Aluminosilicates in biomass thermolysis gas refining

E. M. SULMAN*, YU. V. LUGOVOY, YU. YU. KOSIVTSOV, K.V. CHALOV, I.S. SMIRNOV, A. I. SIDOROV, A. A. STEPACHEVA Department of biotechnology and chemistry Tver State Technical University A.Nikitin Str., 22, 170026, Tver RUSSIA

Abstract: - In this paper the influence of different catalyst on the catalytic thermolysis of different biomass wastes was studied. Synthetic and natural zeolites were used as catalysts for thermolysis. During the test it was mentioned that the pore size of additives had a strong effect on the catalytic activity and promoted the hydrocarbons formation. Also it was found the positive influence of the molded compositions on the structural and sorption characteristics and a role of catalyst in the subsequent thermolysis reaction. Moreover within the laboratory scale the catalytic refining method of gaseous products was developed and described for further commercial use. The natural aluminosilicate had increased the gaseous product yield in 2 times compared to non-catalytic process. The gases produced by fast thermolysis can be used as an alternative to fossil fuels.

Key-Words: - biomass treatment, catalytic thermolysis, aluminosilicate catalysts, thermolysis gas, thermolysis liquid.

1 Introduction

According to the modern ecological and environmental requirements the biomass waste utilization becomes more and more important task. The thermal treatment conducted in the inert media is a most perspective method among other methods of biomass utilization for the production of heat, electricity, liquid fuels and carbon sorbents. The ecologically most effective and iustified technological solution that allows achieving the maximum yield of useful products is fast thermolysis [1-5].

The use of catalysts during thermolysis increases gaseous and liquid products yield; branched hydrocarbons in liquid thermolysis fraction increase the concentration of aromatic compounds. These features cause a significant interest for the studying of catalytic thermolysis in the whole world [6, 7].

Also there is one more significant advantage of catalytic thermolysis: the selectivity of this method much more higher compared to non-catalytic process. So these products carry the higher quality, can be used as a transportation fuels, it is an important benefit of catalysts application in the waste thermolysis process [8-13].

Among thermolysis techniques the fast thermolysis can be allocated. This method provides high automation level, continuous cycle of the process, high yields of gaseous and liquid products; and the chance of the secondary processes is very low, that increases the quality of products.

However at present time for the electricity generation on plant-based biomass waste the fast thermolysis technologies requires the increase of initial material conversion to the combustible gases with high heat value and low resin content [1].

Thermocatalytic refining of gaseous products of fast thermolysis is a technological method directed on the reducing of high-boiling fractions content and resins. The thermolysis gas goes through the catalyst refining layer which promotes the thermal destruction of high-boiling components and resins. The significant amount of gaseous hydrocarbons is forming during the thermocatalytic destruction of thermolysis gases resins. This stage also increases the combustion heat of the thermolysis gaseous products.

But the most typical problem of catalysts for gaseous products thermal refining is the high cost and quick activity loss due to the pollution formation on the catalyst surface [16]. That is why the task of development of check and effective catalyst is still actual task.

Therefore the study of fast thermolysis process involving the stage of thermolysis gas refining can help to solve the problems of renewable feedstock processing and make it more applicable for commercial use.

2 Experimental

2.1 Materials

To study the catalytic thermolysis at low temperature the samples of biomass with the 30% decomposition degree and 5% ash content were used. The samples of flax shive, hazelnut shell and sunflower seed husk were chosen and used as the feedstock for the fast low-temperature thermolysis process.

Such natural aluminosilicate materials as bentonite clay, kaolin clay, clay mergel, cambrian clay as well as synthetic zeolites (H-Mord-20, H-Beta-25, HY, H-ZSM-5 and H-Beta-150 purchased by "Zeolyst International" (USA)) were used as the catalysts of the biomass waste thermolysis.

2.2 Apparatus

On Fig. 1 t he laboratory reactor for the fast thermolysis of biomass with a section of a thermal catalytic purification is presented.



Fig. 1. Experimental reactor for the fast thermolysis of biomass

The fast thermolysis of biomass was performed under inert atmosphere (nitrogen) so before the test the system was purged by the 80 liters of nitrogen.

