

## ARTICLE

# SORPTION OF WATER FROM PETROLEUM PRODUCTS BY POLYACRYLAMIDE-BASED SUPERABSORBENT

Dinar D Fazullin, Nikita M Novikov\*, Gennady V Mavrin, Ilnar A Nasyrov

Department of Chemistry and Ecology, Naberezhnye Chelny Institute, Kazan Federal University, RUSSIA

## ABSTRACT

Maintaining of high quality of petroleum products is an urgent task, since the use of low-quality fuel containing dissolved or emulsified water can increase the likelihood of rapid deterioration or breakdown of an internal combustion engine which uses the fuel. Water is present in petroleum products and in oil in various states: in a dissolved state, in a free state, and in the form of an emulsion. The transition of water from one state to another is determined by the following factors: pressure, temperature, pH, viscosity and chemical composition of the fluid. If free water is removed by conventional methods such as settling, coalescence, and centrifugation, then removal of bound water (emulsified and dissolved water) is a difficult task. The method of chemical absorption of water was investigated for the purification of gasoline from dissolved water, and polyacrylamide-based superabsorbent and cellulose fiber were considered as absorbents. The filtration rate of gasoline with a content of 10.6% emulsified water through a layer of sorbent 10 cm and a diameter of 0.9 cm was 4.3 cm<sup>3</sup> / min. The degree of removal of water by the absorbent containing 30% polyacrylamide was 99.8%. The absorbent can be used to clean fuels from emulsified and dissolved water.

## INTRODUCTION

At oil-producing and oil-refining enterprises there is an acute problem of utilization of water-in-oil emulsions formed during the production of a number of petroleum products. Water in petroleum products is in a dissolved, emulsified and free state. To separate these types of emulsions, various processes and devices are used, which work is based both on centrifugal and gravitational forces, separation using reagents and various adsorbents, and on specific processes such as ultrasound, magnetic field, and radio emission [1-3].

The recently spread on the market coalescent filters which well separate water (for example, filter elements manufactured by Pall Company), do not work efficiently enough when there is a large amount of mechanical impurities in the initial diesel fuel.

In [4], the authors used calcium oxide to remove moisture from petroleum products. Oil containing water was passed through a tube filled with an adsorbent under dynamic conditions at a speed of 0.5 m / h and a temperature of 20-25° C. The consumption of calcium oxide was more than 0.21% by the volume of refined petroleum products. To remove the formed calcium hydroxide flakes, the authors used filtration methods.

Also in the literature there are many works on the drying of various petroleum fractions and petroleum products: fuels, oils, olefins, alcohols, etc. with the use of NaA molecular sieves. Compared with the existing methods of drying oil and petroleum products based on heating them to the water evaporation temperature, drying with the use of molecular sieves has significant advantages. Its disadvantages are: clogging of pores and the formation of gels on the surface, what leads to a decrease in the filtration rate, which requires frequent replacement and regeneration of zeolites.

The patent for the method of processing diesel fuel provides for that fuel is heated; the volumetric content of water in the fuel is adjusted to 1-4 % and the fuel is homogenized. Then, by means of a filtering porous partition made of a hydrophobic material with a cleaning fineness of 1-10 microns, joint processes of dehydration and fine filtration are carried out [5].

In the study [6], superhydrophobic and super-ophilous silane-modified cotton fibers were obtained. The obtained fibers showed selective sorption capacity for oils from water, a high sorption capacity, and high sorption rate. Fibers also have outstanding superhydrophobic stability against various aggressive solutions and hot water, which allows them to be used to separate oils from harsh waters. The efficiency of separation water from oil is more than 91%.

In the study [7], nanoparticles of Fe<sub>3</sub>O<sub>4</sub> and a subsequent hydrophobic modification were applied on the surfaces of cotton fibers. The results show that the prepared fibers exhibit excellent superhydrophobicity and magnetic sensitivity. Compared to the original cotton fibers, the sorption capacity of the modified fibers as to hexane, toluene, chloroform, gasoline, and diesel fuel increases by 70.8%, 58.5%, 23%, 37.3% and 30.5%, respectively.

