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Д.В. Сокольский атындағы «Жанармай,
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Х А Б А Р Л А Р Ы

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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Y.S. Ikhsanov, N.A. Meirbekov, K.M. Shalmagambetov

Al-Farabi Kazakh National University
Center of Physico-chemical Methods of Research and Analysis
Republic of Kazakhstan, Almaty.
E-mail: erbol.ih@gmail.com, nurkanat.m@gmail.com, kairshan@yandex.ru

PRODUCTION OF NITROCELLULOSE FROM CELLULOSE CULTIVATED IN SOUTH KAZAKHSTAN UNDER SUPERCRITICAL CONDITIONS

Abstract. This article presents the results of a study of the process of producing nitrocellulose from Kazakhstani cellulose raw materials using supercritical technology.

Nitration can be carried out both directly and indirectly. Direct nitration processes include the reactions of replacing a hydrogen atom by a nitro group or the addition of nitrating agents via a multiple bond, and indirect nitration involves replacing other atoms or groups of atoms with a nitro group (for example, halogens, sulfo groups). Indirect nitration methods include oxidation reactions of nitrogen-containing substances to nitro compounds, as well as condensation reactions leading to nitro compounds.

At the same time, the traditional method of nitration of cellulose is quite “dirty” from an environmental point of view, since it spends a huge (several thousand times more than the volume of nitrocellulose obtained) amount of water for the subsequent stage of washing nitrocellulose from nitration mixture residues after nitration.

This factor significantly increases the cost of water decontamination and links production to large reservoirs, which is not always possible, especially in arid regions.

In addition, due to the relatively small conversion of the nitration process using a nitrating mixture, the production of nitrocellulose requires the construction of large-scale production workshops. Which is also not always justified.

Associations with the above are of great interest to alternative nitration technologies, in particular nitration under supercritical conditions.

The aim of this work is to study the processes of nitration of cellulose in a supercritical static reactor.

For the experiment, the nitration method was chosen in a static supercritical reactor in a carbon dioxide medium using nitric oxide V as a nitrating agent.

As a raw material, cotton pulp of the 1st grade was used.

The initial reagent for producing nitric oxide V was nitric acid with a concentration of 65%

The process was carried out in a static reactor.

As a result, a white fibrous mass was obtained, similar in appearance to cellulose, readily soluble in acetone and insoluble in water, the density was 1.63 g / cm³, based on the density, analysis of the melting temperature and the nature of the combustion, we can conclude pyroxylin with a nitrogen content of 12.05 - 12.4%.

Keywords: cellulose, nitration, supercritical conditions, nitrocellulose.

Introduction. Nitration is one of the most important reactions of organic synthesis and is widely used in laboratory practice and production [1-3].

Nitration can be carried out both directly and indirectly. Direct nitration processes include the reactions of replacing a hydrogen atom by a nitro group or the addition of nitrating agents via a multiple bond, and indirect nitration involves replacing other atoms or groups of atoms with a nitro group (for example, halogens, sulfo groups). Indirect nitration methods include oxidation reactions of nitrogen-containing substances to nitro compounds, as well as condensation reactions leading to nitro compounds.

The nitration processes are well studied and mastered by industry, and with their help a large number of highly demanded products are obtained, in particular cellulose nitrates, which are one of the most widely used cellulose ethers, the industrial production of which began back in the 19th century. Different applications of cellulose nitrates are determined by their specific properties. High mechanical strength and the ability to transfer to a plasticized state, good solubility and compatibility with available plasticizers - all this provided high volumes of production of cellulose nitrates for the manufacture of gunpowder, rocket fuel, varnishes, paints [4-9].

At the same time, the traditional method of nitration of cellulose is quite “dirty” from an environmental point of view, since it spends a huge (several thousand times more than the volume of nitrocellulose obtained) amount of water for the subsequent stage of washing nitrocellulose from nitration mixture residues after nitration [10-14].

This factor significantly increases the cost of water decontamination and links production to large reservoirs, which is not always possible, especially in arid regions.

In addition, due to the relatively small conversion of the nitration process using a nitrating mixture, the production of nitrocellulose requires the construction of large-scale production workshops. Which is also not always justified [15-17].

Associations with the above are of great interest to alternative nitration technologies, in particular nitration under supercritical conditions.

The current environmental and social environment urgently requires new approaches to the synthesis of organic substances. In particular, there is a shortage of energy and water resources, which puts the issue of rational use in the forefront. One of the solutions to this problem is the use of carbon dioxide in the supercritical state as a reaction medium [18].

At a pressure of more than 74 atmospheres and a temperature of more than 30 ° C, carbon dioxide passes into a supercritical state, in which its density is like that of a liquid, and its viscosity and surface tension are like that of a gas. Such properties make supercritical carbon dioxide an effective non-polar solvent [19-25].