The biomass waste feeds were injected into the batch hopper 1. Than the feed was delivered inside the reactor 4 by screw drivers 2 a nd 3. The residence time of the feed in the reaction zone of reactor 4 was less than 5 seconds. The temperature was controlled by the electric furnace 5 and varied in the range 450-650 °C. The thermolysis products further passed through the discharge hopper 6 were the solid product was removed from the flow. The cyclone 7 provided the dust collection meanwhile the refined from the tars and high-boiling residue were performed by the catalytic column 8. The

gaseous samples were taken before and after catalytic column 8 to estimate the catalytic activity. Then the volatile products further passed through

the condenser 9 where liquid fraction was separated from the flow and collected in the flask 10. A fter that the gaseous products passed through the catalytic refining system 11. The purified gases were collected in the special gas collection system 12.

The weight of feed injected into the reactor was 500 g. The duration of the test was 30 min. To evaluate the rate of thermodestruction of initial source in the presence of the catalysts the rate of gaseous products evolution was controlled during the experiment.

2.3 Analysis

The examination of the thermal stability of biomass feeds was performed by at hermogravimetric analysis. Thermogravimetric analysis was performed by NETZSCH TG 209 F. The samples were heated at a constant heating rate -10 °C/min under the nitrogen at the temperature range 50-600 °C.

The C₁-C₄ hydrocarbon analysis of gaseous products was performed by Crystallux 4000M, the following parameters were used: consumption of gas-carrier (N_2) _ 120 mL/min; N_2 pressure 1.5 kg s/sm^3 ; duration of the analysis – 30 min; sample volume – 1 mL; column: carrier – silica gel 0.4 mm; column length 1 m; temperature 50°C; temperature of detector – 100°C. Volume concentrations of methane, carbon oxides and hydrogen were measured by GAZOKHROM 2000, the following parameters were used: flow rate of the gas-carrier (He) - 30 cm³/min; sample volume - 0.5 cm^3 ; thermostat temperature was 40° C.

The elemental composition of silica-alumina materials was analyzed by X-ray fluorescent spectrometer "Spectroscan-Max". Surface area and pore size distribution of studied clays were measured by Beckman CoulterTM SA 3100TM.

3 Results and discussion

3.1 Catalysts characterization

The surface analysis of H-Beta-25 and H-MORD and samples of clays can be seen in Table 1.

The objective estimation of the availability of the catalytic sites relates to the value of the specific surface area of the catalysts. According to the Tables 1 and 2 among all clay samples the

maximum values of the specific surface area and the pore volume are reached for bentonite clay. The presence of pores with different sizes inside the clays samples positively affects hydrocarbons synthesis. While the large pores provide the effective delivery raw material and extraction of products, the small size pores contribute to the hydrocarbons synthesis [17].

The results of the pore-size distribution measurements (Table 2) indicate that mainly the structure of all clay samples is presented by the mesopores.

Table 1. Surface areas	and pore	sizes	of inve	estigated
silica-alumina material	s			-

Silico					Surface
olumino		area,			
aiuiiiia		м ² /g.			
	Polymorph A		Polymorph B		
H-Beta-	Strait Curved		Strait	Curved	907
25	channels	channels	channels	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
Kaolin clay		-		-	9
Bentonite clay	_		_		59
Cambrian clay	_		_		30
Clay mergel	_		_		20

Table 2. Pore size distribution

Pore	Pore distribution, %					
diameter, Å	Bentonite Kaolin Cambrian clay clay 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		

3.2 Thermogravimetric analysis of biomass

There are number of a process condition effecting on the conversion of a raw biomass to products. The most important one is a temperature.

The various parameters affect on the conversion of the feedstock. The temperature setting of the process is one of the most important ones. First of all the temperature dependence of thermal decomposition of biomass samples was estimated by the differential thermal analysis (Fig. 2).

During all tests the dehydration of water was found at the temperature range 80-180 °C.

The series of peaks with the significant weight loss at the temperature range 210-450 °C correspond to the thermal destruction of different biomass components – hemicellulose, cellulose and lignin respectively [18].

Since the high conversion is a one of the most important parameters, the temperature range 450-650 °C was accepted as optimal for the further studying.





3.3 Temperature dependence of biomass conversion

As it was mentioned above the temperature range of the process is key parameter that influences on t he mass distribution of the thermolysis products. The increase of temperature provides the growth of gaseous and liquid products yields. However at the same time the high temperature increases the cost of the process that leads to the increase of prime cost of the final product.

