Catalytic co-pyrolysis of polymeric waste and biomass as the method for energy and ecology problems solution

Esfir M. Sulman[1*], Yury Yu. Kosivtsov[1], Alexander I. Sidorov[1], Antonina A. Stepacheva[1]
and Yury V. Lugovoy[1]

***Abstract*—**The paper is devoted to the processing of solid domestic wastes by thermotreatment methods. It was revealed that the use of iron subgroup metal chlorides as a catalyst for co-pyrolysis of polymers and biomass allowed decreasing the apparent activation energy in 30 kJs/mol compared to a non-catalytic process. The application of chlorides of iron subgroup metals can lead to the increase in the yield (up to 25%) of gaseous products with high calorific value. The addition of cobalt chloride with the concentration of 2% (wt.) at the process temperature 450 ^{o}C was an optimum concerning the substrate conversion.

***Keywords*—**catalytic co-pyrolysis, polymeric wastes, metal chlorides, biomass.

I. INTRODUCTION

AT present, one of the significant results of anthropogenic influence on nature is the formation of a great amount of solid domestic wastes, particularly polymers, which are characterized by the stability to the natural degradation. Polymeric waste is approximately twelve per cent of the total domestic waste and its amount is constantly growing. The main type of consumption polymeric waste used tires [1, 2].

Taking into account the development of modern industry the production of polymers annually increases by 5-6%. One of such polymers is diene rubber which is used in different fields of industry. In the world half of the produced synthetic and natural rubbers (more than 15 billion tons per year) is consumed by automobile tires production. Finally all the produced tires become waste after some time. In Russia the annual volume of the discarded tires is estimated at over 1 billion tons [3]

In the world there are different technologies of waste and worn-out automobile tires processing. These techniques provide the use of rubber waste for energy generation through the combustion, as well as the chopping of tires to produce rubber crump, rubber powder and reclaimed rubber [4-9].

In Russia combustion remains the main method of tire disposal [3]. However this process involves a lot of problems. Burning of tires results in the formation of such chemicals as biphenyl, anthracene, fluorine, pyrene, benz(α)pyrene, which become the main hazard for humans while going into the atmosphere. Two of these compounds – biphenyl and benz(α)pyrene are the strongest carcinogens. Dumped or buried automobile tires decompose for minimum 100 years under the natural conditions. The contact of tires with rainfall and ground waters leads to the leaching of numeral toxic organic compounds: diphenylamine, dibutylphthalate, phenantrene etc., which contaminate the soil. Furthermore rubber is a macromolecular substance and it belongs to thermoreactive polymers which unlike thermoplastics can not be processed at a high temperature. This fact accounts for the problem of reusing rubber waste [4].

In the more developed countries (USA, Japan, Germany, Switzerland etc.) for a long time semi-production experimental plants (with the capacity of 7…15 thousand tons of the raw materials per year) have been used for the pyrolysis of waste tires [2].

While processing the organic wastes there can be obtained a combustible gas [5-10], a gaseous raw material (syn-gas) for the synthesis of liquid fuel (Fisher-Tropsch synthesis) [11-13] and methanol synthesis [14], liquid fuel and solid carbon residue [15-17].

Lately, great attention has been paid to the search of the methods of the increase of pyrolysis process effectiveness to raise the yield of liquid and gaseous products. For this purpose different catalysts such as Ni chlorides and nitrates [18], alkali and alkaline-earth metal oxides and carbonates [5, 6, 19], cuprum salts [20], zeolites [19, 21] are widely used. The latest research in the field of thermodestruction of polymeric waste is devoted to the study of co-pyrolysis of polymers and biomass [22-27] both in the case of non-catalytic process [22-24] and in the presence of zeolites [25], Ni-Mo catalysts [25], Red Mud and ReUS-Y catalysts [26].

We have recently studied catalytic co-pyrolysis process of biomass (peat) and oil-containing waste using both aluminosilicates and metal chlorides. It was revealed that the addition of bentonite clay allowed increasing the yield of gaseous and liquid products by 8 and 10% respectively [28].

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[1] Tver State Technical University, Department of biotechnology and chemistry, A.Nikitin Str., 22, 170026, Tver, Russia, phone/fax: +74822449317, e-mail: sulman@online.tver.ru.

*Corresponding author: phone/fax: +74822449317, e-mail: sulman@online.tver.ru.

So in this work we studied co-pyrolysis of rubber waste and biomass (peat) to investigate the influence of catalysts on co-pyrolysis products yield.

