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## Thermal Decomposition of Biomass and Glycerol in Vibro-Liquefied Bed in the Presence of the Catalysts of Deep Oxidation

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### Abstract

Features of the thermal decomposition (pyrolysis, steam reforming) of carbon-containing raw material in the vibro-liquefied bed of inert material and in the presence of the catalysts of deep oxidation were studied. It was shown that the presence of catalysts in wood pyrolysis ensures more complete transformation of condensable organic substances (resins) into light gaseous products (CO, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>). For a model oxygen-containing organic substrate (glycerol), it was shown that the conversion of glycerol during its steam reforming in pseudo-liquefied bed of the catalysts of deep oxidation follows several routes including gasification with the formation of CO, H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub>, polycondensation of the products of glycerol dehydration with the formation of coke, steam gasification of coke. Similar processes are realized during the combustion of biomass at the stage of pyrolysis and gasification in the boiling bed. It was shown that efficient catalysts in the steam reforming of glycerol exhibit high activity in the process of oxidation of glycerol and biomass. Investigation of the process of catalytic combustion of aqueous solutions of glycerol showed that the degree of oxidation reaches 99.3–99.9 % with the use of the catalysts of deep oxidation. Oxidation process runs with the highest efficiency in the presence of PK-12-73 catalyst.

**Key words:** catalyst of deep oxidation, combustion of solid fuel, pyrolysis, gasification, steam reforming, biomass, glycerol, vibro-liquefied bed, boiling bed

### INTRODUCTION

Combustion of solid fuel (coal, peat, biomass, shale *etc.*) is a complicated physicochemical process involving heating, pyrolysis and gasification of fuel particles, vapour reforming and oxidation of volatiles, combustion of the coke residue [1, 2]. During combustion in fluidized bed of the catalyst, volatile substances emitted in the pyrolysis of solid fuel do not inflame but interact with catalyst surface with the formation of the products of deep oxidation – CO<sub>2</sub> and H<sub>2</sub>O [3]. These volatiles include CO, hydrogen, methane, saturated and unsaturated hydrocarbons, as well as complicated organic compounds. In particular, in the case

of rapid pyrolysis of wood, along with solid products (coal residue) and combustible gaseous ones (CO, H<sub>2</sub>, CH<sub>4</sub>), liquid products (tar) are formed; they contain water and a complex mixture of hydrocarbons – the products of lignocellulose destruction (the fragments of lignin, lower aldehydes, ketones, acids, alcohols, phenols, furfural, glycerol) [4]. On the catalyst surface, depending on the nature of catalytic centres, hydrocarbons can interact not only with oxygen but also with water giving rise, for example, for methane, hydrogen and CO [5]. Thermal decomposition and oxidation of biomass in the presence of the catalysts of deep oxidation (DOC) in general is presented in Fig. 1.

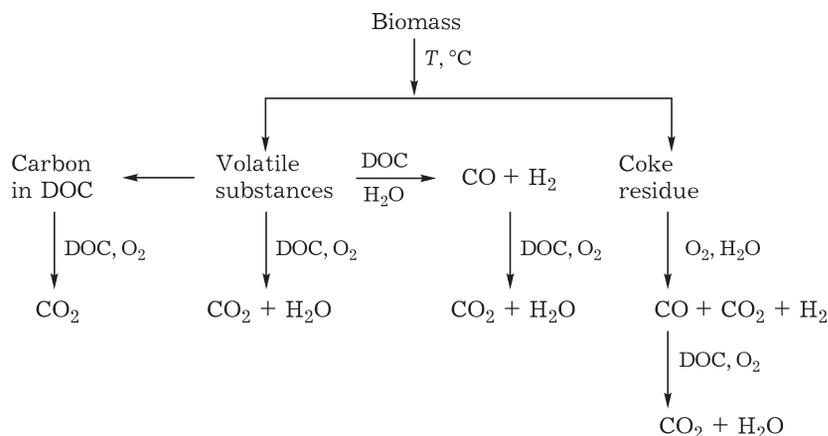


Fig. 1. Routes of thermal conversion of solid biomass in the presence of  $O_2$  and the catalysts of deep oxidation (DOC).

