VOL. 11, NO. 7, APRIL 2016 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

FUEL GAS PRODUCTION THROUGH LOW-TEMPERATURE CATALYTIC PYROLYSIS OF FLAX SHIVES

E. M. Sulman, Yu. Yu. Kosivtsov, A. I. Sidorov, A. A. Stepacheva and Yu. V. Lugovoy
Department of Biotechnology and Chemistry, Tver Technical University 22, A. Nikitina st., Tver, Russia
E-Mail: sulman@online.tver.ru

ABSTRACT

A study of low-temperature catalytic pyrolysis flax shives. The relevance of research is related to the need to waste management of agricultural production. Wastes from the production of flax granulated into granules of 5… 25 mm. As the catalyst used silica-alumina materials and zeolites. The use of silica-alumina natural materials as the additions to a flax tow matrix allows improving structural (strength, porosity) and sorption characteristics (sorption rate) of the molded compositions and can serve as a catalyst during their subsequent thermal conversion. The introduction of a certain amount of mineral additions improves the processability of the molding process; the mass plasticity rises and the initial molding moisture decreases by 10 … 15% approximately.

Keywords: low-temperature catalytic pyrolysis, flax shives, silica- alumina materials, pyrolysis gases.

1. INTRODUCTION

At present the problem of the use of local raw-material sources of energy (biofuels and peat in particular) becomes important due to the increasing costs of energy carriers [1]. Flax straw and shive can move beyond their lowly status as a waste product [2]. This unique natural source belongs to partly renewable energy sources.

To use such a fuel effectively the scientific base for novel processing technologies meeting the modern requirements is necessary. First of all it relates to the manufacturability and affectivity of the processes and also to ecological compatibility of new productions. The processes of thermal biofuels treatment (pyrolysis and gasification) are the most widely used ones.

Modern technologies of solid fuels pyrolysis could be divided into groups according to the following characteristics: heating rate (quick and slow pyrolysis); pyrolysis media (vacuum pyrolysis, hydropyrolysis, methane-pyrolysis), process temperature (low-temperature - lower than 700ºC and high-temperature - higher than 700ºC) [3].

The main process taking place during the pyrolysis [4] is cracking - destruction of -C-C- bounds of organic molecules chains and also total or partial removal of functional groups with the formation of various organic and inorganic compounds - water, hydrogen, ammonium, carbon oxide and dioxide. One of the possible ways to decrease the power inputs for the implementation of thermal treatment processes of biogenic raw-materials with the production of combustible gases mixture is gasification - heating of biofuels using expulsion by various gases [5]. Traditionally gasification is carried out in the reactors with fixed or pseudo-liquefied bed, with air, oxygen or steam blowing or their combination.

The analysis of the literature devoted to the catalytic thermo-conversion of biofuels shows that the use of catalytic systems decreases the temperature of pyrolysis and gasification processes [6], increases the rate of initial hydrocarbons decomposition and thus eliminates many disadvantages of technologies based on torch combustion of solid fuels: complexity of heat-generators and boilers constructions, necessity of usage of special and, as usual, expensive equipment for the neutralization of toxic substances evolving during thermal decomposition (sulfur and nitrogen oxides, dioxins, furan, polyaromatic hydrocarbons).

Among numerous developed and proposed catalysts of pyrolysis potassium vanadate, indium oxide, calcium oxide, magnesium oxide, some zeolites (mordenite modified with nickel) are the most investigated ones [7]. Alkali catalysts (sodium carbonate, potassium carbonate and etc.) were found to increase considerably the yield of synthesis gas during the gasification by steam at the temperature ranged from 550°C to 750°C. Transition metals salts reveal high activity at the initial stage of the reaction, but they are deactivated during the process [8].

Leading European countries and the USA actively develop novel catalytic materials for the pyrolysis and gasification of organogeneous raw-materials. The examples are: zeolites ZSM-5 [9], zeolites catalyst DC-11 [10], mineral silica-alumina materials MCM-41 [11], Al-MCM-41, Al-SBA-15 [12, 13], silica, Al_2O_3, γ-Fe_2O_3, Fe_3O_4, α-FeOOH [14], clays [15], Ni/Al [16], boric and phosphoric acids [17], zinc chloride [18], KNO_3-B_2O_3/Al_2O_3 [19], Co/MgO [20], Pd-Pt-La/Al_2O_3 [21]. Catalysts on the base of zeolites and like-zeolites minerals are the most prospective ones for the thermal treatment of biofuels. Thus the affectivity of thermo-chemical conversion of biomass to fuels is considerably increase while using silica-alumina catalysts which accelerate the decomposition of high-molecular substances, increase selectivity, allow controlling the obtaining of the products having the required volatility and inflammability limit.