II. EXPERIMENTAL

TO study the process of co-pyrolysis of biomass and polymeric cord the samples of eriophorum-sphagnum peat with 30% degree of composition and ash content 5% were used. The polymeric cord was divided into fractions by mechanic separation of rubber (51.6%) and polymeric fibers (48.4%).

The chlorides of iron subgroup metals were used as catalysts in the co-pyrolysis process. The catalytic activity of chlorides of transition metals in the processes of temperature decomposition of organic polymeric compounds is well known [29, 30]. The ions of iron subgroup metals promote the increase of the reaction rate of C-C bond breaking making possible the formation of light hydrocarbons with high calorific value.

Co-pyrolysis process

The co-pyrolysis process of polymeric cord and peat was carried out in the designed laboratory unit shown in Fig. 1. The laboratory setup consists of a stationary steel-batch reactor (1), electrical heater (2) equipped with heat controller with patch thermocouple. The heating maximum is 1000 ºC.

Reactor is equipped with a sampler (3), hydrolock (4), and a hoses system used for the transportation and collection of gaseous products in the eudiometer.

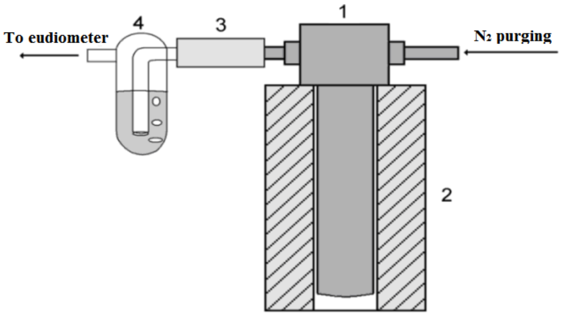

Fig.1 experimental setup for the co-pyrolysis process

The co-pyrolysis process study was conducted in one step for 100 minutes varying both temperature (in the range 350 – 600 ºC) and the catalyst concentration

Analysis

During the experiments the masses of solid, liquid and gaseous products were determined, also the qualitative and quantitative analysis of the pyrolysis gaseous products mixture was done.

The gaseous products analysis was carried out using analytical complex on the base of gas chromatograph [31].

The catalytic influence of metal chlorides was evaluated using the total amount of the obtained gases and the heat of combustion of the gaseous products.

The kinetic modelling of the co-pyrolysis process and the calculation of the activation energy were done using thermogravimetric analysis and differential scanning calorymetry methods according to the method of Freeman-Carroll.

III. RESULTS AND DISCUSSION

INFLUENCE of the catalysts on the products yield

The use of catalysts in the process of temperature decomposition of organic materials is firstly focused on the increase of the yield of liquid and gaseous products used as fuels.

The solid carbon-containing residue yield of peat and polymeric cord co-pyrolysis obtained in the temperature range 350 – 600ºC is shown in Fig. 2.

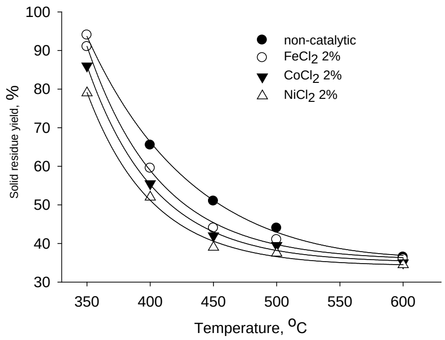

Fig. 2 the dependence of co-pyrolysis solid residue yield on the process temperature for the investigated catalysts and non-catalytic process

The catalytic activity of metal chlorides in the peat and polymeric cord co-pyrolysis (regarding the decrease of the solid residue yield) increased in the row $FeCl_2 \rightarrow CoCl_2 \rightarrow NiCl_2$.

However the activity presented does not affect the gaseous hydrocarbons formation. The highest yield of the combustible gases was observed while using cobalt chloride as the catalyst (Table 1).

Table 1. The dependence of the weight distribution of peat and polymeric cord co-pyrolysis products on the reaction temperature

T,º C	Products, %(wt.)	non-catalytic	$FeCl_2$ 2%	$CoCl_2$ 2%	$NiCl_2$ 2%
400	gas	12.4	13.5	15.1	16.2
	liquid	22.1	27.2	31.5	32.8
	solid	65.5	59.3	51.4	51.0
450	gas	16.5	18.1	20.3	20.8
	liquid	32.3	37.2	39.1	40.2
	solid	51.2	44.7	39.6	39.0
500	gas	18.1	19.4	21.1	21.6
	liquid	38.3	39.3	40.2	41.9
	solid	43.6	41.3	38.7	37.5
600	gas	20.2	21.5	23.0	23.0
	liquid	43.4	42.5	41.7	42.5

	solid	35.9	36.0	35.3	34.5

Influence of the catalysts and temperature on the gaseous products calorific value

One of the key parameters which allow estimating the qualitative characteristics of the gaseous fuels is the calorific value of the gaseous mixture. The dependence of volumetric calorific value of co-pyrolysis gaseous products on the catalyst type and temperature is shown in Fig. 3.

