

DEVELOPMENT OF COMPLEX TECHNOLOGIES FOR BIOMASS PROCESSING

Bessmertnykh A.V., Kosov V.V. and Zaichenko V.M.*

*Author for correspondence

Joint Institute for High Temperatures Russian Academy of Sciences,
13 Izhorskaya str.,
Moscow, 125412,
Russian Federation,
E-mail: zaitch@oivtran.ru

ABSTRACT

Results of experimental investigations in the field of bioconversion are presented. There are considered two technologies. One technology is connected with pyrolytic conversion of biomass into calorific gas which can be used as a gas fuel for power unit on the base of gas-piston engine. It is shown that as a result of biomass pyrolysis and the subsequent cracking of emanating products by their filtration through charcoal at the temperature 1000°C it is possible to receive 1.4m³ of gas with specific calorificity about 3000 kcal/m³ per one kg of original raw material. Other technology is a technology of joint biomass and natural gas processing with production of pure carbon materials and hydrogen. The final products of this technology are the strong composite material containing up to 98% carbon and the gas mixture enriched with hydrogen. The hydrogen content in gas mixture at the reactor outlet is defined by the efficiency of the process of heterogeneous pyrolysis of natural gas and may reach 90% (volume). As a raw material for both technologies the wood waste and peat are considered.

INTRODUCTION

Developing the technologies for conversion of different kinds of biomass into gas fuel and pure carbon materials is rather an actual problem both from the point of view of natural resources conservation, and from the point of view of creating autonomous plants to produce both electricity and heat operating on local kinds of fuel. Very attractive natural raw material is wood and peat. Wood and peat fall under category of renewable hydrocarbon resources. About 70% of the territory of the Russia is covered with forests, which makes up about 23% of world reserves. The development of efficient methods of processing the waste of the lumbering and wood-working industry is a very urgent problem from the standpoint of environmental protection, because the decay of wood waste is accompanied by emission of carbon dioxide, phenol

compounds and other harmful substances while the thermal effect of attendant chemical reactions is not utilization. In regard to peat reserves in Russia, which account for about 42% of those around the world, they are equivalent to about 70 billion tons of standard coal that exceeds the total oil and gas resources [1]. Growth of peat reserves only in Russia is estimated at 260 -280 million tons per year but only few percent of that quantity is extracted and used now. From the 1960's the use of peat began to rapidly decrease as more natural gas was produced and consumed. The amount of peat consumed in 1990 had dropped by more than a factor of 8 as compared with that in 1965 and its fraction in the country's energy balance had decreased by a factor of 22 for the same period of time. Utilization of raw or partially processed wood and peat for needs of power engineering is represented rather inconvenient and demands essential investments as it leads to radical reconstruction of the whole technological chain of electricity production. An alternative way to use the abovementioned hydrocarbon resources for power purposes links to developing a technology for processing them into high-calorific gas mixtures.

Gasification and pyrolysis are the most popular methods that developed for producing gas fuel from biomass. Both of them have some advantages and disadvantages. Air gasification is the easiest method to convert biomass into gas. However the resulting gas contains up to 60% carbon dioxide and nitrogen and its calorific value is generally around 4 - 5 MJ/m³ which is too low. Overall efficiency of gasification gas power plant is limited to 20%. The gasification products also contain undesirable substances such as tars and dust which are need to be removed [2]. To increase a calorific value of the gasification products oxygen or water steam gasification can be used. The gas produced by oxygen and steam gasification contains no nitrogen and small amount of carbon dioxide. The maximum gas yield reaches 1.3 m³ per kg of raw material and its calorific value is about 11 MJ/m³ [3]. Steam gasification is the

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widespread process because of its simplicity. The main disadvantage of the process is concerned with necessity of steam generation which reduces overall effectiveness of power plant. Use of oxygen for the purpose of gasification demands an air separation unit in technological chain that leads to rise in price of end product.