The temperature influence on the fast thermolysis of the biomass waste conversion was measured in the laboratory reactor at the temperature range 450-650 °C, the size of feedstock was about 1 mm. The dependence of flax shive conversion on the fast thermolysis temperature is shown on Fig. 3.



Fig. 3. The temperature dependence of flax shive on fast thermolysis temperature (2 sec)

As it can be seen on Fig.3 the optimal process temperature is 600 C, the further increase of temperature does not lead to the growth of the gaseous and liquid products yield and decreases the heat value of the obtained combustible gas due to the increase of the yield of low molecular weight gases – hydrogen and carbon monoxide (II).

As well as temperature influence on the conversion, the changes of gaseous products heat values due to different process temperature were studied (Table 3). The experiments showed that the highest heat of combustion (17.14 MJ/m^3) was reached at 600 °C

Table	3.	Influence	of	thermolysis	temperature
on hea	t o	f combusti	on	of gaseous m	ixture

Temperature, °C	450	500	550	600	650
Heat of combustion, MJ/m ³	15.07	15.78	16.43	17.14	15.82

3.4 Investigation of influence of the residence time inside the reactor and particle size of raw material

Not only temperature has an influence on the conversion of biomass. Such parameters as a residence time inside the hot reactor zone and the particles size significantly affect on conversion (Fig. 4 and 5).



Fig. 4. The solid residue formation dependence on the residence time in the fast thermolysis reactor ($d\sim0.5$ mm)

As it can be seen on Fig. 4 the increase of a residence time of biomass inside the reactor over 2 seconds is useless since it leads to the rise of the energy costs and promotes the secondary reaction. According to the Fig.5 the optimal biomass particle size is about 0.5 mm.



Fig. 5. The solid residue yields dependence on a particle size of different biomasses (T=600 °C; t = 2 s.)

3.5 Physicochemical properties of the gaseous products

As it can be seen on Fig. 6 there is an influence of the process time on the heat value of biomass fast

thermolysis combustible gas derived from the studied carbon-containing plant waste.

For all tests the growth in the lower volumetric heat value of the gaseous products was observed during the first 8 minutes of the thermolysis. It can be explained by the gradual displacement of the inert media by the thermolysis combustible gases.

The gaseous products received after the flax shive treatment showed the highest heat value while the gaseous products received during the sunflower seed husk recycling has the lowest heat value. The heat value of the gaseous products of the samples studied after the quazy-steady state settlement was in the range 14-17 kJ/L.



Fig. 6. The dependence of the gaseous product lower volumetric heat value on the process time (T= 600 °C).

Generally the gaseous product heat value is determined by methane and ethane content, therefore the form and the character of the curves of C_1 - C_4 hydrocarbons concentration change agrees well with the data of the kinetics of the gaseous product heat value. The information about C_1 - C_4 hydrocarbons content in gaseous products derived from a flax shive thermolysis can be seen on Fig. 7.





However the thermolysis gaseous products contain a significant amount of tars that reduce the effective use of these gases as a source of energy.

The tar content mainly depends on t he process conditions and the reactor construction, type and moisture of the raw material. That is why the refining of the thermolysis gases is a very important and required process stage. Fig. 8 s hows the tar yield dependence of the feedstock type. According to Fig. 8 the lowest amount of tar formed in the fast thermolysis of hazelnut shell while the highest amount of tar was obtained in the fast thermolysis of sunflower seed husk.



Fig. 8. The tar yield dependence on the feedstock type (T=600 °C, t = 2 s, $d\sim0.5$ mm)

3.6 Influence of catalysts on the heat value of thermolysis gases

In our previous work [19] it had been decribed the positive catalytic effect of synthetic zeolites and natural alumosilicates. The heat value dependence of combustible gases on the content of bentonite clay and synthetic zeolite was investigated within the current work and is presented on Fig.9 and 10, respectively.



at 600 °C

The use of additions allows obtaining the higher content of hydrocarbons in a gaseous mixture. It leads to the increasing of the heat value of received gaseous mixture due to the higher content of alkanes and alkenes. The average value of specific heat value of combustion was 1.5-2 times higher compared to the products received from the non-catalytic process.



products on the concentration of synthetic zeolites at 600 °C

The comparison of different addition is represented on Fig. 11, it can be seen the heat value dependence of combustion on di fferent types of the catalyst at 600 °C. As it can be seen from Fig. 11, among natural alumosilicate minerals the bentonite clay was the most effective one.



