SCIENTIFIC JOURNAL
OF THE MODERN EDUCATION & RESEARCH INSTITUTE

• The Kingdom of Belgium

BEST PROFESSOR

of the Univercity Republic of Kazakhstan

SPECIAL EDITION

ON THE RESULTS OF ADVANCED TRAINING PROGRAMME

«INNOVATIVE METODS OF TEACHING AND LEARNING»

12-19 June 2016 г.

Date of issue: 15 November 2016

King's Day

THERMAL CATALYTIC RECYCLING OF CARBON CONTAINING WASTES – A REVIEW

Aubakirov Ermek Aitkazynovich (miral.64@mail.ru),
Tashmukhambetova Zheneta Khalilovna (zheneta@mail.ru),
Burkhanbekov Kairat Edilbekovich (burhanbekov@mail.ru)

Al-Farabi Kazakh National University, Almaty

Abstract

Статья рассматривает одну из важнейших современных тенденций экономичесThe authors provide a review of the many years of work in the field of thermal catalytic recycling of carbon-containing wastes, such as worn out automobile tires and household waste plastics. A special attention is given to the processing of these wastes with new efficient catalysts based on natural zeolite and non-deficient polymetallic waste of ferroalloy production.

Keywords: recycling, tire, plastic, shale, catalyst, zeolite, polymetallic waste.

1. INTRODUCTION

In recent years, the majority of the advanced countries are working intensively on improving and developing new technologies for recycling of worn out automobile tires. As well, they try to improve the performance of individual stages of developed technologies that significantly increases the efficiency of the method in a whole. At the same time, great attention is paid to the environmental aspects in the recycling of these wastes, namely, for the creation waste-free and low-waste resource-saving processes.

Most carbon-containing wastes and worn out automobile tires are hard biodegradable and non-destructive wastes [1] and they represent great potential threat to the environment, because their accumulation leads to the formation of dumps [2]. The slow destruction of the tires caused by natural and climatic factors and rodents leads to the formation of particulate matter in the form of small crumbs, which are dispersed in the environment and carried away long distances by the wind. Storage places of used tires are transformed into a huge area of accumulation of a large number of living organisms [3, 4]. Due to this, it is necessary to develop effective recycling ways of used tires, which will simultaneously solve the problem of secondary use, environmental protection and the production of other types of energy sources [5-7].

1.1. Statistical data on world production and the accumulation of waste tires

According to world statistics, the production of tires for 1996 was around 10-11 million tons. In the same year it was produced about 250 million tires in the USA and around 6 million tires in Switzerland respectively [8]. According to data for 2005, numbers of used tires were 2.5 million tons in North America and 2.5 million tons in Europe and 0.5-1.0 million tons in Japan. In 2005, the amount of used tires in China was about 1 million ton and it is growing annually by 12% [9]. Moreover, in 2010 the annual waste tire growth in Europe reached 3.3 million tons, and the total number for the whole of Europe at that time was 5.7 million tons. Over the last 15 years, in the European Union the ways of waste tire recycling has changed dramatically. For example, in 1996 approximately 50% of the total mass of waste tire has been sent to landfill, but now the figure is only 4% [10].

1.2. The average statistical composition of an automobile tire

The complex composition of tires makes them difficult to recycle. The main component of tires is rubber, which is a chemically cross linked polymer and it has high firmness, so car tires cannot be recycled into other forms without serious degradation. On the other hand, the tires are complex mixtures of different materials, such as natural and synthetic rubber, carbon black, metal cord and other organic and inorganic components [6].

A typical tire could contain up to 30 different types of synthetic rubber, 8 different natural rubbers, in addition to a range of different carbon black fillers and up to 40 different additive chemicals [11].

The main rubber types used are in production, typically, styrene-butadiene-rubber, natural rubber (polyisoprene) and polybutadiene rubber [12].

