The Research of the Natural Halloysite Nanotubes Those are Enriched with Ni and Co Oxides in the Production Process of Environmentally Friendly Diesel Fuels

Tarana Aslan Mammadova[1], Mutallim Maharram Abbasov[2], Aynur Rovshan Hasanova[3], Anar Amil Namazov[4]

[1]*Doctor of Technical Sciences, Head of the Laboratory of Renewable Fuels, Yu.G.Mamedaliyev Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences, Baku, Azerbaijan*
[2]*Doctor of Pedagogical Sciences, Leading Researcher of Laboratory of Renewable Fuels, Yu.G.Mamedaliyev Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences, Baku, Azerbaijan*
[3]*PhD Student, Technologist of the Laboratory of Renewable Fuels, Yu.G.Mamedaliyev Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences, Baku, Azerbaijan*
[4]*BSc Student, Chemist of Laboratory of Renewable Fuels, Yu.G.Mamedaliyev Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences, Baku, Azerbaijan*

---***---

Abstract - *Nowadays, alumosilicates are being used as catalysts for miscellaneous refining processes of petroleum hydrocarbons. Currently, the preparation of catalysts based on the natural alumosilicate (halloysite) nanotubes is one of the modern directions of the application of nanocatalyst to different petrochemistry and oil-refining processes.*
In the proceeding, the hydrotreating process of mixture of diesel fraction with 10 % (by mass) cottonseed oil has been investigated by using free halloysite samples and their modifications with Ni and Co oxides as catalysts, at 330-350°C of temperature, under 5.0 MPa of hydrogen pressure and with 1 hour-1 mass velocity of introduced feedstock.
It has been revealed that, the total sulfur content was 0.0209-0.0193 % (by mass) when the halloysite samples were enriched with Co and Ni oxides separately. The desulfurization depth was 75.5-77.4 % (by mass) respectively. The usage of the halloysite samples those are enriched with Co and Ni oxides together provides a decrease in the total sulfur content up to 0.002 % for diesel fraction. The desulfurization depth is 97.6 % (by mass) for it.

Key Words: **cottonseed oil, hydrotreating, diesel fraction, "green diesel", Ni and Co oxides, halloysite**

1.INTRODUCTION

The research of the oil based alternative energy carriers is very essential for the development of alternative energy resources. In modern world, the fuel which is obtained from biomass and biological sources attracts quite enough attention. The first and second generation biodiesel are widely investigated among the different alternative fuel samples. The first generation biodiesel fuel is produced by the transesterification process of vegetable or animal oil with short chain aliphatic alcohols (methanol, ethanol).

The "greendiesel" process has an important role in the production of the second generation biofuels. The essentiality of this process is that the vegetable oils transform into long chain aliphatic paraffins and enhance the cetane number by joining the diesel fuel via hydrotreating process, it means at 330-350°C of temperature, under 3.5-5.0 MPa of hydrogen pressure. At the same time, the endangered petroleum resources are saved [1-3].

The transformation of vegetable oil acids into paraffins can be seen in two directions in the presented conditions:

1. By decarboxylation reaction (with the production of CO_2 and normal paraffins)

$$C_{17}H_{35}COOH + H_2 \rightarrow C_{17}H_{36} + CO_2$$

2. By hydrodeoxygenation reaction (with the production of water and normal paraffins)

$$C_{17}H_{35}COOH + 3H_2 \rightarrow C_{18}H_{38} + 2H_2O$$

The direction of the process is determined by the ratio (C_{17}/C_{18}) of the paraffins those have either 17 or 18 carbon atoms in the chain.

Currently, this process is mostly operated by using hydrotreating catalysts. However, the transformation of the vegetable oils by the second direction results the production of water in the process. These water molecules destroy the structure and decrease the duration of maintenance of the hydrotreating catalysts. That is why, the first direction of the transformation of vegetable oils is desired [2].