Fig. 11. The quantitative influence of additives on the heat value of combustion

As it can be seen from Fig. 11 there is significant difference in the behaviors of natural and synthetic alumosilicate additives during weight changes, due to the different structure of these substances. Besides, natural alumosilicates while added in considerable amount in reaction mixture, along with catalytic influence were also heating carriers, considerably increasing of the heat conductivity of the biomass substance and promoting more uniform heating.

Also, while using mineral clays the considerable increase of the amount of C_1 - C_4 hydrocarbons in gaseous products was observed. These values were almost two times more, than heat value of gaseous product received during non-catalytic thermolysis.

3.8 The investigation of the catalyst activity in the gas refining process

Within the current research the thermolysis gas refining from tars was performed by thermocatalytic method. The thermolysis gases flow was passed through the heated layer of the alumosilicate catalyst containing iron subgroup metal at various concentrations (0, 1, 2, 5 a nd 10wt.%)

Following metals (5wt.%) supported on zeolite H-ZSM-5 were used as catalyst: Fe, Co, Ni. During the present research the optimal granule size of catalyst was 1 mm. The optimal catalyst size was chosen according to the unit capacity of the gaseous product formation and the system pressure. First of all Co-containing catalyst was found the most effective one (Fig. 12).



Fig. 12. The concentration of tars in the thermolysis gas after refining process (flax shive, T=600 °C, t = 2 s., $d \sim 0.5$ mm)

As it is can be seen on Fig. 12, firstly the use of zeolite catalysts promotes the purification of thermolysis gas, secondly the use of Co-containing catalyst allows to reduce tar yield to 0.00wt.%.

The use of Me-alumosilicate catalyst in gas refining stage leads to the changes of the gas volume and heat value of combustion. It is occurred through the changes of the concentration of hydrogen, C_1 - C_4 hydrocarbons and carbon oxides compared to non-refining process.

Obviously the type and concentration on surface of active metals affect on the catalyst activity followed by differences of products yields (Fig. 13 and 14)

The volume concentration of C_1 - C_4 hydrocarbons increased in 1.39; 1.66 and 1.52 times using 5% Fe-ZSM, 5% Co-ZSM and 5% Ni-ZSM catalysts respectively compared to non-catalytic process. Also the hydrogen concentration was increased compared to non-catalytic process; moreover the growth of H₂ yield increase from Fe to Ni catalysts.

The increase of metal content in catalysts (Fig. 14) leads to the increase of H_2 concentration. It can be explained by the dehydration reaction of thermolysis organic products in the presence of iron subgroup metals [20]. However the simultaneous growth of H_2 and solid residue formation on the catalyst surface is economically unfavorable.



Fig. 13. Gas composition dependence on the metal supported on H-ZSM-5 during the flax shive thermolysis (T=600 °C; t = 2 s, particles size -0.5 mm)



Fig. 14. Gas composition dependence on the metal concentration on the surface of ZSM-5 (T=600 °C; t = 2 s., particle size of flax shive 0.5 mm; metal concentration – 5wt.%)

The influence of the studied catalytic materials on the thermolysis gases composition can be explained by the catalyst high activity during high temperature destruction processes and thermal decomposition of tars and high-boiling fractions of thermolysis liquid products. The catalysts studied also affect on t he carbon oxides (II) and (IV) yields (Fig. 13 and 14).

According to the data on the gaseous product composition (Fig. 13) the optimal Co content in the zeolite catalyst is 2% (wt.). Such metal content in the catalyst allows increasing C₁-C₄ hydrocarbons concentration and removing the resins from the combustible gas of the fast thermolysis of studied biomass types.