During pyrolysis of solid hydrocarbon raw material, heating is carried out without air access, and, therefore nitrogen is absent in the end products. Products of biomass pyrolysis are non-condensable pyrolysis gas, char and liquid fraction consisting of tar and pyrolytic liquor. Calorific value of gas produced in the process of biomass pyrolysis is considerably higher than calorific value of gas produced in the air gasification process. Composition of pyrolysis products depends both on biomass properties and on a number of technological parameters such as heating rate, final temperature, characteristic time of residence in reaction zone and so on. Insignificant degree of processing of initial raw materials into pyrolysis gas is main disadvantage of this technology. Significant increase the gas yield can be achieved by high-temperature conversion of liquid fraction. For this purpose both the catalytic [4] and non-catalytic [5, 6] methods can be used. In the present paper the scheme similar to the scheme offered in [6] for processing of wood sawdust is considered. Experimental feasibility of the technology based on such scheme was partially presented in [7]. Synthesis gas consisted from carbon oxide and hydrogen and char are the end products of this technology.

Char is a brittle porous material with carbon content about 90%. It would be possible to use it in various industrial applications, for example metallurgy, if its stress-strain property is not too low. The other technology which is presented in this paper allows to produce a hard carbon composite material with carbon content up to 98% from char. Composite is formed as a result of deposition of pyrocarbon on the surface of char in the process of heterogeneous pyrolysis of gaseous hydrocarbons which are blown through reaction volume filled by char [8]. The gaseous mixture at the exit of reactor contains hydrogen which concentration may be easily varied by change in operating parameters and may reach 90% (volume) and more. As the gaseous hydrocarbons in this technology natural gas, low-pressure gas field, oil gas and hydrocarbon waste gases of different industrial enterprises may be used.

Comparison of behavior of different biomass types (wood and peat) during their processing by means of two abovementioned technologies, experimental research of the influence of different factors (temperature, heating rate, residence time) on the composition and volume of the producible gaseous mixtures, the quantitative characteristics of the heterogeneous pyrolysis of saturated hydrocarbons in the process of their filtration through the porous carbonic medium were the purposes of this paper.

EXPERIMENTAL CONDITIONS

All the experiments were carried out at the setup similar to used in [7, 8] and schematically presented in Figure 1. It consisted of a high-temperature reactor A, a gas supply system and a gas expense controller G at the entrance of reactor, and a

system of extraction and analysis of gas at the exit of reactor including condenser B, eudiometer C and chromatograph. The samples of the gas for chromatography were taken out in the point D. The reactor was a stainless steel tube with an inside diameter of about 37 mm, which was placed within two-section furnace with independent heaters for each section. Each section was 300 mm length. The heaters allowed varying the temperature inside the reactor from 100 to 1200°C. Such construction of the furnace made possible to use the reactor in one and two chamber regimes.

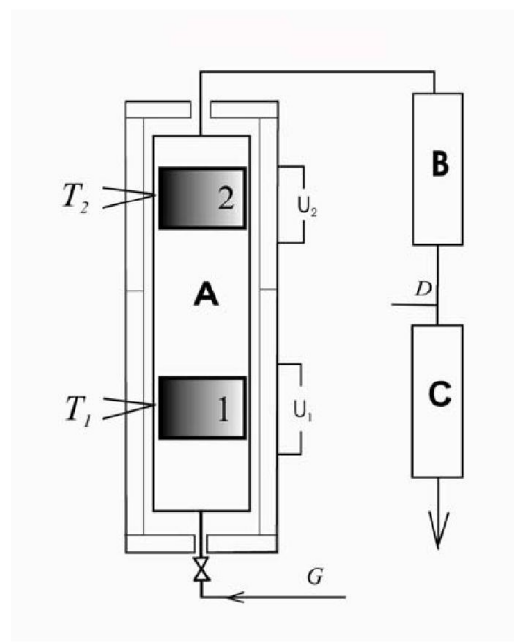


Figure 1 Experimental installation scheme

In the first case the top chamber of reactor was not heated up and was empty. During experiments the behavior of different raw materials situated in bottom chamber at the stage of pyrolysis, activation and also the process of pyrocarbon deposition from gaseous hydrocarbons on the surface of char were investigated. The gas supply system made it possible to carry out experiments in different gas media and monitor the volumetric gas flow through the reactor. The pressure in reactor was equal to 10^5 Pa.