In the work [8], a hollow fiber membrane was used to remove water from motor fuel. The removal of water is as follows: oil containing emulsified water flows along one side of the hollow-fiber membrane; air flowing

### KEY WORDS

Oil products, gasoline, water sorption,

Received: 21 Oct 2018  
Accepted: 24 Dec 2018  
Published: 6 Jan 2019

### \*Corresponding Author

Email:  
novikovchem@yandex.ru  
Tel.+8 (8552) 42-62-40

on the other hand removes water from the oil through a hydrogel membrane available within the wall of the hollow fiber membrane. The water content in the emulsion was 1-4%. The degree of removal of emulsified water was more than 90%. The disadvantage of this method of removing emulsified water is clogging of the pores of the membranes, what leads to an increase in working pressure.

In the studies [9-13], separation of emulsified water from petroleum products performed with the use of absorbents from various composite resins, carbon nanotubes modified by teflon fibrils, super hydrophilic oleophobic sponges, aerogels, zeolites, calcium chloride, nanoparticles and other sorption materials.

Also, to remove water from gasoline, ethanol is added to the fuel in a volume of from 1 to 15% [14].

## METHODS

The scientific significance of solving the problem lies in the development of methods for the cleaning of petroleum products from emulsified and dissolved water based on chemical adsorption methods. For the cleaning of petroleum products from dissolved water, a method of chemical water absorption was investigated, and superabsorbent based on polyacrylamide and cellulose fiber were considered as absorbents (desiccants).

The absorbent was obtained from polyacrylamide and recycled cellulose fiber. The recycled cellulose fibers have different lengths, from 100 microns to 2000 microns. The thickness of the cellulose fibers is from 10 to 100 nm. Cellulose fibers are insoluble in water, acids and alkalis, and in organics; they hold and absorb liquid well. Cellulose fibers are the main component of the sorbent on the surface of which polyacrylamide powder with a size of 100-300 microns is applied.

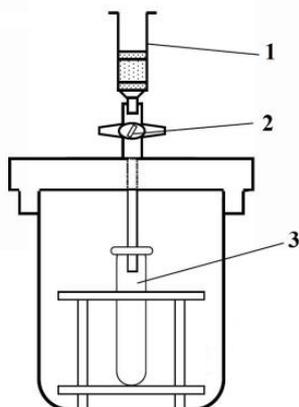
Super absorbents (SA) are hydrophilic polymer networks that, when swelled, absorb and retain huge amounts of water and aqueous solutions, going into gels. The water-holding capacity of super absorbents ranges from 50-100 g / g to 2200 g / g. For example, for the commercially available water-holding polymer "Aquasorb" this value is more than 500 grams of water per gram of absorbent. Hydrogels are obtained by the method of radical polymerization of acrylic acid or its salts (acrylates) at temperatures above 56 oC in an atmosphere of nitrogen or carbon dioxide. A crosslinking agent is introduced into the reaction mass to create a three-dimensional structure at the stage of polymerization. In this case, crosslinking occurs simultaneously with the growth of the polymer. The mass content of cellulose fiber in the sorbent is 70%, and 30% of polyacrylamide.

Dissolved and emulsified water was removed from the model emulsion prepared as follows. 30 ml of water and 10 g of sodium dodecyl sulfate were added to 300 ml of gasoline AI-92. To obtain an emulsion, the mixture was stirred at 3000 rpm for 15 minutes.

The model emulsion was filtered under dynamic conditions through a column filled with a sorbent weighing 2 g, the height of the sorbent was 10 cm.

The filtration rate was determined by passing 100 ml of gasoline and emulsion through a column with absorbent for a certain time.

The scheme of the laboratory installation for absorption of the inverse emulsion of the "water in oil" type in dynamic conditions is shown in [Fig. 1]. Original emulsion is fed into the column with filter loading, the emulsion is filtered through a polymer load under the action of gravity, and the filtrate is collected in a flask.