Carbon dioxide, used in a supercritical state as a reaction medium, has a number of properties inherent in gases. Moreover, it has a number of attractive properties that provide additional benefits when using this gas as an aid in extraction.

- universal dissolving ability with respect to organic compounds, physiologically does not cause concern, because is the final product of the metabolism of a number of living organisms, including humans.

- In relation to the conditions of supercritical fluid extraction, carbon dioxide is chemically inert and does not enter into chemical interactions with reagents.

- CO_2 is relatively safe for the environment, which suggests the possibility of creating an environmentally friendly type of production.

- Carbon dioxide is one of the most accessible and widely used gases in the food industry.

The aim of this work is to study the processes of nitration of cellulose in a supercritical static reactor.

Materials and Methods. For the experiment, the nitration method was chosen in a static supercritical reactor in a carbon dioxide medium using nitric oxide V as a nitrating agent.

The raw materials used were cotton pulp of the 1st grade according to GOST 3818.0 produced by Khlopkoprom-Cellulose LLP in 2019.

The initial reagent for producing nitric oxide V was nitric acid GOST 4461-77 with a concentration of 65% (requires additional strengthening by distillation with oleum).

Results and discussion. The synthesis of pyroxylin under supercritical conditions involves several stages

1 Preparation of nitric acid and bring it, but a sufficient concentration.

Since nitric acid is manufactured industrially and delivered to the market, it has a concentration of not more than 62%, which is insufficient for the nitration reaction and the production of nitrogen pentoxide, it is necessary to strengthen it.

The strengthening process consists in the distillation of nitric acid in a mixture with oleum in a ratio of 1: 3 at atmospheric pressure without access to atmospheric water. As a result, nitric acid with a strength of more than 80% was obtained.

2 getting nitric oxide.

Since the nitration process was selected under supercritical conditions, nitric pentoxide (Nitric Oxide V, N_2O_5) was used instead of the traditional nitrating mixture.

To obtain it, it is necessary to add phosphorus V (P_2O_5, phosphorus pentoxide, phosphoric anhydride, phosphorus pentoxide) to frozen concentrated nitric acid (melting point −41.59 °C, recommended process temperature -78.5 °C).

The reaction must be carried out in the environment of ozone O_3 for which an ozonizer is introduced into the installation.

After addition of phosphorus oxide V, the reaction proceeds at a temperature of 28.0 °C. Under these conditions, nitrogen pentoxide is sublimated and transferred to a collection tank, which is also recommended to be cooled to sub-zero temperatures (from -20 to -40 °C). At the same time, ozone must circulate in the system throughout the process.

The reaction proceeds according to the formula:

$$2HNO_3 + P_2O_5 \rightarrow 2HPO_3 + N_2O_5$$

And in parallel with the reaction:

$$2NO_2 + O_3 \rightarrow N_2O_5 + O_2$$

Figure with the image of the installation for laboratory synthesis of nitrogen pentoxide is shown in figure 1.

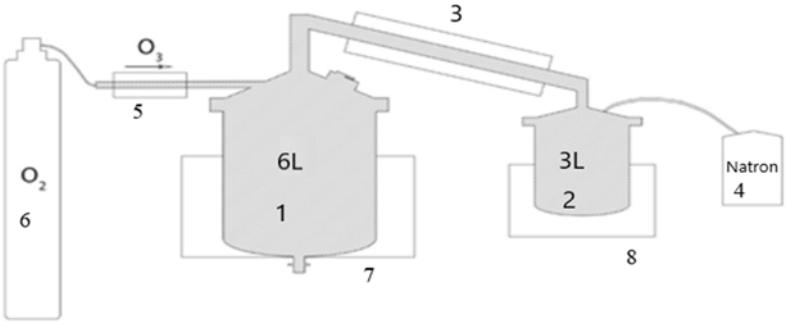


Figure 1 - apparatus for the synthesis of nitrogen pentoxide

Concentrated nitric acid (concentration of more than 75%) is loaded into the reactor 1 and cooled to the freezing point using a refrigerator 2, then phosphorus oxide V is introduced into the reactor 1 in a ratio of 1/1, after which ozone is obtained by passing oxygen from the cylinder 6 through the ozonizer 5, during the reaction, the resulting nitrogen pentoxide is sublimated and condensed in the receiver 2 through the refrigerator 3, while the receiver 2 is also cooled by the refrigerator 8 to stabilize the nitric oxide V, the released and unreacted oxide nitrogen IV is neutralized in tank 4.

As a result, white nitric pentoxide crystals (figure 2) and nitric oxide IV vapors as a by-product will be obtained in the collection.

The reaction yield is 53% based on 100% nitric acid.

