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Praha 8 – Karlín, Lyčkovo nám. 508/7, PSČ 18600
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Section 1. Biotechnology

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EVALUATION OF HOW TO APPLY DEEP LEARNING IN BIOMEDICAL ENGINEERING

Nazrin Ismayilova [1]

[1] Bachelor student of Silesian University of Technology

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Abstract

Recent developments in image processing have contributed to the advancement of rapidly developing technological systems. Studies on image processing, especially in the health field, have increased its popularity. Despite the success achieved on existing methods, whether it is medical images or images in other fields; the deep learning model is a model that contributes more in terms of time and performance compared to existing methods. While processing is done on single-layer images with existing methods, high-performance results can be obtained on multi-layer images with the deep learning model. The most important feature of deep learning is that it processes the operations on the image in a single go and can discover parameters that need to be entered manually. In addition, the fact that technology companies are turning to deep learning has increased their competitive power among themselves, and the methods they have built on deep learning in scientific terms have started to be preferred more than existing methods. In the biomedical field, which is one of the areas with limited dataset access, datasets have recently been obtained rapidly.

Keywords: *CNN, deep learning, image processing, biomedical, biomedical imaging*

Inroduction

In a world where digitalization is rapidly spreading, obtaining data has become quite simple. Deep learning models have achieved significant success with the increase in the amount of data. Each deep learning model is unique with its architecture and components. These models have minimized the errors received in many areas, thus leaving traditional methods behind. At the same time, it has been seen that higher successes are achieved by minimizing human influence. Creating models similar to the human nervous system has taken the field of artificial intelligence to an advanced level. Deep learning models have been used especially in areas such as image analysis, audio analysis, robotics, autonomous vehicles, gene analysis, cancer diagnosis and virtual reality, and have achieved excellent results compared to human performance.While used in the relevant field, attention has been paid to prevent time loss, improve memory and power usage, and avoid stacking layers on top of each other.

With the continuous development and advancement of deep learning technologies, new opportunities and challenges will arise. Designing more complex, automated decision-making systems, ensuring that systems learn, understand and make decisions better, understanding objects and events in data types such as images, videos, and text, developing more effective learning methods under limited data conditions, using knowledge learned in one field in another, understanding the ethical relationship between deep learning, and developing human-focused, fair artificial intelligence are inevitable areas to focus on in the future. Researchers and experts can expand the boundaries of deep learning and achieve new successes by working in these areas.

Image processing is a technology that obtains fast results with various interface software in a computer environment for the functions performed by the human eye. Various models have been developed in this technology and these models have also contributed to the scientific studies. Using image processing and clustering methods, many categories of analysis are performed on the image such as shape detection, labeled classification, shape separation, and structuring into subclasses (Zhang J., Y. Xia, Y. Xie, M. Fulham, and Feng D., 2017). The most preferred model in the results of these analyses is the deep learning model, which is a sub-branch of machine learning. Deep learning, which has a multi-layered structure according to the machine learning method and is inspired by the functioning of the human brain, has been attracting increasing interest recently (Koitka S. and Friedrich C. M. , 2016). Image processing experts and academicians at universities use machine learning in application areas such as analyzing videos, classifying images obtained as a result of analysis, learning natural language, etc.

In this process, machine learning uses "Graphics Processing Unit" (GPU) to achieve revolutionary fast and high-performance results. When GPUs are compared to "Central Processing Unit"s (CPU), GPUs are preferred because they have a performance superiority of 10 to 100 times in their applications. In particular, networks are deepened with hidden networks in the Artificial Neural Network (ANN) architecture. This means a lot of memory consumption. Excessive memory consumption can be met by having sufficient hardware in terms of both time and performance. That's why GPUs are preferred instead of CPUs. Deep Learning is the name of the system that can automatically extract features from training sets containing labeled images and allows the use of multi-layered neural networks together, unlike machine learning. It has begun to be used in many areas such as image and sound analysis, robot technology, remote sensing, genetic analysis, cancer and disease diagnosis, etc.

The reason why it is preferred so much is that it can provide fast and high results. This situation has sometimes exceeded human criteria. In these areas, especially large companies (Google, Facebook, Samsung, Microsoft, Intel etc.) continue their investments and studies intensively. Today, the increase in the number of cameras used in every field and the detection of objects in the images obtained from cameras, just like the human eye, has made the machines achieve incredible results with the deep learning model in image processing. In this way, thousands of image sets have shown very successful results with the deep learning model (https://keras.io/ Accessed: 12-Mar-2018).

Academicians working on image processing have focused on image processing studies in the biomedical field in recent years and have increased their activities on deep learning as a model. Another important reason for the interest in deep learning models is that there is enough data to be trained and the physical infrastructure required for processing this data is ready. This article touched on the comparison of deep learning models supported by various companies with existing architectures in the biomedical field. The most important reasons for focusing on the biomedical field are:

The data sets obtained in this field can be obtained more easily and quickly compared to the past, and a new solution method has been found with the deep learning model compared to classical methods. In addition, the lack of past information on deep learning models in the biomedical field, the faster and higher detection of various diseases in image processing in a field that is important for human life such as health, can be listed as reasons. Before examining the studies in the biomedical field, it will be useful to give brief information about deep learning models and their related libraries.

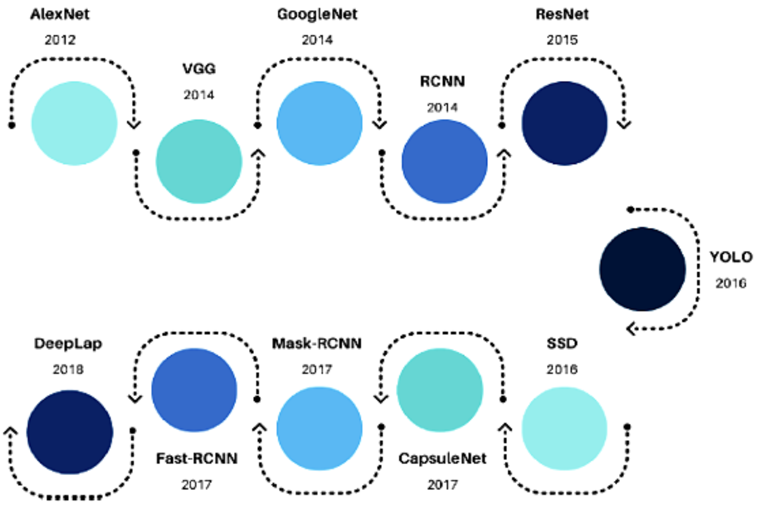
2. Deep Learning Libraries:

Deep learning has led to major breakthroughs in many areas. Of course, the most important factor that enables this is that there are many library files written in various programming languages (Java, C#, C++, Python, etc.) on deep learning. "TensorFlow, Lasagne, Keras, MXNet, Caffe, Torch, etc." are the most preferred libraries. These libraries support many deep learning models such as multilayer neural networks (MLNs), recurrent neural networks (RNNs), feed-forward networks. Caffe: It is a library written on deep learning and image processing. It can also be run on application languages such as Python and Matlab. The most important feature of the Caffe library is that it has pre-trained models (Y. Jia et al, Jun. 2014). Keras: It is a high-level deep learning library written on the Python programming language. Its most important feature is that it can also run on the Tensor Flow Library (https://keras.io/ (Accessed: 12-Mar-2018). TensorFlow: It is an open source deep learning library supported by Google. It makes it easier to build deep networks on GIUs. It is generally preferred for numerical calculations in image processing (https://www.tensorflow.org/ (Accessed: 12-Mar-2018). Torch: It is a library that simplifies even the most complex problems and prepares the algorithm for solving the problem in a fast and flexible structure. Torch can work on image processing, audio processing, video, image, etc. formats. The programming languages it supports are Lua and Python. MXNet: This library is known as a multi-language library because it is supported by programming languages such as R, Python, Scala, Julia. In this way, it is possible to compare the work done in different programming languages.

3. Deep Learning Models

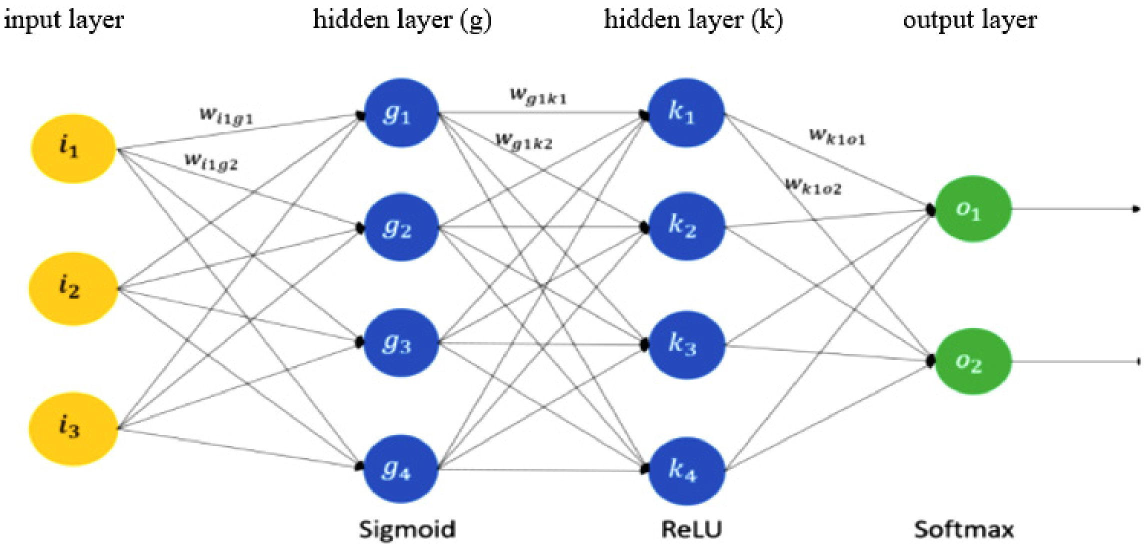
As a result of the digitalization of today's age, the amount of data is rapidly increasing exponentially. This situation has contributed to the developments and successes in the field by increasing the amount of data that the algorithms of methods such as deep learning need to be successful. Deep networks perform the learning process on raw data by obtaining the necessary data from the representations in the relevant layer. Each model built on its architecture is of particular importance. Alex Net, ZF Net, GoogLeNet, Microsoft RestNet, R-CNN, Fast R-CNN and Faster R-CNN models can be listed among the models considered important. In these models, logics such as preventing time loss, improving memory and power usage, and creating a structure that does not stack layers on top of each other have been adopted. Figure 1 shows the development of models developed with the deep learning method over time.

Figure 1. *Methods developed with deep learning architectures (Saleem vd., 2019)*



The Alex Net model, developed on the deep learning architecture in 2012, proved once again how valuable the deep learning approach is by winning the ImageNet competition. While the error rate of computerized object identification was 26.2%, the error rate was reduced to 3.6% with Microsoft RestNet as a result of the continuous development of the architectures. The success of deep learning models has ensured high success in many areas where the architecture is used. The successes it has achieved have enabled the development of many practical applications of machine learning, the expansion of the field of artificial intelligence and its popularity. Deep learning is formed by the combination of artificial neural networks, layers, activation functions, weights and backpropagation algorithm components. It is a learning process in which multilayer neural networks are used to produce output from input data. In order to explain the terms more clearly, it is possible to make the following explanation: ANNs are mathematical models inspired by the biological nervous system. The network structure of the ANNs in Figure 2 can be examined. ANNs are formed by connecting nerve cells (neurons) with a network structure. Neurons, which are processing units, receive input data, perform calculations using weights and activation functions, and transmit the results to other neurons. Deep learning ANNs use this modeling approach.

Figure 2. *Schematic representation of multilayer artificial neural network*



Activation functions are used to calculate the outputs of neurons and represent the non-linear properties of neurons in signal transmission. It can be said that activation functions such as Sigmoid, ReLU (Rectified Linear Unit), and Tanh are widely used. In deep learning networks, the concept of weight is used for the connection between input data and output data, and the concept of bias is used to adjust the activation threshold of cells. These parameters are learned and updated during the training of the network. The training process in question is carried out with the backpropagation algorithm. This algorithm calculates the amount of error between the outputs of the network and the real values backwards and updates the weights with this error information. In this way, the network can learn the relationships between input data and outputs and make more accurate predictions. The selection of such algorithms directly affects deep learning performance. Another factor affecting performance is the design of the deep learning architecture and the layer arrangement. Deep learning architectures will be examined in detail under a separate heading. Deep learning networks process data through layers, each layer forming a specific group of operations. It can be said that it is responsible for the operations on data and the flow of information. With the development of ANNs and the increase in the number of hidden layers, the ESA architecture, which is referred to as a deepening network, has entered an incredible rise. The main difference that distinguishes this architecture from ANNs is that it prevents memorization during the training phase of the network structure. ESA is a deep learning model that can automatically extract the features of images and perform complex tasks. ESAs consist of more than one layer and complete the training process by processing the input data layer by layer. The layers used in the ESA architecture include the convolution layer, the smoothed linear unit layer (ReLU), the pooling layer, the fully connected layer, the Dropout layer and the classification layer. The convolution layer creates activation maps by applying filters to the input image.

The flattened linear unit layer breaks the linear structure of the network and pulls the negative values to zero. The pooling layer is used to reduce the input size and reduces the size by taking the maximum values or averages on the data coming from the convolution layer. The fully connected layer is connected to all fields of the previous layer and calculates the weight matrix. The Drop Out layer closes random nodes to prevent the network from memorizing and increases the diversity of the network. The classification layer performs the classification process and predicts objects in deep learning architectures. These layers form the basis of deep learning models and are used together to perform the learning process. The convolution layer extracts features in the image, while the ReLU layer breaks the linear structure. The pooling layer reduces the size, while the fully connected layer calculates the connections. The DropOut layer prevents memorization, while the classification layer predicts the results. The combination of these layers is used to increase the performance of deep learning models and perform various tasks.

Deep Learning has started to attract more attention, especially with the competitions organized by ImageNet since 2012, and deep learning models have started to be preferred in image classification in the competitions. To give some preliminary information about these popular models:

Alex Net, which made its name in the 2012 ImageNet competition, was trained with approximately one million images and is a deep learning model with a very high success rate in classifying images. This model was modeled to classify a thousand objects (Krizhevsky A., I. Sutskever, and Hinton G. E., 2012).

ZF Net: This model was designed inspired by the AlexNet model and better results were obtained compared to AlexNet. It won first place in the ImageNet competition in 2013. The difference compared to AlexNet is that the filter size is 7×7 and the number of steps is 2. In addition, it used the “Cross Entropy”, “Probabilistic Gradient Descent” and “ReLu” algorithms in its own architecture. The ZF Net architecture consists of 7 layers (Zeiler M. D. and Fergus R., 2014).

Goog LeNet won first place in the ImageNet 2014 image classification competition. In the ImageNet competition it entered in 2012, it increased its success rate from 89.06% to 93.33% in 2014. The GoogLeNet architectural structure consists of 22 layers, and this architecture has proven that increasing the number of layers increases the performance of the classification process when the dataset is too large. In order to prevent overloading of large-sized images, it filters images of various sizes such as “1 × 1, 3 × 3, 5 × 5” in the same time frame.

Microsoft ResNet: The RestNet architecture contains more layers than other architectural structures and has 152 layers in its structure. The number of layers contains almost 7 times more layer parameters than the GoogLeNet architecture. RestNet came first in the ImageNet image classification competition held in 2015. While the human error rate is accepted as 5–10%, RestNet reduced this rate to 3.57% in the competition held in 2015 (Wu S., S. Zhong, and Liu Y., 2017).

Res NeXt model: This model is a model that classifies images with deep learning developed by the Facebook software company. It adopts the strategy of “dividing, transforming and merging” image inputs with several special filter methods (1×1, 3×3, 5×5 etc.); It has a homogeneous multi-branch architectural structure. The ResNeXt model is inspired by ResNet and VGG models.

R-KSA model: The purpose of this model, known as regional KSA, is to correctly detect objects on the image. This architecture is the architecture that detects objects on images taken from different angles or at different times of the same environment and gives us the relationships between objects. It analyzes the image from different sized windows for each image by performing a region selection search and classifies pixels according to their color, texture and density for each object definition (Girshick R., J. Donahue, T. Darrell, and Malik J., 2014).

The most important shortcoming of the B-KSA model is that it spends a lot of time while training the dataset. To overcome this deficiency, the "Faster B-KSA" model was developed. With this model, instead of running thousands of times for each image; one image is run and the other images are accepted without running the values of the image that was run (Girshick Ö. R. , J. Donahue, T. Darrell, and Malik J., 2014).

4. Deep Learning in Biomedical Field:

Recently, especially studies conducted with deep learning models have achieved successful results in various fields, while activities in the biomedical field have also increased rapidly. With the access to large-scale data sets in this field, the intensity of deep learning studies on biomedical has started to increase rapidly. This section mentions academic studies on deep learning in the biomedical field. One of the studies conducted in the classification of biomedical images: The use of the fine-tuned KSA method in the classification process. With the fine-tuning method, the existing KSA model is trained with ready data sets and the weight updates of the model are obtained. Later, when different data sets ARE left to be trained in the model, the feature and classification process are faster since the weight updates are made in advance.

5. Discussion and Conclusion

Deep learning is a branch of artificial intelligence. The aim is to extract features faster, more efficiently and most importantly automatically in image processing and reflect them in the result. In traditional methods, this function is entered manually. Perhaps the best feature of deep learning models is that they allow the use of many designed models and many traditional methods in the classification of an image. When we compare deep learning models with each other, the most important disadvantage is that they consist of a large number of layers and parameters. Most of the deep learning architectures work in a stacked manner, that is, in order. Although some of the layers operate in parallel in their own structures, this situation can be seen as a disadvantage in the deep learning model. The complexity of the architectures can also negatively affect the performance obtained. As a result, in this article we have compiled, brief information was presented about the recent studies in the biomedical field related to deep learning. Deep learning models and libraries were mentioned at a basic level for those who want to work in the biomedical field, and the use of these models with traditional methods and their effects on the performance results obtained were mentioned.

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Contact: nazrin.ism2006@gmail.com

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Section 2. Chemistry

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STUDY OF THE EFFECT OF COMPLEX ADDITIVES THAT INCREASE THE OCTANE NUMBER AND ACT AS INHIBITORS FOR AUTOMOTIVE GASOLINES ON A COPPER PLATE

Akhmedov Orif Jumanazar o'g'li [1], ***Fayziev Jakhongir Bakhromovich*** [1],
Beknazarov Hasan Soyibnazarovich [1], ***Djalilov Abdulahat Turapovich*** [1]

[1] Tashkent Research Institute of Chemistry and Technology

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Abstract

In writing this article, we studied the physical and chemical properties of octane-boosting and inhibitor-functioning additives for automotive gasolines based on various local and foreign sources. Based on the reviewed literature, we synthesized a new type of complex additive that increases the octane number and acts as an inhibitor. When these additives were tested in AI-80 gasoline at concentrations of 1, 3, 5, 10, and 15 percent, they were found to increase the octane number by up to 14 units, as confirmed by the UIT-85 apparatus. To evaluate the inhibitor function in gasoline, stearylamine was added at concentrations of 0.001, 0.002, 0.005, and 0.01 percent. The results demonstrated that at a 0.01 percent concentration, the inhibitor prevented discoloration of the copper plate.

Keywords: *Gasoline, vernier caliper, copper plate, acetone, nylon rope, RON, MON, stand, test tube, water bath, corrosion, hydrochloric acid, electronic balance, oil, engine, corrosion, inhibitor, octane number, oxygenate, oxygen, methanol*

Methanol is a highly polar organic solvent that significantly alters the physicochemical properties of gasoline when added to it. During the combustion process in the engine, methanol reacts by generating free radicals, leading to the formation of oxidation products such as formaldehyde and carbon monoxide, which can cause corrosion of the engine's metal components. Due to methanol's high heat of vaporization, it can remain in liquid form and flow onto the cylinder walls without fully evaporating, washing away the lubricating oil layer on the piston. This reduces the protection against corrosion to some extent. Additionally, methanol reacts with sulfur-containing compounds and other additives present in gasoline, accelerating the corrosion of the engine's internal system. This limits the concentration of methanol that can be safely added to gasoline (Ahmedov O., Beknazarov H., Fayziyev J., 2024; Kapustin V. M., 2013; Wang Z., Liu H., Reitz R. D. 2017; Prakash A. et al., 2017).

When the volumetric content of methanol in gasoline reaches 3%, it begins to cause severe corrosion of metal components in the engine's internal fuel system, including copper, iron, aluminum, and steel (Ahmedov O. J., Beknazarov H. S., Fayziyev J. B. 2024; Gureev A. A., Azev V. S., 1996).

The addition of methanol to fuels in internal combustion engines has a corrosive effect on metals such as copper, iron, aluminum, and steel. When the methanol content reaches 3%, it significantly enhances the corrosive properties of gasoline, and as the methanol concentration increases, corrosion intensifies further. Therefore, modifying engine materials and adding corrosion inhibitors, as well as producing blended gasoline with a low methanol content, are among the key measures to prevent corrosion (Ahmedov O.J, Beknazarov H. S., Fayziyev J. B., 2025; Gustiana Awaludin Sobarsaha, Nuryoto Nuryoto, Jayanudin Jayanudina. 2021; Sharaf Faruk. 2018).

Based on the above findings, we developed an additive containing an inhibitor and studied its effect on a copper plate. To examine the impact of this additive when applied to AI-80 gasoline, we gathered the necessary equipment and reagents for the experiment (Ahmedov O. J., Beknazarov H. S., Fayziyev J. B., Djalilov A. T., 2024; Lipin P. V. et al., 2022).

A highly purified copper plate, prepared according to Standard GB/T 5096–1985 (Petroleum products – Determination of corrosiveness to copper), is taken and polished using fine sandpaper (200–600 grit). The copper plate is then washed with 99% acetone and thoroughly dried. Afterward, it is weighed using an analytical balance, and its width and thickness are measured with a vernier caliper.

The prepared copper plate is securely fastened to a stand using a nylon rope and immersed in an additive-containing gasoline solution with 0.01% mass of inhibitor, submerging it to two-thirds of the test tube's height. The test tube is then placed in a 60 °C water bath and left for 30 minutes. After the exposure, the sample is removed, and its surface is examined for signs of corrosion. Stearylamine, derived from stearic acid, is used as the inhibitor in this process. The copper plate is then thoroughly washed first with 20% hydrochloric acid and then with acetone, after which it is dried. Finally, its mass is measured using an electronic balance, and the corrosion rate of the copper layer is calculated.

Formula for Calculating Corrosion Rate **X=G/S** is used to calculate the degree of corrosion.

Here, X is the corrosion rate (g/m²); G is the mass of the plate after the experiment (g); S is the metal surface area (m²).

The inhibitor was tested at a concentration of 0.01%, and the results can be seen in the following table 1.

Table 1. *Gravimetric analysis of copper plate mass loss with and without inhibitor application*

№	Prisadka (landing)	Initial plate mass g	The mass of the plate after the reaktion is in g	The lost mass g	Corrosion rate-g/m²
1.	Prisadka without added inhibitor	22.4	22.152	0.248	88.571
2.	Inhibitor added prisadka	22.4	22.355	0.045	16.071

The corrosion mechanism in the darkening of the copper plate proceeds as follows. When water is present in methanol-containing gasoline, it leads to acidic corrosion and electrochemical corrosion of metals, causing the ionization of the acid. This enhances the acidic corrosion of active metals and activates other corrosive processes. The main reactions occurring at the cathode and anode are as follows:

Anod: $2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^-$

Katod: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

An oxide layer (composed of Cu_2O and CuO) forms on the surface of the copper plate.

Over time, the mixture of oxides reacts with water, leading to the formation of copper hydroxides. The solution absorbs CO_2 from the air, resulting in the formation of copper carbonates ($(CuOH)_2CO_2$, $CuCO_3$). The resulting mixture of salts and oxides forms a uniform and dense oxide film, which makes the copper plate less susceptible to corrosion.

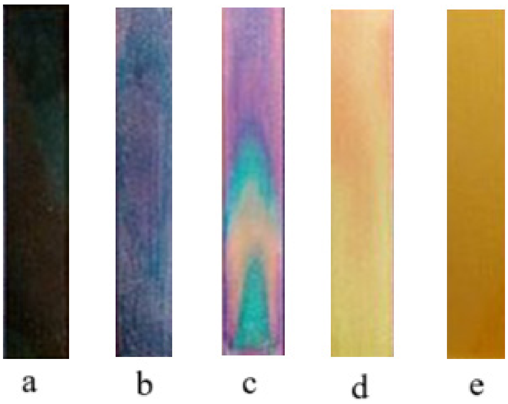
Considering the effect of temperature on copper plate corrosion, the higher the temperature, the more active the intermolecular interactions between the additive and gasoline components become, and the thermal motion of the solution molecules intensifies. This accelerates the desorption of the adsorption layer on the surface of the copper plate, exposing the metal surface and leading to an increase in the corrosion rate.

On the other hand, as the temperature increases, the solubility of gases such as O_2 and CO_2 in water decreases, which has a beneficial effect on inhibiting copper corrosion. However, based on experimental data, it was found that within the temperature range of 20–90 °C, the concentration of copper ions initially decreased, then increased, and the minimum copper ion concentration was observed at 60 °C.

Corrosion inhibitors are compounds composed of polar and non-polar groups, which act as surface-active substances that are soluble in oil. When a corrosion inhibitor is added to the base oil, it forms an oil solution similar to a colloidal solution, which is an unstable dispersion system. The polar groups containing elements such as oxygen, nitrogen, phosphorus, and sulfur adsorb onto the metal surface.

The synthesized complex additive, which functions as both an octane booster and an inhibitor, was tested on a copper plate according to GOST D 130/IP 154, and changes in the plate's color were observed. This complex additive was applied to gasoline at different concentrations (1, 3, 5, 10, and 15%) to study its effect on increasing the octane number. At the same time, its effect on the copper plate was examined in both inhibitor-added and inhibitor-free conditions. It was proven that using the inhibitor at 0.01% concentration provided optimal results.

Figure 1.



In this image, the effect of the complex octane-boosting additive without an inhibitor on AI-80 gasoline was tested. The observations are as follows:

(a) Without an inhibitor, the copper plate darkened significantly, which, according to GOST D 130/IP 154, is rated as 4b on the scale.

(b) When 0.001% inhibitor was added, the plate turned dark brown, rated as 4a on the scale.

(c) With 0.002% inhibitor, a noticeable color change was observed, rated as 3a on the scale.

(d) When 0.005% inhibitor was applied, the discoloration was significantly reduced, showing slight improvement, and was rated as 2b on the scale.

(e) With 0.01% inhibitor, the best result was achieved, with minimal color change, and it was rated as 1b on the scale according to GOST D 130/IP 154.

Among these results, the best performance was observed at 0.01% inhibitor concentration, which provided the most effective corrosion protection.

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Contact: Ahmedovorif686@gmail.com

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SYNTHESIS OF A NEW DERIVATIVE OF 5-FLUOROURACIL BASED ON 2-CHLORO-N-(4-IODOPHENYL)ACETAMIDE AND STUDY OF ITS BIOLOGICAL ACTIVITY AGAINST CANCER CELLS

Ochilov Shohzod Ergash ogli [1], ***Yusufov Mukhriddin Saidovich*** [1],
Otavaliyev Ibrohim Hamidullo ogli [1], ***Abdushukurov Anvar Kabirovich*** [1],
Matchanov Alimjon Davlatboyevich [2]

[1] The National University of Uzbekistan named after Mirzo Ulugbek, Tashkent

[2] Institute of Bioorganic Chemistry named after acad. A. S. Sadykov, Tashkent

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Abstract

In this work, a new compound was synthesized by the reaction of 2-chloro-N-(4-iodophenyl) acetamide with 5-fluorouracil. The process was carried out in two stages, first, the chloroacetylation reaction of 4-iodoaniline was carried out and in the second stage, the new product was synthesized based on the reaction of the obtained compound with 5-fluorouracil. The structure of the product was confirmed by^{1}H,^{13}C NMR, IR and Mass spectrometry. The liquefaction temperature, reaction yield, solubility of the obtained product were determined and the biological activity was studied in 3 types of cancer cells: Hela (cervical cancer cell), HT-29 (colon cancer cell) and MCF-7 (breast cancer cell).

Keywords: *5-Fluorouracil (5-Fu), chloroacetyl chloride, 4-iodoaniline, 2-chloro-N-(4-iodophenyl) acetamide*

Introduction

Today, the synthesis of new drugs for the treatment of cancer is of great importance in the pharmaceutical fields. Although many anticancer drugs have been developed and are used in the treatment of cancer, most of them have adverse effects. 5-Fluorouracil and its derivatives have been used for many years in the treatment of tumor diseases: gastrointestinal, colon, head, neck and breast cancer. 5-Fluorouracil is a strong anticancer agent, but it also has many negative side effects. Patients who used 5-Fluorouracil experienced adverse effects such as inflammation of the mouth and intestines, hair loss, and central nervous system damage. However, many derivatives of 5-fluorouracil have been shown to have much better biological activity than 5-fluorouracil.

