



NON-CONVENTIONAL METHODS OF PREPARATION OF POLYMER WASTE TO CATALYTIC PROCESSING INTO THE FUEL

Zheneta Kh. TASHMUKHAMBETOVA,^a Yermek A. AUBAKIROV,^a Larissa R. SASSYKOVA,^{a*}
Kairat E. BURKHANBEKOV,^a Maria F. FAIZULLAEVA^{b,c} and Nurbubi K. ZHAKIROVA^a

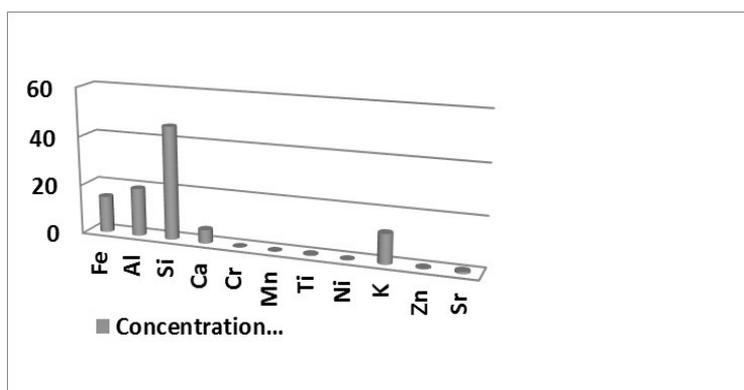
^a Al-Farabi Kazakh National University, 71, al-Farabi, Almaty, Kazakhstan, 050040

^b Scientific Research Institute of New Chemical Technologies and Materials, 95^a, Karasaibatyr, Almaty, Kazakhstan, 050012

^c Korkyt Ata Kyzylorda Universsity, 29a Aiteke bi str., Kyzylorda, Kazakhstan

Received May 16, 2017

The influence of non-conventional methods of preparation of raw materials on the basis of waste rubber and plastics on hydrogenation thermal catalytic processing by preliminary treatment by ultrasound, irradiation, cryogenic treatment with liquid nitrogen along with mechanical grinding was investigated. The catalysts of the process are the composites based on polymetallic wastes of ferroalloy production (WFP) and activated by acid treatment of the natural zeolite of the Kazakh Taizhuzgen deposit researched by X-ray fluorescence, X-ray diffraction and nitrogen porosimetry. It was found that the greatest yield of a liquid product is observed when the raw material is processed by ultrasound with the intensity of ultrasonic waves $I = 5 \text{ W/cm}^2$; 150 seconds. The irradiation of raw materials somewhat reduces the yield of liquid fractions and increases the formation of gas. Processing raw materials with liquid nitrogen, followed by mechanical grinding, allows changing the structure of the organic mass, which affects the yield, composition and quality of the products.



INTRODUCTION

Perspective non-conventional methods of physical and chemical influence are methods of cryogenic processing by liquid nitrogen, by ultrasound, radiations and other methods.^{1,2} The most effective way is their resonant processing. The phenomenon of cavitation is followed by concentration of energy which is capable to change physical and chemical properties of raw materials on the basis of carbon-containing waste, causes a depolymerization, increases the content of light hydrocarbons in the obtained liquid products. Cavitation is followed also by partial destruction of

molecules, with formation of free radicals which are capable to initiate the liquefaction process. The similar effect renders a way of preliminary radiation exposure and cryogenic processing of raw materials on the basis of solid carbon-containing waste.³⁻⁶ In recent years, along with the mechanical grinding of the solid carbon-containing raw materials based on waste, non-conventional methods of physical and chemical effects, such as sonication, cryogenic treatment and irradiation, are used.⁷⁻¹¹

The aim of the study was to determine the effect of preliminary cryogenic treatment, ultrasonic treatment and irradiation of raw materials based on polymer waste on the change in the yield and the

* Corresponding author: larissa.rav@mail.ru

group hydrocarbon composition of the products of their thermocatalytic hydrogenation. In this research an attempt of development of resource-saving technology was made for the solution of a problem of complex and harmless utilization of polymeric materials on the basis of worn tires, rubber-containing and plastic waste, polymetallic wastes of metallurgical industries. Composites based on polymetallic wastes of ferroalloy production (WFP) and acid-activated natural zeolite-heulandite-clinoptilolite of Kazakh field Tayzhuzgen were used as catalysts of the process. Previously, the surface and structural properties of composite catalysts were studied using X-ray spectroscopy and X-ray phase analysis.¹²

RESULTS AND DISCUSSION

Surface and structural properties of composite catalysts based on natural zeolites and WFP were studied using X-ray spectral, X-ray phase analysis and BET method. X-ray phase analysis of catalysts

based on activated zeolite and WFP is presented in Figs. 1-3. According to the given diffractograms of the zeolite, three crystalline phases corresponding to the heulandite of the composition $\text{Ca}(\text{Ca}_{3,6}\text{K}_{0,8}\text{Al}_{8,8}\text{Si}_{27,4}\text{O}_{72}\cdot 26,1\text{H}_2\text{O})$, clinoptilolite of the composition $\text{Ca}(\text{K}, \text{Na}_2\text{Ca}_2(\text{Si}_{29}\text{Al}_7)\text{O}_{72}\cdot 24\text{H}_2\text{O})$ and quartz were identified in them. As follows from the diffractograms of the WFP, alumina and silica are equally present in it, which are manifested in the form of additive signals (Fig. 2). The textural properties of catalysts by the method of adsorption porometry of BET were investigated and their specific surfaces were determined (Table 1).