The two chamber regime was used for investigation of pyrolysis of different raw materials, composition and yield of gas produced in process of its thermal conversion. Raw material 1 (see Figure 1) was placed into the bottom chamber. Char 2 obtained by pyrolysis of the same raw material was placed in the top chamber. The depth of char bed was equal to 50 mm. Before experiments the top chamber was heated up to temperature T_2 that was held further at the constant level. After that the temperature of the bottom chamber was raised at the rate 10°C/min. Thus, gases and vapour formed during pyrolysis of initial raw material passed through the porous carbon bed with the fixed temperature T_2 (further this mode is designated as «pyrolysis with cracking»). As a result of homogeneous and heterogeneous chemical reactions in the high-temperature zone a decomposition of pyrolysis gases and vapour took place.

Conversion degree depended both on the temperature T_2 and on the residence time in a high-temperature zone. The output gas mixture passed through the condenser B. Non-condensable gas came into the eudiometer C. Comparison of the composition and the output of the gases formed at presence and absence of the char in the top chamber of the reactor gave an opportunity to compare efficiency of conversion of initial raw material into combustible gas under different operation conditions. Wood and peat pellets were used as initial raw material. Humidity of the samples was 6% and 10% for wood and peat respectively.

PYROLYSIS OF WOOD AND PEAT PELLETS

The different raw materials pyrolysis experiments were carried out in one chamber regime of reactor. During the experiments raw material was heated in oxygen-free medium from room temperature to 1000°C. The fulfilled experimental investigations showed similar behavior of peat and wood pellets during their thermal processing. The change in the temperature of samples and the corresponding change in their mass are presented in Figure 2. The data shown in Figure 2 correspond to a heating rate of approximately 10°C/min. It can be seen that the loss of mass occurs mainly in the temperature interval from 200 to 600°C and ranges from 65 (for peat pellets) to 75% (for wood pellets) of the initial mass. The change in the mass with a further increase in the temperature is insignificant and is equal to around 5% of the initial mass in the temperature interval from 600 to 1000°C. The obtained char is a brittle porous material containing around 80 and 90% of carbon for peat and wood pellets, respectively. This difference mainly depends on the difference of ash level of the initial raw materials. Changing the heating rate from 2 to 35°C/min resulted in the mass of char decreasing by no more than 10% and the specific volume of open pores increasing by around 20%. The specific volume of open pores for char from wood and peat pellets is equal to 0.5 and 0.28 cm³/g, respectively.

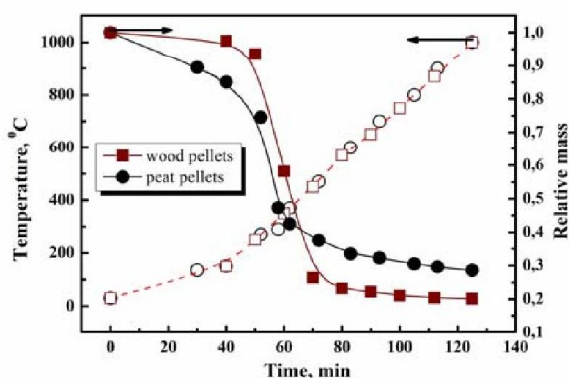


Figure 2 Temperature change and relative mass loss of wood and peat pellets in the pyrolysis process