5-Fluorouracil (5-Fu) was first synthesized in 1957 and is one of the anticancer agents routinely used to treat tumors such as colon, stomach, and breast cancer (Cunningham D., James R. D., 2001). Due to the lack of tumor selectivity of 5-Fu, its therapeutic use causes serious damage to the bone marrow, gastrointestinal tract, and central nervous system. To overcome these problems, many modifications of the structure of 5-Fu have been made, and a number of drugs have been synthesized with its amino acids, peptides, phospholipids, and polymers (Zhang F. M. et al., 2006). 5-Fu is a cytotoxic agent that inhibits rapidly proliferating cancer cells in conventional chemotherapy.Researchers have tried various methods to reduce the toxicity of 5-Fu, including strategies to modify its chemical structure and to deliver the drug to a specific site.

Several low molecular weight derivatives of 5-fluorouracil have been developed, including 5-fluoro-2'-deoxyuridine, 1-(2-tetrahydrofuryl)-5-Fu, and 3,5-dioctanoyl 5-fluoro-2-deoxyuridine (Malet-Martino M., Martino R. 2002; Wang J. X., Sun X., Zhang Z. R., 2002). Many compounds of 5-Fu containing a nitro group in the aromatic ring have been obtained, and their cytotoxicity and radiosensitizing activity have been studied.

The coupling of 2,4-dinitrophenylamine with 5-fluorouracil through three carbon atoms resulted in the formation of 3[3-(2,4-dinitro-phenylamino)-propyl]-5-fluoro-1-H-pyrimidine-2,4-dione, which has radiosensitizing properties, but not cytotoxicity, under aerobic conditions (Khalaj A. et al., 2006). In addition, 2,4-dinitrobenzoyl, 2,4- and 3,5-dinitrobenzoyl, 2,4-dinitrophenylacetyl derivatives of 5-Fu were reacted with di-T-butoxycarbonate $(Boc)_2O$, 4-Dimethylaminopyridine (4-DMAP), K_2CO_3, KI salts and DMFA, acetonitrile solvents at 78 °C for 4 hours. The structure of the obtained products was confirmed by IR, NMR and Mass spectrometry methods[6]. New sulfonyl derivatives of 5-Fu (5-fluoro-1 (arylsulfonyl) pyrimidine-2,4 (1H, 3H)-diones) were synthesized by the reaction of 5-fluorouracil with sulfonyl chloride (Yan X. et al., 2009).

Polymeric conjugates of 5-Fu play an important role in the pharmaceutical industry. In particular, the conjugate of polyethylene glycol with 5-fluorouracil, which is a smooth, spatially uniform 44.3 ± 5.8 nm nanoparticles with the participation of recombinant human serum albumin, has advanced the pharmaceutical and therapeutic fields (Sharma A., Kaur A., Jain U. K., Chandra R., Madan J., 2017). Scientists have synthesized a new derivative of 5-Fu based on pectin (PT), a high-molecular polysaccharide. In the process of obtaining this derivative, the monochloroacetic acid derivative of 5-Fu was first synthesized, then a solution of pectin in DMSO was added to the resulting product and stirred at 50^{o} C for 96 hours, then ethanol was added to the reaction mixture and filtered.

The obtained 5-Fu-PT derivative was dried at 60 ^{o} C for 24 hours and then subjected to HPLC analysis, and the analysis showed that 5-Fu-PT did not contain free intermediate 5-Fu-acetic acid (Wang Q. W., Liu X. Y., Liu L., Feng J., Li Y. H., Guo Z. J. and Mei Q. B. 2007; Liu L. et al., 2008). Nowadays, obtaining metal complexes and developing drugs based on them is one of the urgent tasks of the chemistry field. Therefore, a new ruthenium-based 5-Fu complex [Ru(5-FU)(PPh3)2(bipyr)]PF6, which has a high cytotoxic effect on cancer cells, was synthesized in analytical purity and high yield. Its apoptosis induction effect in human colon carcinoma HCT116 cells was evaluated (Silva V. R. et al., 2018).

In recent years, Uzbek scientists have synthesized the paraaminoazobenzene derivative of 5-Fu in high yield. In the reaction process, an intermediate product based on chloroacetyl chloride of paraaminobenzene was initially obtained, and 5-Fu was reacted with it in DMFA solvent to obtain the target product. The biological activity of the product was studied in cancer cells (Ochilov Sh. E. U. et al., 2024). Based on the above data, we also synthesized a new 4-iodoaniline-based compound of 5-Fu to reduce the negative effects of 5-Fu, improve its properties such as selective action, high biological activity and easy solubility in water. Its structure was confirmed using Mass,^{1}H,^{13}C NMR and IR spectroscopy. The biological activity of the resulting product was studied in 3 types of cancer cells: Hela (cervical cancer cell), HT-29 (colon cancer cell) and MCF-7 (breast cancer cell).

Experimental part

The M-560 device was used to measure the liquidus temperature of the obtained product.^{1}H and^{13}C NMR spectra were obtained in DMSO solvent on VARIAN MR

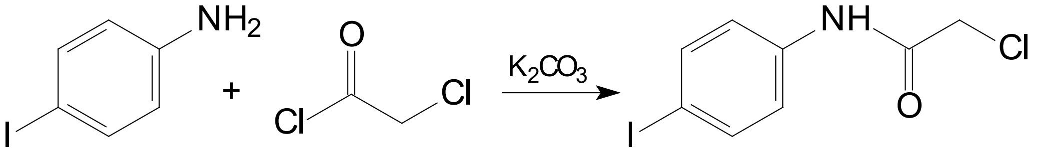
400 MHz spectrometers. Mass analysis was studied using high-resolution mass spectrometry (HRMS) AB SCIEX QSTAR Elite. IR spectra (KBr pellet) were studied on Perkin Elmer FT-IR/NIR Spectrometr Spectrum 3, 4000–400 cm^{-1}.

Results and discussions

Synthesis method

The synthesis of a new derivative of 5-fluorouracil based on 4-iodoaniline was carried out in two stages. First, 0.01 mol (2.955 g) of 4-iodoaniline was placed in a 100 ml round-bottomed flask and dissolved in 50 ml of acetonitrile. 0.01 mol (1.38 g) of K_2CO_3 was weighed and added to the mixture on an analytical balance. The solution was stirred with a magnetic stirrer at a temperature of –1–3° C for 30 min in a cold condition, and 0.01 mol (0.8 ml) of chloroacyl chloride was added dropwise. Then, the reaction was carried out for 2 h, and then the mixture was checked by TLC (hexane: acetone, 2–3). The intermediate 2-chloro-N-(4-iodophenyl)acetamide was obtained in 80% yield.

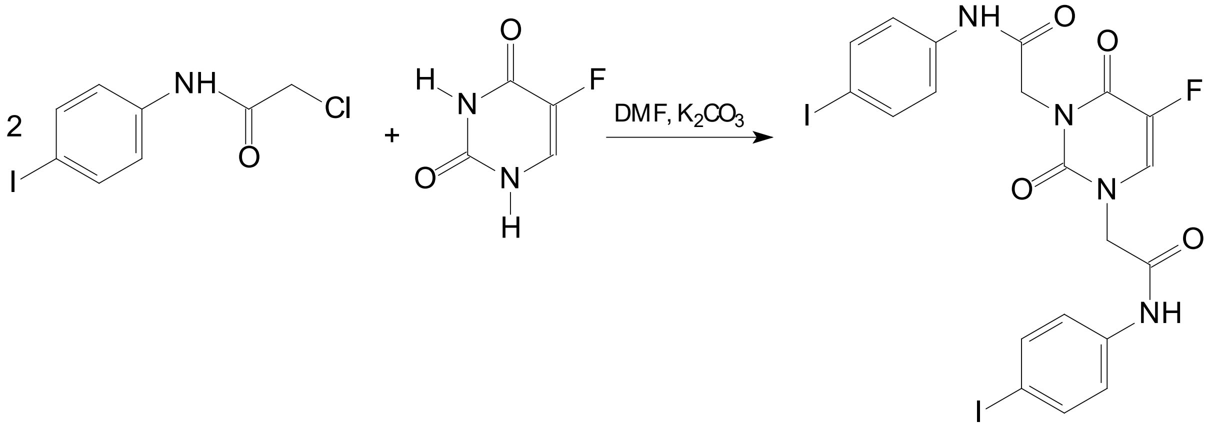
Scheme 1. *The first stage of the reaction*



Name: 2-chloro-N-(4-iodophenyl)acetamide

In the second step of the reaction, 0.625 mmol (0.081 g) of 5-fluorouracil was dissolved in 10 ml of DMFA at room temperature and K_2CO_3 (1.25 mmol, 0.1725 g) was added. Then, 1.25 mmol (0.37 g) of 2-chloro-N-(4-iodophenyl)acetamide was added under stirring and the reaction was carried out for 5 h at room temperature. The reaction mixture was checked by TLC (hexane: acetone, 2: 3) and cleaned.

Scheme 2. *Synthesis of the target compound*



Product name: 2,2'-(5-fluoro-2,4-dioxopyrimidine-1,3(2H,4H)-diyl) bis(N-(4-iodophenyl)acetamide)

Yield: 74%; m.p.: 275–277 °C. R_f = = 0.71.^{1}H NMR (400 MHz, DMSO-D6) δ 8.28 (s, 1H), 8.26 (s, 1H), 7.65 (dd, J = 8.9, 6.5 Hz, 3H), 7.41 (dd, J = 11.2, 8.9 Hz, 3H), 4.64 (s, 3H), 4.60 (s, 3H), 3.33 (s, 1H).^{13}C NMR ((101 MHz, DMSO-D_6) δ 165.22, 164.77, 156.67, 156.41, 149.70, 138.48, 138.36, 137.51, 137.45, 137.15, 130.56, 130.22, 121.87, 121.27, 121.22, 109.57, 87.16, 86.94, 51.11, 43.95. HR-ESI–MS: m/z 648.92 [M - H]$^+$ calcd for $C_{20}H_{15}FN_4O_4I_2$. IR (KBr pellet): ν=3281.51 (NH, 1736.15 (–C=O, amid), 1645.13, 1596.95 (–C=O, 5-Fu), 1382.97 (–CH_2-C=O), 1197.72 (C-F) см$^{-1}$.

Figure 1. *IR spectrum of 2,2'-(5-fluoro-2,4-dioxopyrimidine-1,3(2H,4H)-diyl) bis(N-(4-iodophenyl)acetamide)*

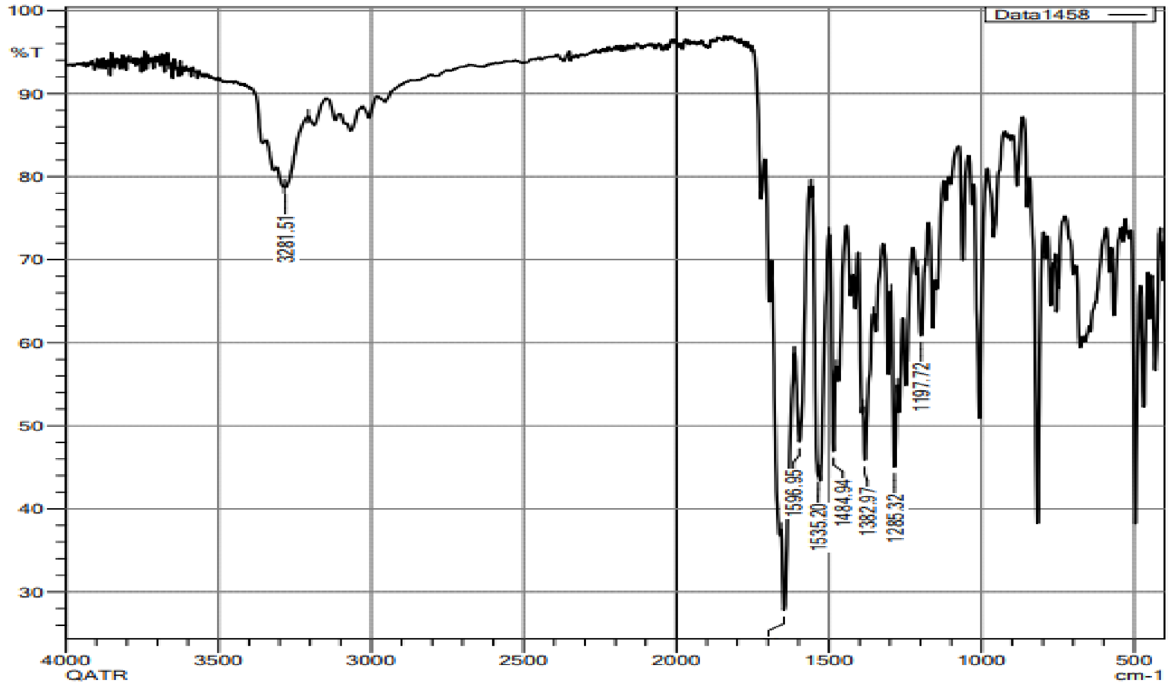
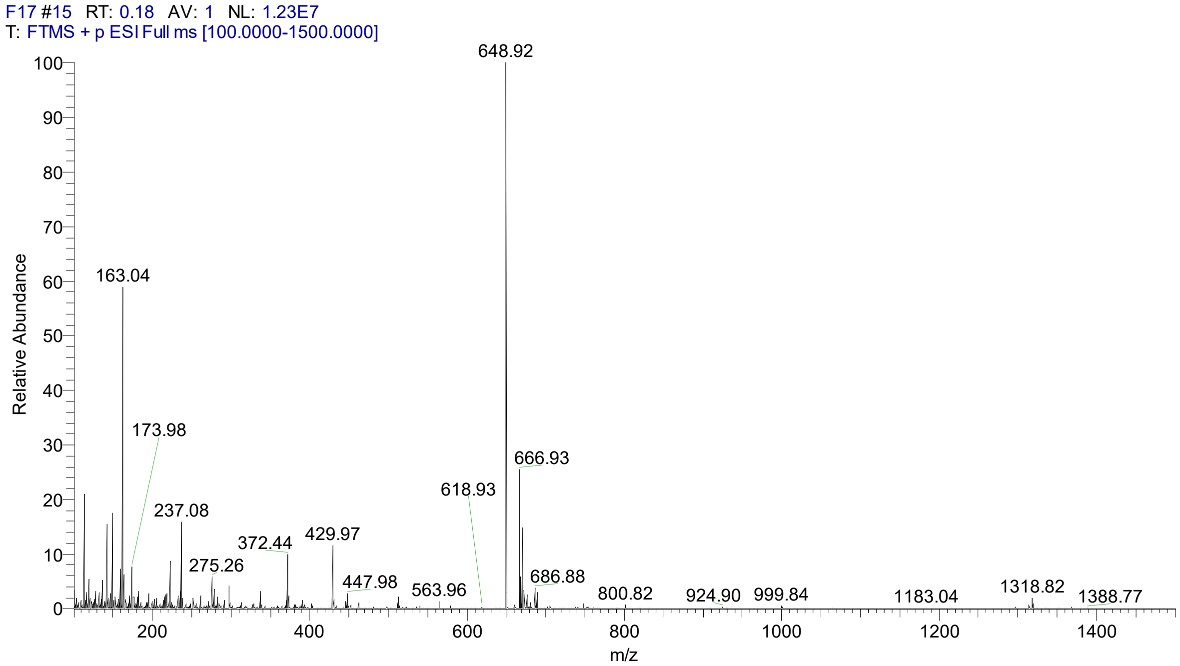


Figure 2. *Mass spectrum of 2,2'-(5-fluoro-2,4-dioxopyrimidine-1,3(2H,4H)-diyl) bis(N-(4-iodophenyl)acetamide)*



Biological activity

The biological activity of 2,2'-(5-fluoro-2,4-dioxopyrimidine-1,3(2H,4H)-diyl)bis(N-(4-iodophenyl)acetamide) was studied in 3 different types of cancer cells (50 mmol/l). The product showed an inhibition rate of 87.63% (5-Fu=27.08%) for Hela (cervical cancer cell), 82.90% (5-Fu = = 40.75%) for HT-29 (colon cancer cell) and 64.20% (5-Fu = 41.49%) for MCF-7 (breast cancer cell). The IC_{50} values of the product were Hela=10.73±0.54 μM and HT-29 = = 5.19 ± 0.26 μM, respectively.

Conclusion

2,2’-(5-Fluoro-2,4-dioxopyrimidine-1,3(2H,4H)-diyl)bis(N-(4-iodophenyl) acetamide) was synthesized for the first time and its chemical structure was confirmed using IR,^{1}H,^{13}C NMR and Mass spectrometry methods. When the biological activity of the obtained compound was studied in terms of its inhibitory properties against Hela (cervical cancer cell), HT-29 (colon cancer cell) and MCF-7 (breast cancer cell), it was observed that the inhibitory activity of the obtained substance on Hela cell was 3-fold stronger than 5-Fu, 2- fold more active than 5-Fu against HT-29 and 1.5- fold more active than 5-Fu against MCF-7 cells.

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Contact: shahzodochilovnuu@gmail.com

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STUDY OF SPECIFIC PROPERTIES OF THE OXIDIZED RICE STARCHES MODIFIED WITH DIFFERENT OXIDANTS AND ELECTROCHEMICAL METHOD

Sharipov Muzafar [1]

[1] Department of Chemistry and oil-gas technologies, Bukhara state university

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Abstract

The physicochemical properties of native rice starch, electrochemical modified rice starch and oxidized rice starch were also studied parallel using rapid visual analysis (RVA), X-ray diffraction pattern (XRD) and dynamic rheometry. Al samples of oxidized starches showed lower swelling power (SP) and solubility and higher paste clarity in comparison with native starch. These results suggest that the undesirable properties in native, chemical and electrochemical oxidized rice starch samples could be overcome through all types of oxidation. Oxidized starch by electrochemical method showed the highest ability to resist shear of all oxidized starch samples.

Keywords: *rheology, electrochemical oxidation, gel formation, pastes clarity, swelling power*

Introduction

Oxidized starch comes from oxidation modification of original starch in order to overcome its shortcomings, such as limited hydrophilic character and chemical reactivity, poor solubility and poor functional properties (Wang Y. J., Wang L., 2003). The successful oxidation modification has made starch, which is high availability in nature, renewable and biodegradable, becomes a useful polymer in a wide range of applications (Raina C. S., Singh S., Bawa A. S., Saxena D. C., 2006). Oxidized starch shows much better water solubility, excellent film-forming properties, lower viscosity at high solid content, less retrogradation and better clarity than native starch (Kaur M., Oberoi D. P.S., Sogi D. S., Gill B. S., 2011). The unique properties of oxidized starch have diversified starch's applications in paper and textile industries for providing surface sizing and thickening properties (Singh J., Kaur L., Mc Carthy O. J., 2007).

In general, oxidized starch is prepared by reacting starch with oxidants (e.g., hydrogen peroxide, hypochlorite, periodate, ozone, bromine, chromic acid and permanganate) under certain reaction conditions (Li J., Vasanthan Th., Bressler D. C., Tyler R. T., 2010). The most common starch oxidizers used in production are sodium salts of hypochlorites and periodates, and also hydrogen peroxide (Sangseethong K., Termvejsayanon N., Sriroth K.). The mechanism of the chemical modification process with different oxidizers occurs differently. Researches the utilization of hydrogen peroxide for the oxidation of starch necessitates the presence of iron ions (Tolvanen P., Mäki-Arvela P., Sorokin A. B. Salmi T., Murzin D.Yu., 2009). Nevertheless, the oxidation process is not fully achieved, and there is limited enhancement of the adhesive properties. The utilization of potassium permanganate and sodium periodate is deemed environmentally unfriendly due to their hazardous nature, susceptibility to poisoning and explosions, difficulties in handling at elevated temperatures, and potential risks during experimental procedures (Kato Y., Matsuo R., Isogai A., 2003; Wilpiszewska K., Spychaj T., 2008).

As is known application of starch in many industries is demanded with modifying its structure and properties, and methods of modification would not change feature and individuality of this natural polymer. Among numerous ways of modifying of structure and properties of polymers chemical modification takes special place (Ashogbon A. O., Akintayo E. T., 2014). As the way of creation of materials with the improved complex of properties this way will receive development and in the further. And successes in this area first of all should be connected with the physical and chemical approach to an estimation and generalization of already existing extensive experimental and theoretical material from the point of view of the polymeric nature of reacting particles.

Some years in department of chemistry within the limits of the state project on development of technologies of reception of the modified starch, with the purpose of its application in the textile industry are conducted research. The objective of this study was to prepare the modified rice starches such as oxidized starch by various oxidants in various mediums. It was found that the levels of chemical and electrochemical oxidation used in this study did not cause any significant changes pastes clarity. Oxidized starch by chlorate showed lower ability to resist shear in comparison to native starch, while it showed higher ability to resist shear in comparison to oxidized starch by permanganate.

Material and methods

The experimental material consisted of starches of rice produced from rice flour at the Bukhara region as well as rice starch and rice flour starch. The above-mentioned starches were subjected to the oxidation process by means of three methods: 1. Starch subjected to electrochemical processing was performed according to Litvyak *et al.* (Litvyak V. V., Lovkis Z. V., Rebenek E. V., Kupchik M. P., 2007). Briefly, laboratory electrolyze represents electrolyze cell with the anode and the cathode, made of stainless steel, In quality anolite 25%-s' starched suspension acted, in quality catolite were used – 4% th solutions NaCl. Electrochemical processing spent during 60 mines at the force of current 0,6 A. The constant value of force of in currents of 1 hours supported by gradual reduction of pressure by electrodes with 220 to 50 V. Modification was performed at the temperature 25–35 °C.

2. Permanganate oxidation of starch. The cleared suspension of starch containing 25% of solids moves in a vessel of continuous action. Before suspension into a vessel enter the set quantity of sulfuric acid, and then permanganate of potassium. Suspensions maintain temperature in a reactor 30–40 °C for what provide heating of initial suspension to the specified temperature. The expense of sulfuric acid about 1–2% to suspension solids, permanganate of potassium 0,1–0,2%. Time of stay of suspension in a vessel makes about 2 hours that provides end of reaction of oxidation and disappearance of coloring of the suspension appearing after introduction of an oxidizer. After the termination of reaction suspension will partially neutralize a solution кальцинированной soda and simultaneously dilute to concentration of 10%.

3. Modification with sodium chlorate(I) was performed according to methodology of Forsell *et al.* (Forssell P., Hamunen A., Autio K., Suortti P., Poutanen K., 1995). Briefly 400 g of starch was dispersed in water to give 25% suspension. After the addition of 4 g of sodium chlorate(V) solution was performed at room temperature by mixing the starch suspension in alkaline medium (pH=10.0) for 60 min and subsequent neutralization of the reaction mixture with 1 mol/L H_2SO_4 solution to reach pH=7.0. Modification was performed at the temperature 35–45 °C.

Then, the modified starches were washed, dried, disintegrated, and sieved. Starch oxidation was performed according to procedure which was optimalized in previous trials (ISO Norm 112144, 1996); (2) the content of aldehyde groups, according to Zhang (Zhang L., Liu P., Wang Y., Gao W., 2011); (3) The pasting properties of rice starch were measured according to our previous method by using a Rapid Visco Analyzer (Thermo Scientific, HAAKE); (4) X-ray diffraction (XRD) patterns of the samples were characterized by an XRD-6100 instrument (Shimadzu) Sample preparation was carried out were made by cold pressing of the polymer in the form of monolithic round tablets 2 mm and a diameter of 18 mm.

Results and discussion

Analyze of functional group on modified rice starches

In the process of starch oxidation, the destruction of its macromolecules occurs simultaneously with oxidation. Under the action of an oxidizing agent, hydroxyl groups are converted into aldehyde groups, and with further exposure to an oxidizing agent, the latter are oxidized to carboxylic acid groups (Table 1).

Table 1. *Content of carboxyl groups (%) and aldehyde groups (g CHO/100 g d.w.) in oxidised starches*

Starch samples (temp. of oxidation, °C)	Carboxyl groups in oxidised starches (%±SD)		Aldehyde groups in oxidised starches (%±SD)	
Electrochemical oxi-dized (with NaCl sol.)	0.018±0.003 (25 °C)	0.061±0.003 (35 °C)	0.102±0.0052 (25 °C)	0.157±0.0027 (30 °C)
Oxidized by perman-ganate of potassium	0.301±0.017 (30 °C)	0.433±0.029 (40 °C)	0.021±0.0012 (35 °C)	0.079±0.004 (40 °C)
Oxidized by sodium chlorate (V)	0.226±0.005 (35 °C)	0.380±0.011 (45 °C)	0.014±0.0001 (40 °C)	0.053±0.0015 (45 °C)

The only exception was rice starch in which the highest number of carboxyl groups was observed upon modification with permanganate. Oxidant amount is an important part in the oxidant preparation of starch program. For it directly influence the molecular structure change of carboxyl content and oxidation starch (Halal S. L. M., Colussi R., Pinto V. Z., Bartz J., Radunz M., Carreño N. L.V., Dias, A.R.G., Zavareze E. R., 2015). It has been established that the content of carbonyl ($-CHO^-$) and carboxyl ($-COOH^-$) groups characterizes the degree of oxidation and degradation of starch macromolecules. In this regard, the content of carbonyl and carboxyl groups in starch samples isolated with different degrees of oxidation was changed. Analysis of the content of carbonyl and carboxyl groups is carried out according to the methods described.

An analysis of the results compiled for the content of aldehyde groups (Table 1) enables concluding that rice starch was the most susceptible to hydrolysis with the electrochemical method, as it was characterized with the highest increment of aldehyde groups compared to the other methods. Compared to the other methods, permanganate caused the lowest rise in the number of aldehyde groups, which confirms the results of our previous investigations (Sanchez-Rivera M. M., Garcia-Suarez F. J. L., Velazquez del Valle M., Gutierrez-Meraz F., Bello-Perez L. A., 2017).

Gel formation

Starch gelation is complex process involving three main stages. First, starch grains swell reversibly by attaching a small amount of water. When the temperature rises, a large amount of water is added, accompanied by a strong swelling of the grains with an increase in their volume by hundreds of times and an increase in the viscosity of the solution; this stage is irreversible. Swelling of starch occurs due to rupture of hydrogen bonds and hydration of polysaccharide macromolecules. At the last stage, soluble polysaccharides are extracted with water, the grains lose their shape, turning into bags suspended in solution. This starch gel structure is the primary structure (Kuakpetoon D., Wang Y., 2006).

Experiments conducted on the functional properties of our modified rice starch have indicated some similarities with corn or wheat starches (Sasaki T., 2005). Oxidized rice starch with chlorate salts paste presents a fibrous rheology similar to corn starch paste. Starch hydrogels are a typical example of systems exhibiting non-Newtonian liquid properties (Sharipov M. S., 2022). Compositions of unmodified rice starches are highly structured. The maximum permissible concentration for native rice starch during gel formation turned out to be 5% (m / v) but for oxidized rice starch 7% (m / v) and the effect of concentration in this process is shown in Figure 1. Oxidized rice starch hydrogels also showed average transparency properties in pastes compared to wheat and corn starch. In hot conditions (90 °C) the paste of the native rice starch was completely transparent, but in cold conditions (15 °C) the paste was very opaque.

Figure 1. *Chilled hydrogels of rice starch (bottom oxidized) and native (top unoxidized) (obtained from 5, 6, 7% pastes, respectively)*

However, the modified starch pastes were transparent in both states. Freeze thaw stability is an important aspect regarding the characterization of starches (Beninca C., Colman T. A.D., Lacerda L. G., Carvalho-Filho M. A.S., Demiate I. M., Schnitzler E., 2013).

It has been established that electrochemical treatment of a starch suspension makes it possible to obtain starch, which forms a transparent paste that is not prone to gelation. In oxidized starches, a decrease in the tendency of the paste to retrogradation is observed, which is noticeable in comparison with native (unmodified starches) (Fig. 2). Electrochemically oxidized rice starch hydrogels are a typical example of systems exhibiting non-Newtonian liquid properties.