According to X-ray spectral analysis, in the initial catalysts, metals with variable valence, such as Mn, Ti, Fe, Cr, are present along with Si and Al, which makes them suitable for use in the researched process (Fig. 4, 5).

Thus, it was found that the catalysts under investigation are characterized by the presence of active centers and good texture properties.

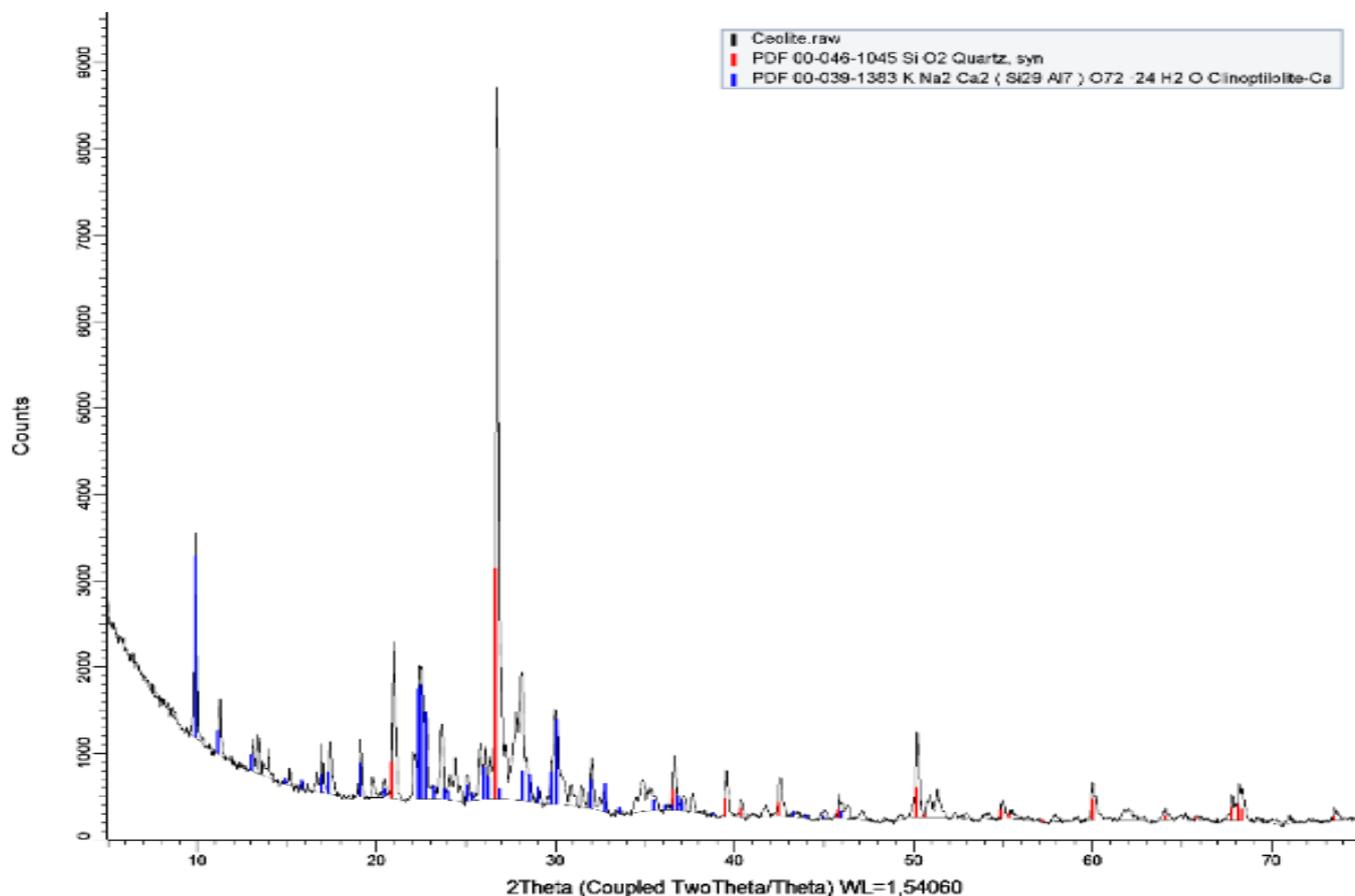


Fig. 1 – Diffractogram of a sample of zeolite with the detection of clinoptilolite and quartz.