Taking into consideration of this factor, besides the hydrotreating catalysts miscellaneous zeolite based, as well as the nanostructured catalysts are used in order to direct the decomposition of the triglycerides to decarboxylation process. As the natural halloysites are nanotubed alumosilicates, their usage for this process is in the focus of attention. Nowadays, natural halloysites are manufactured by a number of companies of the different countries such as the USA, China, and France [4-5].

The usage of the halloysites-natural nanotubes those are modified with the oxides of transition metals as catalysts for the hydrotreating process of the mixture of conventional diesel fraction with vegetable oils is relevant to the purpose.

In comparison to the other alumosilicates, halloysites ($Al_2Si_2O_5(OH)_4{\cdot}2H_2O$) belong to the kaolinite mineral family with high Al/Si ratio and they are nanotubes with natural structure which consists of outer silicon oxide and inner aluminum oxide layers. The chemical content of both halloysite and kaolinite are similar ($Al_2O_3{\cdot}2SiO_2{\cdot}nH_2O$, n=4 and 2<n<4 respectively), the only difference is about the amount of water. Halloysite contains more water molecules (4) than kaolinite. The half of the water of halloysite is in the form of hydroxyl group, the remaining half is in the form of water molecule (H_2O). The water between the layers are fixed, and they are connected with hydroxyl groups. For the hydrated mineral, the thickness of the layers is 10 Å, however for the dehydrated mineral, it decreases up to 7.2 Å. The length of the halloysite tubes is in the interval o 0.5-2.0 µm.

The hydrotreating process of the mixture of mineral based diesel fractions with vegetable oils has been opereted by using the combination of the AQKD-400 hydrotreating catalyst with different synthetic and natural zeolite based catalysts – such as Omnikat – 210P, Zeokar – 600 and halloysites at the Institute of Petrochemical Processes of ANAS. As a result, it has been determined that the usage of halloysites with AQKD-400 catalyst which is currently being used in Baku Oil Refinery named after H.Aliyev shows the most effective results than the other catalytic complexes in the mentioned industrial hydrotreating process (at 330-350°C of temperature, under 3.5 MPa of hydrogen pressure). It has been revealed that, AQKD-400/Halloysite catalytic complex provides the highest C_{17}/C_{18} ratio (1.54) (Chart-1.) and maximum yield of diesel fraction.