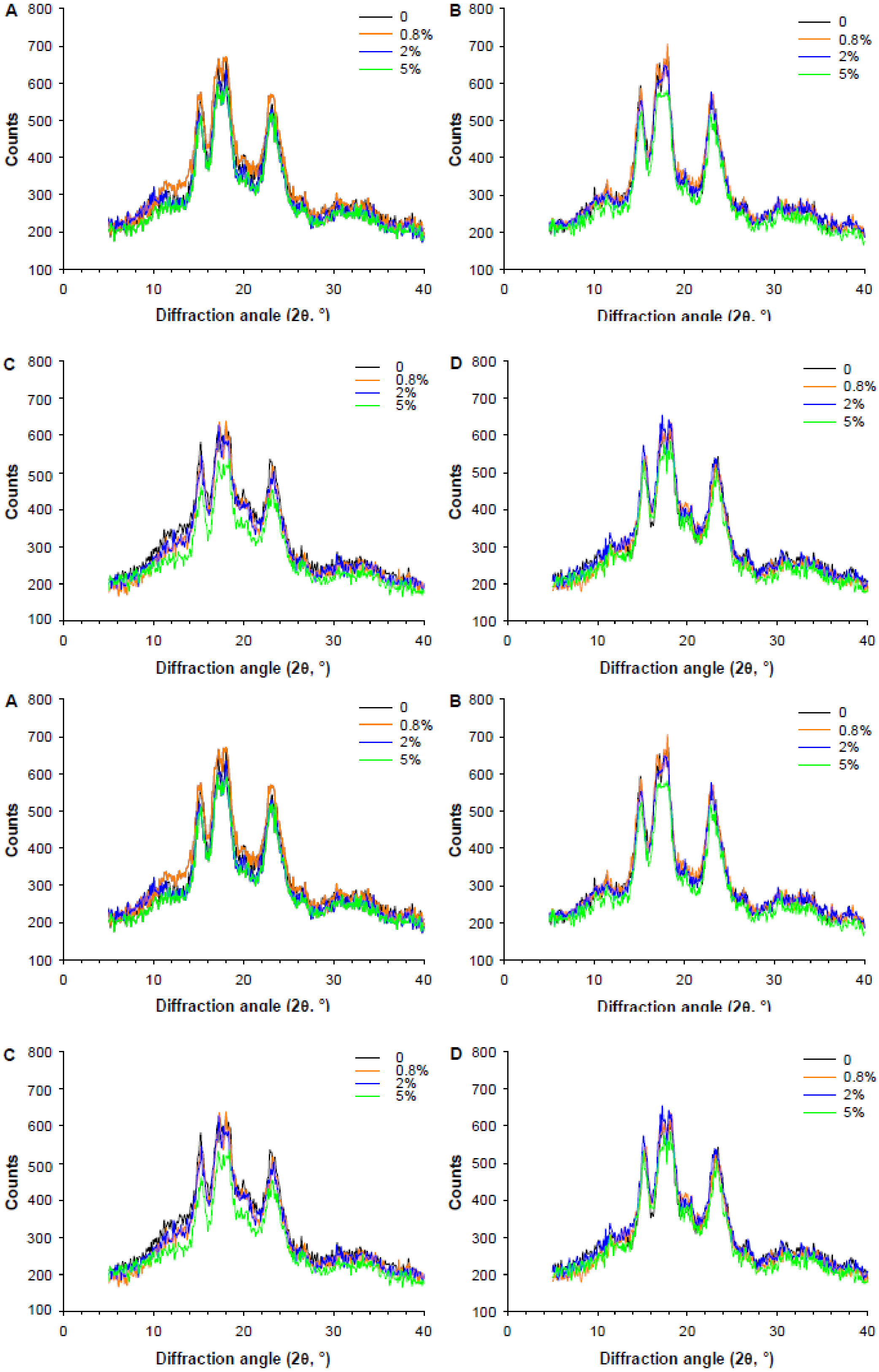
Figure 2. *Pastes of native (top) and electrochemically modified (bottom) rice starch*

Hydrogels of modified rice starches are highly structured. In hot conditions (70 °C) the native starch paste was completely transparent, but in cold conditions (–5 °C) the paste was very opaque. However, the modified starch pastes were transparent in both states. Freeze thaw stability is an important aspect regarding the characterization of starches. These changes (along with decrease in molecular weight) cause a decrease in the gelatinization temperature and viscosity of starch pastes.

X-ray analysis

In the process of starch oxidation, changes occur both in the amorphous and in the crystalline regions of the starch grain. This re-echoed the accepted fact that cross-linking mainly take place in the amorphous regions of the starch granules and did not alter the crystalline patterns of starches. In this case, an increase in the degree of crystallinity of oxidized starch is observed (Tillayeva D. M., Sharipov M. S., 2021). Analysis results are shown in figure 3.

Figure 3. *X-ray diffraction results of native (a) and oxidized rice starch's modification product of its oxidation by electrochemical method (b) chlorate of sodium (c) and permanganate (d)*

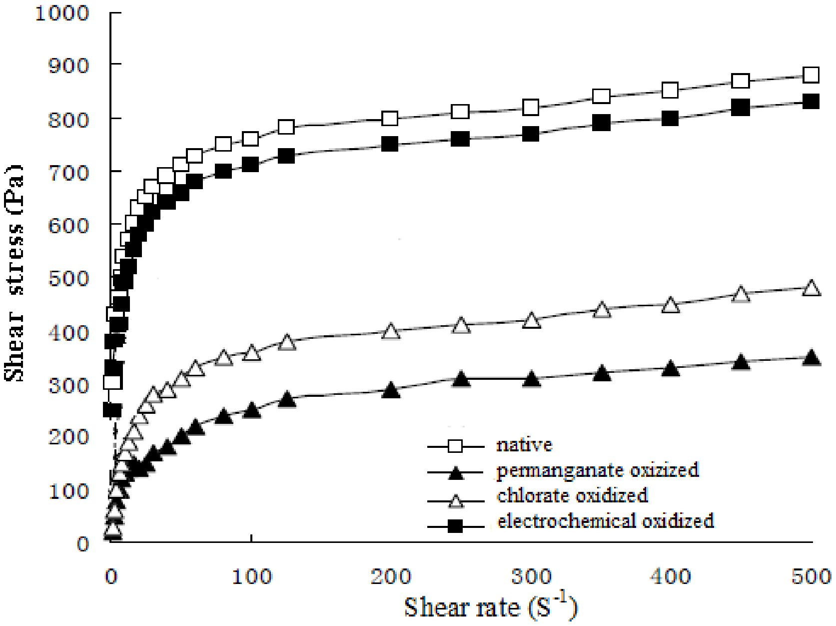


X-ray structural analysis showed that during the oxidation of rice starch by electrochemical and chemical oxidation, changes in the supramolecular structure of starch are insignificant: a slight decrease in the degree of crystallinity is observed starch after its oxidation, which manifests itself in a decrease in the intensity of reflexes at angles of 19.5 and 22.0 degrees (Fig. 3). As a result of the gelation process, an increase in the hydration and mobility of the chains of macromolecules takes place (Tillayeva D. M., Sharipov M. S., 2023). In a later work, using high and low angle X-ray diffraction methods, the researchers discovered disk-like regions with increased electron density, having a crystalline structure of β-form of amylose, in destructive starch gels (Zhong Y., Tai L., Blennow A., Ding L., Herburger K., Qu J., Xin A., Guo D., Hebelstrup K. H., Liu X., 2022). The degree of crystallinity of the gels was 16–22% as shown. The authors believe that the sol-fractions of the molecule are hydrated, and double helices are formed upon dehydration of long segments of branched and linear molecules. Above the critical concentration, double helices aggregate, forming crystal cores that grow into disk-like regions (Pfister B., Zeeman S. C., 2016).

Flowing Characteristics

The results from the previous studies indicated that rice starch samples were pseudoplastic and shear thinning liquids. As shown by the flow curves in Figure 4, shear stress of all native and modified starch samples increased with increasing shear rate.

Figure 4. *Shear stress as a function of shear rate for native and oxidized rice starch samples*



At the same shear rate, native starch showed the highest shear stress, while oxidized starch with permanganate showed the lowest shear stress. Gibinski et al. indicated that high values of shear stress pointed to a high stability of the structure of the starch (Gibinski M., Kowalski S., Sady M., Krawontka J., Tomasik, P., Sikora M., 2006). According to these authors electrochemical modified starch had the most stable structure and the strongest ability to resist shear, the structure of oxidized starch was weakened and lost the ability to resist shear.

Conclusion

However, a partially degraded network was not resistant to shear and could not maintain the integrity of starch granules after oxidation by permanganate, resulting in a decrease in shear stress. Oxidized starch by chlorate showed lower ability to resist shear in comparison to native starch, while it showed higher ability to resist shear in comparison to oxidized starch by permanganate.

Oxidized starch by electrochemical method showed the highest ability to resist shear of all oxidized starch samples. The reaction order of oxidized modification had a significant influence on the physicochemical proper of starch granules.

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Contact: m.s.sharipov@buxdu.uz

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COMPOSITION OF LIQUID PARAFFINS AND THEIR FLOTATION PROPERTIES IN MODEL SAMPLES

Vakkasov S. S. [1]***, Turobzhanov S. M.*** [2]

[1] Jizzakh Polytechnic Institute

[2] Tashkent State Technical University named after I.Karimov

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Abstract

The article recommends optimal parameters for the process of obtaining liquid paraffin based on hexane, which is a secondary product of the chemical industry. Comparing the composition of domestic and "foreign analog" aprotic solvents, it is found that the efficiency is higher in solutions with a relatively large amount of the main component, the concentration output is 3.2% higher in the "foreign analog" solvent with the same consumption of two apolar collectors, the content of KCl in the float product due to the influence of local liquid paraffin the amount was found to be 0.9% more.

Keywords and phrases: *liquid paraffins, used hexane, hydrocarbon mixture, model samples, flotation properties*

Introduction

Today, in the world, natural and environmentally friendly raw materials – liquid paraffins are used in medicine to relieve constipation, in the treatment of encopresis, as a binding agent or ointment in the production of capsules and tablets in pharmaceuticals, as a moisturizing and cleansing agent for skin and hair in cosmetology, in the production of paraffin paper in light industry, as flotation of reagents in the chemical industry. used in enrichment. Therefore, identifying new sources of liquid paraffins, creating effective technologies for their separation and putting them into practice remains one of the important tasks.

A number of scientific researches are being conducted in the world to identify and separate cheap sources of liquid paraffins. In this regard, special attention is being paid to expanding sources of liquid paraffins not only from oil reserves, but also from secondary hydrocarbons of the chemical industry, developing innovative methods of separation, using sylvinite ore as a highly efficient selective collector in flotation enrichment, developing and testing technologies for obtaining liquid paraffins. As it is known (Patent. No. 925793), they suggest using kerosene as a source of liquid paraffins. Typically, kerosene contains up to 30% aromatic hydrocarbons, which adversely affect the selectivity of beneficiation of sylvinite ores by flotation. In addition, naphthalene hydrocarbons are carcinogenic substances, so it is not important to involve them in the process.

As aprotic solvents, it is proposed to use gas oil and crude oil extraction products. Foamless flotation apparatus was used to study the collection properties of oil reagents. In the tests, the reagents were first dispersed with the feed in a foamless flotation apparatus. This made it possible to exclude the separation of the emulsion during the flotation process itself. The collection characteristics of the initial products of different composition and the technology of obtaining their fractions were also studied (Baichenko A. A., Ivanov G. V., Bocharova E. M., 1999; Baichenko A. A., Ivanov G. V., Bocharova E. M., Bauer L. N., Min R. S., Kukushkin V. V., 1999; 1999; Petukhov V. N., Kukushkin V. V. 1999; Petukhov V. N., Kukushkin V. V. 1999; Savinchuk L. G., Kukushkin V. V., Aglyamova E. R. 1999).

Sources (Khan G. A., Gabrielova L. I., Vlasova N. S., 1986; Ya L., Shubov, S. I., Ivankov, N. K. Shcheglova. 1986; Ya L., Shubov, S. I. Ivankov. 1992) list some aprotic reagents, such as clarified, tractor and oxidized kerosene, household stove fuel, apolar aromatic reagents AAP-1 and AAP-2, activated flotation reagent AF-2 and thermogasoyl. Clarified kerosene is widely used in the early stages of flotation and is still widely used in a small number of factories. The predominance of saturated compounds in kerosene has a more selective effect on coal flotation than aromatized kerosene, but the flotation rate is slightly lower. The advantages of clarifying kerosene are the absence of a specific smell, ease of use, smooth process, and low cost. Kerosene does not foam, and at high consumption it exhibits anti-foaming properties. For coal flotation, clarified kerosene is used only in combination with a heteropolar reagent. Its consumption is 1–3 kg/t.

Chemically, kerosene is a mixture of saturated, unsaturated and aromatic hydrocarbons. A large amount of unsaturated and aromatic hydrocarbons containing 16–24 carbon atoms per molecule compared to clarified kerosene (17%), allows tractor kerosene to increase its flotation ability. During the flotation of coals of the middle stage of metamorphism, its consumption is 1–1.5 kg / t, in the flotation of low metamorphism – 1.5–2.5 kg / t.

The purpose of the study

The secondary product of the chemical industry is the development of technology for obtaining liquid paraffins based on used hexane and the identification of their effective areas of application.

The waste of JV "Uz-KorGasChemical" LLC, which was chosen as a **research object,** is liquid paraffin produced by dissolving various hydrocarbons in secondary hexane. Liquid paraffins are mostly saturated hydrocarbons with linear structure having carbon numbers C5–C18.

Experiments section

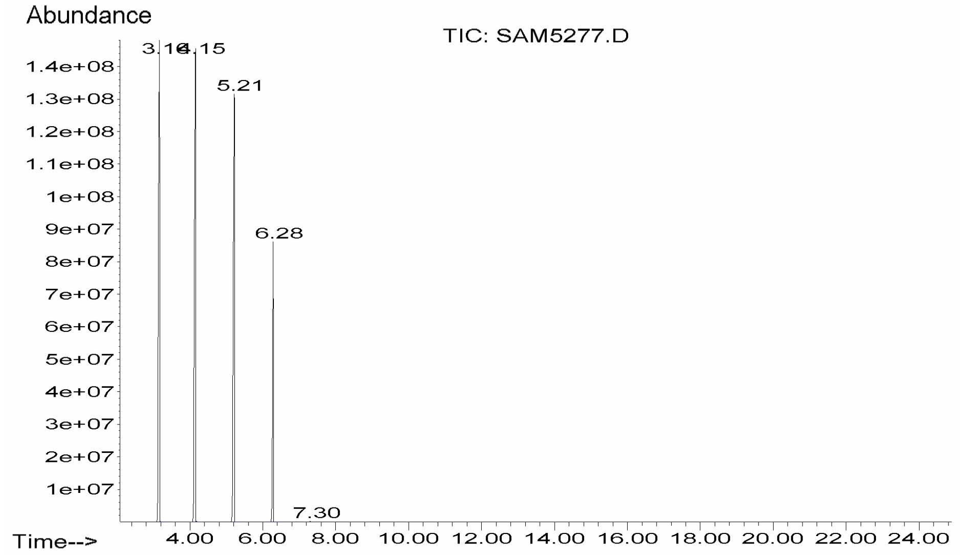
Recycled hexane is known to contain low molecular weight and high molecular weight compounds according to regulations. Therefore, the main task of achieving this goal is to separate the mixture into low molecular and high molecular components. In the first distillation, the light volatile part was separated to separate the liquid paraffin mixture, and then the main part of the product was separated.

The cubic residue was separated from the residual mass of the main component by filtration.

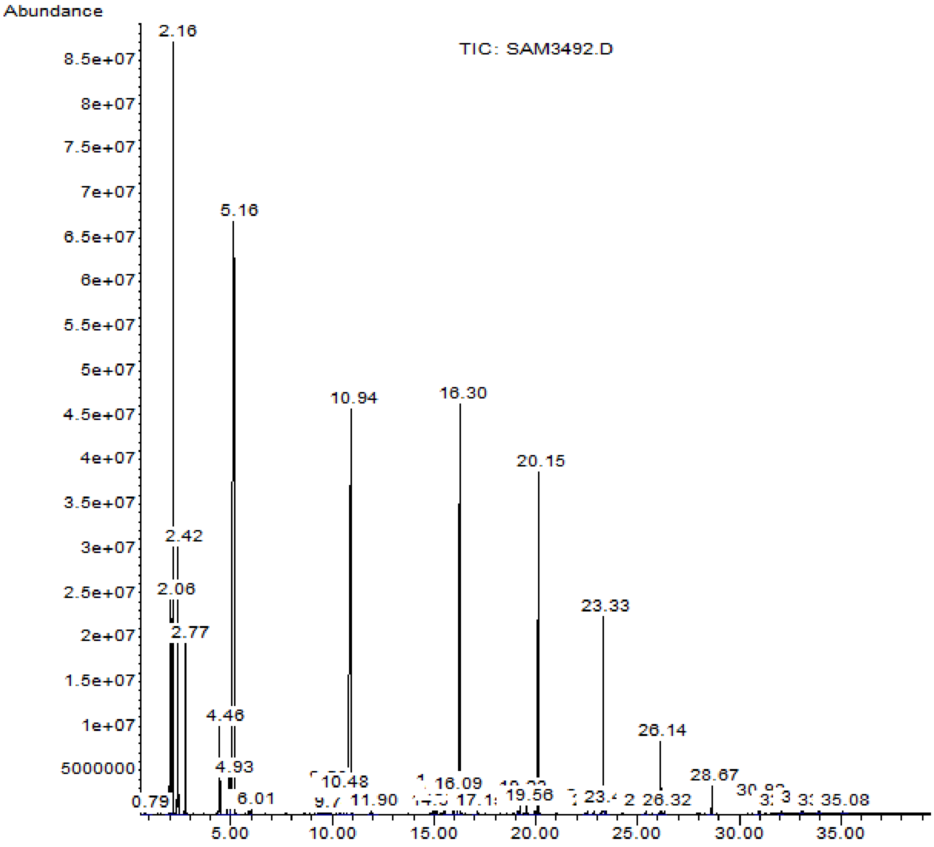
To determine the composition of the initial and obtained flotation reactants, we used chromate-mass spectroscopy in a 5% solution of phenylmethylsiloxane in dimethylsiloxane using a 30m × 0.25 mm capillary column using an Agilent Technology GS 6890 / MS 5973N device, using hydrogen as a carrier gas and an injector temperature 280 C, the temperature of the MS source 230 C, MS square field temperature was 180 C. When programming the temperature of the column thermostat from 100 to 280 C, the temperature rise rate is 10 C/min, and the sample volume is 1 μl. The resulting chromatogram is shown in Figure 2.4 (b). At the same time, Figure 2.4 (a) shows the chromatogram of liquid kerosene – an imported foreign analogue.

Figure 1. *Chromatogram of studied samples: a) imported paraffin; b) domestic liquid paraffin*

a) 1) tetradecane; 2) pentadecane; 3) n-cetane; 4) n-heptadecane; 5) n-octadecane



b) 1) 2-methylpentane; 2) 3-methylpentane; 3) hexane; 4) cyclopentane; 5) cyclohexane; 6) 2-ethylhexane; 7) trans-1-ethyl-3-methylcyclopentane; 8) n-octane; 9) ethylcyclohexane; 10) octane; 11) 5-methylnonane; 12) 9-methylleucosan; 13) 3-methylnonane; 14) 2-heptenal; 15) dean; 16) 1-cyclohexyl; 17) 4-ethyldecane; 18) undecane; 19) 3-methyl-undecane; 20) 1-hexyl-3-methylcyclopentane; 21) dodecane; 22) 1-hexylcyclohexane; 23) tridecane; 24) 3-methyltridecane; 25) n-tetradecane; 26) 5-methyltetradecane; 27) pentadecane; 28) n-hexadecane; 29) nonyl-cyclohexane; 30) 5-methylpentadecane; 31) n-octadecane; 32) cyclohexylmethane; 33) n-eicosan; 34) n-docosane; 35) 2-methylcyclodecanone; 36) n-tetracosane; 37) Z, Z-3,13-octadedecedien-1-ol; 38) hexacosane



Analysis of results

The obtained results show that the imported paraffin analogue contains saturated hydrocarbons with carbon numbers ranging from C14 to C18. However, the composition of the waste is multi-component. It consists of low molecular and medium molecular hydrocarbons of cyclic and acyclic structure. Chromatograms show peaks characteristic for unsaturated hydrocarbon radicals, as well as for hydroxyl radicals that disappear after cubic residue separation. Peaks characteristic of pentane, hexane and heptane isomers also disappear after distillation.

The resulting aprotic solvent liquid paraffins were used in the process of flotation beneficiation of potassium ore, and the reagents were first tested on model samples. The gas chemical complex of JV "UzKorGasChemical" LLC prepared local liquid paraffins (MSP) obtained on the basis of secondary hexane as an apolar solvent, R1 – R3 composition solutions. As an object of comparison, "foreign analogue" (FA) purchased from abroad and used by JSC "Dekhkanabad potash plant" for beneficiation of sylvinite ores was used.

Table 1. *Results of flotation of liquid paraffins in model samples at a temperature of 22 ± 1 C*

Indicators	**Model samples**					
	P_1		**P_2**		**P_3**	
	FA	**DLP**	**FA**	**DLP**	**FA**	**DLP**
Yield, %:						
Concentrate	42,3	39,1	31,5	31,2	17,5	19,4
residual	57,7	60,9	68,5	68,8	82,5	80,6
Mass fraction of KCl, %:						
Concentrate	89,2	90,1	89,4	88,9	87,4	87,9
residual	21,26	24,25	7,55	8,12	5,70	3,84
Separated KCl, %:						
Concentrate	75,46	70,46	84,5	83,21	76,56	85,26
residual	24,54	29,54	15,5	16,79	23,44	15,74

It can be seen from the table that the "foreign analog" solution has a high concentration in solutions with a relatively large amount of the main component. If these two apolar collectors are compared with the "foreign analogue" and domestic liquid paraffin in terms of the concentrate yield and the amount of KCl in its content, it can be seen that the concentrate yield is 3.2% higher in the first apolar solvent at the same consumption. But at the same time, under the influence of local liquid paraffin, the amount of KCl in the flotation product is 0.9% higher, which indicates that local liquid paraffin is more effective. These results are of practical importance and are the basis of high selectivity activity of native liquid paraffin. Hence, the mass ratios of the initial salts in the model samples greatly affect the efficiency and selectivity of the apolar solvent.

The original model example shows that as the temperature of the initial solution increases, the total amount of salts in the saturated brine increases mainly due to the increase in the amount of potassium chloride. But an increase in temperature causes an increase in the surface activity of the additives in the composition, as well as the activity of the collecting reagents. Therefore, the temperature dependence of the efficiency of apolar collectors was also studied. Figures 2 and 3 show the results of these studies.

At the limits of all investigated temperatures, the concentrate yield is higher in the imported foreign analogue: an increase in temperature from 10 C to 40 C increases the concentrate yield by 23%, with an increase in aproton consumption by 5 g/t, a 5% increase was observed in the R1 model sample even at low flotation temperatures. With an increase in temperature at 45 C, there were no sharp changes in the yield of the concentrate.

Figure 2. *Yield of flotation concentrate of R3 model sample when collector consumption is 10 g/t: 1) FA; 2) DLP*

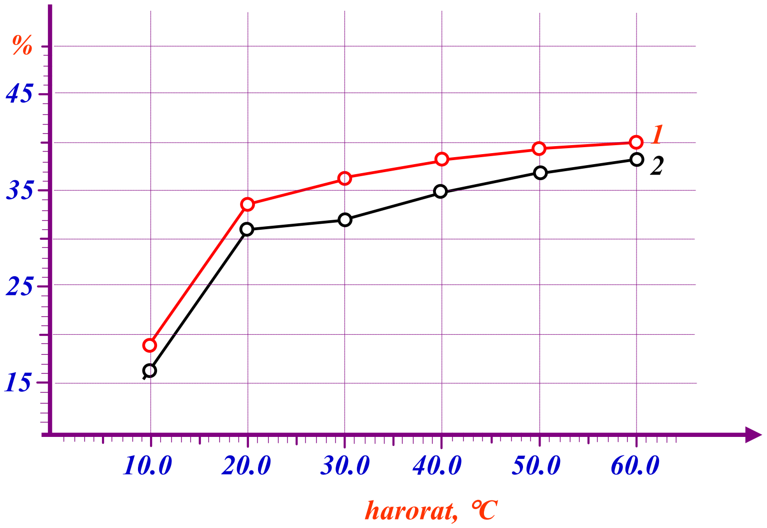
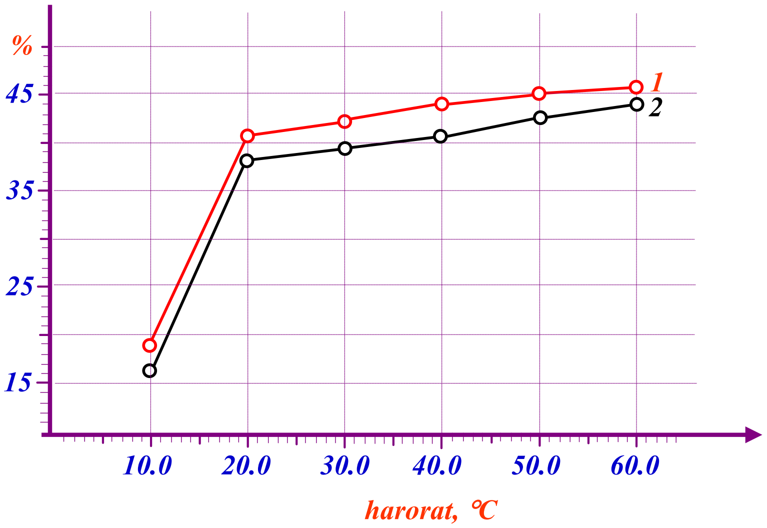


Figure 3. *Yield of flotation concentrate of R3 model sample when collector consumption is 15 g/t: 1) FA; 2) DLP*



At low temperatures, when native liquid paraffins are used as an aprotosolvent, the concentrate yield is low, but at high temperatures, it is possible to see an improvement in the concentrate yield.

Summary

The results of the comparative analysis of flotation sodium show that the flotation activity of the imported apolar solvent is lower than that of domestic liquid paraffins. This can be justified by the presence of high-molecular carbon rods with a cyclic structure and relatively large molecular sizes, which accelerate hydrophobization of floating potassium chloride particles in the composition of local liquid paraffins.

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Contact: bmoxichexra@bk.ru

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THE EFFECT OF THE CHARACTERISTICS OF THE CATIONIC COLLECTOR AND APOLYAR SOLVENT MIXTURE IN DETERMINING THE ACCEPTABLE CONDITIONS OF THE FLOTATION PROCESS

Vakkasov S. S. [1]**,*Turobzhanov S. M.*** [2]

[1] Jizzakh Polytechnic Institute

[2] Tashkent State Technical University named after I. Karimov

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Abstract

The literature focused on the study of flotation processes was analyzed and it was found that the use of fatty amines in a mixture with hydrocarbons as a collector has a positive effect on the flotation enrichment of sylvinite ores. The composition of liquid paraffins obtained from imported and domestic secondary products was determined and compared by chromatographic analysis. Liquid paraffin derived from domestic secondary products has been shown to improve the flotation process, increase the separation of KCl into the concentrate, and reduce the consumption of valuable amine, thereby reducing the cost.

Keywords: *flotation, flotation reagents, collectors, izvlechenie, Selvinite ore, potassium chloride, liquid secondary raw materials, chromatographic analysis, liquid paraffins, residual hydrocarbons*

It is known that flotation is carried out due to the adsorption of air molecules on the mineral particles of the components under the influence of substances called “flotation reagents”. The progress of the flotation enrichment process and its result are mainly determined by the reactive mode of flotation, i.e. assortment, type and method of their application. This regime is mainly determined by the physico-chemical properties of the mineral, its degree of dispersion, as well as conditions for finished products (Bobrakova A. A., 2013; Yunash A. A., 2004; Mergenbaatar N., 2005; Effective reagents for flotation of high-ash coals 2020).

In the flotation process, for the best enrichment result, several flotation reagents are usually used, their actions are interconnected and depend on the concentration of each of them. Therefore, excessive consumption of one reagent requires an increase in the consumption of other reagents, and an increase (or decrease) in their concentration can lead to deterioration of the technological performance of the entire process. Experiments have shown that the lowest possible consumption of reagents provides lower costs for the processing of mineral raw materials and better results of the enrichment process. Despite the accumulated theoretical and practical experience, the required amount of reagents is always determined for each mineral raw material using laboratory flotation experiments shown in industrial conditions (The concept of flotation examples of flotation reagents. 2009; Algebraistova, N. K. 2009; Garkovenko E. E., Nazimko E. I., Samoilov A. I., Papushin Yu. L., 2002).

The intended purpose of flotation reagents predetermines their suitability for one of three major classes: collectors, foam formers, and regulators.

Collectors are organic in nature and are mainly fixed on the surface of a solid liquid. Foam formers are mainly surfactant organic substances adsorbed at the liquid-gas interface. Regulators are used as additives to thickeners and foamers to increase flotation selectivity or mineral recovery. Representatives of this class are both inorganic and organic substances (Seyed, Hamid & Hosseini, Hamid & Hosseini. 2008; Shengo, Michel & Gaydardzhiev, Stoyan & Ngoy, Pierre. 2014).

The main purpose of the collectors is to hydrophobize the mineral surface, to increase the speed and stability of particles sticking to the air bubbles (Grigoriev A. A. 2001; Shubov L.Ya., Ivankov S. I., Scheglova N. K., 1990).

Liquid paraffins are the solvents that ensure the activity of the collecting reagents in Sylvin flotation.

As liquid paraffins today, '-dichlorodiethyl ether mixed with methyl ethyl or methyl isobutyl ketone in a mass ratio of 1:1 is used, treatment with urea is carried out by adding a solvent of 180–260 weight to the raw material. washing of the material and the complex is carried out in the first step with the specified solvent and in the second step with methyl ethyl – or methyl isobutyl ketone (Rodina, T. A., 2015).