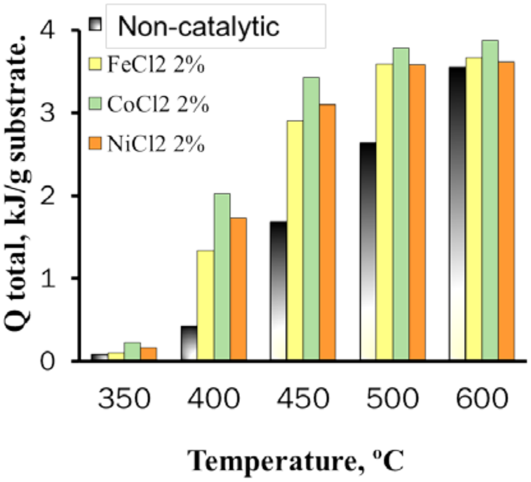

Fig. 3 the dependence of volumetric calorific value of co-pyrolysis gaseous products on the catalyst type and temperature

While using the chlorides of iron subgroup metals the total calorific value of the gaseous products increased and reached out the constant at a temperature 450 ºC. In the case of non-catalytic process the total calorific value of the gaseous products increased with the increase of co-pyrolysis process temperature across the studied temperature range (Fig. 3).

Basing on the value of the total calorific value of the co-pyrolysis gas in the studied temperature range the experiments can be ranged as the following: $CoCl_2 > NiCl_2 > FeCl_2 >$ non-catalytic process.

The influence of the catalysts on the total calorific value of the co-pyrolysis gases decreases with the increase in the process temperature up to over 500 °C and at 600 °C the difference in the values of the heat of combustion of gaseous products in the case of non-catalytic process is insufficient.

Influence of the catalyst concentration on the calorific value of the gaseous products

The influence of the catalyst concentration on the calorific value of gaseous products of peat and polymeric cord co-pyrolysis is shown in Fig. 4.

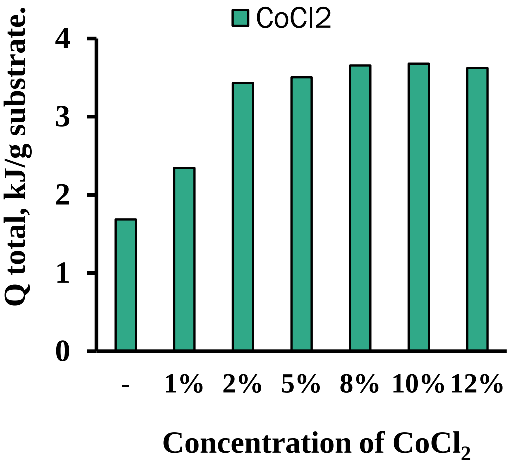

Fig. 4 the calorific value of co-pyrolysis gaseous products dependence on cobalt chloride concentration

The increase in the catalyst concentration resulted in the decrease of the lower calorific value of the gas. This fact can be explained by the increase in the low molecular weight gaseous hydrocarbons yield.

The total composition of co-pyrolysis gaseous products depending on cobalt chloride concentration is shown in Fig. 5.

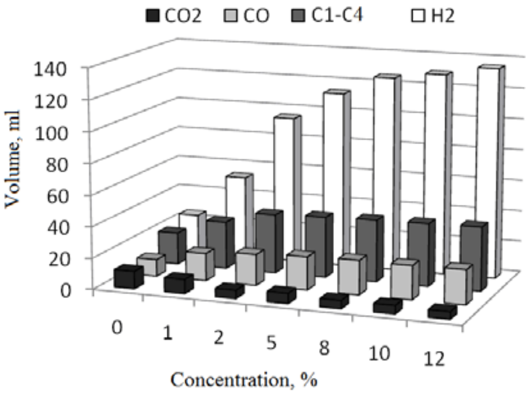

Fig. 5 the gaseous phase composition in dependence to $CoCl_2$

As it was noted the use of cobalt chloride leads to the increase in the formation of C_1-C_4 hydrocarbons, hydrogen and carbon oxide (II). The use of this catalyst also allowed decreasing carbon oxide (IV) formation. However the increase in $CoCl_2$ concentration over 2% did not affect hydrocarbons concentration.