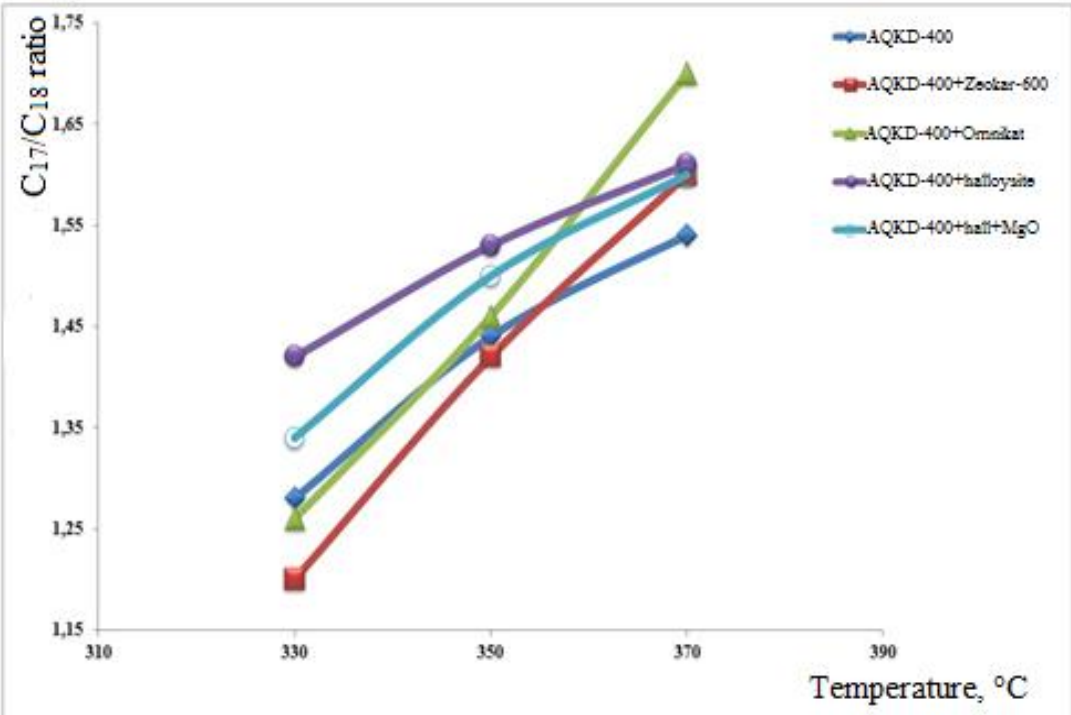


Chart-1: The graph of the ratio of the C18 paraffins to C17 paraffins depending on temperature

The portion of the second cracking reactions are lower than Omnikat – 210P and Zeokar – 600 catalysts those are synthetic zeolites and have stronger acid centers during research of the halloysites in the hydrotreating process of the mixture of diesel distillate with 10% vegetable oils. That is why, the production yield of the diesel fraction is higher by 1.8-2.5 % than the mentioned catalytic systems [8].

2.EXPERIMENTALS

2.1.Materials and Methods

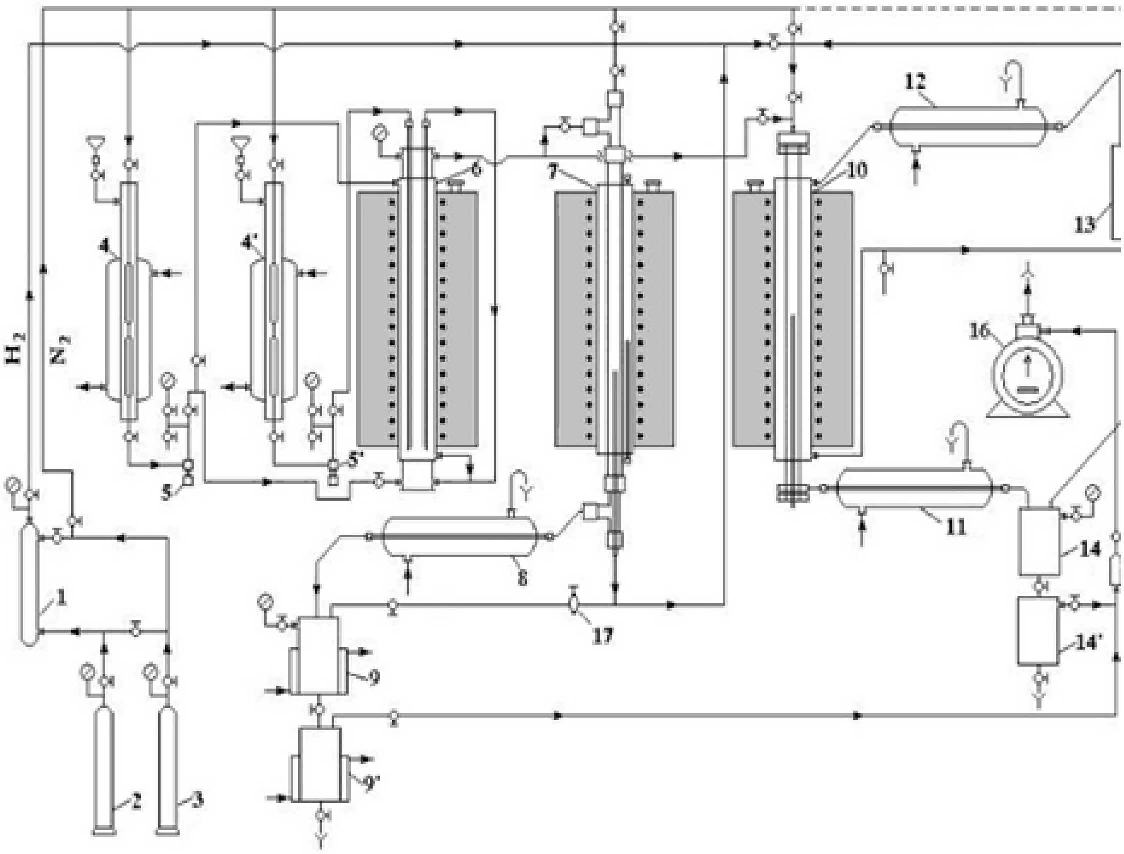
In the presented proceeding, the initial form and the modifications of halloysite nanotubes with transition metals have been investigated as catalysts for the hydrotreating process of the mixture initial refining diesel fuel with 10 % cottonseed oil. For this purpose, new catalyst samples have been prepared by modifying the halloysite samples with the oxides of Ni and Co both separately and together. The phase and elemental content as well as the thermal properties of the modified samples have been determined by X-Ray