The authors of (Mineral processing Design and Operations. 2020; Ukushkin V. V., 1999; Kukushkin V. V., Petukhov V. N., Osina NLO, 2003) suggested the use of kerosene, gasoil, etc. as a collecting reagent. Depending on the raw materials and processing conditions, they have different compositions and are in the form of a complex mixture of organic substances. The diversity of their composition makes it difficult to study the effect of kerosene and kerosene during flotation. However, it is difficult to determine which components of kerosene and gas oil are the most flotation active, and what to consider when choosing reagents for these conditions is complicated.

As aprotic solvents (Petukhov V. N., Osipa N.Yu., Kukushkin V. V. et al., 2003; Khan G. A., Gabrielova L. I., Vlasova N. S., 1986; Ya L. Shubov, Ivankov S. I., Shcheglova N. K. 1990; Ya. L. Shubov, Ivankov S. I., 1992), some aprotic reagents, such as clarified, tractor and oxidized kerosene, household stove fuel, apolar aromatic reagents AAP-1 and AAP-2, activated flotation reagent AF-2 and thermogasoyl are listed. Clarified kerosene is widely used in the early stages of flotation and is still widely used in a small number of factories. The predominance of saturated compounds in kerosene has a more selective effect on coal flotation than aromatized kerosene, but the flotation rate is slightly lower. The advantages of clarifying kerosene are the absence of a specific smell, ease of use, smooth process, and low cost. Kerosene does not foam, and at high consumption it exhibits anti-foaming properties. For coal flotation, clarified kerosene is used only in combination with a heteropolar reagent. Its consumption is 1–3 kg/t.

It is known from industrial practice that the yield of the concentrate and its purity in most cases are related to the mass fraction of soluble and insoluble salts in the saturated solution of sylvinite, which changes with temperature changes, and thus the efficiency of the reagents entering the flotation suspension system, the reaction of the reagents with the aqueous medium and the surface of the phase separation. also changes. As a result of these changes, the total technological process indicators can also change in a positive or negative direction.

There are many sources that have studied indicators related to temperature increase in the range of 30–35 C from saturated salt solutions to the processes of flotation beneficiation of potassium ore (Da Li, Pingmei Duan, Zhiping Du, Fangqin Cheng, Yunshan Guan. 2015).

In the natural conditions of our republic, the air temperature is high (35–45 C) in the months of July and September, which affects the flotation process and the passage of waste reagents, which are valuable as enrichment residues, is observed. It is urgent to determine the composition of reagents that allow high technological efficiency of potassium chloride enrichment of sylvinite ore at low and, especially for us, high temperatures.

Separation of potassium chloride from the mineral resources of our country – sylvinite ore by flotation enrichment, and the production of potassium fertilizers based on it is carried out according to the technology of OAZ "VNII Galurgii" of the Russian Federation, and operates at the expense of raw material crushed to 1 mm from the Tubegatan mines.

Therefore, in the course of our research, we considered it necessary to study the optimal technological parameters of flotation beneficiation of Tyubegatan ore silvin in the presence of synthesized collecting reagents.

In the technological process of JSC "Dekhkhanabad Potash Plant", mechanical or flotation cleaning is carried out with the help of SFM to slurry potassium chloride from natural sylvinite in a flotation enrichment system, then a mixture of alkylamines with apolar additives and depressants is used as a collector.

Saturated matochnium solution of JSC "Dekhkanabad Potash Plant" was chosen as the object of research. The density of this saturated matrix solution is 1244 kg/m^3, the amount of the main component is 18–35% by mass. and T_1, T_2 and T_3 contents were selected. The original ore also contains clay inclusions with a large specific surface in the amount of 4–15%, and the rest of the ore mass consists of sodium chloride (NaCl) and other soluble salts, which adversely affect the flotation beneficiation process of other sylvin (KCl).

The temperature of the climatic chamber is below 10 °C and not above 40 °C. All experiments to determine the effectiveness of the new reagents, with varying amounts of potassium chloride and insoluble residues, were carried out on samples with ore sizes no larger than 1 mm. Preparation of ore for flotation was carried out by cleaning it from the initial slurry.

When the temperature of the matochny solution is increased from room temperature to 40 C, the total amount of salts in the saturated saline solution increases from 30.8 to 33.1%, mainly due to potassium chloride, because at such temperatures the solubility of potassium chloride KCl increases compared to sodium chloride NaCl.

The results of laboratory studies on determining the flotation activity of cationic and apolar collectors against potassium chloride under different conditions made it possible to choose the effective working concentrations of the obtained reagents and determine the optimal conditions for use in beneficiation of natural ore.

For the experiments, domestic liquid paraffins extracted on the basis of secondary hexane were selected and compared with foreign analogues. As flotation components, reagents used in the technological system of "Dekhkanabad potash plant" JSC were selected.

The sylvinite ore smaller than 1 mm in size was first thoroughly cleaned in slurry and flotation process was carried out at a transfer rate of 15–40 g/t. It was found that in the composition of winter brand QA-2 amine containing 2% S20 < 24 fraction, local liquid paraffins exhibit a concentrate content of 71.24%, at consumption of 30 g/t (melting temperature 35 ± 1 C).

In the presence of summer YoA-1 with 22% S20 < 24 fraction in the local liquid paraffin collector, it was observed that potassium chloride separation reaches 90%. At the same time, the separation of potassium chloride from T-3 base solution using this composition made it possible to increase from 28.2 to 32.1%, while the separation of potassium chloride from ore with T-1 and T-2 composition was 35 C when 25 g/t was used. will have maximum efficiency.

Local liquid paraffin collector consumption of 30 g/t transfer winter and summer amine content S20 < 24 5, 10 and 15% by mass. It was found that the yield of concentrate increases by 0.8, 0.96 and 1.2%, and the level of potassium chloride separation increases by 1.0, 2.1 and 4.2%.

The results of the experiments show that at relatively low temperatures Amine: Liquid Paraffin (LP): Vacuum Gasoline (VGO) in the ratio of 35: 8: 2 had effective indicators. In the temperature range from 2 to 30 C, the same composition shows results close to the indicators of “base” industrial reagents

Table 1. *Results of flotation of sylvin in various samples with the presence of “Base” industrial and recommended reagents*

Results	A composition of collectors					
	SA-1 + SA-2: PEG: FA (40: 4: 8)			AmInes: DLP: VG (40:10:2)		
	T-1	T-2	T-3	T-1	T-2	T-3
Yield, %:						
concentrate	16,0	24,7	35,2	15,1	23,3	35,4
residual	84,0	75,3	64,8	84,9	75,7	64,6
Mass fraction of KCl, %:						
concentrate	67,3	86,8	83,1	68,2	86,9	83,9
residual	2,4	5,8	8,9	3,8	7,3	8,3
Separated KCl, %:						
concentrate	79,76	83,1	83,4	76,3	78,5	84,6
residual	20,24	16,9	16,6	23,7	21,5	15,4

When conducting laboratory experiments with the introduction of vacuum gas oil into an aqueous solution of amine, it was observed that the amine surface was covered with a film due to the formation of a difficult emulsion. At the same time, the resulting film can be removed by preliminary mixing of liquid paraffin and vacuum gas oil. As a result, a stable emulsion of amine and modifier is formed. Increasing the amount of amine to 40 g/t and the amount of apolar solvent to 15 g/t causes a sharp increase in the efficiency of the flotation process. At the same time, it is seen that flotation studies are higher than the indicators of the “base” regimes when reagents emulsified in the amine solution of vacuum gas oil are used. The separation of potassium chloride in the initial concentrate is 89.8%, compared to the “base” mode, it is 86.8%. Thus, the use of the reagent component in the same order is maintained at a high level even at temperatures of 35 C and above.

During the research, it was also observed that the flotation process of silvin can be controlled by changing the consumption of collectors. Taking this into account, the dependence of the proportions of the components of the aggregate composition on the indicators of sylvinite flotation was studied.

The sylvinite flotation was studied in conditions where the temperature of the matochny solution was higher than 40 C in the following proportions of the components of the collecting composition: Amine: summer amine (SA-1), winter amine (WA-2), foreign paraffin analogue (PA), domestic liquid paraffins (DLP), polyethylene glycol (PEG), vacuum gas oil (VGO), pine oil. Modified compositions were prepared by mixing components: 1) Amin+SA-2; 2) The ratio of SA-1+SA-2 is 59:41. Aggregate ratio to amine is unchanged at 35 g/t transfer. Amine: The dosage of apolar collecting reagents is strictly controlled. As a result of research, it was found that reducing the amount of amine in the mixture from 70 to 55% by mass improves the indicators of flotation beneficiation of sylvinite ore: the yield of the initial concentrate from the T-3 base is from 35.2 to 36.9%, and the degree of separation of KCl is from 83.4 to 84.0 increases to %. In the course of research, if the flotation process is carried out at high temperatures with a modified composition consisting of winter amine SA-2 and local liquid paraffins, it will be possible to completely replace foreign analogues. It should be noted that when using the SA-2+DLP+VGO flotation composition, the yield of the concentrate reaches 37.6%, and the separation of potassium chloride reaches 83.7%. Thus, with an increase in the percentage of collecting components added to the amine composition, its efficiency and potassium chloride flotation indicators increase. shows that it can be recommended for flotation beneficiation.

The material selected for enrichment has a large amount of water-insoluble additives, which during processing are transferred to a fine, difficult-to-filter soil slurry. The amount of soil sludge in the composition is within the limit of 3–12%. The component that needs to be separated is sylvin – potassium chloride, which is present within wide limits in the composition and makes up 18–35% of the total amount. The composition also contains sodium chloride, which has little effect on the flotation process. Flotation is carried out in solutions enriched with salts. The solution is characterized by strong foam formation, high viscosity and surface tension. Using liquid paraffin obtained in laboratory conditions, natural sylvinite was used in the process of separation of potassium chloride in flotation devices. in parallel, experiments were conducted with standard imported liquid paraffins (Table 2).

Table 2. *Comparative results of standard industrial and experimental liquid paraffin composition in flotation beneficiation of sylvinite ores*

№	Indicators	Standard liquid paraffins		Obtained liquid paraffins		Standard on MTX
		amount	KCl, %	Amount	KCl, %	
1.	Raw material	408	31.53	408	31.53	
2.	Potassium chloride obtained	130.5	89	132.31	89.2	≥ 83
3.	Residue	277.5	3.5	275.69	3.5	≤ 3,8

The obtained results show that the secondary product of "Uz-KorGasChemical" JSC – liquid paraffins obtained on the basis of used hexane, can replace the imported standard product in all its characteristics.

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Contact: bmoxichexra@bk.ru

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SINTHESIS OF BENZOPYRIMIDIN-4-ONE AND 3-H SUBSTITUTED DERIVATIVES BASED ON THEM

Zulpanov Fazliddin Abduxakimovich [1]***, Elmuradov Burkhon Juraevich*** [1]***,***
Zakhidova Aziza Bakhromovna [2]***, Arzanov Ravshan Xurramovich*** [3]

[1] Akad. S. Yu. Yunusov Institute of the Chemistry of Plant Substances,
Academy of the Republic of Uzbekistan, Tashkent, Uzbekistan

[2] Branch of Russian Mendeleev University of Chemical Technology
in Tashkent Faculty of Chemical Technology

[3] School № 3, Samarkand District, Uzbekistan

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Abstract

As a result of studying the synthesis and biological activity of condensed heterocyclic compounds, new drugs have been developed, including derivatives of 3-alkylquinazolin-4-one, and their bioactive derivatives have been identified. The development of new drugs based on them is relevant.

Keywords: *o-aminobenzoic acid, formamide, cyclization, alkyl halides, alkylation, quinazolin 4-one, 3-alkylquinazolin-4-one, IR, 1H and 13C NMR*

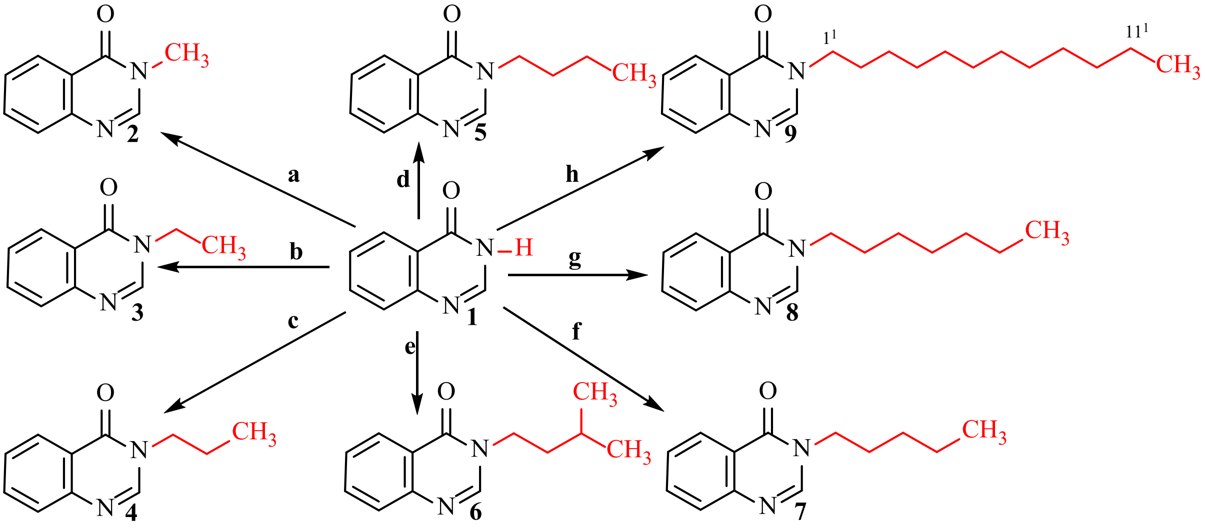
Introduction

Compounds containing a benzopyrimidin ring are considered to have very high medicinal activity. In recent years, various peripa-rations based on many representatives of derivatives formed on the basis of heterocyclic compounds containing benzopyrimidin have been introduced into agricultural and medical practice. Compounds based on benzopyrimidin are widely used against viruses, microbes, fungi, colds and cancer (Xiaoqing Wu, Mingdong Li, Wenhua Tang, Youguang Zheng, Jiqin Lian, Liang Xu, Min Ji., 2011), and as stimulants for plants (Kalpana Singh, P. P. Sharma, A. Kumar, Anurag Chaudhary and R. K. Roy. 2013). In recent years, the incidence of socially significant diseases: cardiovascular diseases (Giovanni Marzaro 2007–2010), diabetes (Expert Opinion on Therapeutic Patents), cancer (Mikra, C., Bairaktari, M., Petridi, M.-T., Detsi, A., Fylaktakidou, K.C., 2022) and viral diseases (Shi-Ben Wang, Xian-Qing Deng, Yan Zheng, Yan-Ping Yuan, Zhe-Shan Quan, Li-Ping Guan. 2012) has been increasing. An example of this is that benzopyrimidin is included in such drugs as imatinib (Raffaella Sordella, Daphne W. Bell, Daniel A. Haber, Jeffrey Settleman. 2004), erlotinib (Martin H. Cohen, John R. Johnson, Yeh-Fong Chen, Rajeshwari Sridhara, Richard Pazdur. 2005), afatinib (Pawan K., Premnath D., Muhammad T., Mazlee S., Yaman M., Nurul S., Muhammad S. et al., 2019), gefitinib (Martin H. Cohen, John R. Johnson, Yeh-Fong Chen, Rajeshwari Sridhara, Richard Pazdur. 2005; Xiaoqing Wu, Mingdong Li, Yang Qu, Wenhua Tang, Youguang Zheng, Jiqin Lian, Min Ji, Liang Xu. 2010; Martin H. Cohen, Grant A. Williams, Rajeshwari Sridhara; Gang Chen, W. David McGuinn, Jr., David Morse Sophia Abraham, Atiqur Rahman, Chenyi Liang, Richard Lostritto, Amy Baird, Richard Pazdur. 2004), which are used against tuberculosis and cancer. In lung cancer, it increased overall survival by 19% and improved progression-free survival (PFS) by 29% compared to chemotherapy (Elmuradov B.Zh., Yakubov U. M., Zhurayev B. B., Tadjimukhamedov K. S., Zakhidov K. A., 2017). These data were approved by the United States Food and Drug Administration (FDA) (Elmuradov B.Zh., Yakubov U. M., Zhurayev B. B., Tadjimukhamedov K. S., Zakhidov K. A., 2017). Anticancer drugs prepared from compounds of the benzopyrimidin family have shown a very low level of toxicity. In this regard, especially the N-3 state electrophilic substitution reactions, i.e. synthesis of new types of derivatives with various halogen compounds of alkyl halides, and with the change of their functional group, it is possible to find new types of fundamental systematic laws and among them, bioactive compounds.

Methods and results

Results and discussion. Bicyclic benzopyrimidin-4-ones are of great practical and theoretical interest. Among the derivatives of benzopyrimidin-4-ones, biologically active compounds have been identified, which are used in medicine and agriculture against various harmful microorganisms. Therefore, it is very important to create efficient synthesis methods of new potentially biologically active derivatives of this class of compounds. For this purpose, in our research, we have identified convenient and effective methods of heterocyclization reaction involving o-aminobenzoic acid and formamide. For this purpose, we considered it appropriate to synthesize new alkyl derivatives as a result of carrying out electrophilic exchange reactions in the 3-position of benzopyrimidin-4-one **(1)**, to determine the regularities in the homologous series of introduced alkyl compounds.

Initially, when benzopyrimidin-4-one is heated in the presence of o-aminobenzoic acid and formamide, two mole of water are separated. As a result of the reaction, we managed to obtain substance **1** in a quantitative yield (98%). Various new types of alkyl compounds were synthesized by interacting benzopyrimidin-4-one with alkyl halides in the 3rd state. This work was carried out in an oil bath at 70–80 °C with the participation of various homologues of alkyl halides **(2–9)**:



a) methyl iodide; b) etyl bromide; c) propyl bromide; d) butyl bromide; e) *izo*-butyl bromide; f) amyl chloride;g) heptyl chloride; h) dodecyl bromide.

Table 1. *IR-spectra (n, cm^{-1}) of 3-alkylbenzopyrimidin-4-ones (1–9)*

№	C-N	C-H	CH_2	C=O	C=N
1	3129	2980	–	2996	1603
2	3067	2989	2971	1649	1612
3	3067	2964	2990	1653	1598
4	3044	2968	2947	1699	1606
5	3067	2877	2936	1666	1607
6	3043	2971	2948	1698	1609
7	3054	2965	2950	1655	1608
8	3054	2966	2926	1655	1509
9	3052	2931	2921	1656	1508

Experimental Part

Synthesis of benzopyrimidin-4-one (1). 1.37 g (0.01 mole) of o-aminobenzoic acid and 6.37 ml (0.04 mole, 7.2 g p = = 1.13 g/sm^3) of formamide were added to a 100-ml round bottom flask and heated for 2–2.5 hours in an oil bath connected with a reflux condenser at 150–155 °C, The substance is recrystallized from water (H_2O) and as a yield 1.43 g (98%) of substance **1**. Melting point 218–120 °C, Rf=0.63 (system: chloroform: methanol – 10:1) is obtained.^{1}H NMR (400 MHz, DMSO-d$_6$, ppm, δ, J/Hz) δ 12.10 (1H, s, NH), 8.12 (1H, dd, *J* = 8.0, 1.6 Hz, H-5), 7.95 (1H, s, H-2), 7.72 (1H, br t, *J* = 7.5 Hz, H-7), 7.61 (1H, br d, *J* = 7.5 Hz, H-8), 7.44 (1H, br t, *J* = 8.0 Hz, H-6).^{13}C NMR (101 MHz, DMSO-*D*$_6$) δ 161.19 (C-4), 149.37 (C-4a), 145.29 (C-2), 134.00 (C-7), 127.59 (C-5), 126.56 (C-6), 126.34(C-8), 123.43 (C-8a).

Synthesis of 3-metylbenzopyrimidin-4-one (2). Put 1.46 g (0.01 mole) of quinazolin-4-one, 30 ml of ethyl alcohol (C_2H_5OH)and 0.616 g (0.011 mole) of KOH into a 100 ml round-bottomed flask and boil and mix slightly. The reaction mixture is cooled and 3.74 ml (0.03 mole) (4.26 g, d=2.28 g/ml) methyl iodide (CH_3I) is added and heated at 75–80 °C for 8 hours. The resulting reaction mixture was cooled and mixed by adding 40 ml of an aqueous solution of 5% NaOH, and then 80 ml of chloroform was poured over it and stirred for 5–10 minutes, and the chloroform layer was separated using a separatory funnel. Chloroform was removed, and the resulting substance was filtered by adding activated carbon in ethyl alcohol (C_2H_5OH) and the liquid part was evaporated and recrystallized. As a yield, 1.12 g (70%) of product **2** was obtained, melting point 102–104 °C, Rf=0.62 (system: chloroform: methanol – 10:1).^{1}H NMR (400 MHz, CD_3OD, ppm. δ, J/Hz): 8.00 (1H, ddd, J=8.1, 1.6, 0.6, H-5), 7.67 (1H, ddd, J=8.5, 7.1, 1.5, H-7), 7.44 (1H, ddd, J=8.2, 1.2, 0.6, H-8), 7.37 (1H, ddd, J=8.2, 7.1, 1.2, H-6), 3.50 (3H, s, 1`), 2.52 (3H, s, H-9).$^{13}$C NMR (100 MHz, $CD_3OD$, δ, ppm.): 157.51 (C-2), 163.62 (C-4), 120.82 (C-4a), 127.61 (C-5), 126.85 (C-6), 135.56 (C-7), 127.41 (C-8), 148.01 (C-8a), 31.50 (C-1`).

Synthesis of 3-Etylbenzopyrimidin-4-one (3). We put 1.46 g (0.01 mole) of benzopyrimidin-4-one, 30 ml of ethyl alcohol (C_2H_5OH) and 0.616 g (0.011 mole) of KOH into a 100 ml round-bottom flask and mix it slightly. After cooling the reaction mixture, 1.94 ml (2.85 g, d=1.47 g/ml) (0.015 mole) ethyl bromide (C_2H_5Br) was added and heated at 75–80 °C for 7 hours. The resulting reaction mixture is cooled and mixed with 30 ml of 5% NaOH aqueous solution, and 60 ml of chloroform is added and extracted. After chloroform extraction, the substance was recrystallized from ethyl alcohol. As a yield, 1.305 g (75%) of substance **3** was obtained, melting point 99–101 °C, R$_f$=0.62 (system: chloroform: methanol – 10:1).^{1}H NMR (400 MHz, CD_3OD, ppm. δ, J/Hz): 8.08 (1H, ddd, J=8.1, 1.5, 0.6, H-5), 7.67 (1H, ddd, J=8.4, 7.1, 1.5, H-7), 7.51 (1H, ddd, J=8.4, 1.1, 0.6, H-8), 7.42 (1H, ddd, J=8.1, 7.1, 1.1, H-6), 4.13 (2H, k, J=7.1, H-1`), 1.30 (2H, t, J=7.2, H-2`).^{13}C NMR (100 MHz, CD_3OD, δ, ppm.): 156.87 (C-2), 163.32 (C-4), 121.30 (C-4a), 127.76 (C-5), 126.98 (C-6), 135.67 (C-7), 127.42 (C-8), 148.17 (C-8a), 40.92 (C-1`), 13.78 (C-2`).

Synthesis of 3-propylbenzopyrimidin-4-one (4). 1.46 g (0.01 mole) of benzopyrimidin-4-one, 30 ml of ethyl alcohol (C_2H_5OH) and 0.672 g (0.012 mole) of KOH were added to a 100 ml round-bottomed flask and mixed with a little heat. After cooling the reaction mixture, 1.94 ml (1.83 g, d=0.89 g/ml) (0.02 mole) of propyl chloride (C_3H_7Cl) was added and heated at 75–80 °C for 7 hours. The resulting reaction mixture was cooled, mixed with 30 ml of an aqueous solution of 5% NaOH and extracted with 60 ml of chloroform. As a yield, 1.448 g (77%) of substance **4** was obtained, melting point 95–97 °C Rf=0.63 (system: chloroform: methanol – 10:1).^{1}H NMR (400 MHz, CD_3OD+CCl_4, ppm. δ, J/Hz): 8.1 (1H, dd, J=8.13, 1.5, 0.6, H-5), 7.7 (1H, ddd, J=8.4, 7.1, 1.5, H-7), 7.5 (1H, dd, J=8.4, 1.1, 0.6, H-8), 7.4 (1H, ddd, J=8.1, 7.1, 1.1, H-6), 4.14 (2H, k, J=7.1, H-1`), 2.42 (2H, t, J=6.9, H-3`). 1.31 (3H, t, J=7.1, H-2`).$^{13}$C NMR (100 MHz, $CD_3OD$, δ, ppm.): 156.87 (C-2), 164.33 (C-4), 120.31 (C-4a), 126.75 (C-5), 126.98 (C-6), 134.66 (C-7), 127.42 (C-8), 147.17 (C-8a), 39.76 (C-1`), 38.83 (C-2`), 13.72 (C-3`).

Synthesis of 3-Butylbenzopyrimidin-4-one (5). We put 1.46 g (0.01 mole) of benzopyrimidin-4-one, 30 ml of ethyl alcohol (C_2H_5OH) and 0.672 g (0.012 mole) of KOH into a 100 ml round-bottom flask and mix it slightly. After cooling the reaction mixture, add 2.16 ml (2.74 g, d=1.27 g/ml) (0.02 mole) of butyl bromide (C_4H_9Br) and heat it at 75–80 °C for 8 hours. The resulting reaction mixture was cooled, mixed with 30 ml of 5% NaOH aqueous solution, and extracted with 60 ml of chloroform, the chloroform layer was separated, and the resulting substance was recrystallized from ethyl alcohol. As a result, 1.64 g (81%) of substance **5** was obtained, melting point 91–93 °C, Rf=0.64 (system: chloroform: methanol – 10:1).^{1}H NMR spectrum (400 MHz, CD_3OD, δ, ppm, *J*/Hz): 8.32 (1H, s, H-2), 8.23 (1H, ddd, *J*=8.0, 1.6, 0.6, H-5), 7.82 (1H, ddd, *J*=8.5, 7.2, 1.6, H-7), 7.68 (1H, ddd, *J*=8.2, 1.2, 0.6, H-8), 7.55 (1H, ddd, *J*=8.2, 7.1, 1.2, H-6), 4.06 (2H, m, H-1`), 1.77 (2H, m, H-2`), 1.41 (2H, m, H-3`), 0.99 (3H, t, *J*=7.4, H-4`).^{13}C NMR spectrum (100 MHz, CD_3OD, δ, ppm): 149.18 (C-2), 162.61 (C-4), 122.98 (C-4a), 127.39 (C-5), 127.87 (C-6), 135.65 (C-7), 128.53 (C-8), 149.10 (C-8a), 47.86 (C-1`), 32.37 (C-2`), 20.87 (C-3`), 14.00 (C-4`).

Synthesis of 3-*Izo*-butylbenzopyrimidin-4-one (6). We put 1.6 g (0.01 mole) of benzopyrimidin-4-one, 30 ml of ethyl alcohol (C_2H_5OH) and 0.672 g (0.012 mole) of KOH into a 100 ml round-bottom flask and mix it slightly. After cooling the reaction mixture, add 2.16 ml (2.74 g, d=1.27 g/ml) (0.02 mole) of butyl bromide (C_4H_9Br) and heat it at 75–80 °C for 8 hours. The resulting reaction mixture was cooled, mixed with 30 ml of 5% NaOH aqueous solution, and extracted with 60 ml of chloroform, the chloroform layer was separated, and the resulting substance was recrystallized from ethyl alcohol. As a result, 1.6 g (79%) of substance **6** was obtained, melting point 90–92 °C, Rf=0.66 (system: chloroform: methanol – 10:1).^{1}H NMR spectrum (400 MHz, CD_3OD, δ, ppm, *J*/Hz): 8.22 (1H, s, H-2), 8.13 (1H, ddd, *J*=8.0, 1.7, 0.6, H-5), 7.83 (1H, ddd, *J*=8.6, 7.2, 1.6, H-7), 7.66 (1H, ddd, *J*=8.3, 1.2, 0.6, H-8), 7.57 (1H, ddd, *J*=8.3, 7.2, 1.2, H-6), 4.08 (2H, m, H-1`), 1.76 (2H, m, H-2`), 1.43 (2H, m, H-3`), 0.97 (3H, t, *J*=7.4, H-4`).^{13}C NMR spectrum (100 MHz, CD_3OD, δ, ppm): 149.18 (C-2), 162.61 (C-4), 122.98 (C-4a), 127.39 (C-5), 127.87 (C-6), 135.65 (C-7), 128.53 (C-8), 149.10 (C-8a), 47.86 (C-1`), 32.37 (C-2`), 20.86 (C-3`), 14.03 (C-4`).