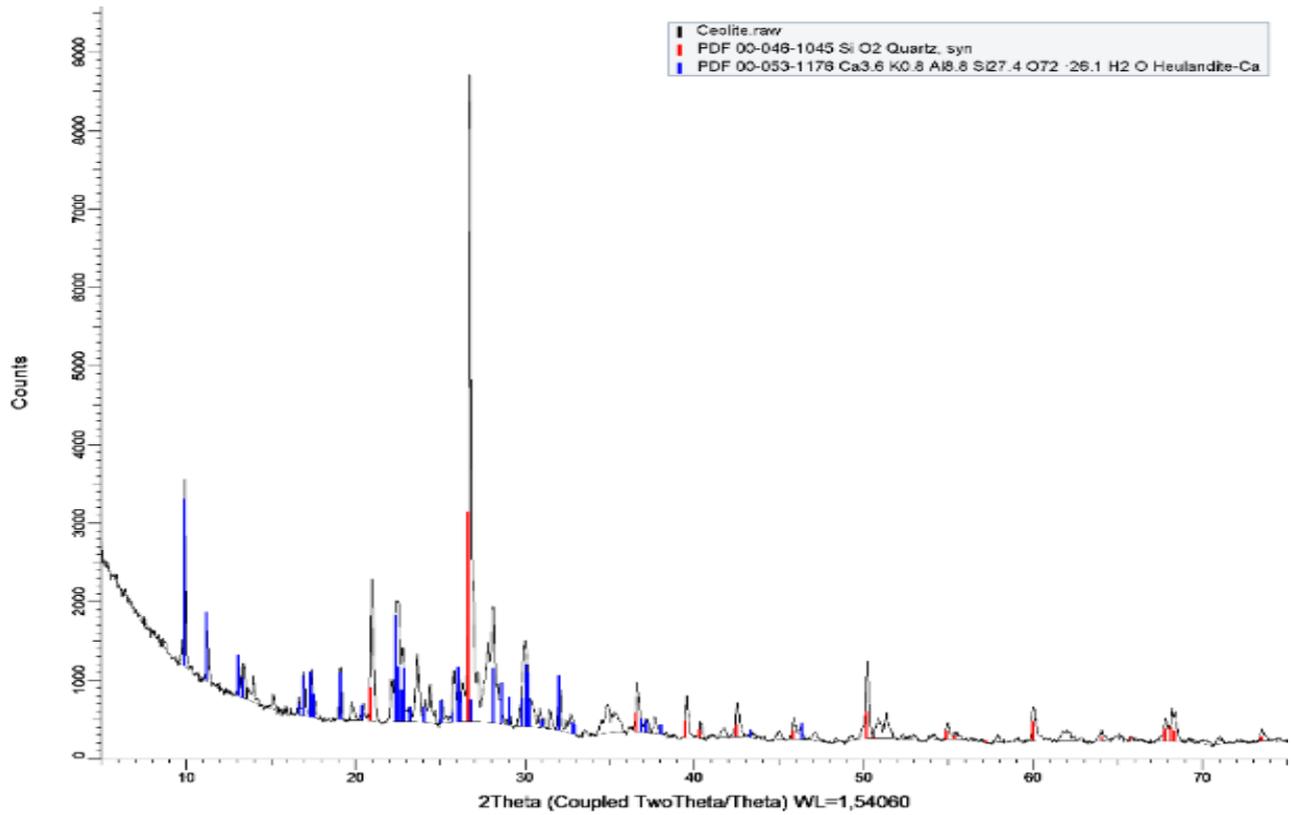


Fig. 2 – Diffractogram of a sample of zeolite with the detection of heulandite and quartz.

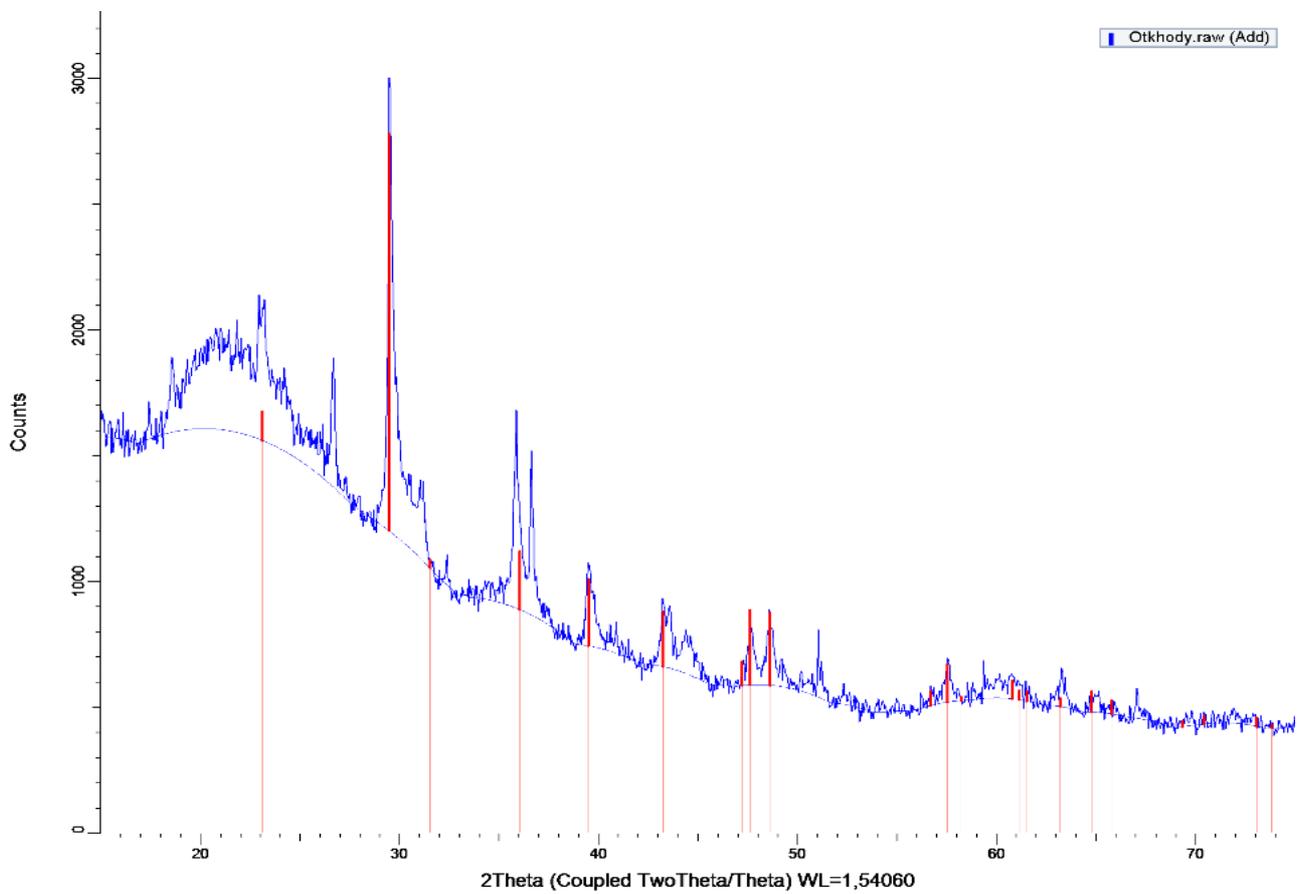


Fig. 3 – Diffractogram of the sample of the WFP.