Therefore the increase in the catalyst concentration over 2% (wt.) is uneconomical because the calorific value does not practically increase with the catalyst concentration increase.

Influence of the temperature on peat and polymeric cord co-pyrolysis process

To explain the obtained experimental data on calorific value of gaseous products of peat and used automobile tires polymeric cord co-pyrolysis it is necessary to study the composition of the gaseous products. The dependence of the obtained gaseous mixture components volumes on the temperature of both non-catalytic process and in the presence of $CoCl_2$ is shown as a diagram in Fig. 6 and 7.

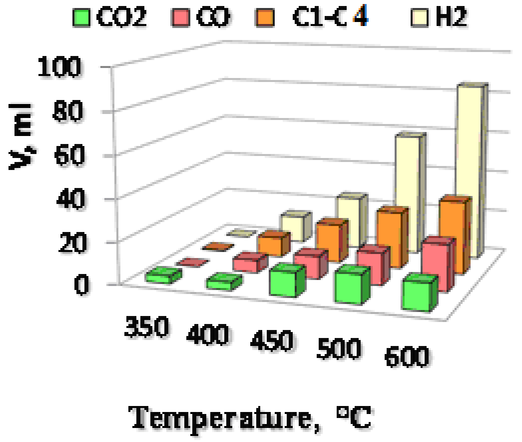

Fig. 6 The gas phase composition depending on the temperature for a non-catalytic process

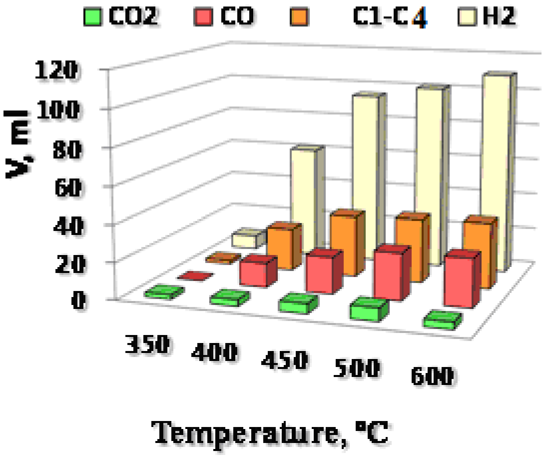

Fig. 7 the gas phase composition depending on the temperature in the presence of cobalt chloride (2% (wt.))

Analyzing the total composition of co-pyrolysis gaseous products composition obtained during both non-catalytic and catalytic processes at the same temperature it should be noted that the use of cobalt chloride leads to the formation of higher volumes of C_1 – C_4 hydrocarbons and carbon monoxide in comparison with a non-catalytic process.

While using cobalt chloride as the catalyst the significant increase in hydrocarbons, hydrogen and carbon oxide (II) in a temperature range 350 - 450 °C was observed. The further increase in the temperature of the catalytic process over 450 °C did not lead to the significant increase in hydrogen and hydrocarbons volume.

Activation energy estimation of peat and polymeric cord co-pyrolysis

The thermal destruction process is a sum of different chemical reactions so the total rate of the weight loss and the rate of destruction light products emission reflect the summarized process. As the result of this fact the reaction order and rate constant, which are the parameters, needed for the quantitative characterization of thermodestruction, in this case are the relative characteristics presenting the sum of chemical transformations.

The results of modelling with the use of Freeman-Carroll method showed that peat and polymeric waste co-pyrolysis process with the formation of gaseous products is well described by the equation of chemical kinetics with fractional order (1):

$$d\omega / dt = k [\omega_0]^n \quad (1)$$

where: [ω] – mass fraction of gaseous products;
t – process time , min;
k – reaction rate constant, s^{-1};
$[\omega_0]$ – mass fraction of substrate;
n – reaction order.

According to the data calculated on the base of thermogravimetric analysis the total reaction order for non-catalytic process is equal to 1.78 (~2); and for the process in the presence of cobalt chloride – 1.07 (~1).

The calculation of the Arrhenius parameters of thermodestruction process was done using Freeman-Carroll method. The values of kinetic parameters of the process and thermodestruction rate constants at 450 ºC for all the studied samples are shown in Table 2.