The most prospective methods of thermo-chemical processing of flax shives are pyrolysis and gasification which include heating of biofuels without the access of air or with the expulsion by steam, oxygen, carbon dioxide or gaseous mixture to obtain combustible gases. Transformation of initial raw material is a complex system of subsequently-parallel reversible or irreversible reactions, among which there are both exo- and endothermic reactions. Such processes have rather high activation energies, that is high temperatures are necessary for their realization. Introduction of the catalysts into the reaction mixture leads to a considerable decrease of the activation energy and allows obtaining greater amounts of hydrocarbons at the same temperature compared to noncatalytical processes [22]. The gas having the required heat of combustion and composition can be obtained (3…30 MJ/m^3) depending on the process conditions. The gases having heat of combustion up to 7 MJ/m^3 are used in power engineering and for technological needs. The heat of combustion of a producer gas obtained from wood or organic waste by the use of steam-air blow is about 6 MJ/m^3. The gases having heat of combustion higher than 7 MJ/m^3 are obtained by the use of steam-oxygen blow under the pressure.

In the work presented the investigations of catalytic properties of natural silica-alumina materials (clays) in the process of flax shives pyrolysis were carried out. The objective of these investigations was screening of the effective catalyst for the processing of the biofuel mentioned. The choice of clays and others silica-alumina materials as the catalysts for the pyrolysis and gasification was based on the effectiveness of theirs influence on the conversion of organic flax substances. Besides, the availability and, thus, the low cost of catalytically active mineral raw material have great importance. Especially because many kinds of such raw materials (clays and other clay materials) can be located near of the agricultural processing [23].

The composition of clays is known to include considerable proportion of minerals, which belong (as well as zeolites) to class of silica-alumina. For example, bentonite clay consists of 70…80 % of montmorillonite having the following composition: (Na, K, Ca) (Al, Fe, Mg) $[(Si,Al)_4O_{10}](OH)_2 \cdot n\,H_2O$. Its structure is organized by the atoms of silicon, aluminium and oxygen, which form tetrahedral group. This mineral has a peculiar structure typical only for so-called clay minerals. For example, it has lamellar structure similar to the structure of mica with very strong cleavage. The lattice of montmorillonite is formed by two external tetrahedral layers and one internal octahedral layer (see Figure-1) [24].

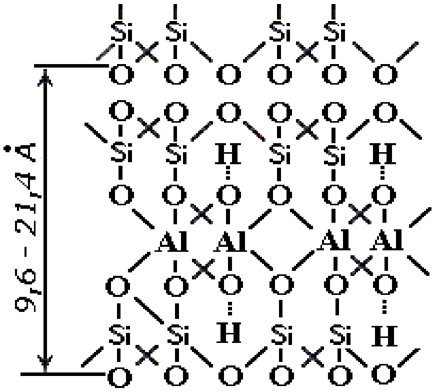

Figure-1. Lattice of monymorillonite.

2. EXPERIMENTAL

To investigate the catalytic influence of clay minerals the samples of bentonite clay, cambrian clay (mineralogical composition of this clay includes kaolin, hydromica and montmorillonite) and kaolin clay, clay mergel and also synthetic zeolites H-Beta-25 и H-MORD (Zeolyst International) were chosen. The choice of bentonite clay is based on the literature data [26], which point out the high content of metal cations in this mineral and the high surface area.

Zeolites NH_4-Mordenite-20 and NH_4-Beta-25, produced by «Zeolyst International», were transferred into catalytically active protonated form of H-MORD and H-Beta-25 by calcination in a muffle kiln.

Mineral materials were introduced in a form of aqueous suspensions in fragmented flax shives in concentration (dry unit weight) of 1, 2, 3, 4, 5 and 10 %. Then spherical granules with size varied (depending on physical-chemical properties of raw material and operating parameters of equipment) from 5 to 25 mm (see Fig. 2) were formed from the obtained mixture in an ablative granulator. These granules dried to equilibrium moisture content (16…20 %) underwent low-temperature pyrolysis. Flax straw and shives with the degree of decomposition of 25…30 % was used as initial raw material.

