THE EXPERIMENTAL RESEARCH OF N-BUTANE PYROLYSIS USING AN AGITATOR

O.A. Kolenchukov[1], K.A. Bashmur*[1], V.V. Bukhtoyarov[1,2], R.B. Sergienko[3], V.S. Tynchenko[1,2,4]

[1]Institute of Petroleum and Natural Gas Engineering, Siberian Federal University, Krasnoyarsk, Russia;
[2]Digital Material Science: New Materials and Technologies, Bauman Moscow State Technical University, Moscow, Russia;
[3]Gini Gmbh, Munich, Germany; [4]Institute of Computer Science and Telecommunications, Reshetnev Siberian State University of Science and Technology, Krasnoyarsk, Russia

ABSTRACT

This research aims to improve the thermal processes of oil sludge treatment. The goal of this research is to determine the impact of the agitator on the output of hydrocarbon gas mixes and hydrogen during the catalytic pyrolysis of n-butane (C_4H_{10}), the product of stage one of the complex oil sludge treatment. To conduct the research, the authors developed a setup for the testing of a pyrolysis reactor with an agitator to assess its efficiency in terms of target n-butane breakdown products, namely hydrocarbon mixes and hydrogen. In this research, the authors used $70Ni–20Cu–10Al_2O_3$ as a catalyst. The components of the obtained gas mix were analyzed using the chromatographic method. The results show that the use of the agitator during the catalytic pyrolysis of n-butane can increase the output of the target product. In particular, the hydrogen output increased by ~7.2% over the reaction period (12 hours) compared to the setup without an agitator. The authors determined that the optimal reaction time for the production of hydrogen and butane-hydrogen mix is 4 hours.

KEYWORDS

Petroliferous sludge;
Hydrocarbon
gas mix;
N-butane;
Catalytic pyrolysis;
Experimental setup;
Reactor;
Agitator.

Introduction

The impacts of factors like the reduction the quality and quantity of fossil energy sources, the enhanced greenhouse gas emission control, and the simultaneous increase in the amount of wastes and demand for power make the development and use of alternative energy sources an increasingly pressing issue. Hydrocarbon gas mixes, as well as hydrogen, are among the promising fuel types of today as they produce less harmful substances when burned compared to conventional fuels [1, 2]. Hydrogen, in its turn, is a harmless fuel as it turns into water when burned.

Currently, oil sludges receive more attention than other industrial hydrocarbon wastes [3]. The key components of oil sludges include valuable hydrocarbons that can be transformed into fuel and other useful products. The oil and gas industry produces a large amount of oil sludges that are dangerous and toxic due to the presence of complex hydrocarbons (aliphatic and aromatic), emulsified oil, resistant organic matters, etc. [4]. The increasing demand for oil products results in the increased formation of oil sludges.