So, in order to understand the details of the combustion of solid fuel (biomass, black and brown coal, peat *etc.*), it is necessary to consider the listed processes separately using either definite conditions either model substrates. Pyrolysis of carbon-containing raw material is of the major stages of its combustion, so it is important to study the effect of DOC on the composition of pyrolysis products. Pine chips were used as the model raw material because wood lignocellulose under pyrolysis emits substantial amount of volatile components, therefore, the indirect influence of the catalysts on the composition of volatile products will be better noticeable. On the other hand, it seemed reasonable to study vapour reforming of oxygen-containing products of biomass pyrolysis in the presence of DOC. Glycerol was chosen as a model compound because it is distinguished by high oxygen content (comparable with cellulose) and has a tendency to form coke through dehydration and aromatization.

At the same time, glycerol is a side product of the production of biodiesel [6, 7] and contains substantial amounts of water and NaCl, which in fact transfers it into the range of industrial wastes. Contaminated glycerol is subjected to biological processing with the formation of target products [7] or is used as fuel [8]. However, the practical experience of flare combustion of watered wastes of glycerol shows that additional amount of fuel is necessary to stabilize the flare, especially if glycerol contains substantial amount of water [8].

The technology of catalytic combustion of fuel that was developed at the Institute of Catalysis (Novosibirsk) is based on a combination of four principles: 1) the use of DOC; 2) fuel combustion in pseudo-fluidized catalyst bed; 3) combustion of the mixtures of fuel and air in the ratio close to the stoichiometric one; 4) combination of heat evolution and heat removal in the same catalyst layer [5]. The presence of the catalyst in the reaction system causes a decrease in the temperature of organic fuel combustion from 1000–1200 to 500–700 °C; high combustion rates are conserved, and complete combustion of fuel-air mixtures is ensured [9, 10]. The application of this technology allows also efficient combustion of low-calorie solid wastes, including those with high humidity, without introducing additional fuel [11].

For the purpose of stage by stage investigation of solid fuel combustion processes, it is proposed in the present work to study pyrolysis and vapour reforming of wood and glycerol in pseudo-fluidized bed of the DOC for organic substances.

## EXPERIMENTAL

Investigation of thermal decomposition of biomass and glycerol in the presence of catalysts was carried out in a laboratory set-up (Fig. 2). The catalyst, 30 cm<sup>3</sup> in volume, was charged into the reactor with the inner diameter of 23 mm. Vibro-liquefied layer of dispersed filler (catalyst or sand) was created with the help of

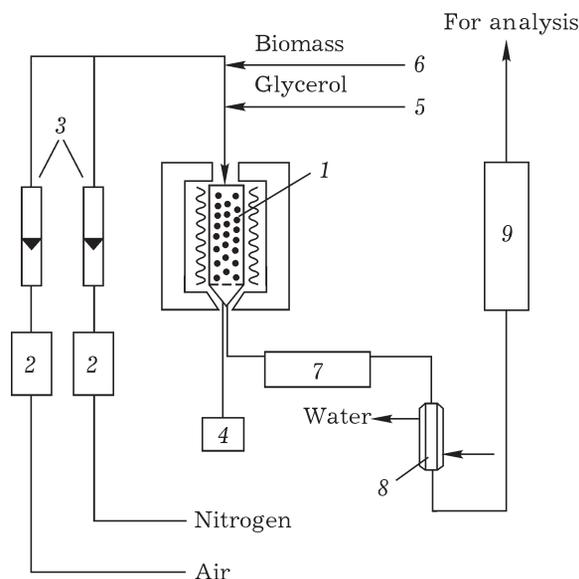


Fig. 2. Laboratory set-up with vibro-liquefied bed of particles: 1 – reactor, 2 – gas dosing units, 3 – gas flow meters, 4 – vibrator, 5 – glycerol input line, 6 – biomass input line, 7 – deposition chamber, 8 – condenser, 9 – drying column with adsorbent.

vibrator combined with the reactor. Vibration characteristics: amplitude 1 mm, frequency 50 Hz. The layer was heated to the working temperature (500–750 °C) with the help of external electric heater. When the necessary temperature was achieved, nitrogen flow rate equal to 4.1 L/h was adjusted. Glycerol flow rate was 16.5 g/h; the molar ratio of water to glycerol was varied from 0 to 4.

For experiments with biomass, pine chips with particle size <0.5 mm were used. The chips were dried preliminarily at 110 °C for 4 h and kept in a desiccator. Chip consumption rate was 3.4 g/h.

Analysis of the gas mixture at the reactor outlet was carried out using a LKhM80 chromatograph. Gases under analysis were H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO, CH<sub>4</sub>, and CO<sub>2</sub>.