Figure-2. Spherical organometallic granules on the base of flax shive.

The investigations on flax shives pyrolysis process were conducted in the experimental reactor described in [25].

The analysis of elemental composition of silica-alumina materials was carried out by X-ray fluorescent spectrometer "Spectroscan-Max". Surface area and pore size distribution for the investigated clays were determined by analyzer Beckman Coulter^{TM} SA 3100^{TM}.

Gas chromatograph "Model 3700" equipped with packed columns filled with silica was applied to measure the concentrations of gaseous hydrocarbons in a gaseous mixture. The temperature of the column was 50ºC, detector - 100ºC. The column length was 1 m. The mean diameter of carrier granules was 0, 3…0, 5 mm. Nitrogen was used as gas-carrier with the flow of 120 ml/min.

3. RESULTS AND DISCUSSIONS

The surface characteristics of catalytic systems H-Beta-25 and H-MORD and samples of clays are presented in Table-1. During the experiments on catalytic pyrolysis of flax shive the elemental composition of samples of clays was investigated (see Table-2).

Table-1. Surface areas and pore sizes of investigated silica-alumina materials.

Silica-alumina	Pore size, Å				Surface area, м^2/г.
	Polymorph A		Polymorph B		
H-Beta-25	Strait channels	Curved channels	Strait channels	Curved channels	807
	7.3 x 6.0	5.6 x 5.6	7.3 x 6.8	5.5 x 5.5	
H-MORD	Perpendicular systems of channels		Parallel systems of channels		605
	6.7 x 7.0		2.9 x 5.7		
Kaolin clay	–		–		9
Bentonite clay	–		–		59
Cambriam clay	–		–		30
Clay mergel	–		–		20

One of the major factors influencing the catalytic activity is the value of the catalyst specific surface. H-Beta-25 and bentonite clay have higher specific surface and pore volume (Tables 1 and 3).

Table-2. Elemental composition of investigated clays.

Component	Concentration, %
Bentonite clay	
$Al_2Si_4O_{13}H_4$	96.88
Ti	0.46
Mn	0.06
Fe	2.47
Ag	0.05
Kaolin clay	
$Al_2Si_2O_6H_4$	99.48
Fe	0.34'
Cambriam clay	
$Al_2Si_4O_6H_4$	95.60
Fe	4.34
Clay mergel	
$Al_2Si_4O_6H_2$	97.56
Mn	0.07
Fe	2.20

Table-3. Pore size distribution.

Pore diameter, Å	**Pore distribution, %**			
	Bentonite clay	**Kaolin clay**	**Cambriam clay**	**Clay mergel**
Lower 6	**0**	**16.40**	**21.35**	**0**
60-80	0	10.06	9.35	0
80-100	0	8.06	7.34	0
100-120	0.11	8.10	6.92	0.12
120-160	0.51	9.77	8.40	0.53
160-200	0.73	8.73	7.45	1.08
200-800	98.65	31.00	29.60	72.48
Higher 800	0.01	7.89	9.58	25.79
Total	100	100	100	100

The results of the investigation of pore volume distribution (Table-4) show that the structure of all the samples investigated is represented mainly by mesopores and also micropores (for kaolin).

Catalytic action of natural silica-alumina minerals and synthetic zeolites was estimated basing on the value of volume of the evolving gaseous mixture obtained during the process of flax shives pyrolysis, on the values of concentrations of hydrocarbons in gaseous mixtures and also on the value of the heat of combustion of combustible gases. The experiments were conducted at a temperature of 400-480ºC, because their conduction at higher temperatures doesn't lead to a considerable increase of the products heat of combustion. The experimental data presented are mean values obtained on the base of the results of five experiments.

The preliminary search experiments showed that the addition to waste of flax proccessing of 2 % of synthetic zeolites and of 30% of natural alumosilicates was optimal. The results of the investigation of the dependence of heat of combustion of combustible gases on the content of bentonite clay and synthetic zeolite are presented in Tables 4 and 5, respectively.

Table-4. Dependence of heat of combustion of gaseous mixture on the concentration of bentonite clay in a substrate (at 460ºC).