Storing such wastes takes up large territories that become unusable for at least a decade until they can recover [5]. Due to their toxic properties, oil sludges cannot be disposed of untreated. Storing untreated oil sludges may reduce the hydraulic conductivity, hygroscopic moisture, and the wetting power of soil, and cause soil degradation due to the upsetting of the air and water regime and the soil matrix
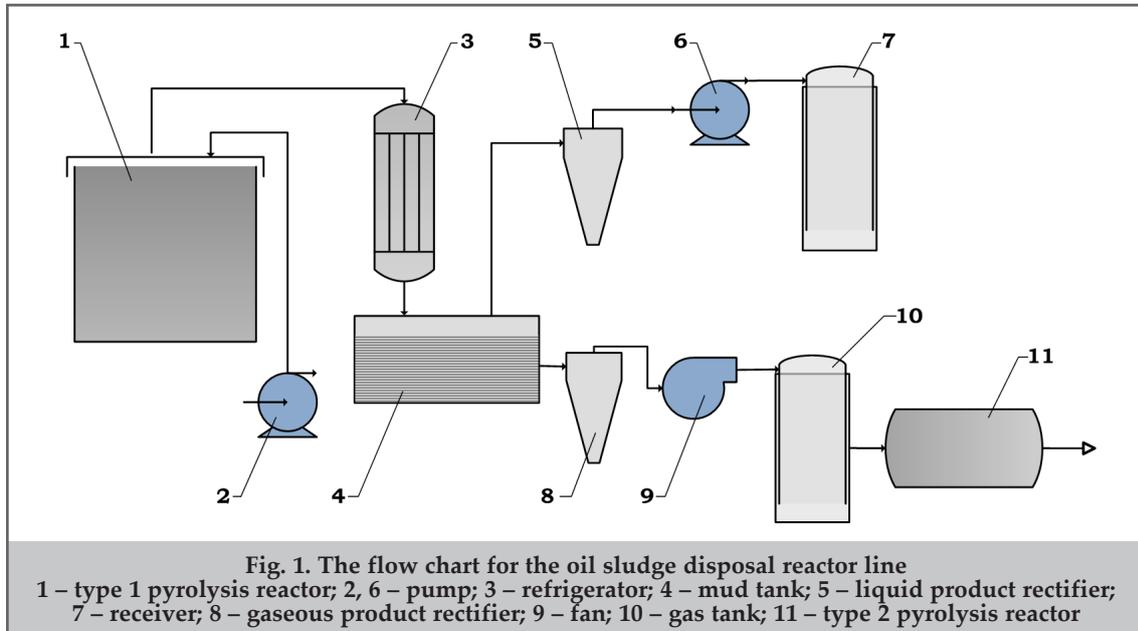
profile [6]. Oil hydrocarbons may enter groundwater posing a serious threat to aquatic ecosystems [7]. Besides, improper oil sludge disposal presents a serious hazard for the health of humans and animals due to the genotoxicity of oil and polycyclic aromatic hydrocarbons [8]. Thus, it is necessary to treat oil sludges in an environmentally safe way to reduce their harmful impacts on the environment.

There are many research works on the disposal of oil sludges, but the Russian Federation lags behind the developed countries in terms of their treatment [9]. The technological cycle restrictions for the oil sludge treatment impact the potential production and usage of valuable products. The pyrolysis-based technology described in [10, 11] is one of the approaches to the deep treatment of oil sludges. The key advantages of this method include the high breakdown rate of the raw material, no need for the additional processing of the raw materials, the possibility of using the breakdown products, relatively low amount of unrecyclable breakdown products, and the self-sufficiency of the method.

The complex technology for the deep processing of industrial organic wastes developed by the authors of this research and partially uncovered in previous publications [12] can be briefly described as follows. The processing like includes two key stages and respective units, the pyrolysis reactors. During these stages, hydrocarbons are broken down into components through the controlled subsequent pyrolytic decomposition. During the first stage, hydrocarbons (liquid, solid, and gaseous) are formed. During the second stage, a gas mix is produced depending on the raw material, the holdup time, hydrogen, and hydrocarbon nanomaterials. The

Fig. 1. The flow chart for the oil sludge disposal reactor line
1 – type 1 pyrolysis reactor; 2, 6 – pump; 3 – refrigerator; 4 – mud tank; 5 – liquid product rectifier;
7 – receiver; 8 – gaseous product rectifier; 9 – fan; 10 – gas tank; 11 – type 2 pyrolysis reactor

technology is shown in figure 1.

Pyrolysis takes place at temperatures between 450 to 1050 °C, which means maintaining this process requires high energy inputs. To reduce the energy costs and increase the target product output, we can use some equipment facilitating the efficient and even distribution of thermal energy through all of the reactor equipment to intensify chemical processes [13]. In particular, we have a hypothesis that heat exchange can be intensified through the use of agitators [14]. This hypothesis has not been confirmed for the pyrolysis of oil sludge decomposition products in any of the experimental research known to the authors.

