke, along with the emission of additional gaseous compounds. When subjecting heavy hydrocarbon raw materials to heating in an inert environment, a biphasic mechanism, comprising primary and secondary decomposition stages, becomes evident. Primary decomposition conventionally occurs approximately at 770 K, while secondary decomposition takes place at elevated temperatures [3].

Various techniques employed for investigating the kinetics of thermal degradation of dense hydrocarbon feedstock reveal different faces of this complex process. Literature sources [4–6] indicate the application of non-isothermal kinetics and dynamic thermogravimetry methods for determination of the kinetic param-

ters of destruction of heavy hydrocarbon raw materials during the processing of the thermogravimetric curve. These methods enable the calculation of activation energy, enthalpy, and entropy of activation.

TGA studies have highlighted the temperature-dependent hydrogenation processes of heavy hydrocarbon raw materials in the presence of catalysts [7–9]. The results of the studies of the hydrogen formation kinetics and mechanisms have showed the catalyst efficiency. As reported in the literature [10], thermogravimetric analysis, concurrently linked to a Fourier transform infrared spectrometer (FTIR) and a gas chromatography (GC), during coal pyrolysis with a nickel catalyst exhibited an augmentation in hydrogen formation within the temperature range of 400–500 °C. Given that this temperature corresponds to the hydrogenation processes of heavy hydrocarbon raw materials, the observed increase in mass loss serves as a predictive indicator for the hydrogenation activity of the catalyst.

The purpose of this study is to evaluate the catalytic activity of NiO/microsphere, CoO/microsphere, and NiCo/chrysotile catalysts by applying differential thermal analysis to primary coal tar (PCT).

Experimental

Technical description of primary coal tar. The coal tar derived from Shubarkol deposit (Karaganda region, Kazakhstan) is classified as a primary tar, indicating that it has not undergone secondary thermal treatments. In contrast to high-temperature coking resin, this tar includes a higher proportion of oxygen-containing compounds, in particular, phenols and unsaturated compounds. The technical details of the coal tar are provided in the paper, referencing the information from the technical description [11].

Procedure for the nanocatalysts preparation. To ensure the formation of an active center with a consistent chemical composition in the catalyst, an important requirement involves depositing active compounds from the solution onto the surface of hard-to-dissolve oxides and ensuring their uniform distribution. The use of catalysts on carriers with a homogeneous distribution of active phase throughout the sorbent volume contributes to a reduction in the consumption of the active component and increases the catalyst's activity [12, 13].

Microspheres [14–16] and chrysotile [17, 18] were chosen as catalysts carriers due to their developed surface area, high thermal stability, and low cost. Microspheres have been obtained from the coal ash originating from Karaganda CHP-3 (Republic of Kazakhstan) by flotation method. The chrysotile mineral used as a substrate for the active centers of nickel and cobalt is sourced as a byproduct from asbestos production at Kostanay Minerals JSC in the Republic of Kazakhstan. This chrysotile mineral is classified as a serpentine raw material with the chemical composition $3\text{MgO}\cdot 2\text{SiO}_2\cdot \text{H}_2\text{O}$.

NiO/microsphere and CoO/microsphere catalysts have been prepared using the “wet mixing” method. 20% aqueous solutions of nickel (II) nitrate $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and cobalt (II) nitrate $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ crystallohydrates (analytically pure, Kupavnareaktiv, Russian Federation) were separately taken. The microspheres were added so that the amount of nickel and cobalt in the resulting solution was 5 % of the total mass of catalyst obtained after completion of the process. The mixture underwent thorough stirring while being heated. Following the formation of a dense mass, it was dried in a drying oven at a temperature of 105 °C. Subsequently, the obtained samples subjected to heat treatment in a muffle furnace at a temperature of 500 °C for 2 hours.

According to the studies [19–22] Ni-Co bimetallic catalysts' activity and stability to coke deposition are superior to the properties of Ni and Co metals taken separately. This is due to the synergy effect between Ni and Co.

In order to remove magnesium and calcium salts contained in the original chrysotile, pre-rinsing was carried out with a 20 % solution of hydrochloric acid. The preparation of the binary catalyst has been realized by dissolving nickel (II) nitrate crystal hydrate (20 %) in water while heating, and then adding alkalized chrysotile to the resulting solution. The resulting mixture was heated and thoroughly stirred until a thick mass was formed. The mass was further dried in a drying oven at a temperature of 105 °C to a constant mass. Then the crystallohydrate of cobalt (II) nitrate was dissolved in water (20 %), and the process was repeated with the dry mass of chrysotile obtained with nickel salt. Further, chrysotile with nickel and cobalt salts was thermally treated in a muffle furnace at a temperature of 500 °C for 2 hours. The mass fraction of nickel and cobalt to the total mass of the resulting catalytic mixture was 5 %.