The chromatographic analysis of composition of the gases evolved during pyrolysis of wood and peat pellets was fulfilled in the temperature range 250 – 1000°C at the heating rate 10°C/min. Gas yield and its composition for wood and peat

pellets are very similar. Major gas components are H₂, CO, CO₂ and C_nH_m. Note that methane constituted the main part in the hydrocarbon mixture C_nH_m. At temperature above 500°C the carbon dioxide content substantially decreased whereas the content of combustible gases (methane, hydrogen and carbon monoxide) increased that led to increase of the calorific value of the product gas mixture. The overall gas yield was equal to 0.29 m³ per kg of initial raw material. The lower calorific value of product gas was equal to $Q_L = 9,6 \text{ MJ/m}^3$. Extraction of the gas evolved in the temperature range 500 – 1000°C leads to the appreciable increase of the calorific value of product gas up to 13 MJ/m³ but the gas yield decreases to 0.18 m³ per kg of initial raw material.

PYROLYSIS AND CRACKING

Increasing the conversion degree of raw material into a combustible gas can be achieved as a result of high-temperature thermal processing of gases and vapors emanating in process of pyrolysis. For this purpose two chamber regime of reactor was used. The data on gas volume (per kg of peat pellets) obtained in the process of heating of the bottom chamber of the reactor at different temperatures T_2 are shown in Figure 3. In the same Figure the similar data received in «pyrolysis» mode are also shown. As follows from the presented data the volume of the gas produced in mode «pyrolysis with cracking» was much more than the volume of the gas produced in «pyrolysis» mode. This difference increased essentially with increasing the top chamber temperature T_2 . Simultaneously reduction of quantity of the liquid fraction collected in the condenser B was observed. For the temperature $T_2 = 1000^\circ\text{C}$ there was no liquid fraction in the condenser that was evidence of full tar and pyrolygneous liquor conversion into gas. Chemical interaction of pyrolygneous liquor with char was confirmed by char mass loss in the top chamber of the reactor which increased with growth of temperature T_2 .

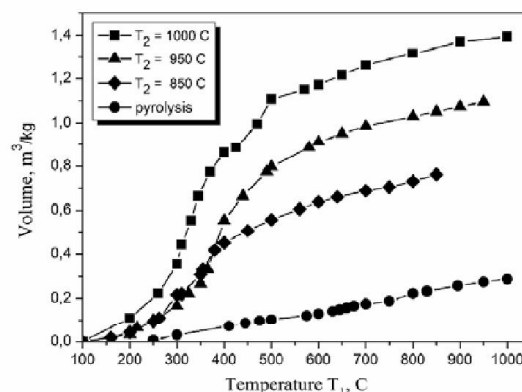


Figure 3 Gas yield per one kg of raw material during thermal processing of peat pellets vs. temperature of the bottom chamber for different regimes

The mass of char formed in the bottom chamber did not depend on the temperature in the top chamber and was about 30% for peat pellets and 20% for wood pellets. It is followed

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from Figure 3 that in mode «pyrolysis with cracking» main volume of gas was generated in the temperature range 250 – 500°C that corresponded to the temperature range of condensable fraction formation during pyrolysis.

Figure 4 shows the results of chromatography of the gas composition during heating of the bottom chamber at two temperatures of the top chamber T_2 . One can see that carbon dioxide and methane content in output gas decreased with the rise of temperature T_2 . For temperature $T_2 = 1000^\circ\text{C}$ the content of carbon dioxide and methane didn't exceed one percent. Thus temperature increase in the top chamber leads to raise the rate of disoxidation of CO_2 and heterogeneous pyrolysis of methane. It should be noticed that for the top chamber temperature $T_2 = 1000^\circ\text{C}$ the gas composition practically does not depend on the bottom chamber temperature at its changing in the range 250 – 500°C, i.e. in the area of main gas release (see Figure 3).