Concentration of bentonite clay, %	**2**	**8**	**10**	**20**	**30**
Q, MJ/m^3	16.27	19.7	20.45	21.14	23.88

Table-5. Dependence of heat of combustion of gaseous mixture on the concentration of synthetic zeolites in a substrate (at 460ºC).

Concentration of H-Beta-25, %	**2**	**20**	**30**
Q, MJ/m^3	20.74	19.56	18.29

In the presence of catalysts the amount of hydrocarbons in a gaseous mixture noticeably increased. The increase of the heat of combustion of gaseous mixture was due to the increased content of alkanes and alkenes obtained with the use of alumosilicate materials. The average value of specific heat of combustion was higher approximately in 1, 5-2 times in comparison with the data received for non-catalytic process.

Table-6 shows the dependence of the heat of combustion on the type of the catalyst at 460°C. As it can be seen from Table-6, among natural alumosilicate minerals the bentonite clay was the most effective one.

The influence of the temperature on the pyrolysis of flax shive in the presence of bentonite clay was investigated. The experiments showed that the highest heat of combustion (23.88 MJ/m3) was reached at 460°C (Table-7).

Table-6. The influence of mixture composition on the heat of combustion of pyrolysis gases.

Component of the substrate	Heat of combustion at 2% of catalyst loading, MJ/m^3	Heat of combustion at 30% of catalyst loading, MJ/m^3
Bentonite clay	16.28	23.89
Cembrian clay	14.66	19.16
Caoline clay	10.65	19.92
Clay mergel	10.71	19.94
H-Beta-25	20.73	18.28
H-Mord	20.75	18.11
Flax shive without any additives	8.51	

Table-7. Influence of pyrolysis temperature in the presence of bentonite clay on heat of combustion of gaseous mixture.

Temperature, °C	440	450	460	480
Heat of combustion, MJ/m^3	18.55	19.04	23.88	23.31

The significant distinction in the percentage of optimal amount of alumosilicate component of the reaction mixture between natural and synthetic alumosilicates was likely due to the different structures of these substances. Besides, natural alumosilicates while added in considerable amount in reaction mixture, along with catalytic action were also heat-carriers, considerably increasing heat conductivity of the mixture and promoting more uniform heating.

While using clay minerals a considerable increase of the amount of the evolved hydrocarbons in a gaseous mixture was observed. These values exceeded the values obtained during the pyrolysis of the sample without any catalysts almost twice (Table-8).

To estimate the kinetic parameters the investigation of the temperature influence in the range of 400…480ºC on the rate of concentration change of the lower hydrocarbons obtained during pyrolysis process was conducted. From the data obtained in can be seen (Table-9) that the value of activation energy for the catalytic process of flax shive pyrolysis is lower almost twice compared to non-catalytic one. At the same time the value of preexponential parameter (k_0) increases in several orders that are due to the increase of reactive centers amount.

As a result of the work performed closed to the optimal conditions of catalytic conversion of flax shives with the production of combustible gases mixture using natural silica-alumina minerals was determined. It was established that bentonite clay has the best catalytic effect on the process of pyrolysis at the concentration of 30 % and at the temperature of 460…480ºC.

The balance of the process can be described in the following way. The flax tow, straw and shives used approximately contain 53.61 % of carbon, 5.96 % of hydrogen, 0.79 % of nitrogen and 40.79 % of oxygen [6]. If nitrogen can be assumed as neglected, this composition approximately corresponds to the following gross-formula: $C_{44}H_{60}O_{25}$. While decomposing in the process of pyrolysis oxygen can contact carbon and form carbon mono- or dioxide or hydrogen and form water. “The excesses” of hydrogen can contact carbon or evolve in a form of H_2. “The excesses” of carbon carbonizes that is remains in a solid phase as coal. Thus, if the higher amount of oxygen binds with hydrogen to form water the lower content of carbon oxides and the higher content of hydrocarbons will be present in a gaseous mixture. On condition of steam condensation the calorific value of gaseous mixture will be higher due to the higher specific content of hydrocarbons.

Table-8. Dependence of hydrocarbons accumulation on the catalyst nature (at 440ºC).

