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Д.В.Сокольский атындағы «Жанармай,
катализ және электрохимия институты» АҚ

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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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OF THE REPUBLIC OF KAZAKHSTAN
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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. Web of 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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**IMPROVEMENT OF PERFORMANCE PROPERTIES
OF DIESEL FUELS WITH MULTIFUNCTIONAL ADDITIVE**

Abstract. The article presents research materials on the evaluation of coagulants properties for growth of resins and oxidation products dissolved in diesel fuel. Micrographs of fuel samples after sulfuric acid attack are given. The evaluation and the research results of alkali attack on the fuel are presented. As a result of aqueous carbamide solution attack on the fuel, the ability of aggregation of resins practically dissolved in diesel fuel was established. The research results of combined compositions of reagents are given. The author notes that combination of sulfuric acid and aqueous carbamide solution when added to diesel fuel allows reduce the content of existent resins by half, while the fuel acidity is reduced by 13%. The article also reveals the patterns of changes in the content of existent resins in the fuel from the duration of sedimentation at different combinations of coagulant compositions. According to the research results, it was established that among the considered agents, the greatest effect of the coagulation process of dissolved impurities in the fuel is achieved by its interaction with the aqueous carbamide solution and sulfuric acid.

Key words: diesel fuel, resins, coagulation, physicochemical parameters, sulfuric acid, alkali, carbamide, sedimentation, removal.

Introduction. Diesel fuels are one of the most popular petroleum products used in agricultural machinery. Composition, properties and quality of diesel fuels used in engines of tractors and automobiles largely determine the resource and reliability of components and parts of fuel equipment and cylinder-piston group.

The reliability of work of tractors, combines and automobiles largely depends on the quality of the used diesel fuel, its performance properties.

Main part. Analysis of fuels stored in oil stores and used in agricultural enterprises showed [1] that fuels purchased from commercial structures from “wheels” in 40-60% of cases had a deviation from the standard values for fractional composition, low-temperature, anti-wear, lubricating properties, content of sulfur and existent resins [2].

One of the problems of poor quality and unsatisfactory condition of diesel fuel used in tractors, automobiles and combines are their storage and transportation conditions.

As is well known, among contaminants present in diesel fuel, besides mechanical impurities and free water, easily removed by physical cleaning methods, it contains dissolved resins, asphaltenes, oxidation products, sulfur, which are practically impossible to remove [1-3].

The main difficulty of removal consists in the absence of means of cleaning the fuel from inclusions of dispersed composition less than 0.1-0.5 microns.

Resins present in fuels and sulfur do not always negatively characterize the quality of the fuel, as they are to a certain extent “lubricating components” [2, 4-7].

On the other hand, increased content of resins, sulfur, and heavy fractions in diesel fuel when it is burned in a cylinder-piston group can cause formation of lacquer and increase in wear of parts of the

cylinder-piston group. In addition, the above components of the diesel fuel adversely affect the economic performance of the engine and exhaust pollution[8-13].

It is possible to remove dissolved impurities from the fuel by filters, centrifuges, separators only by enlarging their dispersion composition, while it is necessary to use physical and chemical methods of cleaning [6-7].

To select and evaluate the possibility of removal of dissolved impurities, several pretreatment methods of the fuel with coagulants were considered, in particular sulfuric acid, alkali and carbamide attack on the fuel [3, 14-21].

Analysis of the fuel under a microscope with magnification $K_{gr} = 110$ times shows that there are no inclusions in the fuel with existent resin content of $60 \text{ mg}/100 \text{ cm}^3$ and mass fraction of sulfur of 0.5% or more.

The following reagents were used to enlarge the dissolved impurities:

1. Sulfuric acid percentagewise to the fuel 0.1-0.5%.
2. Calcined soda solution in water in the ratio 1:5, 1:3, 1:1.
3. Aqueous carbamide solution in the ratio 1:1.

And also their different combinations:

- acid attack, followed by the aqueous carbamide solution attack;
- acid attack, followed by the alkali and aqueous carbamide solution attack;
- alkali attack, followed by the aqueous carbamide solution attack.

In accordance with the research methods, sulfuric acid was alternately added percentagewise 0.1; 0.2; 0.3; 0.4; 0.5% to the diesel fuel with the content of the existent resins $60 \text{ mg}/100 \text{ cm}^3$ and sulfur content, 0.5 mass %.

The fuel temperature was 20°C . The mixture was mixed for 0.5 hours. The coagulation process was examined under a microscope and micrographs were taken. The results of the examination are presented in Figure 1 (a, b, c, d).