Synthesis of 3-amylbenzopyrimidin-4-one (7). Put 1.46 g (0.01 mole) of benzopyrimidin-4-one 25 ml of ethyl alcohol (C_2H_5OH) and 0.72 g (0.013 mole) of KOH into a 100 ml round-bottom flask and heat it a little. After cooling the reaction mixture, add 1.45 ml (1.28 g, d=0.88 g/ml) (0.012 mole) of amyl chloride ($C_5H_{11}Cl$) and heat it at 75–80 °C for 9 hours. The resulting reaction mixture is cooled, mixed with 40 ml of 5% NaOH aqueous solution and extracted with 50 ml of chloroform, the chloroform layer is separated, the substance formed by driving off chloroform is recrystallized from ethyl alcohol (C_2H_5OH). As a result, 1.79 g (83%) of substance **7** is obtained, melting point 88–90 °C, R_f=0.63 (system: chloroform: methanol – 10:1).^{1}H NMR spectrum (400 MHz, CD_3OD, δ, ppm, *J*/Hz): 8.25 (1H, s, H-2), 8.16 (1H, dd, J=8.0, 1.6, H-5), 7.76 (1H, ddd, J=8.3, 7.2, 1.6, H-7), 7.62 (1H, dd, J=8.2, 1.1, H-8), 7.49 (1H, ddd, J=8.2, 7.1, 1.2, H-6), 3.98 (2H, m, H-1`), 1.72 (2H, m, H-2`), 1.31 (2H, m, H-3`), 1.31 (2H, m, H-4`), 0.86 (3H, t, J=7.0, H-5`).$^{13}C$ NMR spectrum (100 MHz, $CD_3OD$, δ, ppm): 149.13 (C-2), 162.59 (C-4), 122.90 (C-4a), 128.55 (C-5), 127.37 (C-6), 135.67 (C-7), 127.83 (C-8), 149.01 (C-8a), 48.10 (C-1`), 29.81 (C-2`), 29.93 (C-3`), 23.30 (C-4`), 14.27 (C-5`).

Synthesis of 3-geptylbenzopyrimidin-4-one (8). We put 1.46 g (0.01 mole) of benzopyrimidin-4-one, 30 ml of ethyl alcohol (C_2H_5OH) and 0.73 g (0.013 mole) of KOH into a 100 ml round-bottom flask and mix it slightly. After cooling the reaction mixture, 1.857 ml (1.615 g, d=0.87 g/ml) (0.012 mole) of heptyl chloride ($C_7H_{15}Cl$) was added and boiled at 75–80 °C for 9 hours. The resulting reaction mixture was cooled, mixed with 30 ml of an aqueous solution of 5% NaOH and extracted with 60 ml of chloroform. As a result, 2.07 g (85%) of substance **8** was obtained, melting point 87–89 °C, R_f 0.64 (system: chloroform: methanol – 10:1).^1H NMR spectrum (400 MHz, CD_3OD, δ, ppm, J/Hz): 8.26 (1H, s, H-2), 8.17 (1H, dd, J=8.1, 1.7, H-5), 7.76 (1H, m, H-7), 7.63 (1H, m, H-8), 7.50 (1H, m, H-6), 3.99 (2H, m, H-1`), 1.72 (2H, m, H-2`), 1.30 (2H, m, H-3`), 1.30 (2H, m, H-4`), 1.23 (2H, m, H-5`), 1.23 (2H, m, H-6`), 0.82 (3H, t, J=6.7, H-7`).$^{13}C$ NMR spectrum (100 MHz, $CD_3OD$, δ, ppm): 149.16 (C-2), 162.63 (C-4), 122.92 (C-4a), 128.58 (C-5), 127.39 (C-6), 135.70 (C-7), 127.85 (C-8), 149.03 (C-8a), 48.14 (C-1`), 29.96 (C-2`), 27.62 (C-3`), 30.23 (C-4`), 32.82 (C-5`), 23.59 (C-6`), 14.39 (C-7`).

Synthesis of 3-dodecylbenzopyrimidin-4-one (9). We put 1.46 g (0.01 mole) of benzopyrimidin-4-one, 30 ml of ethyl alcohol (C_2H_5OH) and 0.896 g (0.016 mole) of KOH into a 100 ml round-bottom flask and mix it slightly. The reaction mixture was cooled and 2.64 ml (2.74 g, d=1.04 g/ml) (0.011 mole) of dodecyl bromide ($C_{12}H_{25}Br$) was added to it and heated at 75–80 °C for 9 hours. The resulting reaction mixture was cooled, mixed with 30 ml of 5% NaOH aqueous solution and extracted with 70 ml of chloroform, the chloroform layer was separated, and the resulting substance was recrystallized from ethyl alcohol. As a result, 2.7 g (86%) of substance **9** was obtained, melting point 86–88 °C, Rf=0.62 (system: chloroform: methanol – 10:1).^1H NMR spectrum (600 MHz, $CDCl_3$, δ, ppm, J/Hz): 8.03 (1H, s, H-2), 8.32 (1H, dd, J=8.1, 1.4, H-5), 7.76 (1H, ddd, J=8.3, 6.9, 1.5, H-7), 7.71 (1H, dd, J=8.2, 1.4, H-8), 7.51 (1H, ddd, J=8.2, 6.8, 1.4, H-6), 4.00 (2H, m, H-1`), 1.78 (2H, m, H-2`), 1.37 (2H, m, H-3`), 1.34 (2H, m, H-5`), 1.28 (2H, m, H-6`), 1.28 (2H, m, H-11`), 1.27 (2H, m, H-9`), 1.26 (2H, m, H-7`), 1.26 (2H, m, H-8`), 1.25 (2H, m, H-4`), 1.25 (2H, m, H-10`), 0.87 (3H, t, J=7.0, H-12`).^{13}C NMR spectrum (150 MHz, $CDCl_3$, δ, ppm): 146.74 (C-2), 161.19 (C-4), 122.32 (C-4a), 126.83 (C-5), 127.33 (C-6), 134.25 (C-7), 127.53 (C-8), 148.26 (C-8a), 47.24 (C-1`), 29.52 (C-2`), 26.80 (C-3`), 29.66 (C-4`), 29.31 (C-5`), 29.45 (C-6`), 29.72 (C-7`), 29.72 (C-8`), 29.57 (C-9`), 32.02 (C-10`), 22.80 (C-11`), 14.25 (C-12`).

Conclusion

An improved method of quantitative yield synthesis of benzopyrimidin-4-onewas developed by carrying out the heterocyclization reaction in the presence of formamide and o-aminobenzoic acid. Synthesis of 3-alkylbenzopyrimidin-4-ones as a result of alkylation reactions of the obtained substance in the presence of alkylating agents of different structures was systematically studied. The obtained substances can be used as important synthons for further modifications. The structure of the obtained substances was analyzed and confirmed using modern physical research methods.

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ON A PROBLEM FOR ONE CLASS OF FOURTH ORDER NONLINEAR SOBOLEV TYPE DIFFERENTIAL EQUATIONS

Samed Aliyev [1], ***Arzu Aliyeva*** [2], ***Sardar Aliyev*** [3]

[1] Faculty of Mechanics and Mathematics, Department of Methods of Mathematics and its Teaching, Baku State University, Baku, Azerbaijan

[2] Institute of Mathematics and Mechanics Azerbaijcan National Academy of Sciences, Baku, Azerbaijan

[3] Faculty of Mechanics and Mathematics, Department of Higher Mathematics, Baku State University, Baku, Azerbaijan

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Abstract

This work is dedicated to the study of certain properties of the classical solution to a one-dimensional mixed problem for one class of fourth order nonlinear equations. By multiplying the equation under consideration by a suitable function and performing subsequent term by term integration, a theorem on the a priori estimation of the classical solution to the mixed problem is proven.

Keywords: *nonlinear equation, mixed problem, classical solution, a priori estimate*

The study examines certain properties of the classical solution to the following one-dimensional mixed problem:

$$\begin{cases} u_{txx}(t,x)-\alpha\, u_{xxxx}(t,x)=F(t,x,u(t,x),u_x(t,x),u_{xx}(t,x),u_{xxx}(t,x)) & (1)\\ \qquad\qquad\qquad\qquad\qquad (0\le t\le T,\ 0\le x\le \pi), & \\ u(0,x)=\phi(x)\ \ (0\le x\le \pi), & (2)\\ u(t,0)=u(t,\pi)=u_{xx}(t,0)=u_{xx}(t,\pi)=0\quad (0\le t\le T), & (3) \end{cases}$$

where $\alpha > 0$ is a fixed number, $0 < T < +\infty; F$ and ϕ are given functions, and $u(t,x)$ is a sought function.

We call a functio ns $u(t,x)$ a classical solution of the problem (1)–(3) if this function and all its derivatives involved in the equation (1) are continuous in $[0,T]\times[0,\pi]$ and the conditions (1)–(3) are satisfied in the usual sense.

In (Khudaverdiyev K., Aliyeva A., 2010), K. Khudaverdiyev and A. Aliyeva studied the existence of a classical solution to a one-dimensional mixed problem for a certain semilinear equation, which is simpler than equation (1). In (Aliyev S., Heydarova M., Aliyeva A. 2024), proven the existence in small of classical solution of the considered mixed problem. But in (Aliyeva A., 2012), the generalized solution and in (Aliyeva A., 2009), the almost everywhere solution of the considered mixed problem was investigated.

We also note works (Aliyev S., Aliyeva A., Abdullayeva G. 2019; Aliyev S, Aliyeva A., 2017; Tekin I., 2021; Tekin I., 2019), of which some approaches are used in this work.

By multiplying the given equation by an appropriate function and subsequently performing term-by-term integration, the following theorem on the a priori boundedness (in certain senses) of the classical solution to the considered mixed problem is proven.

Theorem 3. Let the right side of equation (1) be as follow:

$$\begin{aligned}&F(t,x,u,u_x,u_{xx},u_{xxx})=\\&=f_0(t,u_{xx})\cdot u_{xxx}+f(t,x,u,u_x,u_{xx},u_{xxx})\end{aligned}, \tag{4}$$

where

a) $f_0(t,V)\in C\big([0,T]\times(-\infty,\infty)\big)$; (5)

б) $f(t,x,u_1,\ldots,u_4)\in C([0,T]\times[0,\pi]\times(-\infty,\infty)^4)$ and in $[0,T]\times[0,\pi]\times(-\infty,\infty)^4$

$$\begin{aligned}&f(t,x,u_1,\ldots,u_4)\cdot u_3 \le C\cdot(1+u_1^2+u_2^2+u_3^2)+\delta\cdot u_4^2,\\&0<\delta<\alpha,\end{aligned} \tag{6}$$

where C > 0 is a constant and $\alpha > 0$ is a number appearing in the equation (1).

Then the following a priori estimates hold for all the possible classical solutions $u(t,x)$ of problem (1)–(3):

$$\begin{aligned}&\int_0^\pi u_{xx}^2(t,x)dx \le C_0 \quad \forall t\in[0,T];\\&\int_0^T\int_0^\pi u_{xxx}^2(t,x)dxdt \le C_0\end{aligned}\ . \tag{7}$$

Proof. Let $u(t,x)$ be any classical solution of problem (1)-(3). On multiplying both sides of equation (1) by the functio $2u_{xx}(t,x)$ and integrating the obtained equality in x over $(0,\pi)$, we get:

$$\begin{aligned}&2\int_0^\pi u_{txx}(t,x)\cdot u_{xx}(t,x)dx-2\alpha\cdot\int_0^\pi u_{xxxx}(t,x)\cdot u_{xx}(t,x)dx=\\&=2\int_0^\pi f_0(t,u_{xx}(t,x))\cdot u_{xxx}(t,x)\cdot u_{xx}(t,x))dx+\\&+2\int_0^\pi f(t,x,u(t,x),u_x(t,x),u_{xx}(t,x),u_{xxx}(t,x))\cdot u_{xx}(t,x)dx.\end{aligned} \tag{8}$$

Next, using the last two boundary conditions (3) and condition (6), we obtain that $\forall t\in[0,T]$:

$$2\int_0^\pi u_{txx}(t,x)\cdot u_{xx}(t,x)dx = \frac{d}{dt}\left\{\int_0^\pi u_{xx}^2(t,x)dx\right\}; \tag{9}$$

$$\begin{aligned}&-2\alpha\int_0^\pi u_{xxxx}(t,x)\cdot u_{xx}(t,x)dx=\\&=-2\alpha\cdot\left\{\Big[u_{xxx}(t,x)\cdot u_{xx}(t,x)\Big]_{x=0}^{x=\pi}-\right.\\&\left.-\int_0^\pi u_{xxx}(t,x)\cdot u_{xxx}(t,x)dx\right\}=2\alpha\cdot\int_0^\pi u_{xxx}^2(t,x)dx;\end{aligned} \tag{10}$$

$$\begin{aligned}&2\int_0^\pi f_0(t,u_{xx}(t,x))\cdot u_{xxx}(t,x)\cdot u_{xx}(t,x)dx=\\&=2\int_0^\pi f_0(t,u(t,x))u_{xx}(t,x)\cdot u_{xxx}(t,x)dx=\\&=2\int_0^\pi\left\{\frac{\partial}{\partial x}\int_0^{u_{xx}(t,x)} f_0(t,\xi)\cdot\xi\, d\xi\right\}dx=\\&=2\left\{\int_0^{u_{xx}(t,x)}\xi\, f_0(t,\xi)d\xi\right\}_{x=0}^{x=\pi}=0\end{aligned}; \tag{11}$$

$$\begin{aligned}&2\int_0^\pi f(t,x,u(t,x),u_x(t,x),u_{xx}(t,x),u_{xxx}(t,x))\cdot u_{xx}(t,x)dx\le\\&\le 2\int_0^\pi\left\{C\cdot[1+u^2(t,x)+u_x^2(t,x)+u_{xx}^2(t,x)]+\delta\cdot u_{xxx}^2(t,x)\right\}dx=\\&=2\pi\cdot C+2C\cdot\int_0^\pi u^2(t,x)dx+2C\cdot\int_0^\pi u_x^2(t,x)dx+\\&+2C\cdot\int_0^\pi u_{xx}^2(t,x)dx+2\delta\cdot\int_0^\pi u_{xxx}^2(t,x)dx.\end{aligned} \tag{12}$$

Now, substituting (9)–(12) into (8), integrating the resulting inequality from 0 to t, and using the initial condition (2), we obtain that $\forall t\in[0,T]$:

$$\int_0^\pi u_{xx}^2(t,x)dx + 2\alpha\cdot\int_0^t\int_0^\pi u_{xxx}^2(\tau,x)dxd\tau \le$$
$$\le \int_0^\pi (\phi''(x))^2 dx + 2\pi\cdot C\cdot T +$$
$$+\int_0^t \left\{ 2C\cdot\left[\int_0^\pi u^2(\tau,x)dx + \int_0^\pi u_x^2(\tau,x)dx + \int_0^\pi u_{xx}^2(\tau,x)dx\right] + \right.$$
$$\left. +2\delta\cdot\int_0^\pi u_{xxx}^2(\tau,x)dxd\tau \right\},$$

consequently,

$$\int_0^\pi u_{xx}^2(t,x)dx + 2(\alpha-\delta)\cdot\int_0^t\int_0^\pi u_{xxx}^2(\tau,x)dxd\tau \le$$
$$\le \int_0^\pi (\phi''(x))^2 dx + 2\pi T\cdot C + \qquad (13)$$
$$+2C\cdot\int_0^t \left\{ \int_0^\pi u^2(\tau,x)dx + \int_0^\pi u_x^2(\tau,x)dx + \int_0^\pi u_{xx}^2(\tau,x)dx \right\} d\tau.$$

Next, since $u(\tau,0)=u(\tau,\pi)$ $(0\le\tau\le T)$, then $\forall\tau\in[0,T]$ there exists such a point $\xi=\xi_\tau\in(0,\pi)$, that $u_x(\tau,\xi_\tau)=0$. Then it is obvious that $\forall\tau\in[0,T]$ and $x\in[0,\pi]$:

$$u_x(\tau,x)=\int_{\xi_\tau}^x u_{\xi\xi}(\tau,\xi)d\xi,$$
$$u_x^2(\tau,x)\le\left\{\int_0^\pi \left|u_{\xi\xi}(\tau,\xi)\right|d\xi\right\}^2 \le \qquad , (14)$$
$$\le\pi\cdot\int_0^\pi u_{\xi\xi}^2(\tau,\xi)d\xi = \pi\cdot\int_0^\pi u_{xx}^2(\tau,x)dx$$

$$\int_0^\pi u_x^2(\tau,x)dx \le \pi\cdot\int_0^\pi u_{xx}^2(\tau,x)dx\cdot\pi =$$
$$= \pi^2\cdot\int_0^\pi u_{xx}^2(\tau,x)dx \qquad . (15)$$

On the other hand, using the relation $u(\tau,0)=0$ $(0\le\tau\le T)$, we obtain $\forall\tau\in[0,T]$ and $x\in[0,\pi]$:

$$u(\tau,x)=\int_0^x u_\xi(\tau,\xi)d\xi,$$
$$u^2(\tau,x)\le\left\{\int_0^\pi \left|u_\xi(\tau,\xi)\right|d\xi\right\}^2 \le \qquad , (16)$$
$$\le\pi\cdot\int_0^\pi u_\xi^2(\tau,\xi)d\xi = \pi\cdot\int_0^\pi u_x^2(\tau,x)dx$$

$$\int_0^\pi u^2(\tau,x)dx \le \pi\int_0^\pi u_x^2(\tau,x)dx\cdot\pi =$$
$$= \pi^2\cdot\int_0^\pi u_x^2(\tau,x)dx \qquad . (17)$$

Then, using a priori estimate (15), we obtain from (16) and (17), that $\forall\tau\in[0,T]$ and $x\in[0,\pi]$:

$$u^2(\tau,x)\le\pi\cdot\int_0^\pi u_x^2(\tau,x)dx \le \pi^3\cdot\int_0^\pi u_{xx}^2(\tau,x)dx, \qquad (18)$$

$$\int_0^\pi u^2(\tau,x)dx \le \pi^3\cdot\int_0^\pi u_{xx}^2(\tau,x)dx\cdot\pi =$$
$$= \pi^4\cdot\int_0^\pi u_{xx}^2(\tau,x)dx \qquad . (19)$$

Now, using notation

$$\delta_0\equiv 2(\alpha-\delta)>0$$

and estimate (19), (15) on the right-hand side of (13), from (13) we obtain that $\forall t\in[0,T]$:

$$\int_0^\pi u_{xx}^2(t,x)dx + \delta_0\cdot\int_0^t\int_0^\pi u_{xxx}^2(\tau,x)dxd\tau \le$$
$$\int_0^\pi (\phi''(x))^2 dx + 2\pi T\cdot C + \qquad (20)$$
$$+2C\cdot(\pi^4+\pi^2+1)\cdot\int_0^t\left\{\int_0^\pi u_{xx}^2(\tau,x)dx\right\}d\tau.$$

Then, due to $\delta_0>0$, it is obvious that $\forall t\in[0,T]$:

$$\int_0^\pi u_{xx}^2(t,x)dx \le$$
$$\int_0^\pi (\phi''(x))^2 dx + 2\pi T\cdot C + 2(1+\pi^2+\pi^4)\cdot C\times$$
$$\times\int_0^t\left\{\int_0^\pi u_{xx}^2(\tau,x)dx\right\}d\tau \qquad .$$

Hence, applying Bellman's inequality we obtain that $\forall t\in[0,T]$:

$$\int_0^\pi u_{xx}^2(t,x)dx \le \left\{\int_0^\pi (\phi''(x))^2 dx + 2\pi T\cdot C\right\}\times$$
$$\times\exp\left\{2(1+\pi^2+\pi^4)\cdot C\cdot T\right\}\equiv C_1 \qquad . (21)$$

Then, using a priori estimate (21), we obtain from (20) that $\forall t\in[0,T]$:

$$\delta_0\cdot\int_0^t\int_0^\pi u_{xxx}^2(\tau,x)dxd\tau \le$$
$$\int_0^\pi (\phi''(x))^2 dx + 2\pi T\cdot C + 2(1+\pi^2+\pi^4)\cdot C\cdot C_1\cdot T \equiv C_2.$$

Consequently,

$$\int_0^T\int_0^\pi u_{xxx}^2(\tau,x)dxd\tau \le \delta_0^{-1}\cdot C_2 \equiv C_3. \qquad (22)$$

Now, from (21) and (22) it follows the trueness of a priori estimates (7). Theorem is now proved.

In conclusion, this work serves as a continuation of (Aliyev S., Aliyeva A., 2020), where the a priori boundedness (in a certain sense) of the almost everywhere solution considered mixed problem was studied.

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Contact: samed59@bk.ru

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STUDY OF PENDULUM MOTION USING DIFFERENTIAL EQUATIONS AND THE MAPLE PACKAGE

Chuyanov Xurshid Uralovich [1]

[1] Department of Higher Mathematics. Karshi Engineering Economics Institute

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Abstract

In this paper, the differential equations of mathematical and physical pendulum motion are solved and investigeted using the Maple application package.

Keywords: *differential equation, mathematical pendulum, physical pendulum, general solution, angular acceleration, mass, moment of inertia*

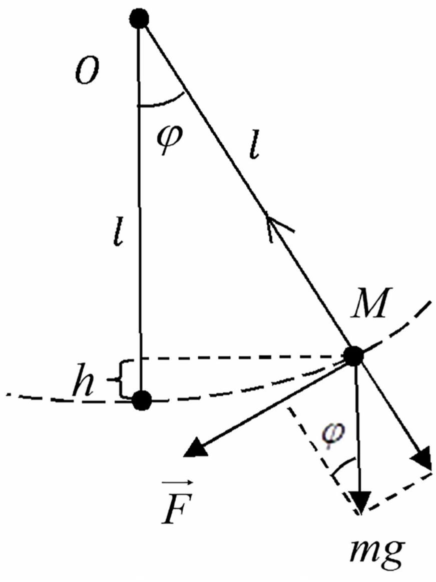
Introduction

The study of mechanical motions leads to the solution of differential equations. Solutions to differential equations cannot always be expressed in terms of elementary functions. Practical packages can be used effectively to test solutions. In the future, we will formulate the equation of motion of the pendulum and explore it using the Maple package. Task statement and solution.

Pendulum motion is used both from a theoretical and practical point of view to solve technological and scientific problems.

A mathematical pendulum is a system consisting of a weightless, inextensible and rod l, suspended at point O, and a material point attached to it with mass m. This pendulum moves in a vertical plane passing through point O. The position of the pendulum is determined by the angle φ between the vertical axis directed downward and the rod, where $\varphi = \varphi(t)$ (t – time).

Figure 1.



According to Newton's second law, the force $\vec{F} = m\vec{a}$ ($\vec{a}$ – is the acceleration vector, $\vec{F}$ is the sum of the tension and gravity forces) acts on the point M with mass m. We project this vector equation onto the tangent to the trajectory at point M. The projection of the tension force is zero and the projection of gravity is $F = mg\sin\varphi$ (see Figure 1). The projection of the acceleration vector is $a = l\varphi''$ (where φ'' is the angular acceleration). Thus,

$$ml\varphi'' = -mg\sin\varphi. \qquad (1)$$

This equation is an autonomous second-order differential equation with respect to the unknown function $\varphi = \varphi(t)$. Its order can be lowered by replacing the variable t with φ, which is possible using equation (1):

$$\varphi'' = \frac{d\varphi'}{dt} = \frac{d\varphi'}{d\varphi}\cdot\frac{d\varphi}{dt} = \frac{d}{d\varphi}\left(\frac{\varphi'^2}{2}\right),$$

$$\frac{d}{d\varphi}\left(\frac{\varphi'^2}{2}\right) = -\frac{g}{l}\sin\varphi \text{ or} \qquad (2)$$

$$d\left(\frac{\varphi'^2}{2}\right) = -\frac{g}{l}\sin\varphi\, d\varphi$$

Integrating equation (2), we o thain:

$$\frac{\varphi'^2}{2} = \frac{g}{l}\cos\varphi + C_1 \ (C_1 = const).$$

Set in this equation $\omega^2 = \frac{g}{l}$, $C_1 = -\frac{g}{l} + C \quad (C = const)$ and get:

$$\frac{\varphi'^2}{2} + \omega^2(1-\cos\varphi) = C. \qquad (3)$$

Equation (3) expresses the conservation of the total energy of the system with mass m, since the kinetic energy is

$$\frac{mv^2}{2} = \frac{m(l\varphi')^2}{2} = ml^2\cdot\frac{\varphi'^2}{2},$$

and potential energy

$$mgh = mgl(1-\cos\varphi).$$

Thus, the total energy of the system:

$$E = \frac{mv^2}{2} + mgh = ml^2\cdot\frac{\varphi'^2}{2} + mgl(1-\cos\varphi) = \\ = ml^2\left(\frac{\varphi'^2}{2} + \frac{g}{l}\cdot(1-\cos\varphi)\right).$$

Therefore, while driving:

$$\frac{\varphi'^2}{2} + u(\varphi) = C, u(\varphi) = \omega^2(1-\cos\varphi)\ (C = const).$$

From here:

$$\varphi' = \pm\sqrt{2(C-u(\varphi))}. \qquad (4)$$

In the phase space (φ,φ') this equation determines the phase trajectories.

If $C<0$, then the trajectory does not exist. If $C=0$, then $\varphi = \pi k, k\in\mathbb{Z}$ are the equilibrium points of the system.

If $0<C<2\omega^2$, then the trajectories will be closed curves corresponding to periodic oscillations of the system.

If $C>2\omega^2$, then the phase trajectories will be open curves, which corresponds to a rotational motion about the point O.

In general, the solutions of equation (4) cannot be expressed by elementary functions. Solutions can be found using Jacobi elliptic functions.

If in the solution the angle φ varies over a small interval, then $\sin\varphi \approx \varphi$, and (1) the equation will take the form of a harmonic oscillator:

$$\varphi'' + \omega^2\varphi = 0.$$

Solutions of this equation are expressed in terms of elementary functions and have the form:

$$\varphi = A\cos(\omega t + \varphi_0),$$

where A – is the amplitude, φ_0 – is the initial phase. This solution describes harmonic oscillations with period $T = \frac{2\pi}{\omega}$.

Therefore, small oscillations of a mathematical pendulum represent harmonic oscillations.

Let's study the trajectories of the mathematical pendulum in phase space at $\omega = 1$ using the Maple package.

$\omega := 1$

$$\omega := 1$$

$$with(plots) : p1 := implicitplot\left(\frac{(\phi')^2}{2} + \omega\cdot(1-\cos(\phi)) = 1, \phi=-4..4, \phi'=-2..2, scaling = constrained, thickness = 2, color = \text{"Niagara DarkOrchid"}\right)$$

$$p1 := PLOT(...)$$

$$p2 := implicitplot\left(\frac{(\phi')^2}{2} + \omega\cdot(1-\cos(\phi)) = 0.4, \phi=-4..4, \phi'=-2.7..2.7, scaling = constrained, thickness = 2, color = blue\right)$$

$$p2 := PLOT(...)$$

$$p3 := implicitplot\left(\frac{(\phi')^2}{2} + \omega\cdot(1-\cos(\phi)) = 1.98, \phi=-4..4, \phi'=-2.5..2.5, scaling = constrained, thickness = 2, color = green\right)$$

$$p3 := PLOT(...)$$

$$p4 := implicitplot\left(\frac{(\phi')^2}{2} + \omega\cdot(1-\cos(\phi)) = 1.73, \phi=-4..4, \phi'=-2.5..2.5, scaling = constrained, thickness = 2, color = \text{"Generic Blue Purple"}\right)$$

$$p4 := PLOT(...)$$

$$p5 := implicitplot\left(\frac{(\phi')^2}{2} + \omega\cdot(1-\cos(\phi)) = 3.2, \phi=-4..4, \phi'=-2.7..2.7, scaling = constrained, thickness = 2, color = black\right)$$

$$p5 := PLOT(...)$$

$$p6 := implicitplot\left(\frac{(\phi')^2}{2} + \omega\cdot(1-\cos(\phi)) = 2.5, \phi=-4..4, \phi'=-2.5..2.5, scaling = constrained, thickness = 2, color = black\right)$$

$$p6 := PLOT(...)$$

$$p7 := implicitplot\left(\frac{(\phi')^2}{2} + \omega\cdot(1-\cos(\phi)) = 4.1, \phi=-4..4, \phi'=-3.2..3.2, scaling = constrained, thickness = 2, color = black\right)$$

$$p7 := PLOT(...)$$

$display(p1, p2, p3, p4, p5, p6, p7)$

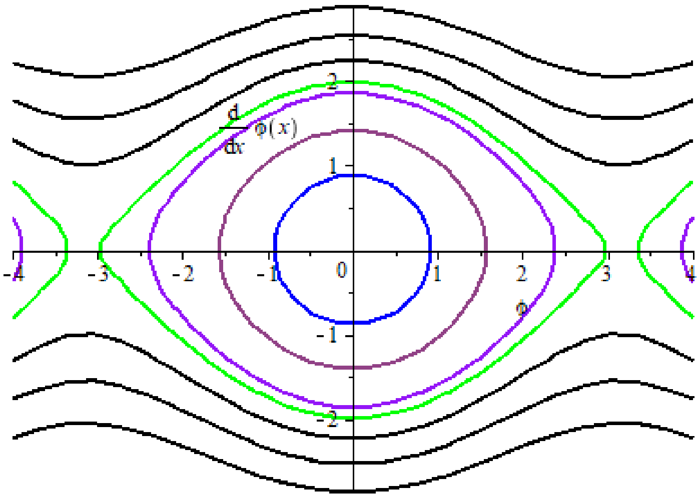


Figure 2.