Differential thermal analysis of PCT. Thermogravimetric studies to determine the effect of catalysts on the kinetic parameters of thermal degradation of primary coal tar LABSYS™ EVO TG, DTA, DSC 1600 °C with thermogravimetric scales connected to DTA and DSC converters, metal-resistive furnace and multitasking software structure controlling various modules (Setaram, France) was carried out in the number

of equipments. In order to avoid the diffusion effect and to ensure process homogeneity during sample preparation, 3 g of Al_2O_3 was placed in a crucible and fired in a muffle furnace at a temperature of 600 °C for 2 hours. Then it was placed in a desiccator for drying. During the study of thermal destruction of primary hard coal tar, 1 % catalyst and dried Al_2O_3 have been added to its 0.2 g mass. Microsphere, NiO/microsphere, CoO/microsphere, chrysotile and NiCo/chrysotile have been taken as the catalytic additives. As per the literature source [23], the optimum quantity of nanocatalyst introduced to the mass of raw materials for the catalytic processing of dense hydrocarbon feedstock during thermal degradation is reported to be 1 %

Two identical Al_2O_3 crucibles with a volume of 100 ml were used for thermal analysis. Their design provides direct measurement of temperature in the substance mass. Samples of the mixture with and without a catalyst were prepared by analytical grinding (~17 mg; measurement accuracy ± 0.01 %). Then they were loaded into one of the corundum crucibles with a volume of 2 ml, the another one was left empty. Both crucibles were placed into the electric furnace of the device and heated linearly from 33 °C to 600 °C at a constant heating rate of 20 °C/min, while the mass change was recorded. At a certain temperature various reactions begin and at this temperature the mass loss of the sample is observed. Thus, the rate of mass loss increases and decreases again after the reaction is completed. Thermal analysis is performed in an oxygen-free environment to avoid oxidation reactions. Nitrogen was taken as a gas medium, the flow rate was 30 ml/min. Processes are carried out in comparative conditions, because the size and granulometric composition of the sample affect the results of the analysis. The type of derivatograms also depends on the gas emission conditions. If the rate of formation of gaseous substances is higher than the rate of their removal, then gaseous products that affect the process of thermal destruction are accumulated inside the sample. In order to prevent accumulation of gases in the derivatograph, their suction is provided.

Results and Discussion

Technical characteristics of coal tar are given in Table 1.

Table 1

Technical characteristics of primary coal tar [11]

Description	Value
Tar density at 20 °C, g/cm^3	1.061
Anhydrous tar density at 20 °C, g/cm^3	1.062
Water content, %	2.2
Mass fraction of the substances insoluble in toluene, %	1.4
Mass fraction of the substances insoluble in quinoline, %	–
Ash content, %	0.12
Phenol content, %	20.6
Naphthalene content, %	1.6
Mass fraction of fractional composition, %	
till 180 °C	5.1
180–210 °C	4.4
210–230 °C	4.8
230–270 °C	15.8
270–390 °C	19.7

The studied coal tar is characterized by a low density, a small amount of water, the absence of crystallizing fractions, a low yield of substances insoluble in toluene, a high content of phenols, a small proportion of naphthalene.

The information about particle's size and distribution, chemical composition and surface morphology of the microsphere, NiO/microsphere, CoO/microsphere catalysts used in thermal degradation of primary coal tar is given in [24], NiCo/chrysotile catalyst's particle's size and distribution, X-ray phase analysis, surface morphology information is given in [25]. The scanning electron microscope (SEM) image of the microspheres (Fig. 1) and the transmission electron microscope (TEM) image of the chrysotile (Fig. 2) are illustrated in the pictures below.