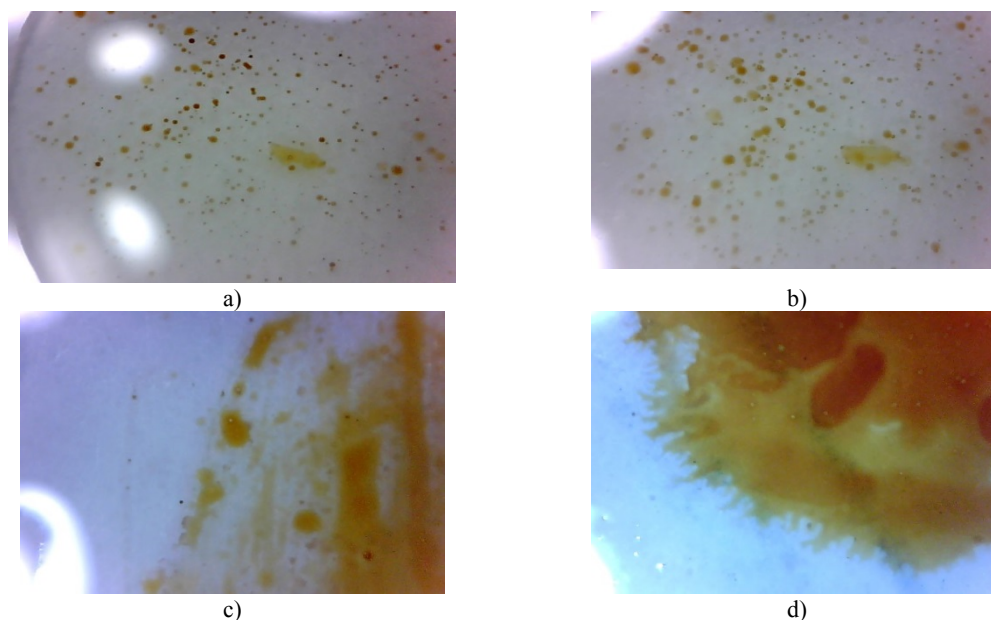


Figure – 1. Micrographs of the diesel fuel samples when adding in it: a) 0.1% of sulfuric acid; b) 0.2% c) 0.3%; d) 0.5%

Figure 1 shows that even a small amount of acid (0.1%) causes the coagulation process and appearance of conglomerates.

With increase in the concentration of acid to 0.3%, increase in the carbon formation is observed. Since the acid can cause increase in the fuel acidity, the acid was evaluated in accordance with GOST, and the content of existent resins in the upper part of the fuel that settled for 30 minutes was measured.

Figure 2 shows the dependence of the change in the fuel characteristics at different concentrations of the added acid.

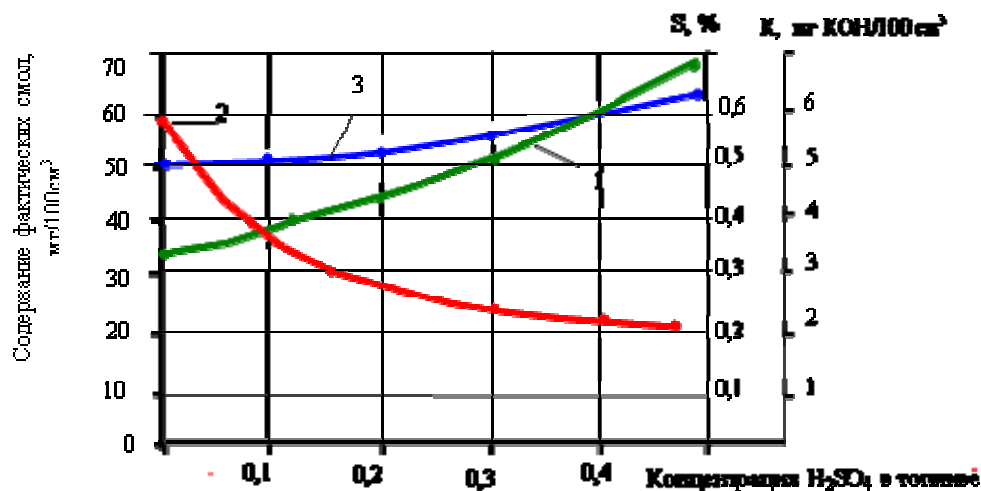


Figure 2 – Change in the fuel characteristics under the sulfuric acid attack

It was established that sulfuric acid allows remove resins from the fuel (Curve 2, Figure 2), however, the value (S) of the sulfur content increases and the acidity (K) of the fuel increases, which is a negative fact.