We must note that the efficiency of agitators can be characterized by the mixing rate [15]. We understand the mixing rate as the mutual distribution of substances after mixing. The mixing rate depends on the intensity of swirling floorage formation by the agitator, as well as the flow and swirl structure, and their energy dissipation. Mixing has a direct impact on heat transfer characterized by the heat transfer factor. The heat transfer factor is a complex value depending on the physical properties of the operating medium, its movement speed, dimensions, agitator blade shapes, etc.
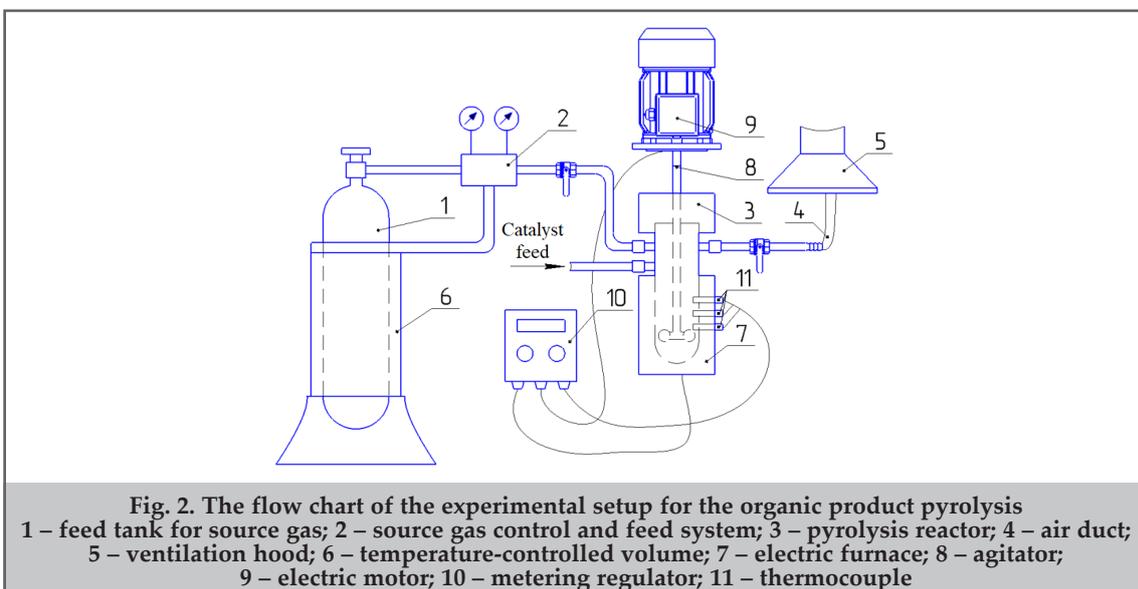
Thus, the goal of this research is to determine the impact of the agitator on the output of target end products during the catalytic pyrolysis of n-butane (C_4H_{10}), the product of stage one of the complex oil sludge treatment.

Methods and materials

To achieve the goal set, we developed an experimental setup for the complex pyrolysis of industrial organic wastes, whose flow chart is shown in figure 2, at the Biofuel Composition Laboratory of Siberian Federal University.

This setup may work in two pyrolysis modes. The first mode is the processing of industrial organic wastes resulting in the production of valuable gaseous (light hydrocarbons), liquid (saturated, unsaturated, cyclic, and aromatic hydrocarbons), and solid (coke, ash) pyrolysis products. The second mode is the treatment of the previously produced light hydrocarbons to produce a gas mix, hydrogen, and nanofiber carbon used as an additive for the manufacturing of various products (composite materials, catalyst carriers, etc).

The operating principle of the experimental setup is as follows. A catalyst is places in the pyrolysis reactor 3 (fig. 2), then it is heated using the electric furnace 7. When the

Fig. 2. The flow chart of the experimental setup for the organic product pyrolysis
1 – feed tank for source gas; 2 – source gas control and feed system; 3 – pyrolysis reactor; 4 – air duct;
5 – ventilation hood; 6 – temperature-controlled volume; 7 – electric furnace; 8 – agitator;
9 – electric motor; 10 – metering regulator; 11 – thermocouple

required temperature is achieved, hydrocarbon gas was fed from the tank 1 where it stored at room temperature. When the gas contacted the catalyst, a gas mix and nanofiber carbon was formed, and some of the gas was sampled for research. The optimal hydrocarbon gas flow, according to [16], was set at 100 l/h gcal. The catalyst weight is 0.1 g.

Pyrolysis was controlled using the two-channel metering regulator 10, type OVEN 2TRM1, accuracy grade 0.5/0.25. To control the reactor temperature, we used three thermocouples 11, type TKhA (K), installed in the thermocouple pocket at equal distances along the height of the reactor.

Before the experiment, the pyrolysis reactor and the pipeline system were blown with a neutral gas, carbon dioxide (CO_2), with subsequent visual inspection of joints. Pyrolysis was carried out at the atmospheric pressure and a reactor temperature of 590±10 °C. The reactor with the catalyst was heated directly after the pressure test in the neutral gas medium. After the set temperature was achieved, we fed the hydrocarbon gas, namely n-butane.