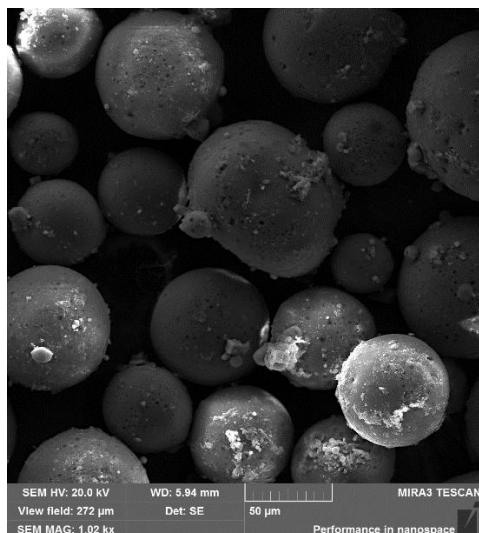


Figure 1. SEM image of the microspheres

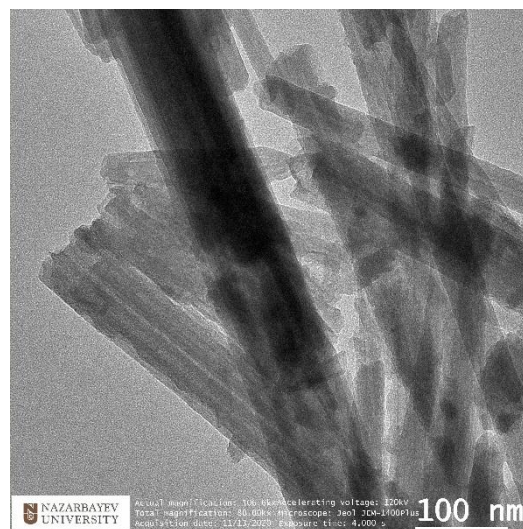


Figure 2. TEM image of the chrysotile

The surface of the microspheres exhibited micropores with sizes ranging from 200 to 400 nm, along with irregularities [24]. The micrographs (Fig. 2) reveal a tightly packed arrangement of chrysotile tubes. However, on a larger scale, the long-range order of chrysotile can be characterized as “amorphously” packed. The mineral contains nanotubes with an inner diameter of approximately 10 nm and an outer diameter of about 60 nm [25].

The method of determining the kinetic parameters of thermal destruction of carbon-containing substances describing the entire part of the one-stage thermogravimetry curve was explained by T.V. Bukharkina [26] and S.Yu. Lyrshikov [27].

The “gross-stage” method of thermogravimetric analysis, as well as Professor Gulmaliev's [28] kinetic parameters (rate constant k , pre-exponential multiplier) for the thermal degradation (heating rate 20 K/min) of heavy hydrocarbon raw material, specifically high-viscosity oil, and its blend with catalysts (including microsphere and NiO/microsphere catalyst) and polymers, has been detailed in the referenced paper [1]. The calculated activation energy (E_a) and pre-exponential multiplier (k_0) were determined according to the method presented in [28].

Notably, elevated values of activation energy and pre-exponential multiplier are observed during the decomposition of high-viscosity oil within the temperature range of 534–759 K, particularly when microspheres and polyethylene glycol are introduced. On the contrary, lower activation energy is noted during the decomposition of a mixture comprising high-viscosity oil, polyethylene glycol, and NiO/microsphere in the temperature range of 520–745 K.

Figure 3 shows thermogravimetric curves of primary decomposition of primary coal tar and its mixture with catalysts.

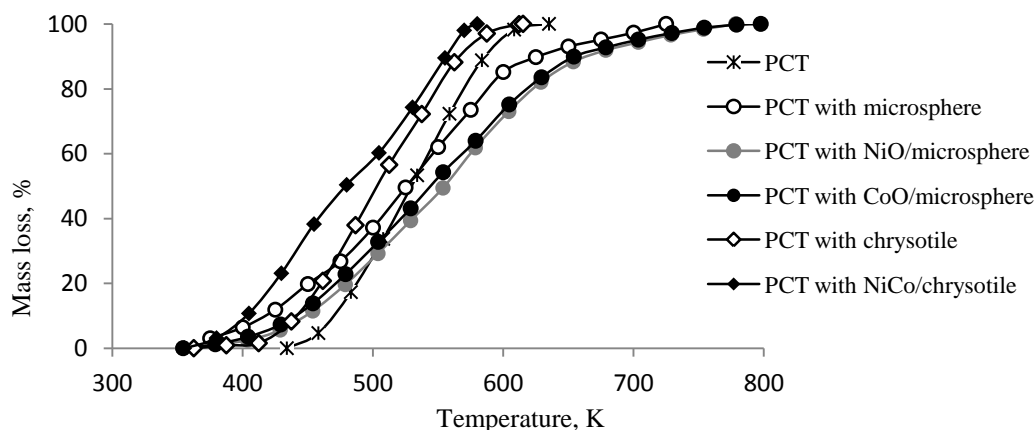


Figure 3. Thermogravimetric curves of destruction of primary coal tar and its mixture with catalysts

As can be seen in Figure 3, during the thermal destruction of unmixed primary coal tar, mass loss begins at 434 K, and when CoO/microsphere and NiO/microsphere are added, mass loss starts at 354 K, when microsphere is added, at 350 K, in case of chrysotile is added — at 407. The onset temperature of mass loss when adding NiCo/chrysotile is 355 K. In the main stage of destruction of primary coal tar, the mass loss process ends quickly in the mixture of NiCo/chrysotile at 577 K, in the mixture of PCT with chrysotile at 623 K, in the destruction of unmixed primary coal tar at 635 K, in the presence of microspheres at 748 K, in the presence of NiO/microsphere at 778 K, in the presence of CoO/microsphere at 798 K.