The content of existent resins (Curve 2, Figure 2) is most actively reduced when the acid concentration in the fuel is 0.1-0.2%, increase in the percentage concentration to 0.5 does not lead to significant resin reduction in the fuel.

Water-miscible calcined soda was used for consideration as alkali coagulants. The mixing concentration was 5:1, 3:1, and 1:1. It is noted that when mixing 5 and 3 parts of soda with 1 part of water, 100% dissolution of soda in water is not achieved. When mixing soda with water in proportions 1:1, a good solubility was noted (more than 80%), in accordance with which further research was carried out with the aqueous solution of 1:1, and the percentage of the aqueous alkali solution to the fuel was taken 0.5:1; 1.5 mass %.

The fuel mixed with the aqueous alkali solution was heated to a temperature of 100°C and then the temperature was kept for 0.5-1 hours with constant mixing.

The evaluation of coagulating ability was carried out under a microscope.

Figure 3 shows micrographs of the fuel samples with different concentrations of alkali water.

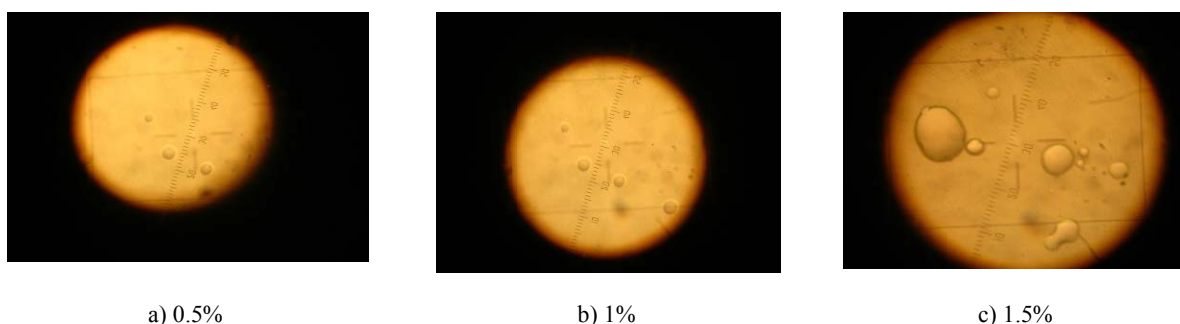


Figure 3 - Micrographs of the diesel fuel samples after the alkali water addition

Analysis of the research results presented in Figure 3 shows that the alkali water at the concentration of its addition into the fuel a) 0.5%; b) 1%; c) 1.5% practically does not have a coagulative effect on the impurities dissolved in the fuel.

If consider the fuel as an ultra-dispersed system with dissolved in it heavy hydrocarbon fractions, sulfur compounds of oil, etc., then the stability of this system can be greatly changed by adding small amounts of electrolytes into it. In lyophobic systems, the addition of electrolytes greatly increases the rate of coagulation. Based on the well-known theoretical laws of coagulation processes, as well as the research results on destabilization of dispersed systems of lubricating oils, the well-known substance – carbamide, which is a mineral fertilizer used in agricultural production, was used to study the coagulating ability of the impurities dissolved in the fuel.

The practical research on the evaluation of the coagulating ability of the dissolved impurities in the diesel fuel under the aqueous carbamide solution attack was carried out on a fuel with the existent resin content of $60 \text{ mg}/100 \text{ cm}^3$ selected on the oil store of one of the agricultural enterprises of West Kazakhstan region and a fuel stored in one of the commercial oil stores in the city of Uralsk of the Republic of Kazakhstan with the content of existent resins of more than $70 \text{ mg}/100 \text{ cm}^3$.

Analyzing the research results, let's note that carbamide is able to aggregate the impurities dissolved in the fuel. With increase in the concentration of the added solution with respect to the fuel, the coagulation of particles increases, and in the process of sedimentation as the concentration of the separating agent increases, a layer of recrystallized carbamide is formed. Figure 4 shows fragments of micrographs of the fuel samples when the aqueous carbamide solutions are added into it.