4 Conclusion

According to the data received the following conclusions can be made:

-the optimal temperature for the fast thermolysis treatment of flax shive, hazelnut shell, sunflower seed husk was about 600 °C;

-the optimal feedstock size was 0.5 mm at the residence time inside the reactor about 2 seconds;

-2% Co-ZSM-5 had the highest activity at the catalyst-substrate mass ratio 1:20;

-the use of zeolite catalysts on the base of iron subgroup metals leaded to the decrease of tars content in the thermolysis gas as well as to the increase C_1 - C_4 hydrocarbons amount, hydrogen and carbon monoxide (II) concentration compared to non-catalytic process. References:

- [1] A.V. Bridgwater Review of fast pyrolysis of biomass and product upgrading, *Biomass and bioenergy*, Vol. 38, 2012, P. 68.
- [2] W.T. Tsai, M.K. Lee, Y. M. Chang Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor, *Journal of Analytical and Applied Pyrolysis*, Vol. 76, No. 1, 2006, P. 230.
- [3] A.V. Bridgwater Biomass fast pyrolysis, *Therm. Sci.*, Vol. 8, 2004, P. 21.
- [4] Yu. Yanqing The role of shape selectivity in catalytic fast pyrolysis of lignin with zeolite catalysts, *Applied Catalysis A: General*, Vol. 447, 2012, P. 115.
- [5] M.A. Jackson, D.L. Compton, A.A. Boateng Screening heterogeneous catalysts for the pyrolysis of lignin, *Journal of Analytical and Applied Pyrolysis*. Vol. 85, No. 1, 2009, P. 226.
- [6] Russian market of cereal crops, *Analytical review*, Vol. 2, 2014.
- [7] G.W. Huber, S. Iborra, A. Corma Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering, *Chem. Rev.*, Vol. 106, 2006, P. 4044.
- [8] S. Yaman Pyrolysis of biomass to produce fuels and chemical feedstocks, *Energy conversion and management*, Vol. 45, No. 5, 2004, P. 651.
- [9] J. Speight *Synthetic Fuels Handbook: Properties, Process and Performance,* McGraw-Hill Professional: New York, NY, USA, 2008.
- [10] C.J. Atkinson, J.D. Fitzgerald, N.A. Hipps Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review, *Plant and soil*, Vol. 337, No. 1-2, 2010, P. 1.
- [11] K. Openshaw A review of Jatropha curcas: an oil plant of unfulfilled promise, *Biomass and Bioenergy*, Vol. 19, No. 1, 2000, P. 1.
- [12] S.A. Khan, L.Ch. Malav, S. Kumar, M. Kumar Malav, N. Gupta, Proceedings of the 4th International Conference on Energy Systems, Environment, Entrepreneurship and Innovation (ICESEEI '15), 2015, P. 382.
- [13] A.S. Hassan, J.D. Udonne, A.S. Afolabi Process Study of Biogas Produced from Cow Dung and Water Hyacinth in a Single Phase Digester Reactor, *System*, Vol. 17, P. 18.
- [14] V. Germanovich, A. Turilin Alternative sources of energy and energy saving. The practical constructions of wind, solar, water, and biomass energy utilization, *Science and engineering*, Moscow, 2014, P. 320.

- [15] J.H. Yuan, R.K. Xu, H. Zhang The forms of alkalis in the biochar produced from crop residues at different temperatures, *Bioresource technology*, Vol. 102, No. 3, 2011, P. 3488.
- [16] T.A. Milne, R.J. Evans Biomass Gasifier "Tars": Their Nature, Formation and Conversion, National Renewable Energy Laboratory Managed by Midwest Research Institute for the U.S. Department of Energy under contract No. DE-AC36-83CH10093 Prepared under Task No. BP811010, 1998, 67.
- [17] Y. Zhang, P. Yoneyama, N. Tsubaki A New Low-Temperature Methanol Synthesis Method, *7th World Congress of Chemical Engineering*, 10-14 July, Glasgow, Scotland, 2005, P. 256.
- [18] P.J. De Wild, H. Reith, H.J. Heeres Biomass pyrolysis for chemicals, *Biofuels*, Vol. 2, No. 2, 2011, P. 75.
- [19] E.M. catalytic Sulman Low-temperature pyrolysis of waste of flax processing using silica-alumina catalytic systems, Recent Advances on Energy, Environment. Ecosystems, and Development: proceedings of the International Conference on Energy, Environment, Ecosystems, and Development (EEED 2015), Barcelona, Spain, April 7 - 9, 2015, P. 75.
- [20] V.A. Roiter *Catalytic properties of substances*, Naukova dumka, Kiev, 1968, P. 720..

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