The natural rubber comes from the Hevea tree, whilst the synthetic rubber is generally derived from petroleum based products [13]. Natural rubber has unique elastic properties and it is an essential element of a tire. Rubber comprises elastomeric polymers characterized by the presence of a network structure that can be temporarily deformed when subjected to external forces.

1.3. Modern recycling technologies of worn out automobile tires

Nowadays, there are several recycling methods of worn out automobile tires: warehousing, burial, decorative use, incineration, recovery, thermal and thermal catalytic recycling [14, 15] into alternative energy sources.

In recent years, thermal catalytic recycling of used tires with heavy oil residue into synthetic motor fuels gets particular relevance [16-18], which is associated with growth of oil refining volume and the formation of heavy residues such as mazut and tar. They can be recycled together with tires into synthetic liquid products, because, it is important for solving problems of comprehensive and rational consumption of raw materials and energy, furthermore, it can be useful for the problems of ecological safety of the environment. Petroleum residues, during the process act as paste-forming agent (PA) for raw materials (to promote diffusion of the components to the catalyst) and hydrogen donor in direction of products conversion.

1.4. Products of thermal recycling of waste tires and ways of their usage

During thermal recycling of waste tires can be produced such products as synthetic oil, gas and solid residue [19, 20]. The synthetic oil may be used as a replacement for traditional liquid fuel, because it has a high calorific value about 41-44 MJ/kg, and also can be a raw material for refinery or source for obtaining variety of valuable organic compounds [21]. Gases generally consist of C_1-C_4 hydrocarbons, which are characterized by a very high energy content, which makes them to be used as energy source for various processes [10, 22]. The solid residue consists of a carbon black and char, which are being formed during the process [10]. After appropriate treating it can be used for the production of activated carbon [22], as reinforcing filler for the rubber industry and household products [23], as an ink [24], as a filter material for water treatment plants [25] and as a solid fuel.

2. THERMAL CATALYTIC RECYCLING OF RUBBER-CONTAINING WASTES

A perspective direction in the recycling of rubber wastes is finding new efficient catalysts. As is known, catalytic activity, selectivity and stability are the main parameters in the selection of the catalyst system. Due to this, the authors have investigated the influence of nature of various catalysts in the thermal recycling of waste tires (Table. 1). In this regard, such catalysts as thermal activated natural zeolite from Tayzhuzgen field, bauxite-095, red sludge, KIO_3 and ferroalloy production waste (FPW) have been studied.

Experiments were carried out on a batch type installation under initial 0.5 MPa pressure of argon and at a temperature of 400 °C with continuous mixing mode for 60 minutes. The ratio of the PA and tire crumbs was 1:1 and the weight of catalyst was 2% of the total amount of feedstock.

Worn out automobile tires Bridgestone B650AQ (made in Japan) cut into 2-6 mm wide pieces were used as the process feedstock.

The source of hydrogen and the binder of the feedstocks was a paste based on heavy oil residues from the «Kumkol» oil field (Southern Kazakhstan), with boiling points above 500 °C [26], which has properties such as low sulfur content and high content of paraffin. As we know, paste agent, catalyst and tire crumbs all together can demonstrate a synergistic effect in the thermal catalytic recycling.

Experiments of the thermal processing of used tires were carried out in the absence and presence of catalyst. Obtained synthetic oil was subjected to distillation at atmospheric pressure and fractions boiling at temperatures before 180, from 180 to 250 and from 250 to 320 °C were isolated (Table 1).