Figure 4 shows the temperature dependence of the rate of mass loss on temperature during thermal destruction of primary coal tar and its mixture with catalysts.

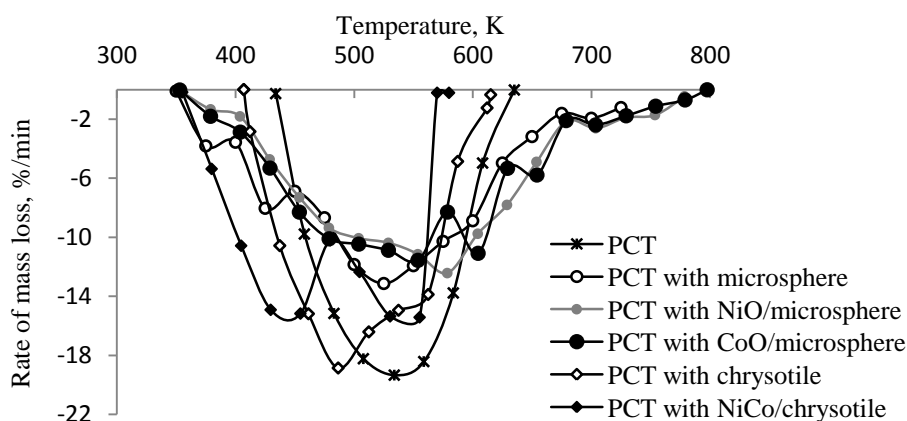


Figure 4. DTG curves of destruction of primary coal tar and its mixture with catalysts

The analysis of the derivative thermogravimetry curves for heavy hydrocarbon raw materials in Figure 4 reveals a staged and variable-speed progression of processes. The introduction of NiCo/chrysotile catalyst and microsphere-based catalysts induces an early onset of thermal decomposition in primary coal tar at approximately 80 K. The inclusion of chrysotile does not alter the maximum rate of thermal decomposition (19 %/min). Notably, the mass loss rates during the thermal decomposition of PCT with the incorporation of microsphere-based catalysts and NiCo/chrysotile are diminished. The maximum rate of mass loss is observed at temperatures of 534 K for unalloyed PCT, 525 K with the addition of microspheres, 579 K with the addition of NiO/microspheres, 554 K with the addition of CoO/microspheres, 487 K with the addition of chrysotile, 455 K, and 555 K with the addition of NiCo/chrysotile.

Microsphere catalysts (CoO/microsphere and NiO/microsphere) affect the duration of the main stage of the thermal decomposition process of primary coal tar. This situation leads to a more decomposition of the resin mass in the main stage. And in PCT and NiCo/chrysotile mixture, thermal destruction takes place in a short time, but at a high speed.

The thermokinetic parameters, namely the pre-exponential factor (k_0) and activation energy (E_a), for primary coal tar and its blend with catalysts, have been determined using the “gross-stage” method [26], and the results are presented in Table 2.

Table 2

Kinetic parameters of thermal destruction of PCT and its mixture with catalysts according to the “gross-stage” method

Composition	Temperature range, K	k_0 , min^{-1}	E_a , kJ/mol
Primary coal tar	434–635	$2.2 \cdot 10^3$	38.4
Mixture of PCT and microspheres	350–748	$1.1 \cdot 10^2$	28.3
Mixture of PCT and NiO/microsphere	354–778	$6.6 \cdot 10$	26.7
Mixture of PCT and CoO/microsphere	354–798	$2.3 \cdot 10$	22.0
Mixture of PCT and chrysotile	407–623	$6.1 \cdot 10^4$	50.0
Mixture of PCT and NiCo/chrysotile	355–577	$2.3 \cdot 10^2$	26.6

According to the Table 2, the activation energy and pre-exponential multiplier of the thermal decomposition of unmixed coal tar is higher than when microsphere catalysts and NiCo/chrysotile are added, that is, these catalysts facilitate the initiation of thermal destruction of PCT. And when chrysotile is added, the activation energy of thermal destruction increases, and the process is slowed down.