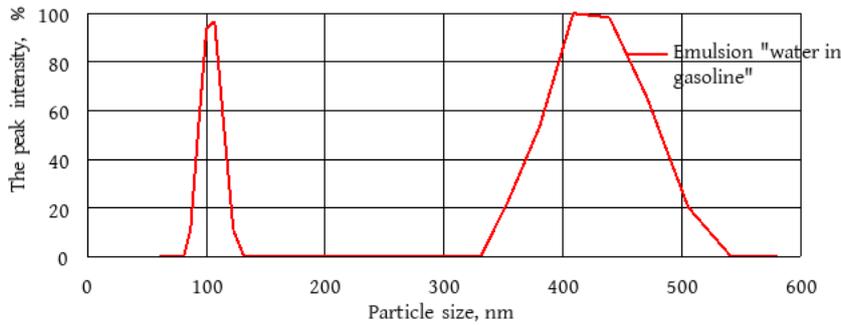
**Fig. 1:** Scheme of laboratory: 1 - column with superabsorbent; 2 - the crane; 3 - a flask for collecting oil.

The water content in petroleum products is determined before and after treatment in accordance with GOST 2477-2014 (Oil and petroleum products; method for determination of water content). The essence

of the method is as follows: the product being tested is heated inside a flask with a refrigerator in the presence of a solvent not miscible with water, which is distilled along with the water in the sample. Condensed solvent and water are constantly separated in the trap, with the water remaining in the graduated compartment of the trap, and the solvent is returned to the distillation vessel.

**RESULTS AND DISCUSSION**

[Fig. 2] and [Table 1] present the results of measurements of particle sizes and  $\zeta$ -potential of the dispersed phase of the inverse emulsion of water in gasoline.



**Fig. 2:** Graphs of particle size distribution of the dispersed phase of the reverse emulsion of water in gasoline.

**Table 1:** The values of the particle size and the  $\zeta$ -potential of the dispersed phase of the reverse emulsion "water in gasoline"

Emulsion	Particle size, nm	$\zeta$ -potential, mV
Emulsion "water in gasoline"	86-124; 355-542	-19 ± 2

According to the data presented in [Fig. 2], the inverse emulsion "water in gasoline" is a poly disperse system with particle sizes from 86 to 542 nm. From the data of [Table 1], it follows that the emulsion has the absolute value of the  $\zeta$ -potential equal to -19 mV and is a stable system. The higher the absolute value of the  $\zeta$  - potential of the emulsion, the stronger the particles repel each other, what does not allow the emulsion to separate.

The filtration rate for gasoline and the inverse emulsion "water in gasoline" through a column with absorbent are presented in [Table 2].

**Table 2:** The rate of filtration of gasoline and emulsion water in gasoline through a column with absorbent (30% polyacrylamide, 70% cellulose fiber)

Name of liquid	Water content in gasoline,%	Filtration rate through absorbent, cm <sup>3</sup> / min
Gasoline	<0.01	9.7
Emulsion water in gasoline	10.6	4.3

The filtration rate of gasoline through the sorbent layer of 10 cm and a diameter of 0.9 cm is 9.7 cm<sup>3</sup> / min, and when filtering gasoline with a content of 10.6% emulsified water, the filtration rate falls to 4.3 cm<sup>3</sup> / min.



**Fig. 3:** Left to right: source gasoline; emulsion with 10.6% water in gasoline; gasoline, purified from water absorbent.

[Fig. 3] shows that the emulsion “water in gasoline” is turbid and has sediments at the bottom of the flask; after filtering the emulsion, the water is trapped in cellulose fiber and is set by polyacrylamide. The cleaned gasoline in [Fig. 3] (right) is transparent. The water content in gasoline was determined by the method of GOST 2477-2014, the results are presented in [Table 3].

**Table 3:** Degree of removal of water from gasoline by an absorbent

Absorbent	Water content in gasoline, %		Degree of water removal, %
	before	after	
10% polyacrylamide, 90% cellulose fiber	10.6	0.5	95.3
30% polyacrylamide, 70% cellulose fiber		<0.01	99.8

From the results of [Table 3], the water removal degree with an absorbent containing 10% polyacrylamide is 95.3%, and when the mass content of polyacrylamide is 30%, the cleaning rate is 99.8%.

Inverse emulsion water in gasoline is a poly disperse system with particle sizes from 86 to 542 nm. Having an absolute value of the  $\zeta$ - potential equal to -19 mV, the emulsion is a stable system. The higher the absolute value of the  $\zeta$  - potential of the emulsion, the stronger the particles repel each other, what does not allow the emulsion to separate.