Table 1. **Influence of the nature of a catalyst on the yield of liquid products in thermal recycling of worn out automobile tires**

Catalysts	$P_{max.}$ (MPa)	Yield of gas (wt. %)	Yield of liquid products, wt. %				Yield of solid residue (wt. %)	Losses (wt. %)
			untill 180 °C	180-250 °C	250-320 °C	Σ_{LP}		
Without catalysts	1.70	8.30	6.90	4.30	10.20	21.40	68.40	1.90
Zeolite	2.30	18.29	11.03	11.67	17.20	39.90	39.71	2.10
Bauxite-094	2.09	15.60	7.50	11.80	11.20	30.50	51.90	2.00
Red sludge	1.95	15.20	5.30	10.70	13.00	29.00	53.80	2.00
KIO_1	1.80	12.13	6.10	5.90	13.50	25.50	60.37	2.00
FPW	2.60	21.96	13.44	10.80	18.70	42.94	32.60	2.50

As follows from these data, the most active catalyst is the FPW. Being that, the total yield of liquids by this catalyst was 42.94 wt. %, which is about 2 times higher in comparison with the process of without catalyst.

All heterogeneous catalysts have problem with rapid deactivation in thermal processes. To solve this problem, in the thermal processing of waste tires was used FPW from Aksu Ferroalloy Plant (Pavlodar region, Kazakhstan). The use such waste as a catalyst can solve the problem of the financial costs for catalyst production and it's regeneration in the recycling of worn out automobile tires, as well as the problem of disposal of these wastes.

Transition metals such as Fe, Mn and Ti were found in content of FPW by X-ray fluorescence and X-ray diffraction analysis methods [27]. In turn, these metal centers may be responsible for hydrogenation and dehydrogenation reactions during the recycling. Furthermore, the presence of Si and Al oxides in the composition of the FPW provides its acidic properties, which can promote cracking reactions during thermal processing. Thus, components of the FPW catalyst provide both metal and acid functions, and it can be regarded as a bifunctional catalyst.

Infrared spectral analysis of the liquid products of thermal and thermal catalytic recycling of tires showed the presence of absorption bands characteristic of alkanes, arenes, aliphatic hydrocarbons, ethers, esters, carboxylic acids and polymethylene fragments $(CH_2)_n$ in spectra.

According to the gas-liquid chromatographic analysis the content of the liquid products was as following: the aromatic – 41.85%, paraffins – 18.16%, isoparaffins – 22.01%, olefins – 7.78%, mixture of alkanes with naphthenes – 10.20% respectively.

As seen from the experimental results, a sufficiently high content of aromatic hydrocarbons in the composition of the final products allows to use them for obtaining an individual aromatic hydrocarbons and various saturated and unsaturated hydrocarbons.

The results of analysis on gas composition of the thermal catalytic process by gas chromatography with mass spectrometric detection showed that it is enriched with C_1-C_4 low molecular weight compounds of alkanes and olefins. The gas density by pycnometrically method was 2.27 kg/m^3, which is consistent with literature data.

According to X-ray fluorescent analysis, a major part of FPW catalyst (90-96 wt. %) remains in the solid residue.

2.1. Thermal recycling of worn out automobile tires with composite catalysts

The chemical composition of the catalyst is an important indicator of its quality. The ion exchange properties and other technological characteristics of zeolites depend on the ratio of silicon and aluminum, and types of cations in their composition [28, 29]. For this purpose, as catalysts of the thermal catalytic recycling of worn out automobile tires, by authors were investigated composites based on FPW and natural zeolite from the Tayzhuzgen field (Eastern Kazakhstan) in different composition.

The presence of macro– and microelements (iron, magnesium, copper, zinc, manganese, titanium and etc.) in the zeolite composition has a positive effect on the catalytic systems. Zeolite-containing catalysts with unique microporous structures and acid-base properties [30] are capable of catalyzing the conversion reactions of C_1-C_5 paraffin hydrocarbons into valuable synthetic products.

The SiO_2:Al_2O_3 ratio of 4.56:1 for the natural zeolite from the «Tayzhuzgen» field is higher than that of the clinoptilolite minerals (3.76-3.90) [31, 32]. Essentially the tested zeolite can be considered to consist of clinoptilolites of Ca, Na, $K_2Al_2Si_{10}O_{24}$·$7H_2O$, and low content of mordenite, quartz resulting in a solid solution of albite-anorthite.