Hydro-carbons	Time, s	Accumulation of hydrocarbons, ml.					
		Flax shive without additives	Bentonite clay	Cembrian clay	Kaolin clay	Clay mergel	H-Beta-25
Methane	720	3.8	7.6	6.6	6.2	8.7	5.2
	1320	6.4	15.3	11.7	11.6	13.9	10.1
	1920	10.4	20.1	14.7	15.0	17.3	12.6
	2880	11.7	23.5	17.5	18.1	20.1	14.8
	4080	12.8	25.5	19.2	20.2	21.9	16.3
	5280	15.7	26.4	20.1	21.4	22.6	17.0
Ethane	720	0.5	1.1	1.0	0.9	1.5	0.7
	1320	1.0	3.3	2.3	2.4	2.9	1.8
	1920	2.1	4.8	3.1	3.4	4.0	2.6
	2880	2.5	5.7	3.8	4.2	4.7	3.3
	4080	2.7	6.1	4.2	4.7	5.1	3.8
	5280	3.4	6.3	4.4	5.0	5.2	4.0
Ethylene	720	0.3	1.1	0.9	0.7	1.1	0.8
	1320	0.59	2.2	1.5	1.4	1.8	1.6
	1920	1.1	2.8	1.8	1.8	2.2	2.1
	2880	1.3	3.0	2.0	2.0	2.3	2.4
	4080	1.3	3.1	2.1	2.1	2.4	2.5
	5280	1.4	3.1	2.1	2.2	2.4	2.6
Propane	720	0.2	0.6	0.6	0.5	0.76	0.7
	1320	0.4	1.5	1.2	1.1	1.3	1.4
	1920	0.9	2.0	1.6	1.5	1.7	1.7
	2880	1.0	2.2	1.8	1.8	1.9	2.0
	4080	1.1	2.4	1.9	2.0	2.1	2.2
	5280	1.4	2.4	2.0	2.0	2.1	2.2

Table-9. Values of activation energies for the process of flax shives pyrolysis.

Gas	E_a, kJ/mol		k_0	
	Not catalytic process	Catalytic process	Not catalytic process	Catalytic process
Methane	85	38	$1 \cdot 10^2$	$7 \cdot 10^6$
Ethane	68	37	$6 \cdot 10^4$	$2 \cdot 10^9$
Ethylene	51	38	90	$5 \cdot 10^4$
Propane	41	22	$3 \cdot 10^3$	$9 \cdot 10^8$

In current work the gas refining from the resins was conducted by thermocatalytic method. The pyrolysis gases were flown through the heated aluminosilicate catalyst layer impregnated by the iron subgroup metal with different concentration.

The use of investigated catalysts allows decreasing the resins content in the pyrolysis gas. The most active catalyst of resin decomposition in pyrolysis gases for all types of investigated materials was Co-containing catalyst (Figure-3).

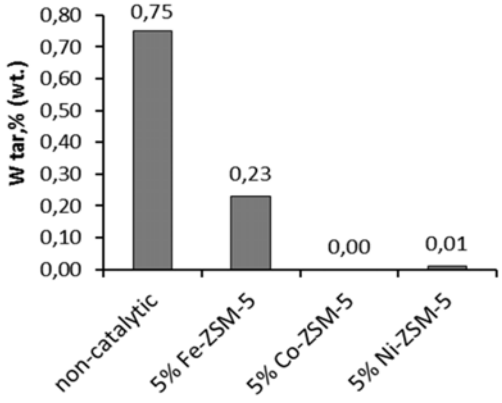

Figure-3. Resin amount in pyrolysis gas.

In the investigation it was found that the catalyst-feedstock mass ratio, granules size and metal concentration on the catalyst surface affect on the catalytic activity in the resins thermal destruction process.

During the experiment it was found that for the complete removal of resins from the combustible gas the catalyst-feedstock mass ratio must not be less than 1:20.

The optimal granule size was chosen in dependence on the reactor capacity considering the gas products formation and the pressure in the system. In the current work the optimal granule size of catalyst was 1 mm.

When using the metal-containing aluminosilicate catalyst to remove the resins from pyrolysis gases the change of gas volume, composition and heat value was observed. For example the use of zeolite catalysts containing the iron subgroup metals leads the increase of the concentration of hydrogen, C_1-C_4 hydrocarbons and carbon oxides (see Figure-4).