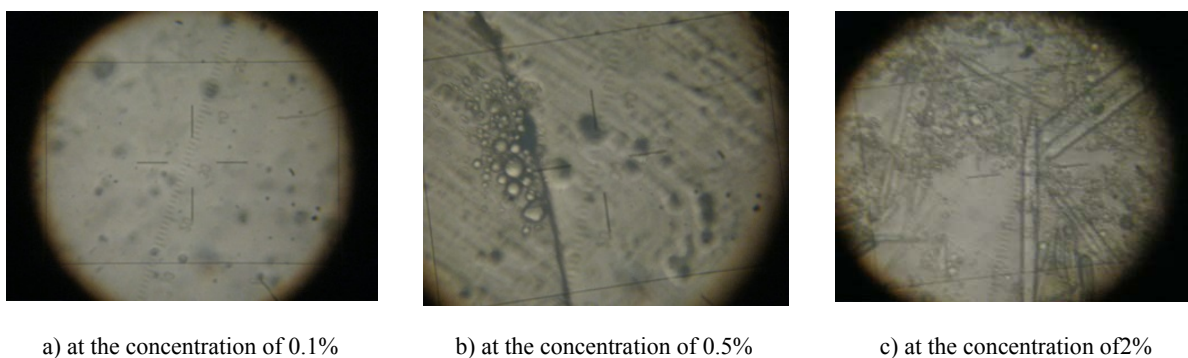


Figure 4 - Micrographs of the fuel samples (the city of Uralsk, Kazakhstan) when the aqueous carbamide solutions are added into it. $T_{\text{fuel}} = 90^{\circ}\text{C}$, the time of sedimentation $t = 90 \text{ min}$

The research found that the optimal concentration of the added 50% carbamide solution is 0.1-0.5% at the temperature $t = 90-100^{\circ}\text{C}$. The optimal time of sedimentation is 60-90 min.

The research evaluated the change in the content of the existent resins in the fuel during the aqueous carbamide solution attack on it (Figure 5).

It should be noted that the content of the existent resins (Figure 5) in the fuel, depending on the concentration of the added aqueous carbamide solution, reduces. However, when it is increased by more than 0.5%, the change in the resin content occurs slightly.

In addition, the content of the existent resins in the fuel after the acid attack on it changed to the value of $25-30 \text{ mg}/100 \text{ cm}^3$. However, the acid increases the fuel acidity, and the carbamide reduces it by 40-45%.

In this regard, the research was carried out on the combined reagent compositions. In particular, the possibility of adding the combinations was considered:

1. 0.1% acid + (50%) 0.5% carbamide solution.
2. 0.1% acid + 0.5% alkali water.

The change in the fuel acidity and the content of the existent resins depending on the duration of sedimentation of different agent combinations is presented in Figure 5.

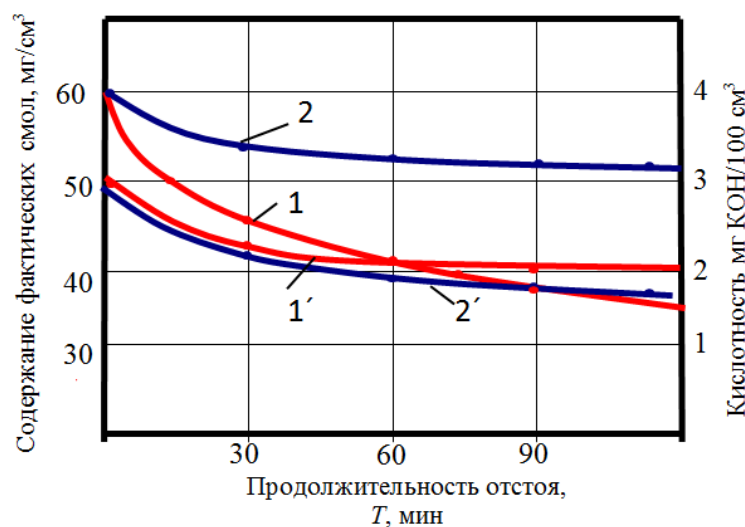


Figure 5 - Pattern of the change in the acidity and the content of the existent resins in the fuel depending on the duration of sedimentation ($T_{\text{addition}} = 90^{\circ}\text{C}$) at different combinations of coagulant compositions: 1, 1' - acid + carbamide solution; 2, 2' - acid + alkali

As is seen from Figure 6, the combination of the sulfuric acid and the aqueous carbamide solution when added to the diesel fuel allows reduce the content of the existent resins in it from $60 \text{ mg}/100 \text{ cm}^3$ to $35 \text{ mg}/100 \text{ cm}^3$, while the fuel acidity 1', 2' reduces from $3 \text{ mg KOH}/100 \text{ cm}^3$ to $2 \text{ mg KOH}/100 \text{ cm}^3$. Compared with the attack on the fuel only with the acid, the content of the existent resins in the fuel with the addition of the combined composition reduced almost the same, but the acidity did not increase, but vice versa – decreased.