The filtration rate of gasoline through the sorbent layer of 10 cm and a diameter of 0.9 cm is 9.7 cm<sup>3</sup> / min, and when filtering gasoline with a content of 10.6% emulsified water, the filtration rate falls to 4.3 cm<sup>3</sup> / min. The emulsion “water in gasoline” is turbid; it has sediments, and after filtration through a layer of sorbent it becomes transparent.

The water removal degree with an absorbent containing 10% polyacrylamide is 95.3%, and when the mass content of polyacrylamide is 30%, the cleaning rate is 99.9%. For comparison, the degree of removal of emulsified water from petroleum products using cotton fiber modified with silane is 91%, and the application of Fe3O4 nanoparticles onto cotton fiber increases the degree of water removal from gasoline by 37% compared to the original fiber [6, 7]. The degree of removal of emulsified water from the engine oil using a hollow-fiber membrane, on which the hydrogel is applied, is more than 90% [8].

Thus, the proposed absorbent from cellulose fiber and polyacrylamide has a high degree of removal of emulsified and dissolved water from gasoline.

## CONCLUSION

According to the research results, it was determined that a superabsorbent consisting of polyacrylamide and cellulose fiber effectively cleans gasoline from emulsified and dissolved water under dynamic conditions. When the content of polyacrylamide is no less than 30% (by weight) in the composition of the absorbent, the water removal degree reaches 99.8%. The fuel filtration rate is from 4 to 5 cm<sup>3</sup> / min. This absorbent can be used to clean fuels and waste solvents from emulsified and dissolved water.

### CONFLICT OF INTEREST

There is no conflict of interest.

### ACKNOWLEDGEMENTS

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

### FINANCIAL DISCLOSURE

None

## REFERENCES

- [1] Osipov OP, Sannikov SG. [2001] Oil refining and petro chemistry. M.: TsNIITNeftekhim. 6:12-14.
- [2] Proskuryakov VD, Smirnov OV. [1992] Cleaning of petroleum products and oily water by electrical treatment. St. Petersburg: Chemistry. 17-18.
- [3] Shepelev II, Tverdokhlebov VP, Fomova NA. [2001] Oil refining and petro chemistry. TsNIIT Neftekhim. 8:14-17.
- [4] Yablokova MA, Ponomarenko EA. [2013] Promising methods for cleaning diesel fuel from water and mechanical impurities. Current problems of science and education. 3. URL: <http://www.science-education.ru/ru/article/view?id=9246> (appeal date: 05/14/2018).
- [5] Zege ON. [1996] The method of processing diesel (mostly watered) fuel, installation for its implementation and a vortex apparatus: RF Patent No. 2054572. 5
- [6] Jintao W et al. [2017] Hydrothermal fabrication of robustly super hydrophobic cotton fibers for efficient separation of oil/water mixtures and oil-in-water emulsions. Journal of industrial and engineering chemistry. 54:174-183.
- [7] Jintao W et al. [2016] Magnetically superhydrophobic kapok fiber for selective sorption and continuous separation of oil from water. Chemical Engineering Research and Design. 115:122-130.

- [8] Li Y et al. Bio-inspired onboard membrane separation of water from engine oil. *Journal of membrane science*. 378:1-2.
- [9] Jingjie H. [2018] Removal of Oil from Water Surface by Novel Composite NSM-g-P(MMA-co-BA) Super Oil-Absorption Resin. *Polymer composites*. 39(4):1051-1063.
- [10] Padmajan SS et al. [2018] Multiwall carbon nanotube reinforced teflon fibrils for oil spill cleanup and its effective recycling as textile dye sorbent. *Journal of environmental management*. 211:198-205.
- [11] Chunping S et al. [2017] A magnetic superhydrophilic oleophobic sponge for continuous oil-water separation. *Chemical engineering journal*. 309:366-373.
- [12] Filho MC et al. [2017] Efficient simultaneous removal of petroleum hydrocarbon pollutants by a hydrophobic silica aerogel-like material. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 520:550-560.
- [13] Ghanbari S, Vaferi S. [2015] Experimental and theoretical investigation of water removal from DMAZ liquid fuel by an adsorption process. *Acta Astronautica*. 112:125.
- [14] El-Faroug Musaab O et al. [2016] Spark Ignition Engine Combustion, Performance and Emission Products from Hydrous Ethanol and Its Blends with Gasoline. *ENERGIES*. 9(12):984.