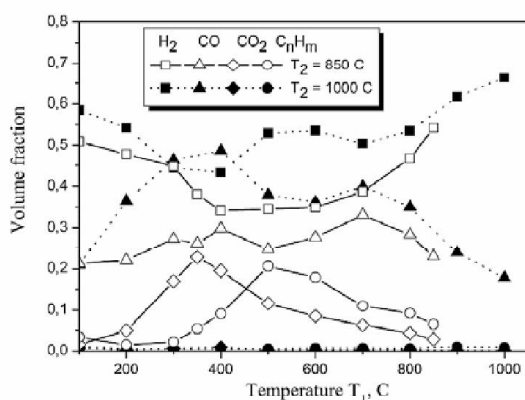


Figure 4 Composition of output gas in mode «pyrolysis with cracking» vs. temperature of the bottom chamber at various temperatures of the top chamber. Raw material – peat pellets

Calorific values of the gas mixtures obtained by thermal processing of wood and peat pellets were calculated on the base of experimental data similar to presented in Figure 4. In Table I and Table II data on content of combustible components in the gas mixtures obtained by thermal processing of peat and wood pellets for different temperatures of the top chamber («pyrolysis with cracking» mode) and corresponding high Q_H and low Q_L calorific values are presented. Similar data for gas mixture obtained in «pyrolysis» mode are shown at the same Tables.

Table I Composition and calorific value of gas mixtures obtained from peat pellets

T_2, C	Volume fractions of combustible components			Calorific value, MJ/m^3	
	H_2	CO	C_nH_m	Q_H	Q_L
850	0,40	0,27	0,08	11,7	10,6
950	0,43	0,40	0,02	11,3	10,4
1000	0,49	0,41	0,01	11,7	10,6
Pyrolysis	0,23	0,19	0,13	10,4	9,6

Table II Composition and calorific values of gas mixtures obtained from wood pellets

T_2, C	Volume fractions of combustible components			Calorific value, MJ/m^3	
	H_2	CO	C_nH_m	Q_H	Q_L
850	0,39	0,28	0,10	12,5	11,5
950	0,47	0,41	0,01	11,5	10,6
1000	0,46	0,46	0,00	11,7	10,9
Pyrolysis	0,28	0,26	0,16	13,4	12,2

The data comparison shows that calorific value of gas mixture obtained in «pyrolysis with cracking» mode practically does not depend on the top chamber temperature T_2 and differs about 10% from calorific value of gas mixture obtained in «pyrolysis» mode. For peat pellets it is more in «pyrolysis with cracking» mode and for wood pellets it is more in «pyrolysis» mode. The gas composition is much more sensitive to the temperature T_2 . As stated above the temperature T_2 increase leads to CO_2 and CH_4 content decrease. For the temperature $T_2 = 1000^\circ\text{C}$ the product gas mixture consists of CO and H_2 in practically equal parts.

If calorific value of the gas mixture obtained in «pyrolysis with cracking» mode slightly differs from calorific value of the gas mixture obtained in «pyrolysis» mode, the gas volumes are essentially different (see Figure 3). That means the «pyrolysis with cracking» mode allows to increase the conversion degree of the initial raw material into gas phase.

HETEROGENEOUS PYROLYSIS OF GASEOUS HYDROCARBONS

At the stage of heterogeneous pyrolysis a gaseous hydrocarbon is blown through a reaction volume with char samples heated up to a given temperature. Reactor was used in one chamber regime. Char samples were received by pyrolysis of wood and peat pellets. Efficiency of the heterogeneous pyrolysis and hence the rate of pyrocarbon deposition depend on different factors such as the specific surface area of char, the temperature at which pyrolysis process carries out, and the composition of gaseous hydrocarbons used at the stage of heterogeneous pyrolysis.

In order to increase the specific surface of char its activation with the help of aqueous vapor was used. Porosity of activated char is related to the decrement of the relative mass in the process of activation. Increase of the mass loss results in increase of the pore sizes and their volume. Dependence of the specific pore volume on the decrement of the relative mass in the process of activation for char samples produced from wood and peat pellets is shown in Figure 5.