The composite catalysts from FPW waste and thermally activated zeolite in ratios 20:80, 60:40 and 80:20 wt. % were used and by the scanning electron microscopy was found, that the mixing of the components leads to the formation of friable amorphous surfaces with vague contours and the foreground is dominated by uniform macroporous structures. These are presumably enriched with oxides of iron (II and III), silica, and alumina as it is known that iron oxides in FPW consist mostly of Fe^{2+}. These data suggest that this composite material may be used as catalysts for the thermal processing of waste carbonaceous materials.

These new composite catalysts for the thermal processing of waste tires were tested in previously established optimal parameters [27] of the process (Table 2).

The data in Table 2 suggest that the yield of liquid products (Σ_{LP}) was more than 2 times higher in the presence of the composite catalyst with ratio 60:40 wt. % compared to the yield without catalyst. Interestingly, the separate components of the composite catalyst appeared to be good catalytic agents but not as much as effective as the composite. Additionally, the total yield of liquid products with FAP catalyst was higher than that obtained with the thermal activated zeolite. It means these constituents show a synergistic effect in conjunction.

Table 2. **Effect of ratio of the FPW:zeolite catalyst on the yield of liquid products during thermal recycling of worn out automobile tires**

Catalysts	P_{max} (MPa)	Yield of gas (wt. %)	Yield of liquid products, wt. %				Yield of solid residue (wt. %)	Losses (wt. %)
			untill 180 °C	180-250 °C	250-320 °C	Σ_{LP}		
Without catalysts	1.70	8.30	6.90	4.30	10.20	21.40	68.40	1.90
Zeolite	2.30	18.29	11.03	11.67	17.20	39.90	39.71	2.10
FPW	2.60	21.96	13.44	10.80	18.70	42.94	32.60	2.50
FPW:zeolite 20:80	2.60	21.19	12.13	11.55	18.42	42.10	34.21	2.50
FPW:zeolite 60:40	2.95	23.90	14.40	16.10	20.30	50.80	22.40	2.90
FPW:zeolite 80:20	2.85	22.79	14.08	15.85	18.47	48.40	26.06	2.75

The gas chromatograph analysis with mass spectrometry showed the presence of C_5-C_{16} hydrocarbons in the first fraction with a boiling point up to 180 °C. Due to the using of the heavy oil residue, in composition of the first fraction there are many kinds of saturated compounds such as octane, nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, and others. Among the olefins there are 1-pentene, 1-hexene, 1-decene, and others. Also, there are a large number of aromatic compounds, such as ethylbenzene, p-xylene, p-cymene and polycyclic aromatic compounds such as toluene, p– and o-xylene, cymene, alkylbenzenes, alkylnaphthalenes and others. It should be noted that in the first fraction in the greatest quantity is contained cymene, which is used as an ingredient for perfumes.

The second fraction with the boiling point between 180-250 °C mainly consists of C_{14}-C_{22} hydrocarbons. The chemical composition of the second fraction presents primarily from aromatic and alkane, also insignificant amount of olefin compounds. Among the aromatic compounds high intensity showed 2-methyl-naphthalene, 2,3-dimethyl-naphthalene and 2,3,6-trimethyl-naphthalene. Alkanes are represented in $C_{11}H_{24}$-$C_{17}H_{36}$ hydrocarbons.

The third fraction with a boiling point of 250-320 °C is composed by C_{11}-C_{27} hydrocarbons. As in the second fraction it contains large quantities of alkane, aromatic and insignificant amount of olefin compounds.

The presence of large amounts of the saturated compounds in the three fractions is due to the possibility of high-temperature thermolysis of feedstock as well as paste agent. The content of the aromatic compounds in the liquid fractions may be caused by the content of styrene-butadiene-rubber in the tire part and aromatic content in the composition of heavy oil residue. The small content of the unsaturated compounds indicates to the possibility of hydrogenation reactions along with thermolysis on the tested catalyst, which has a redox type centers. Sulfur compounds in the liquid fractions are represented mainly by derivatives of thiophene (C_4H_4S).