The pyrolysis reactor is a retort (fig. 2) of heat-resistant inoxidized steel (AISI 310S/20X23H18) that is tightly connected to the metal lid using a threaded joint. We used PENOSIL Premium +1500 °C thermal sealant as a gasket for the metal lid. Reactor retort diameter is 100 mm and its height is 300 mm.

The agitator (fig. 3) is a shaft made of AISI 321 (12X18H10T) steel featuring equally spaced service openings for the installation of mixing elements (blades in our case). The geometry and number of blades may vary. The possibility of controlling these parameters (geometry, number) allows for the setting of their optimal combination to achieve the maximum efficiency of the agitator in the further research.
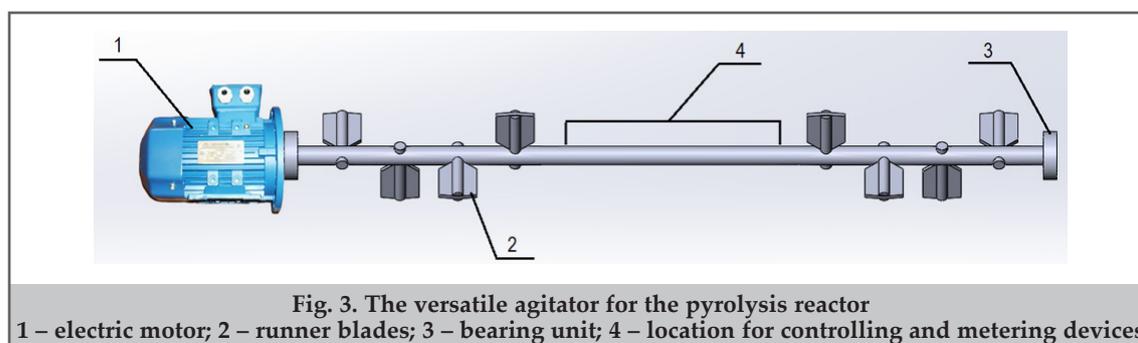
The author of [19] established that the texture promoter (Al_2O_3) in the catalyst has to make up 10% of the weight, and the active metal (Ni) particles in it must be sized between 10 and 40 nm. According to [20], the data obtained from [19] correlate well with the catalytic pyrolysis of propane and butane. Besides, the catalyst serves as a surface of which nanofiber carbon is formed. The recovery of the catalyst was carried out in the hydrogen flow at a temperature of 550 °C during 3 hours.

The research results obtained in [21] show that the use of catalysts during hydrocarbon gas pyrolysis facilitates the increased output of hydrogen and hydrogen-containing mixes, as well as the reduction of the reaction temperature. According to the experimental non-catalytic pyrolysis data, the decomposition of butane was observed at the initial temperature of 450 °C. Up to 625 °C, the reaction produces hydrogen, methane, ethylene, and ethane, if the temperature is above 625 °C, these destruction products are complemented with propylene. The conversion of ~90% is achieved at a temperature of 700 °C with the hydrogen concentration of 18% of volume.

The components of the obtained gas mix were analyzed using a Clarus 600 chromatographer. Gaseous products were sampled every hour, and the total reaction time was 12 hours. The structure analysis of the nanofiber carbon particles formed on the catalyst surface and the impacts of other catalyst types on the process were outside the scope of this research.

The key reaction directions for the butane pyrolysis without the catalyst (1) and with the catalyst (2) can be described using the following expressions:

To measure the concentration of harmful substances in the

Fig. 3. The versatile agitator for the pyrolysis reactor
1 – electric motor; 2 – runner blades; 3 – bearing unit; 4 – location for controlling and metering devices

Since the hydraulic resistance characterizes the completeness of interaction of the flow and the agitator, we used the experimental data [17] to construct regression dependencies for various types of blades and their pitch angles (fig. 4). This justifies the selection of a blade agitator with flat blades.