The change of the relative mass of activated char samples produced from wood and peat pellets in process of the methane heterogeneous pyrolysis as a function of time is given in Figure 6. Note that the dependences presented in Figure 6 were received for the char samples possessed an identical mass decrement in the activation process. It is obvious that similar behavior for the char samples from different raw materials takes place but the value of the deposition rate of pyrocarbon

for char samples from wood pellets is a little more than for samples from peat pellets. It is in agreement with data presented in Figure 5 and indicates that the rate of mass growth depends essentially on the porosity of the sample.

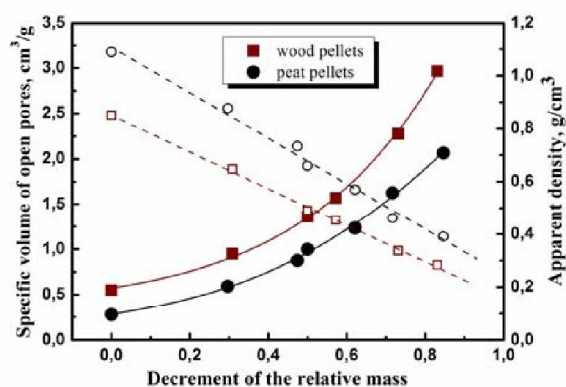


Figure 5 Dependence of the specific volume of open pores (full sign) and apparent density (open sign) on the relative mass loss in the process of activation

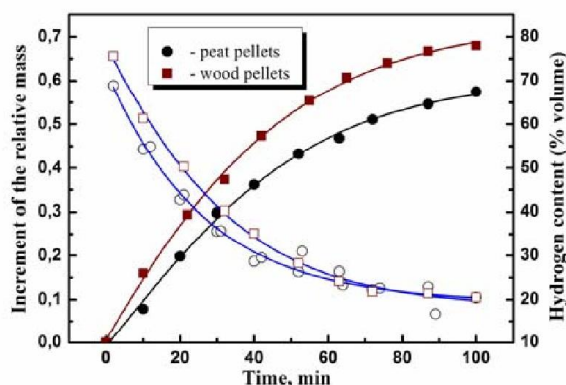


Figure 6 Increment of the relative mass of activated samples (full sign) and hydrogen content at the exit of reactor (open sign) during the process of heterogeneous pyrolysis of methane at 1000°C

From the beginning the deposition of pyrocarbon on surface of the activated samples occurs sufficiently fast. With time the rate of mass gain for activated samples slows down and approaches to the rate for non-activated samples. Such behavior is evidence that active surface area diminishes and becomes even for different samples.

Deceleration of the process of the heterogeneous pyrolysis is verified by the results of the chromatographic measurements of methane and hydrogen content in gas mixture at the exit of the reactor (see Figure 6). The hydrogen content in exhaust gas decreases with time and becomes constant that points to the constant rate of pyrocarbon deposition.

The results of porosity measurements give the opportunity to imagine a character of structure modification of sample in process of the heterogeneous methane pyrolysis: the volume fraction of open pores decreases and the volume fraction of closed pores increases in process of the methane heterogeneous

pyrolysis. After approximately 100 minutes the volume fraction of closed pores is practically constant. This fact indicates that after 100 minutes pyrolysis is in progress on outer surface of the sample practically while inner cavities become closed for methane diffusion though their volume fraction is about 50%.

The foregoing statement is supported by an electron-microscope image of a section of composite material obtained as a result of pyrocarbon deposition on the surface of activated char in the process of heterogeneous pyrolysis of methane (see Figure 7). One can clearly see that a quite significant (of the order of 10 μm) layer of pyrocarbon has already formed on the external surface of the sample, while the internal spaces are still far from being filled.