Figure 2 - Nitrogen Pentoxide Crystals

It should be noted that the crystals of nitrogen pentoxide are extremely unstable and their long-term storage is impractical; for this reason, the obtained pentoxide should immediately go to the 3-stage cellulose nitration.

3 Cellulose nitration

Cellulose nitration is carried out using nitrogen pentoxide in a ratio of cellulose / pentoxide, 1/6

The process takes 15 minutes

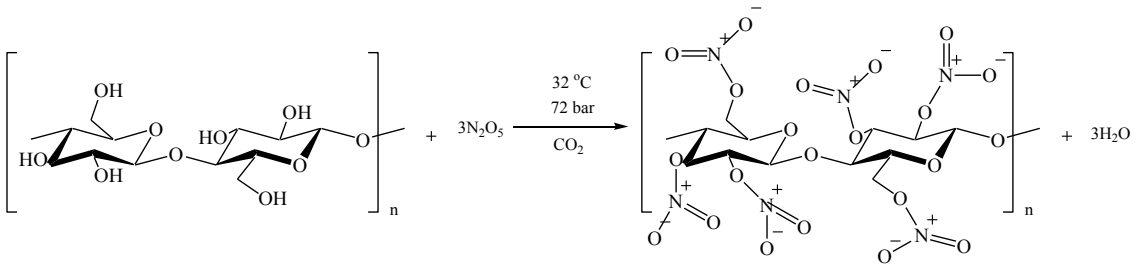
Temperature - 32 ° C

Pressure - not less than 72 atm.

The process was carried out in a static reactor (a reactor with an intensification mixer or a circulation pump for process intensification is recommended)

The reaction yield is almost 100% for cellulose.

The reaction was carried out according to the formula:



As a result, a white loose fibrous mass was obtained, similar in appearance to cellulose, readily soluble in acetone and insoluble in water, the density was 1.63 g / cm³, based on the density, analysis of the melting temperature and the nature of the combustion, we can conclude that pyroxylin with a nitrogen content of 12.05 - 12.4%.

Conclusion. As a result, the first synthesis of pyroxylin from Kazakhstani cellulosic raw materials using supercritical technology was carried out.

The advantages of the process are

-Small water consumption

-Fast reaction

High process selectivity

-High conversion process

-Lack of sulfur compounds in contrast to the traditional nitration method

We continue to work on this process in order to optimize and scale it.

Е.С. Ихсанов, Н.А, Мейрбеков, К.М. Шалмагамбетов

Әл-Фараби атындағы Қазақ ұлттық университеті;
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ОҢТҮСТІК ҚАЗАҚСТАНДА ҚИЫН ЖАҒДАЙДА ӨСІРІЛЕТІН ЦЕЛЛЮЛОЗАДАН НИТРОЦЕЛЛЮЛОЗА ӨНДІРУ

Аннотация. Бұл мақалада суперкритикалық технологияны қолдана отырып, қазақстандық целлюлоза шикізатынан нитроцеллюлоза алу процесін зерттеу нәтижелері келтірілген.

Нитризация тікелей де, жанама түрде де жүргізілуі мүмкін. Тікелей нитраттау процестеріне сутегі атомын нитро тобына ауыстыру немесе бірнеше байланыс арқылы нитраттау агенттерін қосу реакциясы кіреді, ал жанама нитрация басқа атомдарды немесе атомдар тобын нитро тобымен алмастыруды қамтиды (мысалы, галогендер, сульфо топтары). Жанама нитрлеу әдістеріне азот қосылыстарының азотты қосылыстарға тотығу реакциялары, сондай-ақ нитроқосылыстарға апаратын конденсация реакциялары жатады.

Сонымен қатар, целлюлозаны нитраттаудың дәстүрлі әдісі экологиялық тұрғыдан «лас» болып табылады, өйткені ол нитроцеллюлозаның нитратталған қоспадан кейінгі қалдықтарынан кейінгі жуу кезеңі үшін судың үлкен мөлшерін алады (алынған нитроцеллюлозадан бірнеше мың есе көп).

Бұл фактор суды зарарсыздандыру құнын едәуір арттырады және өндірісті ірі су қоймаларымен байланыстырады, бұл әрдайым мүмкін емес, әсіресе құрғақ аймақтарда.

Сонымен қатар, нитрлеу қоспасын қолданып нитраттау процесінің салыстырмалы түрде аз өзгеруіне байланысты нитроцеллюлоза өндірісі ірі өндіріс цехтарын салуды қажет етеді, бұл әрдайым ақталмайды.

Жоғарыда аталған қауымдастықтар альтернативті нитритациялық технологияларға, әсіресе критикалық жағдайларда нитризацияға үлкен қызығушылық тудырады.