Table 2. Kinetic parameters of the processes of combined thermal destruction of polymeric cord and peat

Kinetic parameter	Non-catalytic process	In the presence of $CoCl_2$ 2%
k at 450 ºC	37.34	130.52
E_{act}, kJ/mol	138	104
Pre-exponential factor	$3.98 \cdot 10^{11}$	$4.34 \cdot 10^{9}$
Reaction order	2	1

IV. CONCLUSION

THE use of the combined pyrolysis process of polymeric waste and biomass allows sufficiently increasing thermodestruction process rate and raising liquid and gaseous products yield. The application of chlorides of iron subgroup metals can lead to the increase in the yield (up to 25%) of gaseous products with high calorific value. The addition of cobalt chloride with the concentration of 2% (wt.) at the process temperature 450 °C was an optimum concerning the substrate conversion and allowed decreasing the apparent activation energy of the organogenic raw material thermodestruction process by 30 kJs/mol compared to a non-catalytic process.

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REFERENCES

[1] E.N. Laboy-Nieves “Energy Recovery from Scrap Tires: A Sustainable Option for Small Islands like Puerto Rico” in *Sustainability.* No. 6. 2014. pp. 3105-3121.

[2] Rubber Manufacturers Association. U.S. Scrap Tire Management Summary. Available online: http://www.rma.org/download/scrap-tires/market-reports/MAR-025-Scrap%20Tire%20Market% 202009.pdf (accessed on 21 October 2013)

[3] “Processing and Utilization of Rubber Waste and Used Tires” Available online: http://clean-future.ru/info-pererabotka-i-utilizaciya-othodov-reziny-i-iznoshennyh-avtomobilnyh-shin-pokryshek.html

[4] S.L. Wong. N. Ngadi. T.A.T. Abdullah. I.M. Inuwa “Current state and future prospects of plastic waste as source of fuel: A review” in *Renewable and Sustainable Energy Reviews.* No. 50. 2015. pp. 1167–1180.

[5] P. T. Williams “Pyrolysis of waste tyres: a review” in *Wastemanagement*. Vol. 33. 2013. pp. 1714–1728.

[6] A. Quek. R. Balasubramanian “Liquefaction of waste tyres by pyrolysis for oil and chemicals—a review” in *Journal of Analytical and Applied Pyrolysis*. Vol. 101. 2013. pp. 1–16.

[7] J.I. Osayi. S. Iyuke. S.E. Ogbeide “Biocrude Production through Pyrolysis of Used Tyres” in *Journal of Catalysts*. 2014. Article ID 386371. 9 p.

[8] P.S. Ware “Pyrolysis of waste tyres and future” in *Chemistry & Biology*. Vol. 1. Is. 1. 2015.

[9] M.Samolada. A. Zabaniotou “Potential application of pyrolysis for the effective valorization of the end of life tires in Greece” in *Environmental Development*. No. 4. 2011. pp. 73–78.

[10] K. Murahashi. Y. Kato. Y. Ono “Method and device for gasification of organic matter to recover fuel gas” (Nippon Steel Corp.. Japan). Jpn. Kokai Tokkyo Koho. 2005.

[11] E. Dinjus “Hydrogen and synthesis gas from biomass – a sustainable basis for synthetic fuels” in *7-th World Congress of Chemical Engeneering*. O36-002. Glasgow. 10-14 July. 2005.

[12] P. Mukoma. D. Glasser. D. Hildebrandt. B. Hauseberger “The integration of process synthesis into an experimental program for Fischer-Tropsch Synthesis (FTS) chemistry” in *7-th World Congress of Chemical Engeneering*. P15-022. Glasgow. 10-14 July. 2005.

[13] G. Lewin. H. Bijwaard “Fossil fuels. an energy source for the future” in *7-th World Congress of Chemical Engeneering*. O131-001. Glasgow. 10-14 July. 2005.

[14] B. Skelton. T.E. Bustnes. M.R. Mackley “Development of the oscillatory flow based process for the production of biodiesel transport fuel” in *7-th World Congress of Chemical Engeneering*. O12-003. Glasgow. 10-14 July. 2005.

[15] [15] P. Thy. B.M. Jenkins. R.B. Williams. C.E. Lesher “Slag Formation and potassium volatilization from rice straw blended wood fuel” in *Div. Fuel Chem.*. Vol. 49. 2004. pp. 89-92.