Spherical catalysts were used in the work: IK-12-72 (MgCr<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>) and IK-12-73 (Mg<sub>0.5</sub>Cu<sub>0.5</sub>Cr<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>) manufactured at the Katalizator JSC (Novosibirsk). Catalysts CuO/Al<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>, NiO + NiCo<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> were prepared by impregnation with the aqueous solutions of corresponding nitrates according to the water capacity of the support, with subsequent drying at 50 °C for 4 h and baking at 700 °C for 2 h. The support was  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> manufactured by the Katalizator JSC, with the following characteristics: specific surface according to BET 200 m<sup>2</sup>/g, grain size 2–3 mm, packed density 0.75 g/cm<sup>3</sup>, total pore volume 0.57 cm<sup>3</sup>/g. The characteristics of catalysts are listed in Table 1.

The reference sample was bank sand with particle size 1–1.5 mm.

The amount of carbon in catalysts after thermal processing of glycerol was determined from mass loss after catalyst annealing at 800 °C for 2 h.

Catalytic combustion of biomass (pine chips) and glycerol was carried out in a vibroreactor. The amount of catalyst loaded into the reactor was 30 cm<sup>3</sup>, air flow rate was 90 L/h, biomass consumption was 3.4 g/h, glycerol consumption was 16.5 g/h.

The degree of oxidation of biomass or glycerol ( $\beta$ ) during catalytic combustion was determined from the changes of CO<sub>2</sub> concentration in exhaust gas according to equation  $\beta = [\text{CO}_2]_r / [\text{CO}]_0$  where  $[\text{CO}_2]_r$  is CO<sub>2</sub> concentration at the outlet of the reactor;  $[\text{CO}]_0$  is calculated value of CO concentration for complete oxidation of biomass or glycerol.

Specific surface was determined on the basis of the isotherms of low-temperature nitrogen adsorption obtained using an ASAP-2400 set-up (Micromeritics).

TABLE 1  
Characteristics of catalysts

Catalysts	Content of active component, %	Packed density, g/cm <sup>3</sup>	Specific surface according to BET, m <sup>2</sup> /g
CuO/Al <sub>2</sub> O <sub>3</sub>	15	0.99	175
Co <sub>3</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	20	1.10	151
NiO + NiCo <sub>2</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	20	1.10	147
Mg <sub>0.5</sub> Cu <sub>0.5</sub> Cr <sub>2</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	23	1.02	180
MgCr <sub>2</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	23	1.03	180

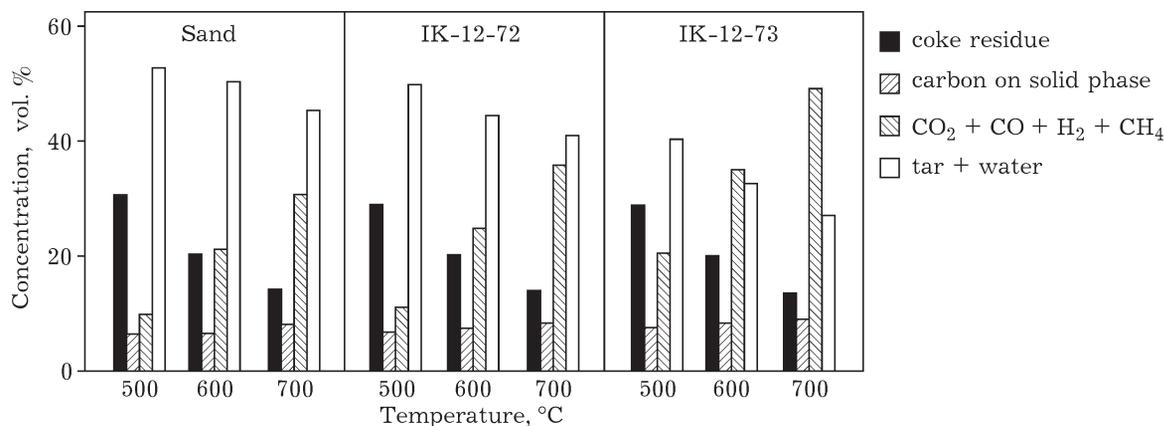


Fig. 3. Composition of the products of pyrolysis of pine chips in the vibro-liquefied bed of the catalysts of deep oxidation (IK-12-72 and IK-12-73) and inert material (sand) depending on temperature.

## RESULTS AND DISCUSSION

The composition of the products of thermal oxygen-free destruction of dry pine chips in vibro-liquefied bed of DOC (IK-12-72, IK-12-73) and inert material (bank sand) depending on temperature is shown in Fig. 3.