In our research, we used the following catalyst: 70Ni–20Cu–10Al_2O_3. The catalyst was prepared by mixing a weighted quantity of pseudoboehmite gel (texture promoter) and nitric acid with a subsequent addition of $Ni(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ and thorough mixing into a paste-like substance. The last catalyst preparation stage involved the addition of a concentrated ammonia solution (as a precipitator) with subsequent drying in the furnace to a temperature of 750 °C. The heating rate was 1 °C/min, and the holding time was 3 hours. The catalyst preparation procedure was similar to that described by the author of [18].

Fig. 4. The dependency of the hydraulic resistance and the blade type and pitch angle
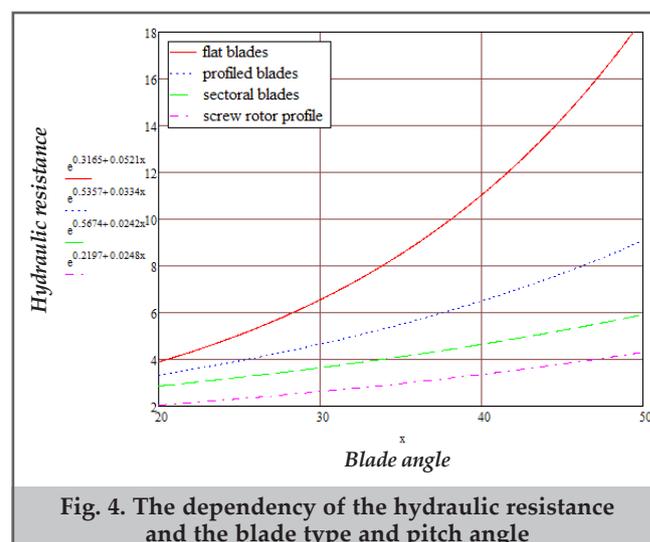
produced gases, we used a Hobbit-T stationary gas analyzer.

Results and discussion

The concentrations of the reaction products with and without the agitator are shown in figures 5 and 6.

From the data obtained we can see that the n-butane pyrolysis can produce three gases: methane (CH_4), hydrogen (H_2), and butane (C_4H_{10}). Besides, it generates C_2-C_3 hydrocarbons whose concentration is shown in general terms on the diagrams (fig. 5 and 6). In both cases, we observed an increase in the concentration of hydrogen over the period of 1 to 2 hours with the further stabilization of its output at 53÷58% over the next 2 hours (from 2 to 4). Starting from the 4th hour of the reaction, the hydrogen concentration reduces, and the concentration of butane increases dramatically, which can be explained by the gradual deactivation of the catalyst. The deactivation is caused by the blocking of the active carbon center. This carbon is made up of nanofiber carbon and carbon nanotubes (carbide cycle mechanism).
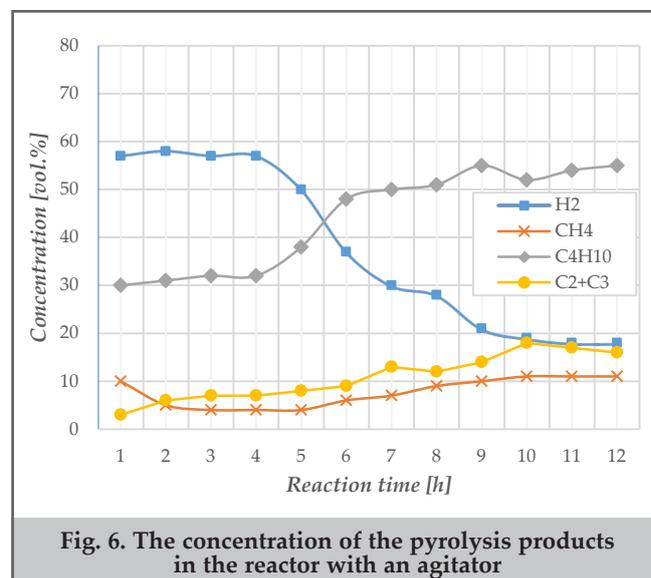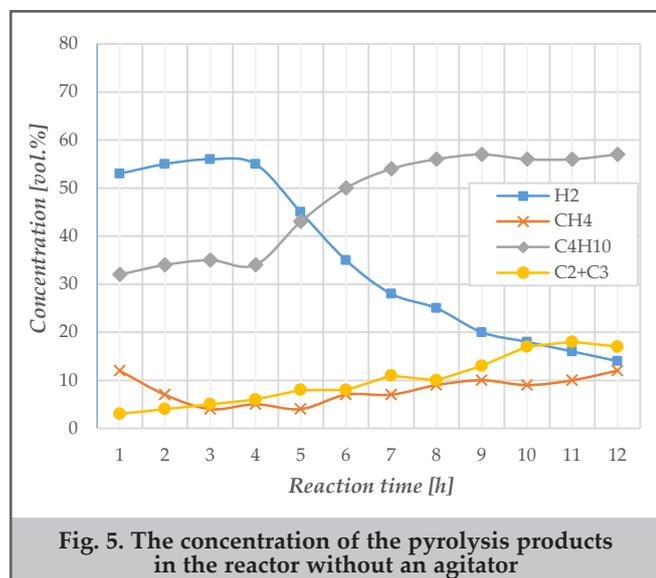
If we compare the results (fig. 5 and 6), we can see that the agitator facilitates an increase in the total hydrogen concentration of ~7.2% for 12 hours of reaction and ~4.6% for 4 hours of reaction. However, to obtain hydrogen or butane-hydrogen mix as end product, it is feasible to carry out the reaction during the first 4 hours as during this time the concentration of hydrogen is at the maximum, and the concentration of auxiliary substances (C_4H_{10}, CH_4, C_2–C_3) is at the minimum. Simultaneously, during the reaction in the reactor with the agitator, the amount of C_2–C_3 hydrocarbons increases and the concentration of butane reduces as more of it is involved in the reaction. The rapid increase in the