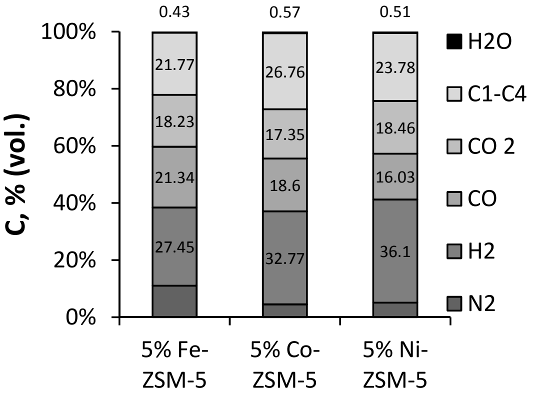

Figure-4. The pyrolysis gas composition obtained using the zeolite catalysts.

In the comparison with the non-catalytic process the C_1-C_4 hydrocarbons volume concentration increases by factor of 1, 39; 1, 66 and 1, 52 using the Fe-containing, Co-containing and Ni-containing aluminosilicate catalyst relatively. The use of these catalysts also leads the content of hydrogen concentration in the gas composition increased from iron to nickel.

The metal concentration on the surface of the aluminosilicate catalyst strongly affects on the catalyst activity in the thermal destruction of the resins in the pyrolysis gas. The increase of metal content leaded the increase of hydrogen concentration that can be explained by the pyrolysis organic product dehydrogenation reaction behavior in the presence of iron subgroup metals [27].

The growth of hydrogen concentration in the pyrolysis gas is followed by the increase of coke-formation on the surface of the catalyst, so the use of the catalysts with high metal content is economically unfavorable.

The sufficient influence of the investigated catalysts on the pyrolysis gas composition can be explained by both of the high catalytic activity in the thermal destruction process and thermal decomposition of high-boiling fractions of liquid pyrolysis products.

4. CONCLUSIONS

The use of catalyst allows decreasing the temperature of pyrolysis from 700ºC to 450…480ºC, decreasing the activation energy almost twice and increasing the rate of pyrolysis.

The data given can be used for further investigations, liquid biofuels and organometallic sorbents production.

The Presented analysis of literature and the experimental data allows coming to the conclusion of the availability of bentonite clay use as the catalytic system in the processes of waste of flax processing pyrolysis for the industrial production of combustible gases as an alternative source of energy [27-29].

ACKNOWLEDGEMENTS

The study was financially supported by the Ministry of education and science of the Russian Federation (RFMEFI57414X0075).

REFERENCES

[1] B.N. Kuznetsov. 1996. Catalytic chemistry of plant biomass. in Soros Educational Journal (Russia). 12: 47-55.

[2] Francis A. Kolla, John J. Balatinecz. Flax shives reinforced thermoplastic resin composition. US Patent US6133348.

[3] V.M. Kostantinov, Yu.B. Chelidze. 2003. Ecological bases of nature management. Moscow Academy.

[4] J. Stevens. 2001. Hot gas conditioning: Recent progress with larger-scale biomass gasification systems. Washington: Pacific Northwest National Laboratory. p. 102.

[5] M. Ising, J. Gil, C.H. 2000. Unger in 1st World Conference and Exibition on Biomass for Energy and Industry. Sevilla, Spain. pp. 1775-1778.

[6] T.N. Mukchina, N.L. Barabanov, S.E. Babash, V.A. Menschikov, G.L. Averkch. 1987. Pyrolysis of carbon-containing raw materials. Moscow “Chemistry. p. 240.

[7] A. Marcilla, A. Gomes, J.A. Reyes-Labarta, A. Giner, F. Hernández. 2003. Kinetic study of polypropylene pyrolysis using ZSM-5 and an equilibrium fluid catalytic cracking catalyst. in Journal of Analytical and Applied Pyrolysis. 68-69: 467.

[8] J. Monnier, G. Tourigny R. 2004. Le van Mao in 13th international congress on catalysis. Paris. France. 2: 216.

[9] A. Marcilla, A. Gomes, S. Menargues, J. García-Martínez, D. Cazorla-Amorós. 2003. Catalytic cracking of ethylene-vinyl acetate copolymers: comparison of different zeolites. in Journal of Analytical and Applied Pyrolysis. 68-69: 495.

[10] D. Serrano, J. Aguado, J. Escola, J. Rodríguez, L. Morselli, R. Orsi. 2003. Thermal behaviour during the pyrolysis of low rank perhydrous coals. in Journal of Analytical and Applied Pyrolysis. 68-69: 481.