Diffractometry (XDR) and Thermogravimetry (Differential Thermal Analysis (TG/DTA/DTG)) methods. The research of the halloysite samples those have been modified with the oxides of Ni and Co reveals that new mineral phases are being created for them and catalysts keep their crystal structure.

The hydrotreating process of mixture of initial refining diesel fraction with 10 % (by mass) cottonseed oil has been operated by using halloysites those have been enriched with Ni and Co oxides as catalysts, at 330-350°C of temperature, under 5.0 MPa of hydrogen pressure and with 1 hour-1 mass velocity of introduced feedstock.

When the halloysite samples are used as free catalysts, pill shaped forms of them are placed in the reactor. In order to provide equal distribution of the feedstock on the catalyst layer and avoid falling down of catalysts from the outlet of reactor, 2 cm of porcelains are placed in the upper and lower part of reactor respectively.

The hydrotreating process of the mixture of diesel fuel with vegetable oil has been operated in the plant which is shown belong (Fig-2.1)



1 - gas collector
2, 3 - gas balloons
4, 4' - feedstock measurement containers
5, 5'- measurement pumps
6 - heater - mixer
7, 10 - middle and high pressured reactors
8, 11, 12 - coolers
9, 9' - separator - cooler, middle pressured reactor
13 - drop container
14, 14' - separators
15 - pressure regulatir
16 - gas meter
17 - throttling valve

Fig-2.1: The technological scheme of the hydrotreating process of the mixture of diesel fractions and vegetable oils

The diesel fraction is given from the container (4) to the bottom entry of the mixer by the measurement pump (5).

The cottonseed oil is given from the container (4') to the top part of the pipe which is attached to the bottom of the mixer by the measurement pump (5'). In the bottom part of the mixer, the diesel fraction and vegetable oil are heated up to 80°C by mixing and entered to the middle pressured reactor which contains catalysts. Before introducing the feedstock, catalysts should be activated in the presence of hydrogen flow at 370-400°C during 2-3 hours.

When the activation process is finished, feedstock pumps (5 and 5') are started to operate, 3.0-3.5 MPa of pressure, 330-350°C of temperature and 1 hour-1 mass velocity are provided by throttling valve (15) which is placed after separators (9' and 14').

The reactors (7 and 10) may be used for higher pressures (7.0-10.0 MPa). These reactors may be operated either parallel or individually.

The product is passed through the coolers (8 and 11) and entered to the separators (either 9, 9' or 14, 14'). Here, the hydrogen which is separated by hydrogen pipe is partially returned to the system, the remaining part is passed through the throttling valve (15) and gas meter (16) and thrown to the atmosphere.

If there is a need for the second step of hydrotreating process, the product of the first step is sent to the reactor (10) from the reactor (7) and the hydrotreating process continues, but the valve (17) should be closed. When the process is finished, the product is entered to the separators (14, 14') by passing through the cooler (11) and then, the obtained gas products are sent to the analysis by passing through the gas meter (16), the liquid products are taken from separator (14').

The initial refining diesel fraction (D2) which contains 10% of light gasoil of catalytic cracking and 10% of light phlegm of coking has been used for the experiments.