Table 1

Data of catalyst analysis by the method of adsorption porometry BET

Index	Catalyst	
	Activated zeolite	WFP
Average volume of pores, cm ³ /g	0.02	0.16
Average pore diameter, Å	104.10	86.60
Specific surface, m ² /g	7.20	108.60

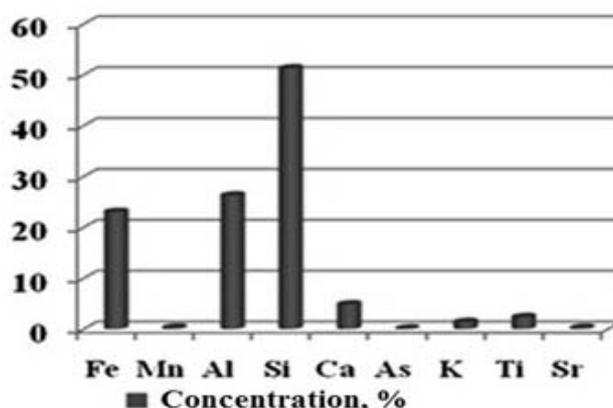


Fig. 4 – Elemental composition of WFP.

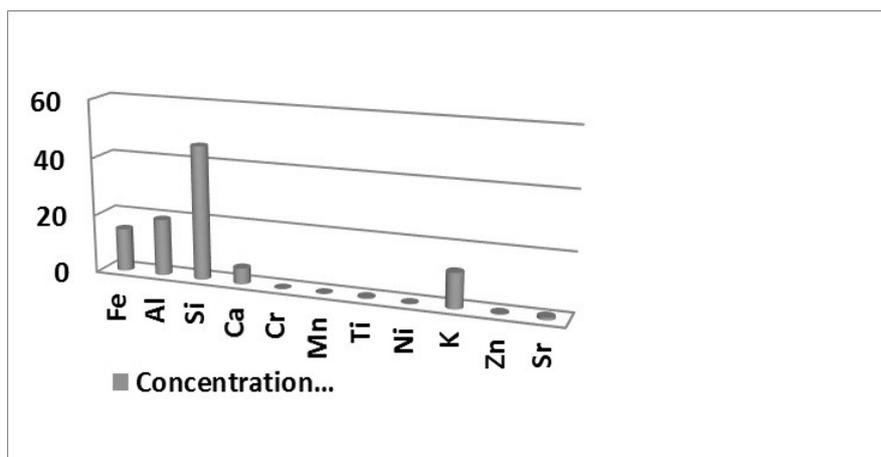


Fig. 5 – Elemental composition of zeolite.

It is known that preliminary processing of raw materials on the basis of industrial and household waste (tires and tubes and plastic) can have in the known physical and chemical ways significant effect on change of their structure and hydrocarbonic structure, and in some cases and reactionary ability that allows to improve technologies of processing of waste and to increase selectivity concerning the obtained range of products.^{13,14} For this reason influence of preliminary ultrasonic processing, radiative effects, cryogenic processing by liquid nitrogen and mechanical crushing of initial raw materials on the basis of waste on the yield and composition of

products of hydrogenation thermocatalytic processing has been studied.

As is known, the effect of cavitation is accompanied by microexplosions, ultrasound, as well as mechanical cuts and collisions with the action of hundreds of cutting pairs moving towards each other at a high linear velocity. The value of this velocity is several tens of meters per second, which makes it possible to cut the dispersible substance on the smallest microparticles by hundreds of thousands of micropulses.^{15,16} The effect of preliminary ultrasonic treatment of rubber crumbs of tires with the degree of dispersion of about 1 to 4 mm in water on the composition

change and the yield of products of hydrogenation thermal catalytic processing on the investigated composite catalysts was studied. Earlier in our works,¹⁷ it has been shown that processing by ultrasound of a rubber crumb with degree of dispersion of 0.6-0.8 mm in water has practically no significant effect on the yield of a liquid product and its fractional composition under optimum conditions of carrying out the process ($T = 400^{\circ}\text{C}$; paste former PF: rubber = 1: 1; catalyst - WFP: zeolite = 40:60; $P = 5-7$ MPa, $t = 60$ min.). In this work it was revealed that a variation of parameters of ultrasonic processing in the range of values of intensity: $I = 1-5$ W/cm²; $t = 50-150$ s of significant effect on dispersion and structural changes of an organic part of rubber and plastic did not render.

The ultrasonic treatment of plastic crumb crushed to a degree of dispersion of about 2 to 6 mm in water in the investigated regimes proved to be practically impractical, since there was practically no cavitation effect on such a strong, fatty and adhesion-resistant material. Therefore, for a research of influence of cavitation processing on composition and the yield of products of hydrogenation thermocatalytic processing it was used a mixture rubber: plastic of composition 1:1 with a size of particles from 2 to 6 mm. The process was carried out on catalyst WFP: zeolite = 40:60 at $T=450^{\circ}\text{C}$; $P=5-7$ MPa; $t=15$ min.; PF: waste = 1:1. Processing of the studied mixture of rubbers and plastic at $I = 1, 3, 5$ W/cm² in the range of values of time of processing 50, 100, 150 sec. at the room temperature does not give accurate regularity on the yield of gaseous and liquid products, and also on the yield of light to 180°C , average $180-250^{\circ}\text{C}$ and heavy distillates $250-320^{\circ}\text{C}$. A total yield of liquid distillate ranges within 54.4 – 61.0 wt.% (Fig. 6). Yield of gases depends on intensity and time of cavitation processing a little.