The kinetic parameters of the thermal decomposition of primary coal tar and its combinations with catalysts, including the rate constant (k), pre-exponential factor (k_0), and activation energy (E_a), were determined using the method of thermogravimetric analysis as outlined in Professor Gulmaliev's work [28]. The calculated values are presented in Table 3.

Table 3

Kinetic parameters of thermal destruction of PCT and its mixture with catalysts according to the “inflection point” method

Composition	Temperature range, K	k , min ⁻¹	k_0 , min ⁻¹	E_a , kJ/mol
Primary coal tar	434–635	$2.3 \cdot 10^{-1}$	$1.18 \cdot 10^2$	27.9
Mixture of PCT and microspheres	350–748	$9.5 \cdot 10^{-2}$	1.06	10.3
Mixture of PCT and NiO/microsphere	354–778	$1.2 \cdot 10^{-1}$	2.52	13.6
Mixture of PCT and CoO/microsphere	354–798	$9.8 \cdot 10^{-2}$	1.13	10.0
Mixture of PCT and chrysotile	407–623	$3.3 \cdot 10^{-1}$	$4.5 \cdot 10^3$	45.7
Mixture of PCT and NiCo/chrysotile	355–577	$1.5 \cdot 10^{-1}$	6.43	15.6

When comparing the thermokinetic parameters determined through the “gross-stage” method and the “inflection point” method for the thermal degradation of pure primary coal tar and its decomposition with a blend of microsphere catalysts, the disparities observed between the methods are consistent. For instance, the activation energies of the thermal decomposition for the mixture of PCT and microsphere, as well as PCT and CoO/microsphere, determined by both methods, exhibit similar values. In both cases, where NiCo/chrysotile is introduced to PCT, the activation energy values closely align with the corresponding thermokinetic parameters of the PCT and NiO/microsphere mixture. Hence, both methods can be equally applied for comparing the kinetic parameters of the thermal degradation of primary coal tar.

The values of the rate constants of the thermal decomposition of primary coal tar, determined by the “inflection point” method are close to each other and relatively low when adding CoO/microsphere and microsphere. The highest rate constant is observed in the mixture of PCT and chrysotile ($3.3 \cdot 10^{-1} \text{ min}^{-1}$). Values of rate constants when NiCo/chrysotile and NiO/microspheres are added to PCTs are close to each other.

The thermal decomposition of primary coal tar of JSC “Shubarkol coal” in the presence of hydrogen donors and catalysts (magnetic part of microspheres and nickel-enriched chrysotile) in the “gross stage” method [3], magnetic microsphere leads to a decrease in activation energy and pre-exponential multiplier compared to chrysotile-based catalyst. And in the “inflection point” method, the addition of two catalysts to the PCT leads to 2–2.5 times increase in the activation energy and rate constants compared to the corresponding parameters of the thermal destruction of the resin without the initial additive.

Conclusions

Comparing the results obtained by two different methods, it can be seen that the microsphere-based catalysts and nickel-cobalt-enriched chrysotile-based binary catalyst decrease the activation energy and rate constant of primary coal tar thermodestruction, and the addition of chrysotile mineral to the system increases both the activation energy and the rate constant of this process.

It shows that the effect of catalytic additives on the thermal destruction of coal tar is directly related to the nature of carriers. While microsphere catalysts extend the range of thermal destruction, chrysotile and the catalyst based on it lead to the rapid completion of the destruction process. This fact as observed in previous works [4, 5] is characterized by the formation of bonds between catalytic additives and heavy hydrocarbon raw materials.

In the presence of the studied catalysts, the rate of thermal destruction of primary coal tar increases in the following order: CoO/microsphere < NiO/microsphere < NiCo/chrysotile.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. **CRedit**: **Darzhan Ergalievna Aitbekova** conceptualization, formal analysis, investigation, visualization, writing-original draft, writing-review & editing; **Murzabek Ispolovich Baikenov** conceptualization, resources, supervision; **Aigul Akizhanovna Muratbekova** writing-original draft, formal analysis; **Abylaikhan Nurlanuly Bolatbay** investigation, formal analysis, validation; **Nazerke Zhumagalievna Balpanova** investigation; **Sairagul Tyanakh** investigation; **Fengyun Ma** conceptualization; **Tolkyn Ondirisovna Khamitova** investigation.

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Conflicts of Interest

The authors declare no conflict of interest.

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