The properties of used diesel fraction and cottonseed oil are presented in Table 2.1 and 2.2.

Table-2.1: The properties of used diesel fraction

Pointers	Factual pointers
Density kg/m^3, at 20 °C	850,3
Content:	
Total sulfur content, % by mass	0,0855
Fractional composition, °C:	
Initial boiling point	189
10 %	218
50 %	281
90 %	249
Final boiling point	365
Iodine number, g J_2/100 g	2.5
Total Acid Number, mg KOH/g	-
Kinematic viscosity, at 40 °C, mm^2/sec	2,72
Flash point, °C in closed cruicible	68
Freezing point, °C	-40
Cloud point, °C	-28
Ash content, % by mass	0,002
Coking of 10% residue, % by mass	0,07
Hydrocarbon composition	
unsaturated	4.14
aromatic	18.34
Naphthene + paraffins	77.51

Table-2.2: The properties of used cottonseed oil

The name of the oil	Iodine number g J_2/100 g	Total Acid Number mg KOH/ g	Molecular mass g/mol	Density, kg/m^3 at 20°C	$T_{freezing}$°C	Refractive index
Cottonseed oil (unrefined)	110,0	2,50	780	923,0	-18	1,4758

3.RESULTS AND DISCUSSION

The material balance of the hydrotreating process of the mixture of initial refining diesel distillate with 10 % cottonseed oil is given in Table 3.1.

As can be seen from Table 3.1, when halloysite samples are used as catalysts, the production yield of the diesel fraction from the hydrotreating process of the mixture of initial refining diesel fraction with 10 % (by mass) cottonseed oil is 97.1 %, however the yield is slightly bigger by 95.3 % when halloysite samples enriched with Ni and Co oxides are used.

Table-3.1: The material balance of the hydrotreating process of the mixture of diesel distillate with 10 % cottonseed oil by using enriched halloysite with the oxides of Ni and Co

Pointers	Halloysite	Halloysite+NiO	Halloysite+CoO	Halloysite+NiO+CoO
Initial materials ,% mass.				
Initial refining fraction	88,0	88,0	88,0	88,0
Cottonseed Oil	8,8	8,8	8,8	8,8
Hydrogen	2,4	2,4	2,4	2,4
Products ,% mass.				
Diesel fraction 180-350°C	91,7	93,2	94,1	95,3
Gasoline fraction b.p.-180°C	2,4	1,9	2,0	1,8
Gases C_1-C_4	3,5	2,6	1,7	0,9
Coke	0,9	0,6	0,6	0,5
Water	0,5	0,5	0,5	0,5
Loss	1,0	1,2	1,1	1,0

The quality pointers of the diesel fractions those have been obtained from the hydrotreating process of the mixture of initial refining diesel distillate with 10 % cottonseed oil are given in Table 3.2

As it is obvious from Table 3.2, the total sulfur content decreases from 0.0855 % to 0.0607 % as a result of the hydrotreating process of the mixture of initial refining diesel distillate with 10 % cottonseed oil by using halloysite samples as catalysts at 350°C of temperature, under 5.0 MPa of hydrogen pressure and with 0.5-1 hour-1 mass velocity. The desulfurization depth is 29 % (by mass). The total sulfur content was 0.0209-0.0193 % (by mass) when the halloysite samples were enriched with Co and Ni oxides separately. The desulfurization depth was 75.5-77.4 % (by mass) respectively. The usage of the halloysite samples those are enriched with Co and Ni oxides together provides a decrease in the total sulfur content up to 0.002 % for diesel fraction. The desulfurization depth is 97.6 % (by mass) for it.