3. THERMAL PROCESSING CARBON-CONTAINING WASTES TOGETHER WITH OIL SHALE IN THE PRESENCE OF COMPOSITE CATALYSTS

Using of natural shale as additives to carbon-containing source materials based on industrial rubber wastes and waste plastics facilitates the appearance of a synergetic effect caused by the more intense degradation of organic matter with the predominant formation of liquid products.

It is found [33, 34] that an increase in the conversion and yield of oils was observed on the joint processing of a mixture of coal and polymer wastes. Data on the effective thermochemical processing of heavy petroleum residues in the presence of activating additives were published [35-37]; it was proposed to use oil shales, sapropelites, liptobiolites, and boghead coals as these additives, which contain ≥7 wt. % hydrogen on an organic matter basis.

Kairbekov et al. studied the effect of the additives of Kenderlyk shale [38], which contained about 10% hydrogen and to 77% carbon, on the hydrogenation of carbon-containing wastes and assumed that this shale can be used as an additional source of hydrocarbons and a hydrogenating agent in the process of thermal dissolution.

The organic matter of shale can be more readily converted into liquid and gaseous products in thermocatalytic destruction processes because the hydrogen content of oil shale is higher than that of coal [38-40]. The cleavage of particular bonds in the molecules of hydrocarbons can be controlled by the selective action of a catalyst on functional groups, and hence the processes can be performed selectively. Therefore, a search for new effective catalysts based on natural zeolites and readily available polymetallic ferroalloy industry wastes is of great scientific and practical interest.

The initial materials (worn tires and waste plastics) were ground to a particle size of 3-6 mm, and shale was crushed to a particle size of 0.25 mm. The shale contained the following elements (wt. %): C^{daf}, 74.1-77.3; H^{daf}, 7.3-9.9; N^{daf}, 1.9-2.1; S^{d}_{t} , 0.6-1.3; and O^{daf}, 10.4-16.8. The H:C atomic ratio was 1.18-1.53.

As catalysts of the process were used zeolite from the Tayzhuzgen deposit (Republic of Kazakhstan), which was activated by acid treatment and calcination, and polymetallic ferroalloy industry wastes (Aksu) and they were taken in different zeolite to ferroalloy industry waste ratios.

The process was carried out in a batch system under an argon pressure of 5-6.5 MPa at a temperature 450 °C with continuous stirring during 15 min. The heavy oil residue from the Kumkol oil field was used as PA.

It was established that the catalyst based on ferroalloy industry wastes and zeolite in a ratio of 40:60 was optimal in terms of the total yield of liquid hydrogenation products; this catalyst was characterized by a higher yield of fractions with b.p. to 180 and 180-250 °C. It was found that an optimum concentration of oil shale is 3 wt. %, at which the total yield of the obtained liquid products was 58.28 wt. % (Table 3).

Table 3. **The impact of the oil shale on the yield of liquid products recycling of worn tires and waste plastics on different catalysts**

Catalysts	Yield of gas (wt. %)	Yield of liquid products, wt. %				Yield of solid residue (wt. %)	Losses (wt. %)
		untill 180 °C	180-250 °C	250-320 °C	Σ_{lp}		
FPW:zeolite 20:80	23.54	8.18	8.25	26.77	43.20	23.11	10.15
FPW:zeolite 40:60	20.15	18.15	17.74	22.59	58.28	9.77	11.80
FPW:zeolite 60:40	18.48	13.99	13.31	20.02	47.32	21.80	12.40
FPW:zeolite 80:20	16.97	14.87	18.78	20.77	54.42	17.01	11.60
Zeolite	19.50	15.03	2.32	22.27	39.62	28.28	12.60
FPW	24.12	18.47	2.64	22.28	43.39	22.89	9.60