As, generally, there are changes in the structure of rubbers caused by multiple-factor energy influence in the form of an impulse, which are followed by a mechanical rupture of associative molecules links of rubbers and the vulcanization sulfur, and also hydrodynamic influence by shift of tension in liquid, the cavitation processing by water should promote separation of a metal cord, soot and sulfur and other fillers from an organic part that in turn should cause its easier transformation into liquid and mainly gaseous

products. It was found that the most optimal for the liquid product yield are rubbish and plastic waste, treated with ultrasound at $I = 5$ W/cm²; duration - 150 sec. - 61.0 wt. %.

Influence of radiation exposure of waste of rubbers and plastic on the yield and composition of liquid products in the process of their hydrogenation thermocatalytic processing on catalyst WFP:zeolite= 40:60 has been investigated at $T = 400^{\circ}\text{C}$; $P = 5-7$ MPa; $t = 15$ min.; PF: waste = 1:1 (Fig. 7). The irradiation was carried out by an electron beam with a density of $2 \mu\text{A} / \text{cm}^2$ with a variation in the irradiation dose from 100 to 500 kGy. As can be seen from Fig.7, the total yield of the liquid fraction from the previously irradiated mixture rubber : plastic varies in the range 32.18 - 53.39% by wt. It should be noted that in the irradiation range of 100 and 300 kGy, respectively, high yields of the liquid fraction are observed. The optimum yield of the gasoline fraction is revealed at an irradiation dose of 500 kGy, and for diesel fuel at a dose of 300 kGy.

Also, it was revealed that radiation of rubbers and plastic in the studied interval of doses has no significant effect on the yield of light distillates in the course of hydrogenation catalytic processing. The yield of the gas fraction increased by about 4-5 wt. %. This is due to the destructive splitting of bonds in rubbers and polymer cord during the irradiation, which leads to further easier thermal decomposition of molecules under the influence of high temperature to hydrocarbon gases of the composition C_1-C_4 , carbon oxides, and is also accompanied by the formation of sulfur-containing gases. It can be caused by the prevalence of process of thermolysis over catalytic cracking and hydrogenation transformations of the formed short molecules. As a part of a dry product there are mainly cord components, metals, soot, mineral additives, sulfur, etc. The essential contribution to the formation of a liquid product is made by fuel oil as binding, a source of hydrogen and reagent.

Thus, preliminary investigations of the effect of irradiation of waste rubber and plastics have shown that it reduces the yield of liquid fractions by about 8-10 wt.% and increases gas formation by 4-5 wt.%. Analysis of the hydrocarbon gas composition by the gas-liquid chromatography method showed the presence of paraffins and isoparaffins of the C_1-C_4 composition, olefins and dienes, gas condensate of the composition C_4-C_5 , H_2 , CO , CO_2 , H_2S .^{12, 18} It was found, in the process

of cryogenic treatment of rubber and plastics wastes with liquid nitrogen for several days in a Dewar vessel, that rubber (tires) had external changes, which is possibly due to structural transformations in its organic part. After processing of rubber with liquid nitrogen,

mechanical separation of rubbers and polymer fibers from metal cord and other components took place. After drying in a vacuum drying cabinet, the rubber mixture was separated from the visible fibers and subjected to mechanical grinding in a ball mill.