Both for the catalysts and for the inert material, the amount of the formed coke residue and condensed compounds (hydrocarbons and water) decreases with an increase in temperature, while the amount of CO<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>4</sub> increases. This temperature dependence is characteristic of lignocellulose pyrolysis: volatile components are adsorbed on the surface of sand and catalyst, and undergo further thermal decomposition with the formation of light incondensable gaseous compounds and solid carbon deposits. With an increase in temperature, thermal decomposition becomes more intense, which is indicated by an increase in the yield of CO<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>4</sub>. The amount of carbon deposits on the surface of sand or catalyst is weakly dependent on process temperature and the nature of the material (see Fig. 3). This may be connected with the fact that decomposition proceeds on the surface of catalyst or sand particles blocking the pores of the support, or carbon formed on catalyst surface may be wiped, so the amount of coke residue not connected with the catalyst increases. The observed phenomenon may be due to a combination of both processes.

The release of additional amounts of incondensable gases during wood pyrolysis in the presence of catalysts may be connected with

the catalytic decomposition of hydrocarbons of the condensate in the presence of water vapour. The effect of water vapour on the amount and composition of gases formed in thermal decomposition of hydrocarbons of the condensed phase in the presence of catalysts was determined for glycerol as example.

The data on the change of the composition of dry gases formed in thermal decomposition of glycerol and on the yield of incondensable gases depending on temperature in the layer of IK-12-73 catalyst are shown in Fig. 4. The maximal yield of incondensable gases is observed within temperature range 700–750 °C. With an increase in temperature from 600 to 750 °C the volume concentration of hydrogen remains practically unchanged, while the con-

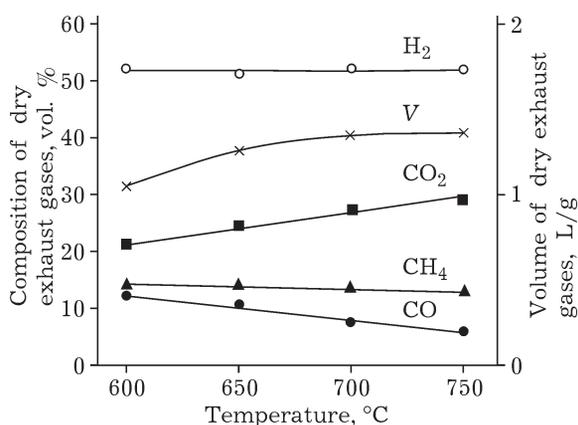


Fig. 4. Dependence of the composition of dry gases in thermal destruction of glycerol (molar ratio of glycerol to water 1 : 4) and the volume of formed gases (V) from 1 g of glycerol on process temperature in the presence of IK-12-73 catalyst.

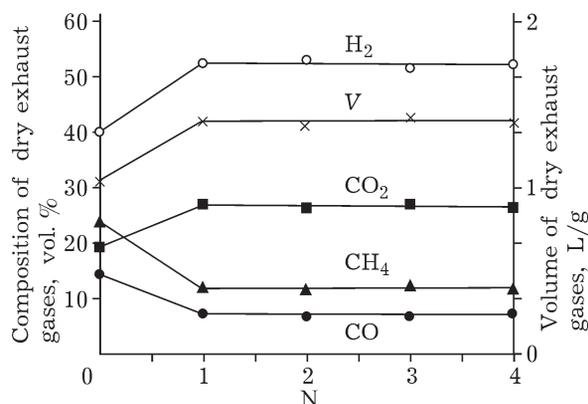


Fig. 5. Dependence of composition and volume ( $V$ ) of dry exhaust gases in the process of thermal destruction of 1 g of glycerol on water/glycerol molar ratio ( $N$ ) at process temperature 700 °C in the presence of IK-12-73 catalyst.

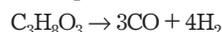
centration of  $\text{CO}_2$  increases gradually, and the concentrations of  $\text{CH}_4$  and  $\text{CO}$  decrease. This may be connected with an increase in the contribution from vapour reforming of  $\text{CH}_4$  and  $\text{CO}$ . It follows from the data on the material balance of carbon and the data on carbon content in the catalyst that thermal decomposition of glycerol proceeds with the formation of incondensable gases and carbon on the catalyst.

With an increase in the molar ratio water/glycerol from 0 to 1, the volume of incondensable gases formed in glycerol decomposition increases (Fig. 5). The concentrations of  $\text{CO}_2$  and  $\text{H}_2$  in these gases increase, while the concentrations of  $\text{CO}$  and  $\text{CH}_4$  decrease. Evidently, the addition of water promotes more complete vapour reforming of these products of glycerol thermal decomposition, such as  $\text{CO}$  and  $\text{CH}_4$ .