[11] G. Nierop, F. van Bergen. 2002. Clay and ammonium catalyzed reactions of alkanols, alkanoic acids and esters under flash pyrolytic conditions. in Journal of Analytical and Applied Pyrolysis. 63: 197.

[12] M. Brebu, M. Azhar, A. Muto, Y. Sakata, C. Vasile. 2002. The role of temperature program and catalytic system on the quality of acrylonitrile-butadiene-styrene degradation oil. in Journal of Analytical and Applied Pyrolysis. 63: 43.

[13] R. Van Grieken, D. Serrano, J. Aguado, R. García, C. Rojo. 2001. Thermal and catalytic cracking of polyethylene under mild conditions. in Journal of Analytical and Applied Pyrolysis. 58-59: 127.

[14] L. García, M.L. Salvador, J. Arauzo, R. Bilbao. 2001. Catalytic pyrolysis of biomass: influence of the catalyst pretreatment on gas yields. in Journal of Analytical and Applied Pyrolysis. 58-59: 491.

[15] H. Eun-Young, K. Jong-Ryeul, C. Jeong-Kun, W. Hee-Chul, P. Dae-Won. 2002. Performance of acid treated natural zeolites in catalytic degradation of polypropylene. in Journal of Analytical and Applied Pyrolysis. 62: 351.

[16] P.T. Williams, A.R. Reed. 2004. High grade activated carbon matting derived from the chemical activation and pyrolysis of natural fibre textile waste. in Journal of Analytical and Applied Pyrolysis. 71: 971.

[17] H.C. Jong, M.J. Sang, H.K. Jun, K.P. Sang, L. 2004. Won-Ho in 13th international congress on catalysis (Paris, France), Palais des Congres. Paris. 2: 217.

[18] N. Kraikul, S. Jitkarnka, A. Luengnaruemitchai in 7th World Congress of Chemical Engineering. 10-14 July. 2005. Glasgow, Scotland. P.245.

[19] K. Tasaka, T. Furusawa A. 2005. Tsutsumi in 7th World Congress of Chemical Engineering. Glasgow, Scotland. pp. 208-209.

[20] A.D. Simonov, N.A. Yazykov, P.I. Vedyakin V.N. 2003. Parmon in 3-d Russia-China Seminar on Catalysis (Novosibirsk). Boreskov Institute of Catalysis SB RAS. Novosibirsk. Russia. p. 35.

[21] T.V. Bukcharkina, N.G. Digurov. 1998. Chemistry of natural energy carriers and carbon materials. School-book. Moscow, D.I. Mendeleyev RChTU.

[22] J. Rabo. 1980. Chemistry of zeolites and catalysis with zeolites. T.2. Moscow “Mir”. p. 422.

[23] Yu. I Tarasevich. 1981. Natural sorbents in water purification processes. Kiev “Naukova dumka. p. 208.

[24] J.A. Martens, P.A. Jacobs, J. Weitkamp. 1986. Attemps to rationalize the distribution of hydrocracked products. in Appl. Catal. 20: 239.

[25] S. Ayabe, H. Omoto, T. Utaka, R. Kikuchi, K. Sasaki, Y. Teraoka, K. Eguchi. 2003. Catalytic autothermal reforming of methane and propane over supported metal catalysts. in Applied catalysis A: General. pp. 261-269.

[26] O.V. Kislitsa, V.V. Alfyorov, A.E. Usanov, E.M. Sulman. 2004. Production of fuel gases by catalytic

destruction of waste of cross-linked rubbery polymers. in Catalysis in Industry. 1: 35.

[27] Keith Openshaw. 2015. Proceedings of the 11th International Conference on Energy, Environment, Ecosystems and Sustainable Development (EEESD '15), 30-41

[28] Shakeel Ahmad Khan, Lal Chand Malav, Sandeep Kumar, Mahesh Kumar Malav, Navindu Gupta. 2015. Proceedings of the 4th International Conference on Energy Systems, Environment, Entrepreneurship and Innovation (ICESEEI '15), 382-395

[29] A.S. Hassan, J.D. Udonne, A.S. Afolabi. 2014. Proceedings of the 9th International Conference on Energy and Environment (EE '14).