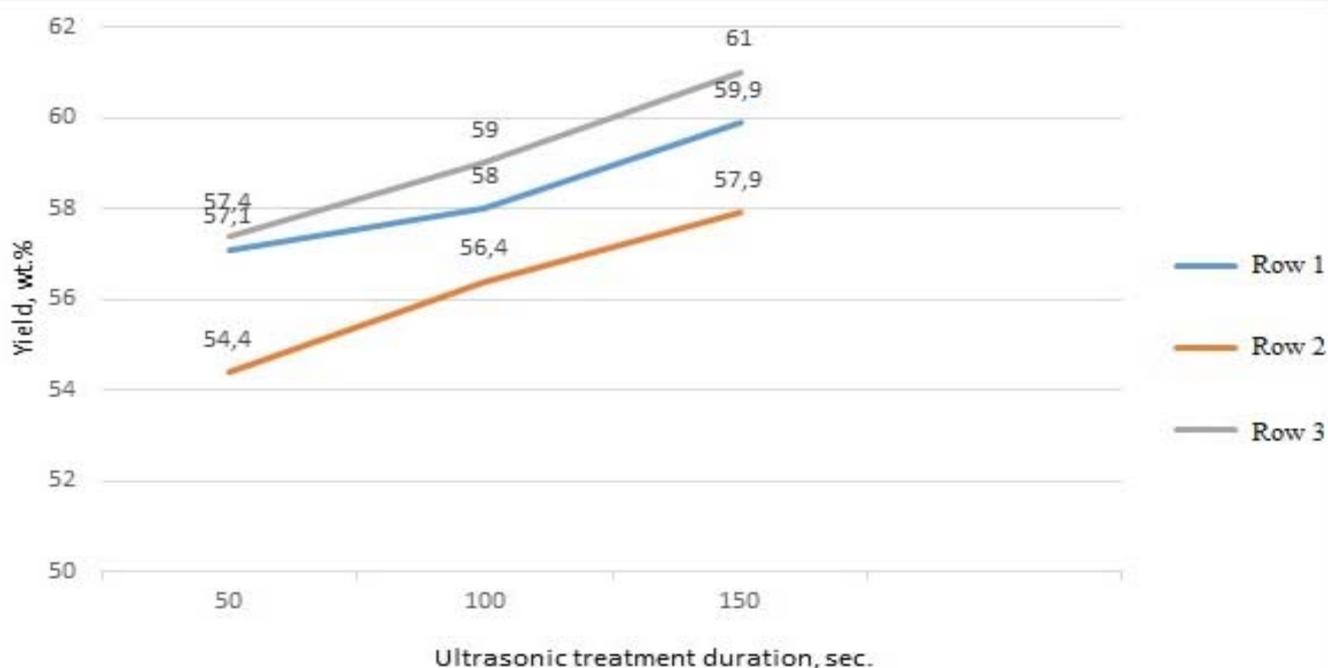


Fig. 6 – Dependence of the yield of the liquid fraction (LF) on the intensity of ultrasound (I) and the processing time (t), rows: 1- I = 3; 2- I = 1; 3- I = 5 (W/cm²); T = 50, 100, 150 (s).

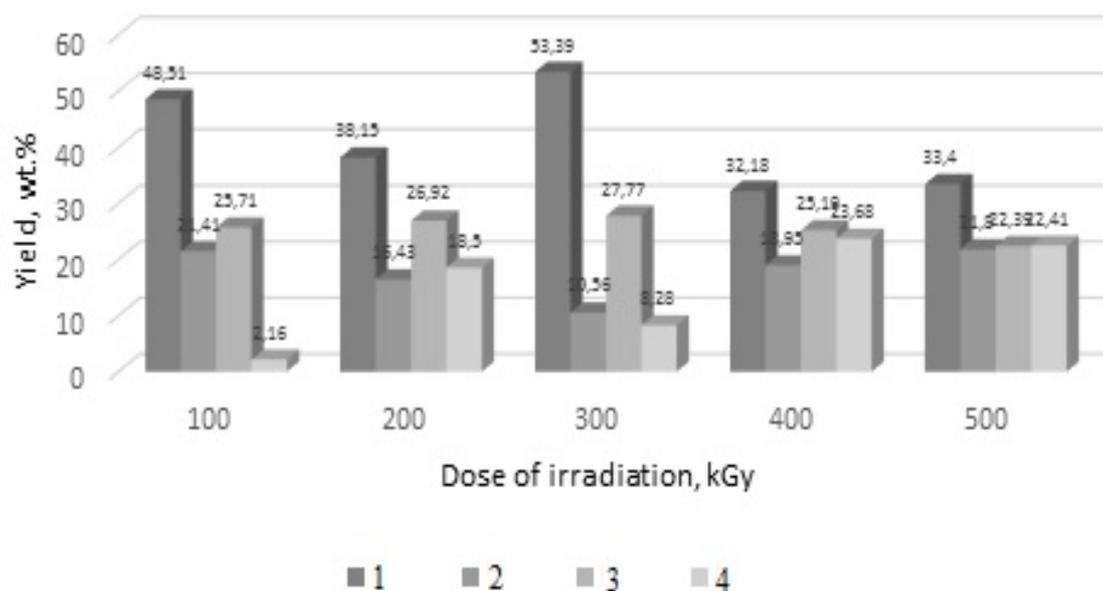


Fig. 7 – Dependence of the yield of the products of processing of radiation irradiated waste of polymers on the WFP: zeolite catalyst t = 40: 60 at T = 400°C; P = 5-7 MPa; t = 15 min.; PF: waste = 1: 1; rubber: plastic = 1: 1 from a radiation dose. Rows: 1-total liquid product; 2 gas; 3-dry residue; 4 – losses.

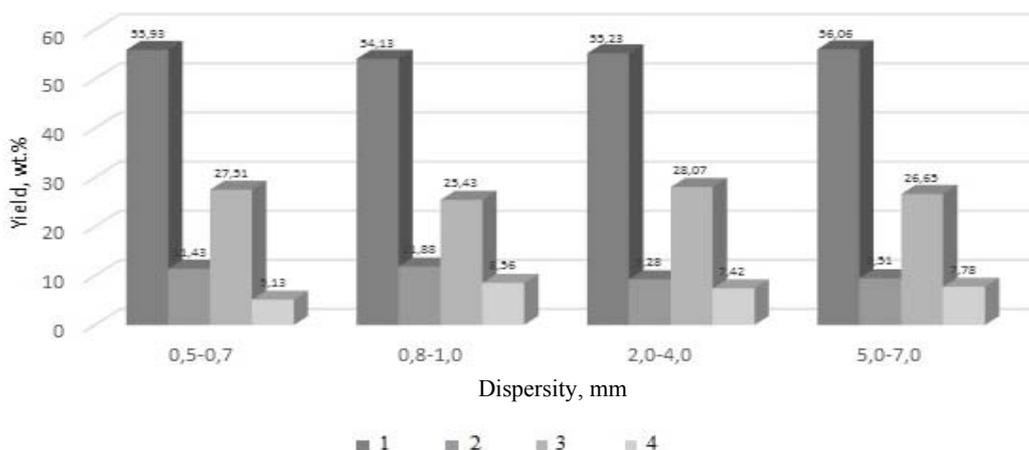


Fig. 8 – Dependence of product yields on the dispersion of rubber treated with liquid nitrogen (WFP:zeolite= 40: 60 (0.67 g), $T = 400^{\circ}\text{C}$, $P = 5-7\text{ MPa}$, $t = 15\text{ min.}$; PF:rubber = 1: 1). Rows: 1 - total liquid product; 2 - gas; 3 - dry residue; 4 - losses.