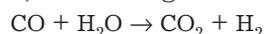
It is known that copper chromite exhibits high activity with respect to  $\text{CO}$  conversion with water vapour [5]. With a decrease in copper content of the catalyst, its activity with respect to  $\text{CO}$  conversion decreases [12].

According to the data reported in [13], the entire process of catalytic vapour reforming of glycerol at a temperature of 500–700 °C can be described with the following set of reactions:

1) vapour reforming of glycerol:



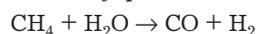
2) steam-to-gas shift reaction:



3) methanization:



In addition, the vapour conversion of methane may proceed at high temperature [14]:



The formation of methane at a temperature within 500–700 °C is observed for all the supported catalysts considered in literature [15–17]. Investigations showed that the most efficient  $\text{CO}$  reforming catalysts with the highest  $\text{CO}$  formation with the maximal conversion of glycerol and minimal formation of methane are catalysts based on  $\text{Rh}$  and  $\text{Ni}$  on  $\text{Al}_2\text{O}_3$  [17]. So, according to the data reported in [15–17], methane formation is exclusively of the catalytic nature, because hydrogenation of  $\text{CO}$  at a temperature within 500–700 °C in the gas phase is impossible. Nevertheless, the formation of substantial amounts of  $\text{CH}_4$  at 700 °C was detected in the experiment with vapour conversion of glycerol in the vibro-liquefied bed of inert material – sand (Table 2).

TABLE 2

Effect of catalyst composition on the yield of the products of thermal destruction of glycerol at 700 °C (catalyst volume 30 cm<sup>3</sup>, glycerol flow rate 16.5 g/h, molar ratio glycerol/water = 1 : 4)

Catalysts	Glycerol flow rate, g/h	Concentration, vol. %				$V_g^*$ , L/g of glycerol
		$\text{CO}_2$	$\text{H}_2$	$\text{CO}$	$\text{CH}_4$	
$\text{NiO} + \text{NiCo}_2\text{O}_4/\text{Al}_2\text{O}_3$	16.5	22.5	57.3	16.0	4.1	1.57
$\text{NiO} + \text{NiCo}_2\text{O}_4/\text{Al}_2\text{O}_3$	31.0	16.8	63.1	18.4	1.6	3.0
$\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$	16.5	21.6	57.0	15.1	6.3	1.54
$\text{CuO}/\text{Al}_2\text{O}_3$	16.5	21.7	53.1	15.9	9.3	1.29
IK-12-72	16.5	25.5	49.3	10.4	14.8	1.21
IK-12-73	16.5	26.9	52.6	7.6	12.9	1.36
Sand	16.5	17.2	48.8	25.1	8.9	0.91

\* Total volume of gaseous products formed from 1 g of glycerol (under normal conditions).



containing catalysts, essential processes are coking and CO conversion. On nickel-cobalt catalyst coking and CO conversion proceed to a smaller extent, and CH<sub>4</sub> content decreases substantially. Due to this fact, this process may be recommended for glycerol utilization through gasification by water vapour with the formation of H<sub>2</sub> and CO as major products. Investigation of catalytic combustion of a mixture of glycerol and water in vibro-liquefied bed of DOC used in the work showed that the degree of glycerol oxidation to CO<sub>2</sub> and H<sub>2</sub>O is 99.3–99.9 % for water/glycerol ratio being varied from 0 to 4 at a temperature of 700 °C. Taking into account the calorific efficiency which is equal to 4324 kcal/kg [20], aqueous solutions of glycerol waste with glycerol content up to 25 % may be burnt in the pseudo-liquefied catalyst bed in autothermal mode with heat utilization in the form of hot water or vapour.

## CONCLUSION

It was established in the investigation of vapour reforming of glycerol in pseudo-liquefied bed of the deep oxidation catalysts that glycerol conversion proceeds along several paths including gasification with the formation of CO, H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub>, polycondensation of the products of glycerol dehydration with the formation of coke vapour gasification of coke. Similar processes take place during the combustion of biomass at the stage of pyrolysis and gasification in the boiling bed. It is shown that efficient catalysts in the vapour reforming of glycerol exhibit high activity in the oxidation of glycerol and biomass. Investigation of catalytic combustion of aqueous solutions of glycerol showed that

the degree of oxidation reaches 99.3–99.9 % when various catalysts of the deep oxidation of organics are used. Oxidation process is most efficient in the presence of IK-12-73 catalyst.

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