Conclusions. Considering the combination “sulfuric acid – alkali”, let’s note that adding 0.1% acid and 0.5% alkali water to the fuel does not allow so much, compared to the first combination, reduce the content of the existent resins, but it helps significantly reduce the fuel acidity. This fact is most likely due to the effect of neutralizing the acid with the alkali.

Analyzing the research results, it can be concluded that among the considered agents, the greatest coagulation effect of the dissolved impurities in the fuel is achieved when it interacts with the aqueous carbamide solution, and the addition of the small amount of sulfuric acid activates the process.

ӘОЖ 621.899

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ДИЗЕЛЬДІ ОТЫНДАРДЫҢ ПАЙДАЛАНУШЫЛЫҚ ҚАСИЕТТЕРІН КӨПФУНКЦИОНАЛДЫ ҚОСПАЛАРДЫ ҚОСА ОТЫРЫП ЖОҒАРЫЛАТУ

Аннотация: Мақалада дизельді отында еріген шайыр мен тотығу өнімдерін ірілендіру үшін коагулянттардың қасиетін бағалау бойынша зерттеу материалдары келтірілген. Күкірт қышқылына ұшырағаннан кейін отын үлгілерінің микросуреттері келтірілген. Сілтілік отынға әсерін бағалау бойынша баға берілді және зерттеу нәтижелері келтірілді. Отынға карбамид су ерітіндісімен отынға әсер етуі нәтижесінде дизель отынында іс жүзінде еріген шайырлардың агрегаирлеу мүмкіндігі анықталды. Реагенттердің қосарланған құрамдарына жасалынған зерттеу нәтижелері келтірілді. су ерітіндісі карбонаты мен күкірт қышқылы комбинациясын дизельдік отынға қосқан кезде нақты шайыр құрамын екі есе төмендетуге мүмкіндік береді, оның үстіне отынның қышқылдығы 13 %-ға төмендейтінін автор атап өтеді.

Сондай-ақ, мақалада коагулянттық композициялардың түрлі комбинацияларында шөгінділердің ұзақтығынан отындағы нақты шайырлар құрамының өзгеру заңдылықтары көрсетілген. Жүргізілген зерттеулердің нәтижелеріне сәйкес, қарастырылған агенттердің ішінде ерітілген коспалардың күйдіру кезінде қышқылдану үдерісінің ең үлкен әсері оның коагуляция мен күкірт қышқылының су ерітіндісімен өзара әрекеттесуімен жүзеге асырылатыны орнатылды.

Түйін сөздер: дизельдік отын, шайырлар, коагуляция, физика-химиялық көрсеткіштер, күкірт қышқылы, сілті, карбамид, тұндыру, жойылу.

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ПОВЫШЕНИЕ ЭКСПЛУАТАЦИОННЫХ СВОЙСТВ ДИЗЕЛЬНЫХ ТОПЛИВ С ДОБАВЛЕНИЕМ МНОГОФУНКЦИОНАЛЬНОЙ ПРИСАДКИ

Аннотация. В статье представлены материалы исследований по оценке свойства коагулянтов для укрупнения растворенных в дизельном топливе смол и продуктов окисления. Приведены микрофотографии проб топлив после воздействия на них серной кислотой. Дана оценка и представлены результаты исследований по воздействию на топливо щелочью. В результате воздействия на топливо водным раствором карбамида установлена способность агрегатирования практически растворенных в дизельном топливе смол. Приведены результаты исследований комбинированных составов реагентов. Автор отмечает, что комбинация серной кислоты и водного раствора карбамида при добавлении их к дизельному топливу позволяет в два раза снизить содержание фактических смол, при этом кислотность топлива снижается на 13%. Также в статье выявляются закономерности изменений содержания фактических смол в топливе от продолжительности отстаивания при различных комбинациях составов коагулянтов. По результатам анализа проведенных исследований установлено, что среди рассмотренных агентов наибольший эффект процесса коагуляции растворённых примесей в топливе достигается при взаимодействии его с водным раствором карбамида и серной кислоты.

Ключевые слова: дизельное топливо, смолы, коагуляция, физико-химические показатели, серная кислота, щелочь, карбамид, отстаивание, удаление.

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