Mechanical grinding of rubber crumb after treatment with liquid nitrogen allowed to extract fractions of approximately the following dispersity: 0.5-0.7; 0.8-1.0; 2-4; 5-7 mm, respectively, which were investigated in the reaction of hydrogenation thermocatalytic processing on a WFP catalyst: zeolite = 40: 60 under similar conditions (Fig. 8).

With increasing dispersion of rubber by treatment with liquid nitrogen and mechanical grinding, the catalytic activity of the investigated catalyst increases, which is apparently due to the formation of an optimal active contact surface of catalyst particles and raw materials under given process conditions. The yield of the liquid product varies by about 3 wt.% and ranges from 54.13 to 56.06 wt.%.

So, the cryogenic processing of rubber with liquid nitrogen and mechanical grinding into pieces with different degrees of dispersion under given conditions for carrying out hydrogenation catalytic processing did not have a significant effect on the fractional composition and yield of the products, although it facilitates an easier separation of inorganic constituents and soot from the

hydrocarbon part of rubbers. Earlier in our work it was shown that at a degree of grinding of rubbers (tires) 0.4-0.6 mm, the yield of liquid distillate was 56.8 wt.%.¹⁸⁻²² As a part of the rubber crumbs crushed to dispersion degree 0.4-0.6 the content of 62 wt.% of rubbers (natural and butadiene - styrene), 3 wt.% of soot and 35 wt.% of other components was found.

Polymer crumb (3-6 mm) after treatment for 1-3 days with liquid nitrogen practically did not undergo any changes and was used in a mixture with crushed rubber with a degree of dispersion of 3-6 mm in the hydrogenation thermocatalytic processing on the catalyst WFP:zeolite= 40: 60; $T = 15\text{ min.}$; PF: rubber = 1: 1; rubber: plastic = 1: 1 at $T = 450^{\circ}\text{C}$ (Table 2). Thus, recycling of rubbish and plastic wastes on the investigated composite catalysts with preliminary treatment of raw materials with liquid nitrogen and subsequent mechanical grinding allows to slightly change the structure of the organic mass, which affects not only the yield and composition of liquid and gaseous products, but sometimes improves their quality.

Table 2

Dependence of the yield of a liquid fraction of processing of plastic and mixture rubber-plastic (dispersion degree = 3-6 mm; $T = 450^{\circ}\text{C}$; catalyst WFP:zeolite with the composition 40 : 60 and 60 : 40; $P = 5-7\text{ MPa}$; $t = 15\text{ min.}$; PF:waste = 1 : 1; rubber-plastic= 1 : 1)

Catalyst WFP:zeolite	V_{gas} , wt.%	Liquid phase, T_{boiling} to 180°C , wt.%	Liquid phase, T_{boiling} 180- 250°C , wt.%	Liquid phase, T_{boiling} 250- 320°C wt.%	Σ liquid phase, wt.%	Weight of dry residue, wt.%	Losses, wt.%
Plastic							
40:60	2.99	10.89	18.43	37.69	67.01	12.0	18.00
60:40	3.64	21.43	5.30	35.63	62.36	13.0	21.00
Rubber-plastic							
40:60	4.99	24.91	25.08	15.98	65.97	13.0	16.04
60:40	4.78	24.10	29.11	8.39	61.60	15.0	18.62

The yield of liquid fraction when processing within 15 min. at $T=450^{\circ}\text{C}$ on catalyst WFP: zeolite of composition 40: 60 was higher and corresponded on plastic – 67.01 wt. %, and on mixture rubber: plastic – 65.97 wt. % (Table 2).

EXPERIMENTAL

The experiment was made on installation of periodic action under pressure from 5 to 7 MPa and temperatures of 400-450°C in a continuous mixing regime. The installation is represented by a stainless steel metal reactor Kh18N10T of the “duck” type with a volume of 0.25 dm³. Thermal heating was realized by means of the heater of the alternating current regulated by the transformer and the ampermeter. Temperature monitoring in the reactor was carried out using a thermocouple with a chromel-copel, the readings were recorded on a KSP-4 instrument whose scale was calibrated for boiling temperatures of water (100°C), melting of tin (232°C), lead (327°C) and zinc (427°C). The pressure in the hydrogenation process was created by argon, the change of which was fixed with a manometer. A mixture of crushed polymeric materials, catalyst and paste former (PF) - black oil with a boiling point > 350°C, heated to 70-80°C, was loaded into the reactor, then the reactor was checked for leaks, purged with argon, a pressure of 0.4-0.5 MPa, then the heating device was turned on. During the hydrogenation process, a pressure change was recorded using a manometer due to temperature increase, gas separation and the presence of volatile components. After the experiment, the heating of the reactor was switched off and the system was cooled to room temperature. The gas formed in the process was collected in a gas meter with a saturated salt solution. The amount of gas formed was determined from the pressure difference.

Ultrasonic treatment of polymeric wastes was carried out on multifunctional laboratory ultrasonic complex MARK-3/22-AL. Cryoprocessing of the rubber and plastic samples under study was carried out with liquid nitrogen in a Dewar vessel. X-ray phase analysis of the catalysts was carried out on an X-ray diffractometer ARL X'TRA. The specific surface area of the samples of catalysts based on activated zeolite and WFP was determined by the method of nitrogen porosimetry on the AUTOSORB-6B unit.