Table-3.2: The quality pointers of the diesel fractions those have been obtained from the hydrotreating process of the mixture of initial refining diesel distillate with 10 % cottonseed oil

Pointers	Halloysite	Halloysite+ NiO	Halloysite +CoO	Halloysite +NiO+CoO
Density at 15°C, kg/m^3	838,6	842,8	843,6	842,0
Fractional composition, °C				
Initial boiling point	180	185	195	196
10%	214	218	220	220
50 %	280	280	285	286
Endpoint of boiling	360	365	368	370
Flash point, in closed cruicible, °C	69	71	71	71
Kinematic viscosity at 20 °C mm^2/sec	2,75	3,1	3,25	3,27
Cloud point °C (should not be high)	-25	-28	-27	-28
Freezing point °C (should not be high)	-35	-37	-39	-40
Acidity mg KOH/100 cm^3 fuel	0,53	0,95	0,85	0,5
Iodine number, g J_2/100 g fuel	1,84	1,4	1,9	1,3
Total sulfur content, % mass.	0,0607	0,0193	0,0209	0,002
Coking of 10 % residue, % mass	0,0016	0,0021	0,0020	0,0011
Hydrocarbon composition, % mass				
aromatic	16,5	13,5	12,8	12,0
unsaturated	1,80	1,0	1,1	1,0
naphthene-paraffin	81,7	85,5	86,1	87,0

When the halloysite samples those are modified with Ni and Co oxides together are used as catalysts, the least amount of sulfur and aromatic hydrocarbons are observed in the diesel fraction that is obtained from the hydrotreating process of the mixture of primary refining diesel fraction with 10 % of cottonseed oil.

It should be mentioned that inspite of the addition of cottonseed oil, the low temperature properties of diesel fuel is not deteriorated and it is compatible with the winter diesel fuel.

REFERENCES

[1] energy-source.ru/publish/tehno/149-centia
[2] Senol O.I., Viljava T.R., Krause A.O.I. Hydrodeoxygenation of aliphatic esters on sulphided NiMo/γ-Al2O3 and CoMo/γ- Al2O3 catalyst: The effect of water, Catalysis Today. Vol.106, 2005,pp.186-189
[3] Kalnes T.N., Marker T., Shonnard D.R. Green Diesel: A Second Generation Biofuel, Int. J. Chem. React. Eng. Vol.5, 2007, pp. 87-93
[4] Joussein E., Petit S., Churchman J., et al. Halloysite clay minerals – a review, Clay Mineral, Vol. 40, 2005, pp. 383-426
[5] Elechkiy A.V., Carbon nanotubes and their emission properties, The achievements of Physics, Vol.172, No.4, 2002, pp.402-438
[6] Aliyev R.R., Reznichenko I.D., Chelyutina M.I., The ecological problems in the production of alumonickel(cobalt)molybdenum catalysts, Catalysts in the industry, No.2, 2005, pp. 33-39
[7] Chelyutina M.I., Reznichenko I.D., Aliyev R.R., Trophimova M.V., The synthesis of the hydrotreating catalysts in petroleum refining, Ecology and Industry,2005, pp 14-17
[8] Mammadova T.A., The research and production of manufacturing environmentally friendly motor oils and addition of petroleum acid and vegetable oil based additives to them, The dissertation for candidature of the doctor of technical sciences, Baku, 2014, pp 265-284

BIOGRAPHY

Tarana Aslan Mammadova is deputy director of Yu.G.Mammadaliyev Institute of Petrochemical Processes for scientific purposes and the Head of the Laboratory of Renewable Fuels. Her main scientific objective is the manufacture of the environmentally-friendly engine fuels.

Mutallim Maharram Abbasov is working as a leading researcher at Yu.G.Mamedaliyev Institute of Petrochemical Processes. His main scientific objective is the production of environmentally-friendly diesel fuels from the secondary refining petroleum products.

Aynur Rovshan Hasanova is working as a technologist in the laboratory of Renewable Fuels and Ph.D student at Yu.G.Mamedaliyev Institute of Petrochemical Processes. Her main scientific objective is the production of "green" diesel with hydrotreating process by modifying of different catalysts.

Anar Amil Namazov is working as a chemist in the laboratory of Renewable Fuels at Yu.G.Mamedaliyev Institute of Petrochemical Processes. His interest areas include preparation of different catalysts and the analysis of petroleum products with chromatographic methods.