hydrogen output and reduction of butane output is only observed during the first hours (from 1 to 5). Later on, the reactor operates with nearly the same parameters as the one without the agitator. After 5 hours, the reaction can be justified for the production of carbon nanomaterials and gas mixes for the fuel power industry.

The increase in the concentration of the target pyrolysis products due to the use of an agitator can be explained by the continuous maintenance of the set reaction temperature throughout the reaction chamber of the reactor. This is achieved through creating a swirling motion of the fed gas by the agitator resulting in a more efficient heat withdrawal from the heated reactor wall by the gas. Another factor behind the increased total concentration is the mixing of the gas and the catalyst due to the intensification of molecule diffusion both to and from the surface of the catalyst.

The analysis of the harmful substance concentration showed that the MAC of harmful substances (CO, CO_2) do not exceed the standards set by GN 2.2.5.3532-18 and GN.2.1.6.3492-17.

To determine the experimental error, the data were processed as follows: Each of the time coordinate samples was taken three times with the further analysis of the qualitative and quantitative composition of the gas mix. Further on, we determined the absolute error Δx and the relative error εa of the experiment according to [22]. All of the measurements were taken for the number of degrees of freedom $k = 3$ and Student's t–test $p = 4.3027$. The calculation results show that the relative error of the measurement results is in the range of $\Delta x = 1.4÷1.9\%$. The relative error can be rounded to a larger value and written down as $\varepsilon_a = ±2\%$.

Fig. 5. The concentration of the pyrolysis products in the reactor without an agitator

Fig. 6. The concentration of the pyrolysis products in the reactor with an agitator

Conclusions

To research the deep complex treatment of industrial organic wastes, we developed and presented an experimental setup for the testing of a pyrolysis reactor with an agitator to assess its efficiency in terms of target breakdown products, namely the butane-hydrogen mix and hydrogen.

The results of the experimental research show that the use of the agitator during the catalytic pyrolysis of n-butane can increase the output of the target product. The increase in the output of gaseous products can be attributed to the even distribution of heat throughout the reaction chamber due to the swirling created by the agitator.

The agitator-based catalytic pyrolysis setup for n-butane helped us increase the hydrogen output by ~7.2% over 12 hours of reaction and ~4.6% over 4 hours of reaction. The relative error amounted to 2%. The optimal reaction time for the production of hydrogen and butane-hydrogen mix is 4 hours due to the maximum hydrogen concentration during this time.