CONCLUSION

The carried-out complex of analyses of composition and physical and chemical properties of catalysts has allowed to draw a conclusion that the studied samples on the basis of polymetallic waste of ferroalloys and the activated natural zeolite on the elemental composition and superficial structure are of interest as available, rather cheap and active catalysts to process of hydrogenation thermocatalytic processing of carbon-containing waste on the basis of worn tires and plastic in motor fuels. In this work it was

shown the possibility of implementation of an integrated approach to preparation of waste of rubbers and plastic by preliminary processing by ultrasound, radiation exposure, cryogenic processing by liquid nitrogen with the subsequent mechanical grinding which lead to increase in degree of dispersion of raw materials, separation of organic mass from the accompanying components and simplification of its transformation into liquid fuel products. It was found that the most optimal for the liquid product yield are rubbish and plastic waste, treated with ultrasound at $I = 5 \text{ W/cm}^2$; $T = 150 \text{ sec.}$ - 61.0 wt.%, and the yield of gases depends little on the intensity and time of cavitation treatment; irradiation of waste rubber and plastics ($D=100-500 \text{ kGy}$) reduced the yield of liquid fractions by 8-10 wt.% and increases gas formation by 4-5 wt.%. It was shown that with increasing degree of dispersion of rubber by treatment with liquid nitrogen and mechanical grinding, the activity of the investigated catalyst increases; the yield of the liquid product changes by about 3% by wt. and is in the range of values 54.13-56.06% by wt. The composition and texture properties of the composite catalyst have been established.

REFERENCES

1. Zh. K. Shomanova, Zh. Kh. Tashmukhambetova, E. A. Aubakirov, R. Z. Safarov and Yu. G. Nosenko, *Int. J. Chem. Sci.*, **2015**, *1*, 367–375.
2. Zh. Shomanova, R. Safarov, Yu. Nosenko, Zh. Tashmukhambetova, A. Zharmagambetova, “World Academy of Science, Engineering and Technology Conference Proceedings”, Barcelona, 2016, p. 71–75.
3. A. G. Chmielewski, M. Haji-Saeid and Sh. Ahmed, *Nucl. Instruments Methods Phys. Res. B*, **2005**, *236*, 44–54.
4. S. Jonna and J. Lyons, *Polym. Test.*, **2005**, *24*, 428–434.
5. F. Parrés, J. E. Crespo, A. Nadal, A. Macias-Garcia and E. M. Cuerda-Correa, *Mater. Sci. Forum*, **2010**, *636–637*, 1421–1427.
6. Ch. Thevy Ratnam, S. Ramarad, M. Khalid, S. Abdull Rashid and Z. Mohamed, *Macromol. Symp.*, **2015**, *353*, 47–54.
7. G. Burillo, R. L. Clough, T. Czvikovszky, O. Guven, A. L. Moel, W. Liu, A. Singh, J. Yang and T. Zaharescu, *Radiat. Phys. Chem.*, **2002**, *64*, 41–51.
8. T. Chen, Y. Shen, W. Lee, Ch. Lin and M. Wan, *J. Clean. Prod.*, **2010**, *18*, 1850–1858.
9. G. R. Daborn and R. Derry, *Resour. Conserv. Recycl.*, **1988**, *1*, 49–63.
10. A. Rowhani and Th. J. Rainey, *Energies*, **2016**, *9*, 1–26.
11. J. I. Osayi, S. Iyuke, S. E. Ogbiede, *J. Catal.*, **2014**, *2014*, 1–9.
12. Zh. Kh. Tashmukhambetova, Zh. K. Kairbekov, E. A. Aubakirov, K. E. Burkhanbekov, M. F. Faizullaeva and

- Zh. K. Shomanova, *Solid Fuel Chem.*, **2016**, *50*, 220–225.
13. E. S. Herrera-Sosa, G. Martínez-Barrera, C. Barrera-Díaz, E. Cruz-Zaragoza and F. Ureña-Núñez, *Int. J. Polym. Sci.*, **2015**, *2015*, 1–8.
 14. G. Ramos, F. J. Alguacil and F. A. López, *Rev. Metal.*, **2011**, *47*, 273–284.
 15. L. Bergman, “Ultrasound and its application in science and technology”, Foreign Literature Publishing House, Moscow, 1957, p. 367–368.
 16. E. M. Soloviev, *Caoutch. rubber*, **1984**, *7*, 42–45.
 17. Zh. Kh. Tashmukhambetova, E. A. Aubakirov, K. E. Burkhanbekov and G. B. Makanova, *News of National Academy of RK, series of Chemistry and Technology*, **2016**, *1*, 18–25.
 18. E. Aubakirov, Zh. Tashmukhambetova, Zh. Kairbekov and K. Burkhanbekov, *Appl. Mech. Mater.*, **2014**, *618*, 136–139.
 19. Zh. Tashmukhambetova, J. Aubakirov, Zh. Shomanova, K. Burkhanbekov, R. Safarov, L. Sassykova, N. Zhakirova and M. Faizullaeva, *Oriental J. Chem.*, **2017**, *33*, 2884–2890.
 20. D. A. Baiseitov, M. I. Tulepov, L.R. Sassykova, Sh. A. Gabdrashova, Z. A. Mansurov, *Bulgarian Chemical Communications*, **2017**, *49*, 600–607.
 21. D.A. Baiseitov, Sh. E. Gabdrashova, A.N. Magazova, O. Dalelkhanuly, Zh. B. Kudyarova, M.I. Tulepov, L.R. Sassykova, Z.A. Mansurov, *Int. J. Chem. Sci.*, **2016**, *14*, 244–250.
 22. Zh. K. Kairbekov, E. A. Aubakirov, Zh. Kh. Tashmukhambetova, M. F. Fayzullaeva, Zh. K. Shomanova and K. E. Burkhanbekov, *Chem. Bull. KazNU*, **2015**, *1*, 90–95.