Let's solve the last equation

$$\varphi' = \pm\sqrt{2\left(c_1 - u(\varphi)\right)}$$

with initial condition $\varphi(0) = \varphi_0,\ \varphi'(0) = 0$.

The solution is expressed in terms of eliptic functions.

We are investigating this solution with Maple. The solution is expressed in terms of the integral:

$$\pm\int_{\varphi_0}^{\varphi} \frac{da}{\sqrt{2\left(u(\varphi_0) - u(a)\right)}} = t.$$

In this case, + is used when the φ' is positive. When pendulum motion starts at an angle φ_0 without an initial velocity, we find its period T.

T period is formed from the following equation

$$-\int_{\varphi_0}^{0} \frac{da}{\sqrt{2\left(u(\varphi_0) - u(a)\right)}} = \frac{T}{4} \qquad \text{or}$$

$$\int_{0}^{\varphi_0} \frac{da}{\sqrt{2\left(u(\varphi_0) - u(a)\right)}} = \frac{T}{4}.$$

We compute this period in the mathematical package Maple when $\varphi_0 = \frac{\pi}{3}$.

$$int\left(\frac{4}{\sqrt{2\cdot\left(\cos(\phi) - \cos\left(\frac{\pi}{3}\right)\right)}}, \phi = 0\,..\,\frac{\pi}{3}, numeric\right)$$

$$6.743001419$$

Therefore, in a mathematical pendulum, the period of oscillatory motion that began at angle $\frac{\pi}{3}$ under its own weight is

$$T = 6{,}743001419.$$

For a mathematical pendulum in the equation with small deviation angles, the period of oscillation is: T = 27:

$$T = \frac{2\pi}{\omega}.$$

If $\omega = 1$, then the period will be 2π. Obviously, its period is greater than 2π in large movements.

In the same way, we can study the equation of motion of a physical pendulum. A physical pendulum is a solid that oscillates freely under the influence of gravity around an arbitrary horizontal fixed axis that does not pass through the center of gravity.

The equation of motion of a physical pendulum with mass m, rotated from the equilibrium position by an angle φ, is reduced to a differential equation of the form

$\frac{d^2\varphi}{dt^2}+\omega^2\sin\varphi=0$, where $\omega^2=\frac{mgl}{I}$, I is the moment of inertia, l is the distance from the center of gravity of the body to the axis of rotation, g is the acceleration of gravity, m is the mass of the body. Solutions to this differential equation have been studied above.

Conclusion

The equation of small movements of a mathematical pendulum is similar to the equation of harmonic oscillations. Using this equation, you can determine the period of oscillation, angular frequency and other dynamic properties of the pendulum. It follows that the period of small oscillations does not depend on the initial values. However, in the general case of (large oscillations), the oscillation period depends on the initial data.

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Contact: xchuyanov77 @list.ru

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GEODESICS ON A PSEUDOSPHERE: ANALYTICAL AND NUMERICAL APPROACHES

Maxsatulloyeva Feruza Maxmud qizi

[1] Faculty of Mathematics, National University of Uzbekistan named after Mirzo Ulugbek

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Abstract

Geodesics on a pseudosphere are examined through analytical and numerical approaches. The pseudosphere, a surface of revolution with constant negative curvature, is characterized using the first fundamental form. The geodesic equations are derived via Christoffel symbols and transformed into a first-order Bernoulli equation. Solutions are obtained both analytically and using Python's LSODA method for numerical integration. Results illustrate the behavior of geodesic trajectories and their dependence on initial conditions. The study provides insights into differential geometry and mathematical physics, highlighting the significance of geodesics in negatively curved spaces.

Keywords: *geodesics, pseudosphere, differential geometry, christoffel symbols, numerical integration, Bernoulli equation*

Introduction

Geodesics, the curves that represent the shortest paths between points on a surface, play a fundamental role in differential geometry and have significant applications in physics, particularly in general relativity and the study of curved spaces.

This work focuses on the analytical and numerical study of geodesics on a pseudosphere. To describe the surface mathematically, we begin with its parametrization and derive the first fundamental form, which characterizes the intrinsic geometry of the surface. Using this foundation, we compute the Christoffel symbols, which are essential in formulating the geodesic equations. These equations, derived from the calculus of variations, describe the natural motion of a particle constrained to move along the surface without external forces. Since the geodesic equations are typically nonlinear second-order differential equations, solving them directly can be challenging. Therefore, we employ a transformation that reduces the geodesic equation into a first-order Bernoulli equation, allowing for more accessible analytical and numerical solutions.

To further analyze the geodesic behavior, we apply numerical methods, specifically the LSODA (Livermore Solver for Ordinary Differential Equations) algorithm, to integrate the equations and visualize geodesic trajectories. LSODA is particularly useful as it adapts between stiff and non-stiff solving methods, ensuring accurate results across different parameter conditions. The numerical solutions provide a detailed exploration of how geodesic paths evolve on the pseudosphere and how their trajectories depend on initial conditions. The results illustrate the fundamental characteristics of motion on negatively curved surfaces, including the divergence of geodesic paths, a hallmark of hyperbolic geometry.

We consider the pseudosphere, which is a surface of revolution formed by rotating a tractrix around its asymptote. Therefore, the pseudosphere, in relation to the tractrix, is given by the following parametrization:

$$x(u,v) =$$

$$= \left(a\cos u\cos v, a\sin u\sin v,\ a\left(cosu + lntg\frac{u}{2} \right) \right)$$

Then

$$x_u = \left(a\cos u\cos v, a\cos u\sin v, a\frac{\cos^2 u}{sinu} \right)$$

$$x_v = \left(-a\sin u\sin v, a\sin u\cos v, 0 \right)$$

For a surface of revolution, the coefficients of the first fundamental form are as follows:

$$E = \frac{a^2\cos^2 u}{\sin^2 u},\ F = 0,\ G = a^2\sin^2 u$$

The Christoffel Symbols are:

$$G^1_{11} = -\frac{2}{\sin 2u},\quad G^1_{12} = 0,\quad G^1_{22} = -\frac{\sin^3 u}{\cos u},$$

$$G^2_{11} = 0,\quad G^2_{12} = ctgu,\quad G^2_{22} = 0.$$

The differential equation of geodesic lines on a surface is given as follows:

$$\frac{d^2v}{du^2} = G^1_{22}\left(\frac{dv}{du}\right)^3 + \left(2G^1_{12} - G^2_{12}\right)\left(\frac{dv}{du}\right)^2 +$$

$$+\left(G^1_{11} - 2G^2_{12}\right)\frac{dv}{du} - G^2_{11}$$

Then,

$$\frac{d^2v}{du^2} = -\frac{sin^3u}{cosu}\left(\frac{dv}{du}\right)^3 -$$

$$-ctgu\left(\frac{dv}{du}\right)^2 - \frac{1+2cos^2u}{cosusinu}\left(\frac{dv}{du}\right)$$

We solve this differential equation for geodesic lines on a pseudosphere. It is a second-order nonlinear differential equation. First, we simplify by letting

$$y = dv/du.$$

This reduces the order of the equation, transforming it into a first-order equation for y. Then,

$$d^2v / du^2 = dy / du.$$

The equation becomes:

$$\frac{dy}{du} = -\frac{sin^3u}{cosu}(y)^3 - ctgu(y)^2 - \frac{1+2cos^2u}{cosusinu}(y)$$

This is a Bernoulli differential equation in y. Let's try the substitution y = 1/z to transform it into a linear equation. After substitution and simplification:

$$z\cdot\frac{dz}{du} = \frac{\sin^3 u}{\cos u} + ctgu\cdot z + \frac{1+2\cos^2 u}{\cos u\sin u}\cdot z^2$$

Bernoulli's equation should be in the following form:

$$\frac{dz}{du} + P(u)z = Q(u)z^n$$

In this case, n = 2, so we write the equation in the following form:

$$\frac{dz}{du} = \frac{\sin^3 u}{z\cos u} + \frac{1}{\tan u} + \frac{\left(1+2\cos^2 u\right)}{\cos u\sin u}z$$

To solve the equation, we use the method of variable substitution. We introduce the following variable: $w = z^{1-n} = z^{-1}$.

Then,

$$\frac{dw}{du} = -z^{-2}\frac{dz}{du} = -\frac{1}{z^2}\frac{dz}{du}$$

We write the equation in terms of w:

$$\frac{dw}{du} - \frac{1}{\tan u}w = -\frac{\sin^3 u}{\cos u}w^2 + \frac{\left(1+2\cos^2 u\right)}{\cos u\sin u}$$

Let's solve this equation. Here,

$$P(u) = -\frac{1}{\tan u}$$

$$Q(u) = -\frac{\sin^3 u}{\cos u}w^2 - \frac{\left(1+2\cos^2 u\right)}{\cos u\sin u}$$

This is still not a linear equation because there is a w^2 term. If the value of w is very small (w ≈ 0), the equation becomes linear if we ignore the quadratic term:

$$\frac{dw}{du}-\frac{1}{\tan u}w\approx-\frac{\left(1+2\cos^2 u\right)}{\cos u\sin u}$$

This is a simple linear equation, which we can solve using the following integrals.

Integrating factor method.

General solution of linear equation:

$$I\left(u\right)=e^{\int P(u)du}$$

$$P\left(u\right)=-\frac{1}{\tan u}\text{, that is way:}$$

$$I\left(u\right)=e^{\int-\frac{1}{\tan u}du}=e^{-\ln|\sin u|}=\frac{1}{|\sin u|}$$

This is used as an integrating factor. Multiplying both sides by *I(u)*:

$$\frac{1}{|\sin u|}\frac{dw}{du}+\frac{1}{\tan u|\sin u|}w=-\frac{\left(1+2\cos^2 u\right)}{\cos u\sin^2 u}$$

Now the left-hand side looks like a complete derivative:

$$\frac{d}{du}\left(w\cdot\frac{1}{\sin u}\right)=-\frac{\left(1+2\cos^2 u\right)}{\cos u\sin^2 u}$$

$$w\cdot\frac{1}{|\sin u|}=\int-\frac{\left(1+2\cos^2 u\right)}{\cos u\sin^2 u}du\ \Rightarrow$$

$$w=|\sin u|\left(\frac{\ln\left(\sin u+1\right)}{2}-\frac{\ln\left(1-\sin u\right)}{2}-\frac{3}{\sin u}+C_1\right)$$

We had introduced the notation *w* = *z* – *1*, and since *y* = *z* – *1*, it follows that *w* = *y*. Since *y* = *dv*/*du*, the equality becomes:

$$\Rightarrow\frac{dv}{du}=$$

$$|\sin u|\left(\frac{\ln\left(\sin u+1\right)}{2}-\frac{\ln\left(1-\sin u\right)}{2}-\frac{3}{\sin u}+C_1\right)$$

To find *v*, we integrate both sides of the equation

$$v=$$

$$=\int|\sin u|\left(\frac{\ln\left(\sin u+1\right)}{2}-\frac{\ln\left(1-\sin u\right)}{2}-\frac{3}{\sin u}+C_1\right)du$$

Thus, the final result of our integral is as follows:

$$v=-\frac{\cos\left(u\right)|\sin\left(u\right)|\ln\left(\sin\left(u\right)+1\right)+\left(-\cos\left(u\right)\ln\left(1-\sin\left(u\right)\right)+2C_1\cos\left(u\right)+4u\right)|\sin\left(u\right)|}{2\sin\left(u\right)}+C_2$$

Numerical analysis of Geodesics on a Pseudospherical Surface

The differential equation governing the geodesics is given by:

$$\frac{dy}{du}=-\frac{sin^3u}{cosu}\left(y\right)^3-ctgu\left(y\right)^2-\frac{1+2cos^2u}{cosusinu}\left(y\right)$$

where *u* represents the parameter along the geodesic, and *y* denotes the derivative of the geodesic function. This equation describes the behavior of geodesic curves on a pseudospherical surface and is solved numerically using the LSODA method.

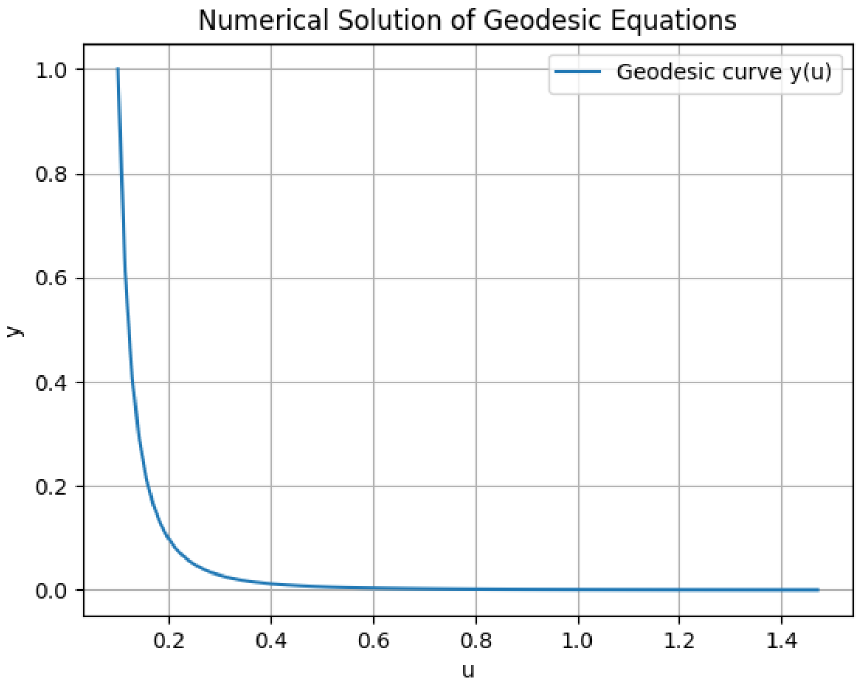
The following Python implementation provides a computational approach to solving and plotting these geodesic curves:

- import numpy as np
- import matplotlib.pyplot as plt
- from scipy.integrate import solve_ivp
- def geodesic_ode(u, y):
- Geodesic equation:
- dy/du = – (sin^3(u)/cos(u)) * y^3 – (cot(u)) * y^2 – ((1 + 2*cos^2(u)) / (cos(u)*sin(u))) * y
- if np.isclose(np.cos(u), 0) or np.isclose(np.sin(u), 0):
- return [0] # Prevent division by zero
- dydu = (–np.sin(u) ** 3 / np.cos(u)) * (y ** 3) \

– (1 / np.tan(u)) * (y ** 2) \
– ((1 + 2 * np.cos(u) ** 2) / (np.cos(u) * np.sin(u))) * y

- return [dydu]
- # Initial conditions
- u0 = 0.1 # Initial parameter value
- y0 = 1 # Initial condition y(0) = 1
- # Calculation interval (avoiding singularities)
- u_span = (u0, np.pi / 2–0.1)
- u_vals = np.linspace(*u_span, 100)
- # Numerical solution using LSODA
- sol = solve_ivp(geodesic_ode, u_span, [y0], t_eval=u_vals,
- method='LSODA')
- # Diagnostic output
- print("Solver success:", sol.success)
- print("Solution shape:", sol.y.shape)
- print("Computed points:", sol.t)
- # Visualization of the geodesic curve

```
• if sol.success and sol.y.shape[0] > 0:
• plt.plot(sol.t, sol.y[0], label=' Geodesic curve y(u)')
• plt.xlabel('u')
• plt.ylabel('y')
• plt.legend()
• plt.grid()
• plt.title(' Numerical Solution of Geodesic Equations')
• plt.show()
```



The graph presented here represents the numerical solution of the geodesic equations.

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Contact: feruzamakhsatulloeva@gmail.com

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Section 4. Technical sciences in general

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THE EFFECT OF POLYMER SULFUR OBTAINED FROM TECHNICAL SULFUR ON BITUMEN ADHESION

[1] ***Yusupov Farkhod,1 Khursandov Bobomurod,1 Yuldashov Fazliddin***

[1] Institute of General and Inorganic Chemistry of the Academy
of Sciences of Uzbekistan. Tashkent, Uzbekistan

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Abstract

The article investigates the optimal conditions, structure, and properties of polymer sulfur obtained from local sulfur raw materials. A composition was developed using secondary phenol and sulfur. Sodium hydroxide was utilized as an initiator in creating the composition. IR spectroscopy was employed to determine the optimal conditions for polymer sulfur. Based on the research results, the interactions between bitumen and mineral material were studied, focusing on the mechanical theory and electrostatic theory of adhesion properties.

Keywords: Composition, polymer, adhesion, destruction, modifier. modification, plastomers, thermoplastic elastomers, copolymer, dispersion, cohesion, viscosity

Introduction

Currently, the chemical, petrochemical, metallurgical, and gas processing industries produce over 70 million tons of elemental sulfur as a by-product. Due to the high corrosive properties of sulfur compounds and their significant environmental impact, processing them is of great practical importance. One of the areas where sulfur and its compounds are widely used is in construction and road building. Therefore, synthesizing polymer sulfur based on elemental sulfur and developing effective methods for producing polymer sulfur-containing bitumen products using this compound are of great importance. Although sulfur is widely used in many areas of chemical production, it is the construction industry that can consume such large quantities of sulfur (W. J. Chung, 2013). In particular, one of the promising directions is the production of sulfur-containing binding materials used in road surfaces. The inclusion of sulfur in road coating binders, on one hand, reduces the cost of road coatings, while on the other hand, it serves to improve the rheological properties of the coating (N. P. Tarasova, 2021). Sulfur does not conduct electricity. It dissolves well in organic solvents such as carbon disulfide, toluene, and pure ammonia. However, it is practically insoluble in water and most inorganic acids. The main physical and mechanical properties of sulfur are shown in the following table (M. Porto, 2019).

Table 1. *The properties of technical sulfur*

Indicators	**Temperature, °C**		
	20	**122**	**150**
Density, g/cm^3	2,1	1,96–1,99	1,6–1,81
Durability, MPa	12–22	–	–
Stiffness on a matching scale	1–2	–	–
Viscosity, Pa·c	–	0,011–0,012	0,0065–0,0070
Surface tension, H/м	–	–	0,055
Heat capacity, kJ/kg	0,7	1,47	1,84

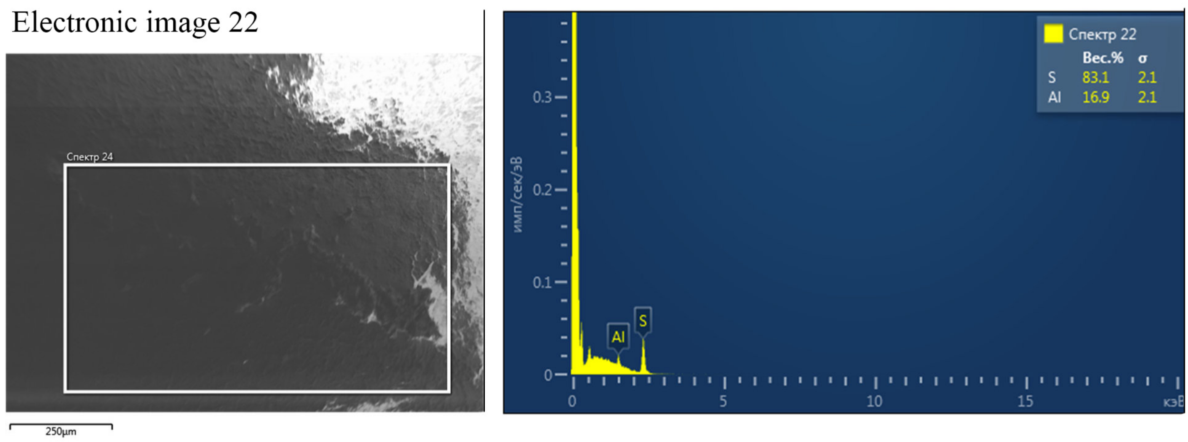
Numerous studies are also being conducted on bitumen modification to obtain high-quality bitumen. Among all bitumen modification methods, polymer modification is considered one of the most popular.(S. Pyshev, 2016) Polymer modification of bitumen involves introducing polymers into bitumen through mechanical mixing or chemical reaction.(V. Gunka, 2021) Among the various polymers studied are plastomers (e.g., polyethylene (PE), polypropylene (PP), ethylene vinyl acetate (EVA), ethylene butyl acrylate (EBA)) and thermoplastic elastomers (e.g., styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), and styrene-ethylene/butylene-styrene (SEBS)).(G. Polacco, 2005) It has been reported that these polymers can improve certain properties of bitumen, such as high stiffness at high temperatures, high crack resistance at low temperatures, good moisture resistance, or extended lifespan.(B. Sengoz, 2009) Polymer modification of bitumen is the introduction of polymers into bitumen by mechanical mixing or chemical reaction.(V. Gunka, 2021) Among the various polymers studied are plastomers (e.g. polyethylene (PE), polypropylene (PP), ethylene vinyl acetate (EVA), ethylene butyl acrylate (EVA)) and thermoplastic elastomers (e.g. styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), and styrene-ethylene/butylene-styrene (SEBS)). It has been shown that these polymers may improve some of the bitumen's properties, such as high hardness at high temperatures, high crack resistance at low temperatures, good moisture resistance, or increased lifespan (B. Sengoz, 2009).

EVA (ethylene vinyl acetate) is a thermoplastic substance formed by copolymerization of ethylene and vinyl acetate monomers. These binders are produced by dispersing the polymer in bitumen at a specified temperature. The modification of bitumen with EVA has the following advantages: increased adhesion of the binder to the mineral filler, improved cohesion (over a wider temperature range), increased resistance to deformation (due to increased viscosity of the binder), increased tensile strength, and reduced temperature sensitivity (C. Rodriguyes, 2015).

Method

Technical sulfur from the Mubarek Gas Processing Plant, secondary phenol, BND 60/90 grade bitumen from the Jarkurgan district of Surxondaryo Region, marble, granite, and gravel were selected as materials for the study. Infrared (IR) spectroscopy was used to examine the structure of polymer sulfur. Elemental analysis was conducted using a scanning electron microscope (SEM) to determine the purity level of technical sulfur, which is a waste product of the Mubarek Gas Processing Plant.

Figure 1. *SEM results of technical sulfur*



Results

Technical sulfur is heated at 125 °C while being rotated at a speed of 60 rpm. During heating, secondary phenol was added in an amount of 4% of the sulfur mass. Sodium hydroxide was used as the initiator. The mixture of sulfur and secondary phenol was stirred for one hour until it reached a homogeneous state. Without stopping the stirring, the temperature was raised to 165 °C, and the mixture was stirred for another 2 hours. Afterward, the liquid sulfur was cooled to room temperature and solidified.

The obtained polymer sulfur was studied based on physicochemical investigations. The interaction between sulfur and phenol was examined using IR spectroscopy, which revealed significant changes in the O-H group region (V_{max}, cm^{-1}: 3374). Peaks at 2917 cm^{-1} and 2850 cm^{-1} indicated the presence of methyl (CH_3) and methylene (CH_2) groups in the composition of aliphatic hydrocarbons. Peaks at 2101 cm^{-1} and 1993 cm^{-1} indicated the presence of triple bond (C=C) groups. The presence of aldehyde or ketone groups was shown by peaks in the region of 1740.72 cm^{-1}. C=C bonds, which are part of the aromatic ring, formed peaks at 1586 cm^{-1} and 1486 cm^{-1}. C-H deformation vibrations in the region of 842 cm^{-1} and 756 cm^{-1} confirmed the existence of a benzene ring. The low-frequency peaks presented in the spectrum at 756 cm^{-1} and 465 cm^{-1} were found to correspond to S-S bonds.

Figure 2. *IR spectrum of polymer sulfur obtained from phenol (secondary phenol) containing additional substances*

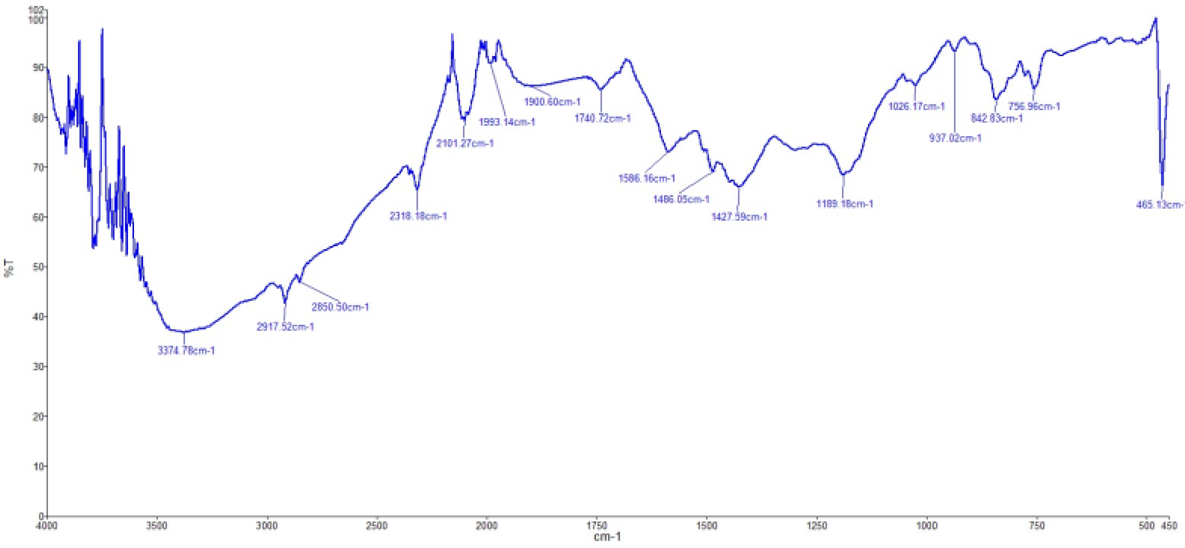


Table 2. *Study and evaluation of the adhesive properties of BND-60/90 bitumen and polymer sulfur-based binders to mineral materials*

The binder	**Mineral material**					
	Granite stones		**Granite gravel**		**Marble**	
	% cover	**score**	**% cover**	**score**	**% cover**	**score**
BND-60/90	76	3	74	2	78	3
BND-60/90 + 3% (PO)	82	3	77	3	86	3
BND-60/90 + 5% (PO)	86	3	84	3	90	4
BND-60/90 + 10% (PO)	92	4	90	4	93	4
BND-60/90 + 15% (PO)	89	3	87	3	89	3
BND-60/90 + 20% (PO)	91	4	89	3	93	4
BND-60/90 + 25% (PO)	93	4	90	4	95	5
BND-60/90 + 30%(PO)	96	5	92	4	97	5
BND-60/90 + 35%(PO)	92	4	88	3	91	4

Based on the data in Table 1, dependency graphs shown in Figures 3 and 4 have been constructed. The highest level of adhesion to granite, gravel, and marble was achieved when the polymer sulfur content was added up to 10%. As we increased the amount of polymer sulfur beyond 10%, the degree of adhesion to the materials decreased.

Note: Explanation of scores: 2 – "unsatisfactory" – the binding film covers less than 75% of the pebbles' surface; 3 – "satisfactory" – the binding film covers up to 90% of the pebbles' surface; 4 – "good" – the binding film covers up to 95% of the pebbles' surface; 5 – "exemplary" – the binding film covers more than 96% of the pebbles' surface (P. Kumar, 2014).

Figure 3. *Adhesion of BND 60/90 road bitumen to mineral materials by adding polymer sulfur in amounts of 3, 5, 10, and 15%*

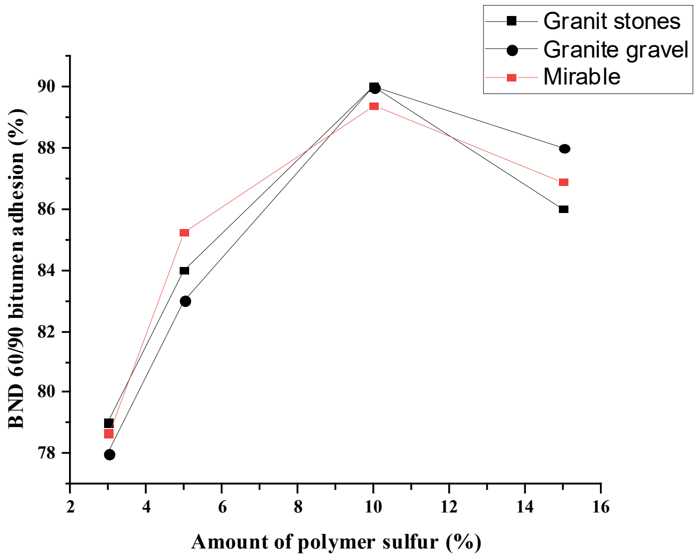
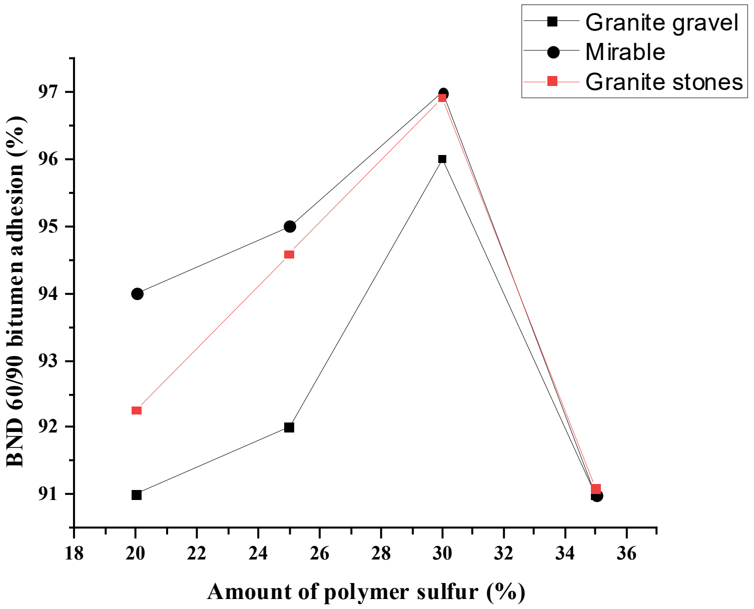


Figure 4. *Adhesion of mineral materials to road bitumen BND 60/90 with the addition of polymer sulfur in amounts of 20, 25, 30, and 35%*



As the amount of polymer sulfur increased, the degree of adhesion to granite stones, granite gravel, and marble increased. The highest adhesion level was achieved when the sulfur content reached 30%. As the amount of polymer sulfur exceeded 30%, its adhesion began to decrease. When we increased the amount of polymer sulfur to 35%, the quality of adhesion with granite, gravel, and marble decreased.