[16] A.G. Gayubo. A.T. Aguayo. A.Atutxa. R. Prieto. J. Bilbao “Deactivation of ZSM-5 zeolite catalyst in the transformation of the aqueous fraction of biomass pyrolysis oil into hydrocarbons” in *Energy Fuels*. Vol. 18. 2004. pp. 1640-1647.

[17] D. Serrano. J.Aguado. J. Escola. J. Rodriguez. L. Morselli. R. Orsi “Thermal and catalytic cracking of a LDPE-EVA copolymer mixture” in *J. Anal. Appl. Pyrol.*. Vol. 68/69. 2003. pp. 481-494.

[18] N. Mishra. S. Pandey. B. Patil. M. Thukur. A. Mewada. M. Sharon. M. Sharon “Facile Route to Generate Fuel Oil via Catalytic Pyrolysis of Waste Polypropylene Bags: Towards Waste Management of >20 mm Plastic Bags” in *Journal of Fuels.* 2014. Article ID 289380. 10 p.

[19] [19] E.V. Antonakou. K.G. Kalogiannis. S.D. Stephanidis. K.S. Triantafyllidis. A.A. Lappas. D.S. Achilias “Pyrolysis and catalytic pyrolysis as a recycling method of waste CDs originating from polycarbonate and HIPS” in *Waste Management.* Vol. 34. 2014. pp. 2487–2493.

[20] R. Aguado. A. Arrizabalaga. M. Arabiourrutia. G. Lopez. J. Bilbao. M. Olazar “Principal component analysis for kinetic scheme proposal in the thermal and catalytic pyrolysis of waste tyres” in *Chemical Engineering Science.* Vol. 106. 2014. pp. 9–17.

[21] Ch. Muhammad. J.A. Onwudili. P.T. Williams “Catalytic pyrolysis of waste plastic from electrical and electronic equipment” in *J. Anal. Appl. Pyrol.*. 2015. http://dx.doi.org/10.1016/j.jaap.2015.02.016

[22] J.D. Martínez. A. Veses. A.M. Mastral. R. Murillo. M.V. Navarro. N. Puy. A. Artigues. J. Bartrolí. T. García “Co-pyrolysis of biomass with waste tyres: upgrading of the liquid bio-fuel” in *Fuel Processing Technology*. Vol. 119. 2014. pp. 263-271.

[23] O. Onay. H. Koca “Determination of synergetic effect in co-pyrolysis of lignite and waste tyre” in *Fuel*. Vol. 150. 2015. pp. 169–174.

[24] M. Brebu. M. Nistor “Co-Pyrolysis Of Various Lignins With Polycarbonate” in *Cellulose Chem. Technol.*. Vol. 48 (1-2). 2014. pp. 69-74.

[25] E. Barta-Rajnai. J. Bozi. Z. Sebestyén. M. Blazsó. E. Jakab. N. Miskolczi. Zs. Czégény “Catalytic pyrolysis of mixtures modeling municipal waste” in *8th International Symposium on Feedstock Recycling of Polymeric Materials (8th ISFR 2015)*. Leoben. Austria. September 07-10. 2015.

[26] M. Brebu. J.Yanik. T. Uysal. C. Vasile “Thermal And Catalytic Degradation Of Grape Seeds/Polyethylene Waste Mixture” in *Cellulose Chem. Technol.*. Vol. 48 (7-8). 2014. pp. 665-674.

[27] S. Fang. Zh. Yu. Y. Lin. S. Hu. Y. Liao. X. Ma “Thermogravimetric analysis of the co-pyrolysis of paper sludge and municipal solid waste” in *Energy Conversion and Management*. Vol. 101. 2015. pp. 626–631.

[28] Y.Y. Kosivtsov, K.V. Chalov, Y.V. Lugovoy, E.M. Sulman, A.A. Stepacheva “Co-pyrolysis of Peat and Petroleum Containing Waste on Ni and CO Containing Catalysts” in *Chemical Engineering Transactions*. Vol. 45. 2015. pp.667-672.

[29] J. Aguado. D.P. Serrano “Feed Recycling of Plastic Waste” *Cambridge: The Royal Society Of Chemistry (Series Editor J.H. Clark)*. 1999. pp. 261.

[30] A.L. Lapidus. V.I. Mashinsky. Ia.I. Isakow. H.M. Minachev “Rewiew of SU Academy of Sciences. Chemistry”. 1978. pp. 26.

[31] O.V. Kislitsa, V.V. Alfyorov, A.E. Usanov, E.M. Sulman, “Production of fuel gases by catalytic destruction of waste of cross-linked rubbery polymers” in *Catalysis in Industry,* №1, 2004, p. 35.