The IR-spectrometric analysis of the hydrogenation products showed the presence of absorption bands characteristic of alkanes, cyclanes, and arenes in the spectra. The spectra of liquid products that boiled away to 180 °C and at 180-250 °C exhibited intense absorption bands at 2956, 2925, and 2871 cm^{-1}, which indicate the presence of the CH_3 group, and absorption bands at 1377 and 1460 cm^{-1}, which are characteristic of the CH_2 group. A great number of peaks in a range of 620-811 cm^{-1} is indicative of the presence of a bond between carbon and sulfur, which is characteristic of compounds such as mercaptans and thiols. The presence of absorption bands at 1459 and 1602 cm^{-1} suggests the presence of aromatic hydrocarbons. Vibrations at 1641 cm^{-1} correspond to unsaturated compounds. Bands at 699 cm^{-1} indicate deformation vibrations in a monosubstituted aromatic ring.

Absorption bands in a range of 620-1030 cm^{-1} were present in the spectra of liquid hydrogenation products; this fact indicated the presence of different functional groups.

4. CONCLUSION

The new catalyst based on polymetallic waste from ferroalloy production (FPW) for thermal processing of worn tires was proposed by authors. By using the FPW, the process can be carried out under more mild conditions and increase the yield of liquid products approximately 2 times in comparison with the process of without catalyst.

Also, highly effective composite catalysts based on natural zeolite from the Tayzhuzgen field and FPW were developed. It is shown that, a composite catalyst in the 60:40 ratios has a maximal activity for the yield of liquid products in the thermal catalytic recycling of worn tires. The highest yield of liquid products was 50.8 wt. % and it is almost 2.4 times more compared to the process of without catalyst.

Experiments on a joint thermal processing of worn tires and waste plastics in the presence of oil shale were carried out by authors. Composite catalysts of FPW:zeolite were composed in various ratios. It is found, that the optimal total yield of liquid products was shown with the composite catalyst of the 40:60 ratio, which is characterized by the high yield of fractions with b.p. up to 180 °C and 180-250 °C. By total yield of liquid products, it was found, that an optimal concentration of oil shale has to be 3 wt. %.

References

1. Miranda M., Pinto F., Gulyurtlu I., Cabrita I. // Fuel. 2013, 103, 542-552.
2. Seghar S., Ait Hocine N., Mittal V., Azem S., Al-Zohbi F., Schmaltz B., Poirot N. // eXPRESS Polymer Letters. 2015, 9(12), 1076-1086.
3. Ucar S., Karagoz S., Ozkan A. R., Yanik J. // Fuel. 2005, 84, 1884-1892.
4. Frigo S., Seggiani M., Puccini M., Vitolo S. // Fuel. 2014, 116, 399-408.
5. Önenç S., Brebu M., Vasile C., Yanik J. // Journal of Analytical and Applied Pyrolysis. 2012, 94, 184-189.