Conclusion

According to the research results, the studied mechanical theory and electrostatic theory demonstrate the importance of the physical properties of granite stones and granite gravel for studying adhesive properties: the surface morphology promotes adhesion and induces selective adsorption, and the nature of the mineral material's surface interacts with adhesive properties. The theories of chemical bonding and thermodynamics have also been thoroughly studied, and the following conclusions have been drawn.

According to the theory of chemical bonds, insoluble stable complexes are formed in bitumen, ensuring adhesive strength in the interphase region of the mineral. Based on the thermodynamic theory, the necessary conditions for adhesive properties and the establishment of a close connection between the two phases have been determined. Based on the two theories of studying adhesive properties considered, the following conclusion was drawn. The smoothness, roughness, surface chemisorption of mineral materials, and various other approaches were observed, and their interaction with bitumen was determined.

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Contact: temirovgolib1995@gmail.com

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STEP-BY-STEP CONTROL OF THE TECHNOLOGICAL PROCESSES IN THE PRODUCTION OF KAPPASPIN SUBSTANCE

Botirov R. A. [1]***, Sadikov A. Z.*** [1]***, Sagdullayev Sh. Sh.*** [1]***,***
Xalilov R. M. [2]***, Bekmurzayeva N. B.*** [2]

[1] Institute of the Chemistry of Plant Substances named after Acad. S. Yu. Yunusov
of the Academy of the Sciences Republic of Uzbekistan, Uzbekistan

[2] Department of Pharmacology and Clinical Pharmacy,
Tashkent Pharmaceutical Institute, Uzbekistan

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Abstract

This article presents the results of experiments conducted to determine the loss of the main product and yield efficiency during the technological stages of producing the Kappaspin substance from the buds and unripe fruits of the *Capparis spinosa* L. plant. It also describes the method for determining the residual amount of the organic solvent ethanol in the cappaspin substance. The results showed that the loss of Kappaspin substance, based on the plant raw material, accounted for 25%, while unaccounted losses were 5%. The yield efficiency of Kappaspin substance was found to be 70%. Furthermore, it was determined that the allowed maximum concentration of ethanol, an organic solvent in the Kappaspin substance, should not exceed 0.5%, or 5000 ppm.

Keywords: *Capparis spinosa L. substance, Kappaspin, analytical method, technological properties*

Introduction

The literature mentions that the unripe fruits and flowers of *Capparis spinosa* L. are rich in vitamins. Its fruit contains mainly vitamins K and B, potassium, calcium, iron, magnesium, and many other elements, displaying various biological activities (Tazhibaev G. G., Inagamov S. Ya., 2023; Farzad Kianersi, Mohammad Reza Abdollahi, Asghar Mirzaie-asl, Dara Dastan & Faiza Rasheed 2020; Sambasivam Manikandaselvi, Pemaiah Brindha, Vellingiri Vadivel. 2018; Murodjon Isagaliev, Evgeny Abakumov, Avazbek Turdaliev, Muzaffar Obidov, Mavlonjon Khaydarov, Khusnida Abdukhakimova, Tokhirjon Shermatov, and Iskandar Musaev. 2022). The above-ground part of *Capparis spinosa* L. contains 0.32% rutin, quercetin, up to 150 mg/% vitamin C, stachydrin, thioglucoside, saponins, coloring substances, while the fruit contains up to 36% sugars, 25–25.6 mg/% vitamin C, 1.46% flavonoids, and thioglucoside. The seed contains 25–36% oil, the root contains 1.2% alkaloids (stachydrin), 0.44% flavonoids, 4.5% sugars, coumarins, and other substances. The buds (flowers) of *Capparis spinosa* L. contain 25% protein, 3% fat, 5% rutin, 150 mg/% vitamin C, and others. Avicenna (Ibn Sina) used *Capparis spinosa* L. to treat respiratory diseases, gastrointestinal disorders, and as a pain reliever, wound healer, and emetic. The primary usable parts of the plant are the flower buds and unripe fruits. Additionally, in the traditional medicine of China, Iran, Morocco, Pakistan, Egypt, and Arab countries, various parts of the plant (roots, stems, and leaves) are widely used (Tlili N., Elfalleh W., Saadaoui E., Khaldi A., Triki, S., Nasri N., 2011).

Mishra P. R. and (Mishra P. R., Panda P. K., Chowdary K. A. and Panigrahi S., 2012) his co-authors studied the effects of the fruit extract of *Capparis spinosa* L. on diabetic conditions in rats. The results showed a decrease in plasma glucose levels, an increase in insulin levels, and restoration of glycogen composition and enzyme activity related to carbohydrate metabolism. Histopathological examination of the pancreas revealed the enlargement of Langerhans islets and a reduction in neutral fats.

At the Institute of Plant Chemistry, scientific research was conducted on the development of a technology for producing the Kappaspin substance, composed of polysaccharide aggregates, from the buds and unripe fruits of *Capparis spinosa* L. (Botirov R. A., Saidova G. E., Mutalova D. K., Sanoev A. I., Sadikov A. Z., Sagdullaev Sh. Sh., 2022). As a result of the studies, a production technology for the Kappaspin substance was developed, and the polysaccharide content, monosaccharide residues, and pharmacotoxicological properties of the obtained samples were determined (Botirov, Ruzali A., Saidova, Gavkhar E., Mutalova, Dilnoza K., Sadikov, Alimdjan Z., and Sagdullaev, Shamansur Sh., 2024; Zhauynbaeva K. S., Botirov R. A., Sadikov A. Z., Sagdullaev Sh. Sh., 2022; Mirzaev, Ruzimov E. M., Botirov R. A., Saidova G. E., Sadikov A. Z. Sagdullaev Sh.Sh., 2023; Bekmurzayeva Nurjamal Baxtiyarovna, Botirov Ruzali Anvarovich, Azamatov Azizbek Azamatovich, Tursunkhodzhaeva Firuza Muratovna, Aytbayeva Aygul Baxtiyorovna, Sadykov Alimdjan Zairovich, Sagdullayev Shamansur Shaxsaidovich. 2024; Bekmurzayeva N. B., Botirov R. A., Azamatov A. A., Tursunkhodzhaeva F. T. Sadykov A. Z., Sagdullayev Sh. Sh., Sultanova R. K., 2024). Continuing our research, we aimed to determine the loss of polysaccharides and yield efficiency during the technological processes of Kappaspin substance production. For this, we determined the quantitative proportion of polysaccharides in the buds and unripe fruits of *Capparis spinosa* L. using the following method.

Materials and methods

An analytical sample of the raw material was taken and ground until it passed through a sieve with 2 mm holes. A 10 g (accurately measured) portion of the ground, sieved sample was placed into a 250 ml volumetric flask with a round bottom, to which 200 ml of water was added. The flask was connected to a condenser and heated on an electric stove for 30 minutes while stirring. The extraction was repeated twice: first with 200 ml of water, then with 100 ml of water. The aqueous extracts were combined and centrifuged for 10 minutes at 5000 rpm. Next, a 500 ml volumetric flask was taken, and a glass funnel with a 55 mm diameter was placed on it, covered with a 5-layer gauze soaked in water. The extract from the centrifuge was passed through the gauze, washed with water, and the volume was adjusted to the mark with water (solution A).

From solution A, 25 ml was taken, placed in a centrifuge tube, and 75 ml of 95% ethanol was added, mixed well, heated in a water bath at 30 °C for 5 minutes, and left for 1 hour. After the designated time, the mixture was centrifuged for 30 minutes at 5000 rpm. The liquid was separated, and the residue was dried at 100–105 °C until a constant weight was achieved. A 16 mm diameter glass filter with holes was used under vacuum pressure (13–16 kPa) to filter the residue. The remaining sediment was filtered again, washed with 15 ml of 95% ethanol-water mixture (3:1), followed by 10 ml acetone and 10 ml ethyl acetate. The filter containing the sediment was dried first in the open air and then at 100––105°C until a constant weight was achieved.

The content of polysaccharides in the plant raw material (X) was calculated based on the absolute dry weight using the following formula:

$$X = \frac{\left(m_2 - m_1\right) \cdot 500 \cdot 100 \cdot 100}{m \cdot 25 \cdot \left(100 - W\right)}$$

Here, m_1 – is the mass of the filter in grams;

m_2 – is the mass of the filter along with the sediment in grams;

m – is the mass of the raw material in grams;

W – is the percentage of mass loss during the drying of the raw material.

The content of polysaccharides in the samples of *Capparis spinosa* L. buds varies between 9.5% and 15.5%, depending on the vegetative phase and the growth location.

In the immature fruits of the plant, this indicator was 4.5–7.8%. Each analysis was repeated at least three times for each sample.

The final technological stage in the production of the substance obtained from the buds and immature fruits of *Capparis spinosa* L. involves the precipitation of polysaccharides in ethyl alcohol and their washing, which necessitated the control of the residual ethyl alcohol content in the substance. To determine the residual ethyl alcohol, gas-liquid chromatography was used. Chromatograms were obtained on a gas-liquid chromatograph under the following conditions, each sample being taken at least 5 times:

- Flame-ionization detector;
- 3.0×2500 mm glass column;
- Sorbent with particle size of 0.16–0.20 mm, N-AW-DMCS;
- 5% SE-52 liquid phase;
- Evaporator temperature 150 °C;
- Column temperature 40 °C;
- Carrier gas (nitrogen) flow rate 30 ml/min.

For obtaining chromatograms, a sample of 0.5 g (accurate weight) of the polysaccharide substance was taken and placed in a 25 ml volumetric flask. 5 ml of water for injection was added to the flask, and the sample was dissolved. The solution was then made up to the mark with the same solvent. The solution was filtered through a glass filter with pores of 0.45 µm, and 1.0 µl of the filtered solution was injected into the chromatograph's injector. Also, a working standard sample of ethyl alcohol was prepared. 25 ml of water, cooled to 10 °C, was added to a 100 ml volumetric flask, followed by 0.2 g (accurate weight) of ethyl alcohol. The mixture was stirred. Then, more water was added to bring it to volume, and the mixture was stirred (Solution A). 50 mL of Solution A was transferred to a 100 ml volumetric flask, and water was added to bring it to volume and stirred (Solution B). 5 ml of Solution B was transferred to a 100 mL volumetric flask, and water was added to bring it to volume and stirred (Solution C). The solution should be used within 30 minutes of preparation. Checking the suitability of the chromatographic system. The ethyl alcohol standard sample (1.0 µL) is injected five times. The chromatographic system is considered suitable if the separation factor between the two components is at least 1.0 and the relative standard deviation of the repeatability is no more than 15%. Identification of ethyl alcohol is performed by comparing the retention times of the peaks of the sample being analyzed and the ethyl alcohol standard. Method. 1.0 µL of the sample to be analyzed and the ethyl alcohol working standard are injected into the apparatus. Five chromatograms are taken, and the area of each peak is recorded. The residual ethyl alcohol content in the preparation (Q, %) is calculated using the following formula:

$$Q = \frac{S_i \cdot 25 \cdot M_m \cdot 100\%}{S_m \cdot M_i \cdot 100_1}$$

"Here; S_i – the area of the peak of the sample being analyzed in the chromatogram, mm²;

25 – the volume of the sample being analyzed, ml;

M_m – the amount of the ethyl alcohol working standard, g;

S_m – the area of the peak of the ethyl alcohol standard in the chromatogram, mm²;

M_i – the amount of the sample being analyzed, g;

100 – the volume of ethyl alcohol, ml.

The efficiency of this method is equal to 1.05. If the efficiency criterion (N) is within the range of 1 to 2, the system is considered efficient.

It was determined that the residual amount of ethyl alcohol in all the samples analyzed was below the allowed upper limit (3550–4800 ppm).

Results and Discussion

During the experiments, the total amount of water-soluble polysaccharides in the raw materials, alcoholic extracts, aqueous extracts, press cake, chloroform extract, aqueous residue, technical product, alcoholic residue, and final product was analyzed. The results of the yields and losses of the main product are presented in the following table (table 1).

Table 1. *Step-by-step control of technological processes (main yields and losses)*

Objects being studied	Amount of Kappaspin substance, %	
	Relative to the mass of the raw material	Yield efficiency relative to the amount in the raw material
Raw material	6	100
Alcoholic extract	0,3	5,0
Aqueous extract	5,4	90
Plant residue (press cake)	0,3	5,0
Chloroform extract	0,3	5,0
Aqueous residue	5,1	85
Technical product	4,5	75
Alcoholic solution	0,6	10
Kappaspin substance	4,2	70
Unaccounted losse	0,3	5,0

Conclusions

As a result of the scientific research conducted, a step-by-step control method for the technological processes of *Capparis spinosa* L. plant's water-soluble polysaccharide yield in industrial production was developed for the Kappaspin substance. According to this method, the losses accounted for in the plant raw material were determined to be 25%, unaccounted losses were 5%, and the yield of the Kappaspin substance was 70%, as established through experiments. It was also determined that the maximum allowable concentration of the organic solvent, ethyl alcohol, in the Kappaspin substance is 0.5%, or 5000 ppm.

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Contact: botiroovr@mail.ru

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PRODUCTION OF PETROLEUM ROAD BITUMEN BASED ON MODIFIED WEIGHTED TARS

Khujakulov Aziz Fayzullayevich [1], ***Abdullayeva Shokhista Shukhratovna*** [1]

[1] Bukhara Engineering and Technology Institute

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Abstract

The reduction of crude oil reserves in the world requires the development and implementation of technologies to increase the depth of oil refining. In this regard, oil refineries are reconstructing the vacuum distillation units of fuel oil in order to maximize the selection of vacuum gas oils, which are valuable raw materials for secondary oil refining processes.

Keywords: *oil, bitumen, tar, oxidation, hydrocarbon, paraffin*

Today, technological progress cannot be imagined without the development of motor transport and the construction of high-speed highways. In this regard, petroleum bitumen as a commercial petroleum product and a binder for the preparation of asphalt concrete is in demand in the national economy of each country.

Petroleum (artificial) bitumen obtained by processing petroleum raw materials is widely used in road construction. Artificial (technical) bitumen – residual refined products of oil, coal, and shale. They are similar in composition to natural bitumen. Natural bitumen is a viscous resinous substance formed from heavy oil fractions as a result of prolonged weathering. It occurs in the form of stratified vein deposits, as well as lakes in places where oil naturally reaches the earth's surface (Makhmudov M.Zh., Khaitov R. R., Narmetova G. R., 2014).

The first designation of bitumen comes from the word "jatu" (Sanskrit), which meant resin released from some trees, which eventually transformed into "Gvitymen" (resinous, sticky), and in Latin, it was simplified to "bitumen" and eventually passed into all European dictionaries (Makhmudov M.Zh., Khalilov A. Kh., Khaitov R. R., Narmetova G. R., 2017).

The use of natural bitumen (asphalt) has been known since the dawn of civilization. The oldest structure using natural asphalt -bitumen-bearing rock was discovered in India (Makhmudov M.Zh., Yomgurov S. A., 2023). It is known that natural bitumen – asphalt was used as an adhesive material in 2500–3000 BC by the people who inhabited the Euphrates Valley. As a construction site

Bitumen was used by the Babylonians (700–500 BC) to build the inner and outer walls of Babylon. During the reign of Semiramis (about 700 BC), a tunnel was built under the Euphrates in Babylon, about 1 km long, made of burnt bricks coated with bitumen. Asphalt was also used in the construction of the famous hanging gardens of Semiramis (Makhmudov M.Zh., Khalilov A.Kh., Khaitov R. R., Narmetova G. R. 2017; Makhmudov M.Zh., Yomgurov S. A. 2023). In ancient Egypt 5,000 years ago, the floor and walls of grain storage barns were covered with asphalt.

In 400–500 BC, fortress walls were built of bricks in Media, bonded with bitumen. The first sections of the Great Wall of China were built on bitumen. Bitumen and asphalt were used for the construction of buildings and towers, water and drainage channels, tunnels, and in medicine for the mummification of corpses, etc. (Dzhamolovich M. M., Ugli Y. S. A., 2024). In the 19 th century, the streets of all cities of the world were paved with stones, and it was only in the period 1832–1835 that the experience of paving city streets and sidewalks of Paris with asphalt was mentioned. Later, in 1835–1840 Bitumen was used in the construction of roads in London, Vienna, Lyon, Philadelphia and other cities (Makhmudov M., Nematov H., Rizayev S. 2023). In connection with the discovery of deposits of bitumen-bearing rocks in France, Switzerland, Germany, in 1700–1800.

In Western Europe, work begins on their use in the construction of floors., sidewalks and waterproofing. In 1835, the first sidewalks were laid in Paris, then in London, three years later in Philadelphia (Murtazaev F. I., Makhmudov M. Zh., Naubeev T. Kh., 2021). Since the middle of the 19th century, in France, the USA, Switzerland and other countries, road surfaces have been made from bitumen-mineral mixtures. For example, the first asphalt concrete coating was first used in France to cover the sidewalks of the Royal Bridge in Paris. In the Russian Empire, the first asphalt pavement was carried out in 1866 in St. Petersburg, and in 1869 in Moscow. In Kronstadt using Hanoverian bituminous rock, although by that time several deposits of bitumen-containing rocks had already been discovered in Russia. The first of them (bituminous limestones) was discovered in Syzran in 1724, and in 1871 an asphalt mastic manufacturing plant began operating in this city. In the USA, cast asphalt prepared using natural bitumen was first used in 1876 (Makhmudov M. Zh., Yomgurov S. A., 2023).

The composition of bitumen is characterized by its elemental and group chemical composition.

Elemental composition of bitumen (% by weight): carbon – 80–85; hydrogen – 8–12.5; oxygen – 0.2–4; sulfur – 0.5–10; nitrogen – 0.2–0.4. The content of some metals in asphalt oil concentrates (such as Arlanskaya) is (% by weight): V – 0.22; Ni; –0.115; Fe – 0.110; Ca – 0.054, etc. The average molecular weight of bitumen does not exceed 700–800 k.e (Makhmudov M. J., Yuldashev T. R., 2023).

Given the wide variety of individual chemical compounds that make up bitumen, data on their group chemical composition is usually used to determine their chemical composition.

The group chemical composition of bitumen provides for the division of all the various individual chemical compounds included in bitumen into three main groups: asphaltenes, resins and oils (maltenes).

Oil is divided into three groups according to its suitability for bitumen production (Maxmudov M. J., Ne'matov X.I., 2023; Llewellyn, P. L. et al., 2008):

1. Highly resinous low-paraffin, resinous low-paraffin, high-resinous paraffin. The composition of such oils corresponds to the condition $A + C - 2.5N \geq 8$, where A is the content of asphaltenes, C is the content of resins, and P is the content of paraffins.

2. Resinous paraffinous, low–resinous low-paraffinous, the composition of which meets the condition $A + C - 2.5\ P$, ranges from 0 to 8 with $A + C$ more than 6.

3. Three types of oil unsuitable for bitumen production: resinous high–paraffin, low-tar paraffin and low-tar high-paraffin, the composition of which meets the condition $A + C - 2.5\ P$, ranges from 0 to 8 with $A + C$ less than 6, and also if $A + C - 2.5\ P$ less than 0.

Heavy resinous low-paraffin oils are the best raw materials for the production of road bitumen.

The presence of de-asphalting asphalts and cracking residues in its composition has a negative impact on the quality of crude oil.

The main goal of forming the qualitative characteristics of raw materials is aimed at forming nanostructured bitumen from it. As is known, oxidation reactions of heavy oil residues occur with the formation of micelle asphaltene nanoaggregates that grow into cluster nanoaggregate structures. The properties of the resulting bitumen binders depend on how the nanoclusters interact with each other, the size of the asphaltene clusters and the rate of formation of the mesh framework of the clusters of asphaltene nanoaggregates.

The decisive factors in choosing a technology are temperature, time, and rate of oxidation reaction.

Professor F. G. Unger (Maxmudov M. J., Ne'matov X.I., 2023) pointed out that "the size and structure of each colloidal particle depend on the equilibrium of the kinetic motion energies of the molecules and the potential of their pair interaction. The conditions of the technological process of formation, existence and destruction of supramolecular structures (associative combinations, micelles, complex structural units, macromolecules) of petroleum dispersed systems of resinous-asphaltene substances determine the structure and physico-chemical properties of bitumen.

Bitumen systems are thermodynamically mobile systems in which hemolytic transitions (of diamagnetic molecules to paramagnetic and vice versa) are continuously carried out and it is paramagnetic molecules and hemolytic processes that cause the rearrangement of the supramolecular structures of petroleum dispersed systems, i.e. they determine the behavior of the system as a whole and the conditions for the formation of the structure when the external conditions of the technological process change.

Analysis of numerous data from various instrumental research methods and their comparison indicate that heavy carbonaceous molecules or individual carbon atoms combine into large structures such as associates, polymers or crystal lattices due to spin excitation and spin polarization through the influence of solvent and temperature."

This allowed us to conclude that there may be an equilibrium dynamics of the colloidal state of such complex objects as bitumen, and to formulate requirements for the parameters of technological effects on petroleum dispersed systems in order to obtain bitumen binders with specified properties.

The main production methods for viscous road bitumen are as follows (Artemova I. I., Kandaurov S.Yu., Bachalov I. S. et al., 2010):

1. Concentration of residual oil fractions by distilling them in vacuum in the presence of water vapor (obtaining residual bitumen).
2. Air oxidation of oil residues (fuel oil, tar, etc.), which makes it possible to obtain oxidized bitumen.
3. Mixing (compounding) of liquid oil residues with viscous residual or oxidized bitumen, solid natural bitumen (asphaltites, gilsonites).

Today bitumen production is emerging as a full-fledged segment of the oil refining industry. The introduction of new technologies in the processing of residual oil components based on the activation of raw materials due to physical and chemical effects using modern equipment, including devices using cavitation effects, ultrasonic and electromagnetic fields, etc., makes it possible to obtain high-quality road bitumen from most oils previously considered unsuitable for bitumen production.

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Contact: makhmudov.mukhtor@inbox.ru

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ANALYSIS OF COMPOSITION AND PROPERTIES OF OIL RESIDUES AND BITUMEN

Makhmudov M. J. [1], ***Komolov R. I.*** [1]

[1] Bukhara Institute of Engineering and Technology

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Abstract

With the increase in the volume of modern housing and road construction in the world, the demand for construction bitumen obtained from petroleum raw materials is also growing. Because petroleum bitumen has many advantages over bitumen obtained from other raw materials used in construction, has the necessary level of protection and strength in construction, and also has many advantages in terms of operational properties. This article presents an analysis of the main physical and chemical properties of oil residues and bitumen and their composition. The results of this analysis serve as a basis for further improvement of the properties of bitumen obtained from petroleum raw materials.

Keywords: *oil, oil residues, bitumen, tar, distillate, paraffinic hydrocarbons, aromatic hydrocarbons*

Introduction

According to the classification given by Kreutzer (Multykh M. E., Privalova N. M., Ezzhalkin M. M., Milovanova V. S., 2008), petroleum asphalt bitumen is visco – liquid or soft and ductile at normal temperature, or solid and brittle products of oil refining or its derivatives.

Objects and methods of research

From a chemical point of view, heavy petroleum residues (HNO) and bitumen are a complex mixture of high-molecular organic compounds of a hydrocarbon and non-hydrocarbon nature, which, along with carbon and hydrogen, include oxygen, sulfur and nitrogen, as well as a number of metals (Fe, Mg, V, Ni, etc.) (Knyazev Yu. V., Budantsev V. V., Frolov V. A., Merkulov S. A., 2015). The elementary composition of bitumen is as follows, mac. %: carbon 80.0–85.0; hydrogen 8.0–11.5; oxygen 0.2–4.0; sulfur 0.5–7.0; nitrogen 0.2–0.5 (Belyaev, V.P., 2013).

Due to the wide variety of compounds that make up TNF and bitumen, it is impossible to isolate any individual substances from this complex mixture in the current state of science and experimental technology. In addition, the bulk of the compounds that make up its composition are substances of a hybrid nature. The only class of compounds that can be isolated from bitumen in a more or less pure form is paraffins. All this is the reason that the chemical composition of bitumen is most often evaluated by the quantitative content of group components in it.

Results and their discussion

Currently, there is a certain opinion about the composition of individual bitumen fractions, their behavior during oxidation and their impact on quality.

It is known that petroleum bitumens consist mainly of three groups of substances: oils – compounds that are soluble in alkanes and desorbed by eluents; resins – compounds that are soluble in alkanes and desorbed from the surface of silica gel with benzene or its mixture with alcohol, but are not desorbed by alkanes; and asphaltenes-compounds that are insoluble in алканах C_{C5}–C7 alkanes$_7$ (Belyaev. 2012).

The oils are a mixture of aromatic and paraffin-naphthenic hydrocarbons. It should be noted that such a different content of hydrocarbon groups in oils affects the properties of bitumen in different ways. The very name of the group of paraffin-naphthenic hydrocarbons indicates the mixed nature of this fraction, which, along with paraffins of normal and iso-structure, may include polycyclic naphthenes, the latter usually exceeding 60% by weight. Polycyclic naphthenes are catacondensed naphthenic rings (4–5) that have alkyl substituents (Belyaev P. S., Zabavnikov M. V., Malikov O. G., 2008).

It is not always possible to isolate paraffin-naphthenic hydrocarbons in their pure form. They almost always contain a certain number of molecules, the chains of which include benzene and even naphthalenecycles, and sometimes cycles that include sulfur (Belyaev P. S., 2005). The only hydrocarbons of this bitumen fraction that do not have a hybrid structure aresaturated hydrocarbonsof normal structure (paraffins) and hydrocarbons of iso structure (ceresins).

According to Pajitnova (Amash, A., 2002), paraffin-naphthenic hydrocarbons are plasticizers in bitumen, and their replacement withmonocycloaromatic hydrocarbons cannot compensate for their plasticizing effect. Solid paraffins have a great influence on the properties of bitumen, their content in raw materials should not exceed 3–6%, and anincrease in these values, accordingto the authors (Nefedov B. K., Gorlova E. E., Gorlov E. G., 2008; Solov'ev E. M., Borisov E. M., Solov'ev M. E., 1998), leads to a sharp decrease in the structural and mechanical strength of bitumen. This served as the basis for creating a classification of oils in terms of theirsuitability for bitumen production.

Bitumen aromatic compounds are polycyclic condensed hydrocarbons that include one or two aromatic rings. Monocycloaromatic compounds are mainly represented by five-ring condensed systems with 2–– 4 metal substituents and one long alkyl substituent. The molecules of bicyclo-aromatic compounds consist of both one and two fragments, but the total number of aromatic rings in the molecules of such compounds is two. In addition, the molecules of mono-and bicycloaromatic compounds contain гетероатомы S, N, and O heteroatoms, but their number is relatively small – one atom per 3–5 molecules. S and N atoms belong to cyclic structures such as thiophene, pyrrol, and pyridine, while hydrogen atoms belong to peripheral functional groups.

Polycycloaromatic hydrocarbons are usually found in small amounts in bitumen. The main structural element of this group of hydrocarbons is condensed naphthalene-type systems, which are part of hybrid structures consisting of three or more cycles. In addition, their separation is difficult and most likely they are a transitionfraction from oils to resins.

Resins have a molecular structure similar to oils (Zinov'ev M., Berezhnaya O. N., Kutsenko G. V., Yarushina O. V., 2001), but are characterized by an even higher degree of condensation. The carbon skeleton of resin molecules is a polycyclic system consisting mainly of aromatic rings with a high degree of condensation and aliphatic substituents. At least 78% of the total number of protons in the" medium molecules " of resins are concentrated in saturated structures, and more than half of them belong to H protons that are not part of metal groups and CH2 groups$_2$, CH located in the a-positions of aromatic nuclei and heterones.