Бұл жұмыстың мақсаты - өте критикалық статикалық реактордағы целлюлозаны нитрлеу процестерін зерттеу.

Эксперимент үшін нитрлеу әдісі ретінде азот оксидін V қолдана отырып, көміртегі диоксиді ортадағы статикалық сынғыш реакторда нитрлеу әдісі таңдалды.

Шикізат ретінде 1-ші класстағы мақта целлюлоза пайдаланылды.

Азот оксиді V алу үшін алғашқы реагент концентрациясы 65% азот қышқылы болды

Процесс статикалық реакторда жүргізілді.

Нәтижесінде целлюлозаға ұқсас ақ борпылдақ талшықты масса алынды, ацетонда оңай ериді және суда ерімейді, тығыздығы, балқу температурасы мен жану сипатын талдау негізінде, 1,63 г/см³ болды, қорытынды жасауға болады. пироксилин құрамында азот мөлшері 12,05 - 12,4%.

Түйін сөздер:. целлюлоза, нитрлеу, сыни жағдайлар, нитроцеллюлоза.

Е.С. Ихсанов, Н.А, Мейрбеков, К.М. Шалмагамбетов

Казахский национальный университет имени аль-Фараби
Центр физико-химических методов исследования и анализа, Казахстан, Алматы

ПОЛУЧЕНИЕ НИТРОЦЕЛЛЮЛОЗЫ ИЗ ЦЕЛЛЮЛОЗЫ, КУЛЬТИВИРУЕМОЙ В ЮЖНОМ КАЗАХСТАНЕ В СВЕРХКРИТИЧЕСКИХ УСЛОВИЯХ

Аннотация. В данной статье представлены результаты изучения процесса получения нитроцеллозы из казахстанского целлюлозного сырья с использованием сверхкритических технологий.

Нитрование может осуществляться как прямым, так и непрямым путем. К процессам прямого нитрования относят реакции замещения атома водорода на нитрогруппу или присоединение нитрующих агентов по кратной связи, к непрямому нитрованию – замену других атомов или групп атомов на нитрогруппу (например, галогенов, сульфогруппы). К методам непрямого нитрования можно отнести реакции окисления азотсодержащих веществ до нитросоединений, а также реакции конденсации, приводящие к нитросоединениям.

В то же время традиционный метод нитрования целлюлозы является достаточно “грязным” с экологической точки зрения, так как затрачивает огромное (в несколько тысяч раз больше объема получаемой нитроцеллюлозы) количество воды на последующую после нитрования стадию промывки нитроцеллюлозы от остатков нитрующей смеси.

Данный фактор значительно повышает затраты на дезактивацию воды и привязывает производство к крупным водоёмам, что не всегда возможно, особенно в засушливых регионах.

Кроме того, по причине относительно небольшой конверсии процесса нитрования с использованием нитрующей смеси, производство нитроцеллюлозы требует строительства масштабных производственных цехов, что тоже не всегда оправдано.

Связи с вышеперечисленным, высокий интерес вызывают альтернативные технологии нитрования, в частности нитрование в сверхкритических условиях.

Целью данной работы является изучение процессов нитрования целлюлозы в сверхкритическом статичном реакторе.

Для проведения опыта был выбран метод нитрования в статическом сверхкритическом реакторе в среде диоксида углерода с применение оксида азота V в качестве нитрующего агента.

В качестве сырья использовалась хлопковая целлюлоза 1 сорта.

Исходным реагентом для получения оксида азота V была азотная кислота концентрацией 65%.

Процесс проводился в статичном реакторе.

В результате получена волокнистая рыхлая масса белого цвета, по внешнему виду похожая на целлюлозу, хорошо растворимая в ацетоне и нерастворимая в воде, плотность составила 1,63 г/см³, на основании плотности, анализа температуры плавления и характера горения можно сделать вывод, что получен пироксилин с содержанием азота 12,05-12,4 %.

Ключевые слова: целлюлоза, нитрование, сверхкритические условия, нитроцеллюлоза.

Information about authors:

Ikhsanov Yerbol Saginovich, PhD, Senior lecturer Department of Chemistry and Chemical Technology of the Al-Farabi Kazakh National University, Kazakh National University, e-mail: erbol.ih@gmail.com, https://orcid.org/0000-0003-4640-9584;

Meirbekov Nurkanat Ayazbayuly, Al-Farabi Kazakh National University, Faculty of Chemistry and Chemical Technology, MSc student of 2-nd course. nurkanat.m@gmail.com, https://orcid.org/0000-0001-6440-3544;

Shalmagambetov Kairzhan Mustafinovich, Doctor of Science, Center of Physico-chemical Methods of Research and Analysis of the Al-Farabi Kazakh National University, kairshan@yandex.ru, https://orcid.org/0000-0002-5660-9208

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