6. Abdul-Raouf M. E., Maysour N. E., Abdul-Azim A. A., Amin M. S. // Energy Conversion and Management. 2010, 51, 1304-1310.
7. Fang Y., Zhan U. M., Wang Y. // Materials and Design. 2001, 22, 123-127.
8. Holst O., Stenberg B., Christiansson M. // Biodegradation. 1998, 9, 301-310.
9. Arabiourrutia M., Olazar M., Aguado R., Lopez G., Barona A., Bilbao J. // Industrial and Engineering Chemistry Research. 2008, 47, 7600-7609.
10. Williams P. T. // Waste Management. 2013, 33(8), 1714-1728.
11. Evans A., Evans R. // Waste and Resources Action Programme. 2006.
12. Williams P. T., Besler S. // Fuel. 1995, 74, 1277-1283.
13. Shulman V.L. // Tyre recycling, Rapra review reports. 2004, 15(7).
14. Williams P. T., Brindle A. J. // Fuel. 2002, 81, 2425-2434.
15. Shah J., Jan M. R., Mabood F. // Journal of Polymers and the Environment. 2007, 15, 207-211.
16. Fan P., Lu C. // Journal of Polymers and the Environment. 2011, 19, 943-949.
17. Khadzhiev S. N., Kadiev Kh. M., Gyulmaliev A. M., Batov A. E., Dandaev A. U. // Solid Fuel Chemistry. 2013, №2, C. 65.
18. Saeng-arayakul P., Jitkarnka S. // Chemical Engineering Transactions. 2013, 35, 1339-1344.
19. Wey M., Liou B., Wu Sh., Zhang Ch. // Air and Waste Management Association. 1995, 45, 855-863.
20. Ahoor A. H., Zandi-Atashbar N. // Energy Conversion and Management. 2014, 87, 653-669.
21. Osayi J. I., Iyuke S., Ogbeide S. E. // Journal of Catalysts. 2014, Vol. 2014, pp. 1-9.
22. Ucar S., Karagoz S., Ahmet R. Ozkan A. R., Yanik J. // Fuel. 2005, 84, 1884-1892.
23. Rodriguez I. D., Laresgoiti M. F., Cabrero M. A. // Fuel Processing Technology. 2001, 72(1), 9-22.
24. Banar M., Özkan A., Akyıldız V., Çokaygil Z., Onay Ö. // Journal of Material *Cycles* and *Waste Management*. 2015, 17, 125-134.
25. Money D. M., Harrison G. // Fuel. 1999, 78, 1729-1736.
26. Aubakirov A. E., Burkhanbekov K. E., Serikov E. B. // MaterialsIX-international scientific-practical conference «Strategiczne Pytania Swiatowej Nauki-2013», 07-15 lutego 2013 roku, Przemysl, Polska, pp. 54-57.
27. Kairbekov Zh. K., Aubakirov E. A., Tashmukhambetova Zh. Kh., Fayzullaeva M. F., Shomanova Zh. K., Burkhanbekov K. E. // Bulletin of the KazNU. 2015, 1(77a), 90-95.
28. Weitkamp J. // Solid State Ionics. 2000, 131, 175-188.
29. Farneth W. E., Gorte R. J. // Chemical Reviews. 1995, 95, 615-635.
30. Akgül M., Özyağcı B., Karabakan A. // Journal of Industrial and Engineering Chemistry. 2013, 19, 240-249.
31. Abdulina S. A., Sadenova M. A., Sapargaliyev E. M., Utegenova M. E. // Vestnik of KazNTU. 2014, 3(103).
32. Akgül M., Karabakan A., Acar O., Yürüm Y. // Microporous and Mesoporous Materials. 2006, 94, 99-104.
33. Osipov A. M., Popov A. F., Shendrik T. G., et al. // http://www.ecologylife.ru/utilizatsiya-2001/nekotoryie-problemyi-sovmestnogo ozhizheniya-uglya-i-othodov-plastmass.html.
34. Osipov A. M., Popov A. F., Grischuk S. V., et al. // *Ecotechnologies and Resources Saving*. 2004, 4, p. 26.
35. Gorlov E. G., Kotov A. S., Gorlova S. E. // Solid Fuel Chemistry. 2009, 1, p. 31.
36. Kotov A. S., Gorlov E. G. // Solid Fuel Chemistry. 2009, №3, pp. 30.
37. Suvorov Yu. P. // Solid Fuel Chemistry. 2006, 6, p. 57.
38. Kairbekov Zh. K., Yemelyanova V. S., Myltykbaeva Zh. K., et al. // Fundamental Research. 2012, 9, p. 924.
39. Kairbekov Zh. K., Maloletnev A. S., Yemelyanova V. S. et al. // Abstracts of Papers. IV Int. Sci.-Techn. Conf. 2013. p.52.
40. Aubakirov E.A., Tashmukhambetova Zh. Kh., Kairbekov Zh.K. et al. // Proc. XII Int. Conf. «Resource-Generating, Low-Waste, and Nature-Conservative Technologies for the Exploitation of Mineral Resources». 2013, vol. 1, p. 554.