The elementary composition of resins is characterized by a high ratio of C and H content (C-79–87%, H– 8,5–9,5%) /36,37/. In addition, resins are characterized by a high content гетероатомов of S, N, and O heteroatoms, as well as metals. Most of the resins are made up ofneutral substances, and a smaller –part is made up of acidic substances. Sulfur is mainly a part of cyclic structures, its contentin resins can reach 10%, and the oxygen content is also high. Nitrogen is not always present in resins, although sometimes its content reaches 2% or more.

Most researchers (Milani, M., 2001) believe that nitrogen compounds (mainly cyclic structures) are so stable that even with the most severe heat treatment, they do not break down and pass into coke. In addition, researchers are of the opinion that resins are a genetically intermediate stagebetween oils and asphaltenes.

Asphaltenes – solid amorphous substancescolored in a dark color, from dark brown to black, have a great influence on the properties of bitumen.

Their density is greater than unity. When heated, they decompose without melting. When stored in the air, especially under the influence of sunlight or other types of radiation, asphaltenes pass into an insoluble state.

Asphaltenes –are the most complex components, which are a mixture of non-hydrocarbon high-molecular compounds of oil. Many researchers believe (Shakhovets S. E., 2006) that asphaltenes are a product of compaction of cyclic compounds, up to the creation of a flat spatialstructure.

Conclusions

A wide range of experimental data on the composition and content of various compounds that are part of heavyHO oils and bitumenis due to both the diversity of the composition of various oilsand different approaches to studying the structure of molecules. More recent studies are based on the association of high-molecular-weightoil compounds fromrelatively low-molecular-weight compounds.

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Contact: makhmudov.mukhtor@inbox.ru

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MODERN METHODS OF PRODUCING PETROLEUM BITUMEN

Makhmudov M. J. [1]***, Komolov R. I.*** [1]

[1] Bukhara Institute of Engineering and Technology

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Abstract

Today, the demand for petroleum bitumen in the world is growing day by day. Because the increase in the volume of construction of new modern structures and roads has caused an increase in demand for these construction bitumen. This article presents an in-depth theoretical analysis of modern and traditional methods for producing construction bitumen based on petroleum raw materials.

Keywords: *oil, oil residues, bitumen, tar, distillate, paraffinic hydrocarbons, aromatic hydrocarbons, naphthenes, polymers, modifiers*

Introduction

The main consumers of bitumen in our country and abroad are road, industrial and civil construction. More than 90.0% of the total bitumen production is spent on their needs. The raw materials for bitumen production are tars of primary oil distillation and other products of secondary processes of processing oil residues (extracts of oil production, extracts of the deasphalting process, cracking residues, etc.), in which high-molecular aromatic compounds, resins and asphaltenes are concentrated (Kemalov A. F., 2003).

Objects and methods of research

Bitumen is obtained by processing residual petroleum products in three main processes used in combination with each other or separately: centering oil residues by distilling them in vacuum in the presence of water vapor or inert gas (residual bitumen); oxidation with air oxygen of various oil residues (fuel oil, tar, semi-tar, deasphalting asphalts, selective oil purification extracts cracking residues or mixtures thereof) at a temperature of 180–300 °C (oxidized bitumen); compounding (mixing) of various oil residues with distillates and with oxidized or residual bitumen (Luksha O. V. Budadien, Opanasenko O. N., Krutko N. P., Loboda Yu. V., 2006).

The production of high-quality bitumen is influenced by the correct selection of the sequence of processes in the general technological scheme of oil refining of various nature (Mullahmetov N. R., Kemalov A. F., Kemalov R. A., Kostromin R. N., 2010).

When using TNF of oils with a high content of resinous-asphaltene substances and aromatic hydrocarbons, the technology provides for an oxidation process that contributes to the formation of an additional amount of structure – forming components-asphaltenes.

Methods for obtaining residual bitumen are based on the concentration of the residue – tar by deep selection of oil fractions from fuel oil in a vacuum column. At the same time, in the lower part of it, ready-made bitumen is obtained without oxidation. For the production of residual bitumen, raw materials with the highest possible content of asphalt-resinous substances are needed; the higher the ratio of asphaltenes: the better the properties and structure of bitumen, the less they are exposed to aging during operation.

Results and their discussion

In Uzbekistan, the main method for producing bitumen with various properties is the oxidation of heavy oil residues with air oxygen.

The composition and physical and chemical properties of commercial bitumen are affected by the technological conditions of the oxidation process. The main factors affecting the tar oxidation process are: the nature of the raw material, the initial softening temperature of the tar, the content of oils, paraffin and naphthenic compounds in it, the oxidation temperature, the flow rate of air supplied for oxidation, the contact surface, the duration of oxidation, the pressure in the reaction zone, the level of the liquid phase in the reactor, etc. (Priyanto S., 2001). The higher the ratio of asphaltenes to resins in oil and the lower the content of solid paraffins, the better the quality of bitumen obtained from them and the simpler the technology of their production.

Obviously, under conditions of bitumen oxidation, the second direction will be preferable, although in mild conditions the first path is also possible. The transition from asphaltenes to carbenes and carbides is noticeably observed during the oxidation of high-resinousmalt at temperatures above 300 °C (Kudryavtseva S. V., 2008; Thompson D. K., 1974).

According to many scientistsфазном окислении нефтяных остат, the accumulation of oxygen-containing products and acids does not always occur during the liquid-phase oxidation of oil residues with air oxygenкислородсодержа, which is usually observed during the oxidation of hydrogensеводородов.

According to the dataof (Kauchukovye modifikatory 1974; Aigul A. I., Linar I. K., 2010), the accumulation of low-molecular oxygen-containing compounds occurs at the beginning of the process and their amount is small: 0.02–0.03%. Other researchers (Islamutdinova A. A., 2010) observed the accumulation of oxygen throughout oxidation. Mostof the oxygen that enters the reactionis released as water. Thus, the role of oxygen in the oxidation of oil residues is mainly reduced to the role of a dehydrogenating agent.

The authors found (Thompson D. K., 1974) that paraffin-naphthenic hydrocarbons are the most resistant to oxidation, and they remain mostlyном, unconverted under oxidation conditions. E in which works reduction. The authors of (Islamutdinova A. A. 2010; Hayrudinov, I. R., Sharifullin, A. A. and Karimov, I. A., 2000) explain the decrease in the concentration of paraffin-naphthenic hydrocarbons observed in (Islamutdinova A. A. 2010; Hayrudinov, I. R., Sharifullin, A. A. and Karimov, I. A., 2000) some studies by distilling the most volatile components.

It is known from the authors work (Shirkunov A. S. 2007) that the oxidation of a mixture of hydrocarbons significantly differs in the rate and mechanism of oxidation of individual substances. In the presence of holonuclear arenes заметно снижается, а алкилированных аренов, the depth of chemical transformations of paraffin-naphthenic hydrocarbons is markedly reduced, while that of long-chain alkylated arenes increases, which was also confirmedin (Hayrudinov, I. R., Sharifullin, A. A. and Karimov, I. A., 2000; Shirkunov A. S., 2007).

The authors of (Khafizov E. R., 2003) present data on the relative oxidation rates at 80 °C of tars and individualhydrocarbons: cumene, decalin, octadecane, and dodecane. The tar oxidation ratewas 0.009 relativeto cumin oxidation, the rate of which is taken as 1.Such low valuesof the relative tar oxidation rate can be explained by the fact that the direction and depth of the process, as well as the nature of the interaction of oxygen with the components, are determined both bythe temperature of the process and by the group compositionof the tar.

Conclusions

Thus, when considering bitumen oxidation, the nature of the feedstock so strongly influences the nature of chemical transformations that it is necessary to select the optimal conditions for each type of raw material separately: temperature, air consumption, etc.

As already noted, TNF of high-paraffin oils is a poor raw material for bitumen production using traditional technology. However, from low-sulfur, high-paraffin oils, TNOs, it is possible to obtain road bitumen by changing the conventional technology. If the generally accepted technological scheme for the production of road bitumen is based on the sequential implementation of the processes of vacuum distillation of fuel oil and subsequent oxidation of the resulting tar to bitumen, then the reverse sequence of processes can be used: air oxidation of a part of fuel oil and vacuum distillation of a mixture of oxidized and non-oxidized fuel oil to bitumen.

However, the steadily increasing requirements for the quality and performance of petroleum bitumen cannot be met by the choice of raw materials alone. Thus, the introduction of new technologies in the processing of residual oil components, based on the activation of raw materials due to physical and chemical exposure, allows us to obtain high-quality road bitumen.

A large number of researchers solve the problem of improving the qualityof bitumen by adding a small number of modifiers, which makes it possible to obtain both materials for roadconstruction andspecial roofing, anti-corrosion, sealing, insulation and other materials. In recent years, there has been a tendency to actively involve various additives in the bitumen production directly in the oxidation process in order to give it the required operational qualities. Thefollowing chapter discusses the oxidation of bitumen in the presence of various additives.

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Contact: makhmudov.mukhtor@inbox.ru

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TYPES AND MAIN CHARACTERISTICS OF ALUMINUM-CONTAINING COAGULANTS

Makhmudov Mukhtor Jamolovich [1],
Haydarov Bekzodjon Abdumalik o'g'li [1]

[1] Bukhara Engineering and Technology Institute, Bukhara, Uzbekistan

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Abstract

Today, various coagulants are used in the world to purify various industrial waters produced in the oil and gas processing industry. This leads to an increased demand for coagulants. This article provides detailed instructions on how to obtain modern coagulants with preserved aluminum, their main characteristics and types.

Keywords: *oil, gas, technical waters, coagulant, aluminum, aluminum sulfate, aluminum oxide*

Aluminum – containing coagulant – $Al_2(SO_4)$ is widely used in the process of water purification. To a lesser extent, aluminum chloride is used, as well as sodium aluminate.

Currently, purified aluminum sulfate in production conditions is mainly obtained from aluminum hydroxide. This method is the simplest and most rational, it allows you to obtain a high-quality product with a low content of iron oxide.

Aluminum hydroxide is an intermediate product in the production of alumina, which is obtained by the Bayer alkaline method mainly from high-quality bauxite. Alumina is produced in smaller quantities from nephelines by sintering them with limestone, as well as from alunites by an alkaline reduction method (Khalilov S. Kh., Makhmudov M. Zh., 2022).

The production of aluminum sulfate consists of two main technological stages – decomposition of hydroxide with sulfuric acid and crystallization of the resulting product. The interaction of aluminum hydroxide with sulfuric acid is described by the reaction:

$$2Al(OH)_3 + 3H_2SO_4 + Q_q = Al_2(SO_4)_3 + 6H_2O + Q_q$$

In (Edelstein A. S., Cammarata R. C., 1998; Ostrovsky N. M., 2007), the solubility of aluminum hydroxide freshly deposited and obtained at alumina plants in dilute sulfuric acid solutions was studied, depending on particle size, impurity content, storage time, and methods for preparing hydroxides. It was found that fine-grained aluminum hydroxide is better soluble in sulfuric acid than coarse-grained. Long-term storage of hydroxide reduces the rate of its dissolution in sulfuric acid. Amorphous hydroxide dissolves faster than crystalline hydroxide.

Aluminum sulfate can be obtained by decomposition of aluminum hydroxide with a stoichiometric amount of 45–50% sulfuric acid at 110–120 °C for 40 minutes. By lowering the acid dose to 95–90%, a product with a higher content of aluminum oxide is obtained with satisfactory crystallizability (Chen S., Yuan, Z., Hanigan D., Westerhoff P., Zhao H., Ni J., 2018).

Aluminum sulfate is produced in periodic or continuous devices with a capacity of 10–150 thousand tons of product per year.

In (Du B. D., He T. T., Liu G. L., Chen W., Wang Y. M., Wang, W., Chen, D.M., 2018; Chuang S. H., Chang T. C., Ouyang C. F., and Leu J. M., 2007) the decomposition of high-iron bauxite with sulfuric acid was studied. Bauxite was characterized by the following chemical composition (in %): Al_2O_3–40.8; Fe_2O_3–27.0; SiO_2–8.7; TiO_2–2.2; CaO – 0.75; MgO – 0.2; Na_2O+K_2O – 0.5; pp.p. – 0.7. With an increase in temperature from 20 to 98 °C and the concentration of sulfuric acid from 10 to 60% extraction of aluminum and iron oxides into the solution increases, reaching 78.9 and 71%, respectively, at 98 °C and 1hour exposure. The degree of extraction of these components at boiling point depends on the duration of the process: with the decomposition of 60% H_2SO_4 bauxite, with an increase in the duration of the process from 5 to 90 minutes, the extraction of Al_2O_3 increases from 67.6 to 94%, and Fe_2O_3 – from 57.3 to 93.1%. boehmite bauxites are worse opened with sulfuric acid. Exposure to 10 n sulfuric acid for 1 hour leads to complete dissolution of gibbsite, partial (by 30%) – kaolinite and insignificant – boehmite. After firing at 550 °C and subsequent decomposition of bauxite for 3 hours, 90% Al_2O_3 is extracted into the solution.

In (Makhmudov M. Zh., Yomgurov S. A., 2023) it is proposed to decompose bauxite with dilute sulfuric acid at 135 °C in a steel reactor lined with acid-resistant tiles.

Initially, 93% H_2SO_4 is fed into the solution, it is diluted with washing waters from sludge washing and heated to a boil, after which bauxite is introduced in small portions to avoid foaming and $Al_2(SO_4)$ is obtained.

The process of obtaining aluminum sulfate from low-quality bauxites is described. Another source of aluminum-containing coagulant is kaolin clays.

In (Dzhamolovich M. M., Ugli Y. S., 2024) kaolins are difficult to open with sulfuric acid. Despite the large number of works devoted to the study of thermochemical transformations of kaolin, there is still no consensus on the mechanism of the process. Based on a complex of studies using physico-chemical methods, including X-ray phase analysis and IR spectroscopy, the mechanism of thermochemical transformations of kaolinite can be represented by the following reactions:

$$Al_2Si_2(OH)_4 \xrightarrow{450\text{-}550^{\circ}C} Al_2O_3 * 2Si_2O_2 + 2H_2O;$$

$$Al_2O_3 * 2SiO_2(OH)_4 \xrightarrow{830\text{-}850^{\circ}C} j\text{-}Al_2O_3 + 2SiO_2;$$

$$3(j\text{-}Al_2O_3) + 2SiO_2 \xrightarrow{900^{\circ}C} 3Al_2O_3 * 2SiO_2.$$

Aluminum alum is also used as coagulants, but they are used less often than aluminum sulfate, which is due to their high cost. In addition, alkali metal sulfates, which are part of aluminum alum, saline the purified water, reducing coagulating properties. Therefore, ammonium-, potassium- or sodium-aluminum alum is used, which has good coagulating properties, as well as more affordable and cheaper ones. Ammonia alum is used for the treatment of chlorinated water (Makhmudov M., Nematov H., Rizayev S., 2023).

An aluminum-containing coagulant can also be obtained from nepheline. In this case, it is advantageous to obtain alum, which is a more effective coagulant.

Nepheline reacts with sulfuric acid at room temperature with the release of a large amount of heat by reaction:

$$(Na, K) / AlSiO_4 / + 2H_2SO_4 + nH_2O \rightarrow (Na, K) / Al(SO_4)_2 * 12H_2O + SiO_2 + (n\text{-}12)H_2O\uparrow$$

The sulfatization process is greatly influenced by the concentration of sulfuric acid and its dose. The higher the concentration of sulfuric acid, the higher the temperature the reaction mass is heated due to the released heat of the reaction. At the same time, more water is released into the vapor phase and alum is formed with a lower content of crystallization water. As a result, anhydrous alum can be formed – double sodium-potassium aluminum sulfates. The choice of the acid concentration is primarily determined by the possibility of separating the silica sludge from the sulfuric acid solution (Ostrovsky N. M., 2007; Chen S., Yuan, Z., Hanigan D., Westerhoff P., Zhao H., Ni J., 2018).

In (Makhmudov M., Nematov H., Rizayev S., 2023), a method for obtaining $Al_2(SO_4)$ was developed from nepheline concentrate by a two-stage method. The product is decomposed in the first stage with nitric acid to produce potassium and sodium nitrates, and in the second stage the solid residue is treated with sulfuric acid to produce aluminum sulfate.

Until recently, the technology for producing aluminum dihydroxosulfate $Al_2(SO_4)_2(OH)$ has not been developed$\cdot 11H_2O$, therefore it was rarely used as a coagulant. However, extensive studies are currently being conducted at the Institute of Colloidal Chemistry and Water Chemistry of the Academy of Sciences of Ukraine, which show the effectiveness of this salt as a coagulant for wastewater and drinking water treatment (Makhmudov M.Zh., Salomov S. S., Savriev M. S., 2021). Aluminum dihydroxosulfate has a number of advantages over aluminum sulfate: it has a higher flocculating ability at low temperatures, requires less alkaline reserve and is effective in a wider range of pH values of the treated water (Aristov Yu.I., 2008).

Aluminum-containing coagulants also include chlorine-containing reagents. Aluminum chlorides and hydroxochlorides – $18Al_2(OH)_nC_{16-n}$ are most often used in water purification from chlorine-containing aluminum compounds. Currently, aluminum pentahydroxochloride – $Al_2(OH)_5Cl$, which has effective coagulating properties, is also widely produced on an industrial scale and is widely used for water purification. Aluminum pentahydroxochloride contributes to the intensive formation of flakes and precipitation of coagulated suspensions. When cleaning waters with a low content of suspended particles and salts, the consumption of this coagulant is significantly lower compared to classical aluminum sulfate. When using aluminum pentahydroxochloride, the range of optimal pH values of the treated waters is significantly expanded.

Aluminum pentahydroxochloride is characterized by lower acidity, so it is effective in purifying waters with small alkaline reserves. In comparison with aluminum sulfate, an equivalent amount of aluminum pentahydroxochloride reduces the alkalinity of water by six times when interacting with calcium bicarbonate. Aluminum pentahydroxochloride contains fewer chlorine ions, therefore, compared with aluminum sulfate, therefore, when used in purified water, there are fewer salts. In addition, the content of residual aluminum in the treated water is noticeably reduced (Patent. 2264589; Desai R., 1992).

One of the effective coagulants is aluminum pentahydroxochloride (Taran, V.N., 2004), which is characterized by higher amounts of water-soluble aluminum compared to other coagulants, and for its solutions there is no need to use anticorrosive protection and stainless steels to preserve pipelines and equipment. This coagulant has a long shelf life (Taran, V.N., 2004).

Chlorine technology is the most advantageous for processing hard-to-open and low-grade aluminum-containing ores, since the technological process provides for the production of aluminum chloride, which can be used as a coagulant (Buluchevsky E. A., 2011).

In (Kuvshinnikov I. M., 1987; Buluchevsky E. A., 2011), technologies have been developed for the production of anhydrous aluminum chloride from various aluminum-containing raw materials. The monograph by B. G. Rabovsky and A. A. Furman (Reshetnikov S. I., 2017) systematizes practical experience and theoretical knowledge in this field.

For oxide raw materials (natural aluminum-containing ores or alumina), chlorination is carried out only with a reducing agent. The reducing agent in this case is coal, clay–like reducing agents are also used – phosgene, generator gas, carbon monoxide, from solid ones – coal pitch and coke. In the presence of these reducing agents, the chlorination process proceeds at temperatures from 1000 to 1100 °C.

Some researchers, in addition to chlorine, suggest the use of carbon tetrachloride, sulfur chloride, hydrogen chloride, etc. as chlorinating agents. It is noted that alumina reacts with hydrogen chloride at a higher temperature, and the reaction itself is reversible. When a small amount of coal is added to the reaction mixture, increased formation of aluminum chloride is noted. When mixing sulfur chloride and chlorine, there is an increase in both reducing and chlorinating properties. Therefore, a lower temperature is necessary for this reaction to occur. The complete interaction of carbon tetrachloride with alumina occurs at a temperature of 390 °C, while $AlCl_3$ is formed.

For alumina, chlorinating agents in the presence of aluminum ores or carbon can also be iron, sodium and calcium chlorides.

In the monograph (Taran, V.N., 2004), several methods for aluminum chlorination are considered, in particular, chlorination in a fluidized bed (the fluidized bed is created by inert materials, for example, sand, or inert gases).

Industrial technological schemes for the production of aluminum chloride, which were developed by Soviet, German and American specialists, are also presented here.

In production conditions, the production of aluminum chloride consists of several stages. At the first stage, concentrated carbon monoxide is produced in special generators in which coal coke is gasified with oxygen. In the second stage, kaolin briquettes are prepared, dried and calcined, the main task of the second stage is the chlorination of kaolin briquettes, which is carried out in the presence of carbon monoxide with chlorine gas in a continuous shaft furnace.

Aluminum chlorides are obtained by the basic reaction:

$$Al_2O_3 + 3Cl_2 + 3CO \longrightarrow 2AlCl_3 + 3CO_2$$

Silicon oxide also reacts with chlorine by reaction:

$$Si_2O_3 + 2Cl_2 + 2CO \longrightarrow SiCl_4 + 2CO_2$$

As shown in (Sircar S., Rao M. B., Golden T. C., 1996), when aluminum and silicon oxides interact with chlorine, the phenomenon of mutual catalysis is noted, when the rate of chlorination of mixtures is higher than when chlorinating individual oxides. According to (Wei, N., Zhang, Z., Liu, D., Wu, Y., Wang, J., Wang, Q., 2015; Xiao, F., Guo, Y., Yang, R., Li, J., 2019), silica and alumina are chlorinated in the temperature range from 550 to 800 °C in the same ratios as in the feedstock.

The literature provides contradictory data on the interaction of chlorine with oxides at higher temperatures. Thus, Kocharovsky (Xiao, F., Ma, J., Yi, P., Huang, J.-C.H., 2008), investigating the chlorination of Polish clays, found that at temperatures above 900 °C, the yield of $AlCl_3$ decreases. Meanwhile, according to Kocharovskys data, confirmed by long-term practice, the yield of $SiCl_4$ in the temperature range from 1000 to 1200 °C reaches minimum values.

These contradictions can be explained by the fact that in (Gritsenko A. I., 1999) the results were obtained in a shaft furnace of continuous countercurrent action, that is, under conditions of a secondary reaction:

$$2Al_2O_3 + 3SiCl_4 \longrightarrow 3SiO_2 + 4AlCl_3$$

In (Natural gas. 2006; Yakushev V. S. 2009; Nagata I., 1966), the results of a study on the chlorination of various types of aluminum-containing raw materials are presented. The authors (Wei, N., Zhang, Z., Liu, D., Wu, Y., Wang, J., Wang, Q., 2015; Gritsenko A. I., 1999) studied the chlorination process of the North Voronezh bauxites, which was carried out in a fluidized bed. It is shown that all oxides included in the bauxite composition are chlorinated in the fluidized bed. The most easily chlorinated are iron and titanium oxides. Optimal chlorination conditions were found, at which the degree of chlorination of iron and titanium oxides reaches 98%, aluminum oxide – 65%, and silicon oxide – 20–35% (Sloan E. D., Koh C. A., 2008).

In (I. A. Zolotarsky, L. I. Voennov, L. Yu. Zudilina, L. A. Isupova, R. A. Zotov, D. A. Medvedev, D. A. Stepanov, A. V. Livanova, E. P. Meshcheryakov, I. A. Kurzina. 2017), a technique was developed for the selective chlorination of bauxites in a fluidized bed to produce aluminum oxide in the temperature range from 800 to 900 °C with a mixture of chlorine and silicon tetrachloride. Chlorination of powdered bauxite in a fluidized bed with 1% carbon makes it possible to remove 65% of iron from it at a temperature of 800 °C, while losing 8% of aluminum (for Uglian bauxite). The chlorination of Prosyanovo kaolin of Ukhta and Severoonezhsky bauxites in the filter layer was studied.

The authors (Reshetnikov S. I., Livanova A. V., Meshcheryakov E. P., Kurzina I. A., Isupova L. A. 2017; Minakova T., 2007) studied the process of chlorination of the mineral part of the Ekibastuz carboniferous rocks. It is shown that during chlorination of these rocks, the yield of iron and silicon oxides is 98–100%, and the yield of aluminum oxide is 91–96%. It is proposed to carry out preliminary hydrochloric acid treatment to pre-release this raw material from silica, or to suppress the process of chlorination of SiO_2 with silicon tetrachloride, to separate silicon and aluminum oxides.

In (Moulton, B. & Zaworotko, M. J., 2001), a series of studies on hydrochloric acid chlorination of carbonaceous rocks of the Ekibastuz deposits was carried out. The authors showed that under certain chlorination conditions, iron oxides can be successfully distilled by 7%, while other oxides of the raw material are not significantly affected.

In (Buleiko V. M., Vovchuk G. A., Grigoriev B. A., Istomin V. A., 2014), a technology for processing kaolin clays from a deposit in Georgia (USA) by carbochlorination was developed. In (Istomin V. A., Fedolov D. M., 2013), a method for processing highly siliceous alumina-containing ores to produce iron oxides was developed, including heat treatment of ore for 30–60 minutes at a temperature from 400 to 500 °C in an atmosphere of chlorine gas. It has been shown that in the presence of natural gas, the yield of iron oxides increases.

A method of purification of aluminum ores from iron has been developed, consisting in reductively sulfidated roasting, chlorination and sublimation of iron chloride (Kalacheva L. P., Fedorova A. F. 2016).

The authors (Maxmudov M. J., Ne'matov X.I., 2023) present a developed method for selective low-temperature reduction of a mixture of iron and aluminum chlorides to metals. It is recommended to carry out the process in an inert gas stream containing hydrocarbons, for example, methane, as well as iron and aluminum chlorides.

The chloride reduction process is recommended to be carried out on the surface of iron, which increases the selectivity of reduction and significantly reduces the temperature of the process: $AlCl_3$ – up to 450 °C, $FeCl_3$ – up to 350 °C, the authors recommend using silicon or manganese instead of jelly, however, on their surfaces the reduction of aluminum chloride occurs at higher temperatures, 950 and 800 °C, respectively.

H. Safiev et al. (Maxmudov M. J., Ne'matov X.I., 2023; Llewellyn, P. L. et al., 2008) studied the decomposition of nepheline syenites from the Turpi deposit of the Republic of Tajikistan by chlorination to produce oxides, and also considered the main thermodynamic characteristics of the processes occurring during chlorination of the main minerals of the nepheline syenite rock (nepheline – $Na_{0,78}K_{0,22}AlSiO_4$, albite – $NaAlSi_3O_8$, microcline – $KAlSi_3O_8$, calcite – $CaCO_3$, hematite – Fe_2O_3 and goethite is FeO(OH). This method is based on the use of coals, carbon monoxide, methane and phosgene and methane as reducing agents. The following probable ways of processes have been identified:

$$M + X + C \longleftrightarrow EX + CO_2,$$

$$M + X + CO \longleftrightarrow EX + CO_2,$$

$$M + X + COCl_2 \longleftrightarrow EX + CO_2,$$

$$M + X + CH \longleftrightarrow EX + CO_2 + H_2O.$$

where: *X is chlorine gas; M is the corresponding mineral; EH is a mixture of chlorides of the corresponding elements in the composition of minerals*

Based on the comments, it can be assumed that feldspar and hematite are chlorinated more effectively when using coal as a reducing agent, and when chlorinating calcite, it is more rational to use methane as a reducing agent. Chlorination of minerals in the presence of a reducing agent – carbon monoxide in the studied temperature range is thermodynamically impossible, and when using phosgene as a reducing agent, all minerals except goethite must be chlorinated equally vigorously.

The conducted studies (Maxmudov M. J., Ne'matov X.I., 2023; Artemova I. I., Kandaurov S.Yu., Bachalov I. S. et al., 2010) have shown the possibility of selective decomposition of Turpi nepheline syenites by chlorination, to obtain a mixture of chlorides of a given composition, depending on the goal. When chlorinating nepheline syenites in the presence of coal, the authors of (Maxmudov M. J., Ne'matov X.I., 2023) achieved sufficiently high degrees of conversion of aluminum oxide to chloride, but at the same time oxides of silicon, calcium, potassium, sodium and iron also pass into chlorides.

The authors of (Vuong D. H., Zhang H. -Q., Sarica C., and Li M., 2009) have developed a method for chlorination of nepheline syenites in a methane atmosphere, consisting of two stages. At the first stage, iron-containing minerals are chlorinated under certain conditions to degrease raw materials, and the second stage consists of chlorination of aluminum-containing minerals. In the second stage, a mixture of chlorides is obtained, which is a good electrolyte for the production of aluminum and chloride melts.

There are several options for conducting the process of chlorine decomposition of these minerals with different initial and final products. Calculations of the temperatures of the beginning of the reaction (T_n), changes in the Gibbs energy (ΔG) and the logarithm of the equilibrium constant (lgK) were carried out using a computer program (Llewellyn, P. L. et al., 2008).

In (Maxmudov M. J., Ne'matov X.I. 2023), the chemical foundations of the chlorine method of processing aluminosilicate ores of Tajikistan were studied, rational conditions for the chlorine process were proposed, and basic technological schemes for the production of aluminum-containing coagulants were developed.

Thus, the high ability of chlorine to enter into chemical reactions, as well as the ability of chlorides to interact with other compounds, make it possible to isolate valuable components from processed raw materials, including aluminum chloride, a coagulant for water purification.

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Contact: makhmudov.mukhtor@inbox.ru

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