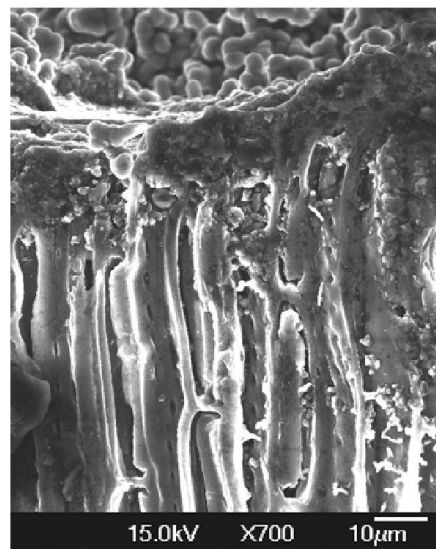


Figure 7 Electron-microscope image of shearing of composite carbon material

For estimation of an influence of the composition of gaseous hydrocarbons on the rate of pyrocarbon deposition the experiments were fulfilled with different saturated hydrocarbons such as methane, propane and butane and their mixtures. It was shown that usage of heavy saturated hydrocarbons causes the pyrocarbon deposition on the active surface of porous carbonic materials to increase essentially. For example the amount of pyrocarbon deposited after 60 minutes of butane pyrolysis at 1000°C was twice as much as in case of methane pyrolysis.

The temperature decrease leads to substantial retardation of heterogeneous pyrolysis. Thus temperature decline in the reaction zone from 920°C to 720°C increases time which is necessary for doubling of mass of the sample in process of heterogeneous butane pyrolysis by an order of magnitude. Similar behavior takes place in the case of heterogeneous methane pyrolysis. So for methane it is need to keep the temperature in the reaction zone at the level of 1000°C. Using of the gas mixtures with addition of heavy hydrocarbons allows decreasing the temperature in the reactor without remarkable productivity slowdown.

As mentioned above at the exit of reactor we have gas mixture enriched by hydrogen. The hydrogen content in gas

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mixture at the exit of reactor depends on operating parameters such as temperature, time of interaction of initial gaseous hydrogen with porous carbon material and so on and can be varied by their change. The data presented in Figure 8 demonstrates such possibility. As a variable parameter the characteristic residence time of methane in reaction zone determined by methane volumetric rate was used.

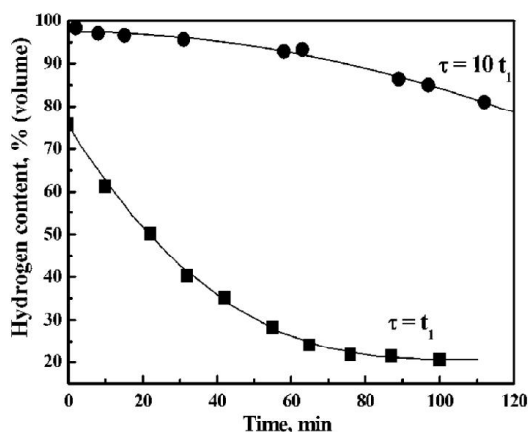


Figure 8 Hydrogen content in (H_2-CH_4) mixture at the reactor exit for different residence time ($t_1 = 1.5s$)

It is followed from data presented in Figure 8 that by selection of proper meaning of the residence time one can firstly to vary the composition of gas mixture at the reactor exit, secondly to hold constant composition during sufficiently long time, thirdly to receive practically complete decomposition of initial gaseous hydrocarbon.

CONCLUSION

As a result of the pyrolysis and the subsequent cracking of emanating volatile products over a char at the temperature $1000^\circ C$ it is possible to increase the conversion degree of initial raw materials and to receive about $1.4 m^3$ of gas with calorific value approximately $11.7 MJ/m^3$ from one kilogram of wood or peat pellets.

Experimental investigations have shown that wood and peat pellets can be used in the technology for integrated processing of raw hydrocarbon materials for obtaining strong composite carbon material and gas mixtures enriched by hydrogen.

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