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Экспериментальное исследование пиролиза н-бутана при использовании перемешивающего устройства

О.А. Коленчуков[1], К.А. Башмур[1], В.В. Бухтояров[1,2], Р.Б. Сергиенко[3], В.С. Тынченко[1,2,4]

[1]Институт нефти и газа, Сибирский федеральный университет, Красноярск, Россия;
[2]Центр НТИ «Цифровое материаловедение: новые материалы и вещества»,
МГТУ им. Н.Э. Баумана, Москва, Россия; [3]Gini Gmbh, Мюнхен, Германия;
[4]Институт информатики и телекоммуникаций, СибГУ им. М.Ф. Решетнева, Красноярск, Россия

Реферат

Исследование направлено на совершенствование термических процессов переработки нефтяных шламов. Целью исследования являлось определение влияния перемешивающего устройства на выход газовых углеводородных смесей и водорода при каталитическом пиролизе продукта первого этапа комплексной переработки нефтешламов – н-бутана (C_4H_{10}). Для проведения соответствующих исследований была разработана установка, отличительной особенностью которой является возможность испытания реактора пиролиза с перемешивающим устройством для оценки его эффективности по выходу конечных целевых продуктов разложения н-бутана – углеводородных смесей и водорода. В настоящем исследовании применялся катализатор 70Ni–20Cu–10Al$_2$O$_3$. Анализ получаемых компонентов газовой смеси производился с помощью хроматографии. Результаты показывают, что применение перемешивающего устройства при каталитическом пиролизе н-бутана способно повысить выход целевого продукта. В частности, по сравнению с установкой без перемешивающего устройства, выход водорода увеличился на ~7.2% за всё время реакции (12 часов). Выявлено оптимальное время реакции для получения водорода и бутано-водородной смеси – 4 часа.

Ключевые слова: нефтесодержащий шлам; газовая углеводородная смесь; н-бутан, каталитический пиролиз; экспериментальная установка; реактор; перемешивающее устройство.

Qarışdırıcı qurğusundan istifadə edərkən n-butan pirolizinin eksperimental tədqiqi

O.A. Kolençukov[1], K.A. Başmur[1], V.V. Buxtoyarov[1,2], R.B. Serqiyenko[3], V.S. Tınçenko[1,2,4]

[1]Neft və Qaz İnstitutu, Sibir Federal Universiteti, Krasnoyarsk, Rusiya; [2]N.E.Bauman adına MDTU-nin «Rəqəmsal materialşünaslıq: yeni materiallar və maddələr» Milli Texnoloji Təşəbbüs Mərkəzi, Moskva, Rusiya; [3]Gini Gmbh, Münhen, Almaniya; [4]M.F.Reşetnev adına Sibir Dövlət Universiteti, İnformatika və Telekommunikasiya İnstitutu, Krasnoyarsk, Rusiya

Xülasə

Tədqiqat neft şlamlarının emalının termik proseslərinin təkmilləşdirilməsinə yönəlmişdir. Tədqiqatın məqsədi qarışdırıcı qurğunun neft şlamların - n-butan (C_4H_{10}) kompleks emalının birinci mərhələsinin məhsulunun katalitik pirolizində qaz karbohidrogen qarışıqlarının və hidrogenin çıxışına təsirini müəyyən etmək idi. Müvafiq tədqiqatların aparılması üçün piroliz reaktorunun qarışdırıcı qurğu ilə sınanmasının mümkünlüyü ilə fərqlənən, n-butanın parçalanmasının son məqsədli məhsullarının – karbohidrogen qarışıqları və hidrogenin çıxışının effektivliyini qiymətləndirmək üçün qurğu işlənib hazırlanmışdır. Bu tədqiqatda 70Ni–20Cu–10Al$_2$O$_3$ katalizatoru tətbiq edilmişdir. Alınan qaz qarışığının komponentlərinin təhlili xromatoqrafiya üsulu ilə həyata keçirilmişdir. Nəticələr göstərir ki, n-butanın katalitik pirolizi zamanı qarışdırıcı qurğunun tətbiqi məqsədli məhsulun çıxışını artıra bilər. Xüsusilə, qarışdırıcısı olmayan bir qurğu ilə müqayisədə, hidrogenin çıxışı bütün reaksiya müddətində (12 saat) 7.2 ~% artmışdır. Hidrogenin və butan–hidrogen qarışığının alınması üçün optimal reaksiya müddəti müəyyən edilmişdir - 4 saat.

Açar sözlər: neftli şlam; qaz karbohidrogen qarışığı; n-butan; katalitik piroliz; eksperimental qurğu; reaktor; qarışdırıcı qurğu.