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Carbon Dioxide Extraction from Biogas by Means of Sorption with the Help of the Inorganic Residue of Integrated Processing of Organo-Containing Wastes

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Abstract

Processes of carbon dioxide extraction from biogas by means of sorption using the inorganic residue from the integrated processing of organo-containing wastes (IPOW) as a sorbent were studied. Advantages of the IPOW process and sorption method are demonstrated, the kinetics of carbon dioxide adsorption on the inorganic residue from IPOW was investigated. It was established that the sorption on the inorganic residue is comparable in its capacities with adsorption on activated carbon. Approximate estimation of the volumes of adsorbers for IPOW set-up with the productivity of 500 t/y with respect to biogas was made. A complete scheme of the IPOW set-up including the unit of the sorption separation of biogas is presented.

Key words: integrated processing of organo-containing wastes, adsorption, biogas, inorganic residue, carbon dioxide

INTRODUCTION

Earlier [1–4] we offered technology of integrated processing of organo-containing wastes (IPOW) with production of fuel gas, hot water and the inorganic residue. Twenty two types of different organo-containing wastes of municipal services, treatment facilities (excess sludge, fresh sludge), agriculture, forestry, *etc.* are investigated *in vitro* and at the pilot plants according to the scheme of IPOW. The IPOW technology includes a number of consecutive and parallel stages: preparation of the waste products; methanogenic waste processing; two-step waste dehydration (the first stage is before methanogenic waste processing, and the second is after it); the thermal destruction of wastes in fluidized bed which can be carried out in two options (pyrolysis/oxidation thermal destruction, a two-step oxidation thermal destruction); cooling of thermal destruction gases to the temperature of 30–35 °C and condensation of water vapour with generation of hot water (80–90 °C); emission of pure carbon dioxide from biogas according to technology Pressure Swing Adsorption (PSA) technology [5], the implementation of technology of intensive plants cultivation in greenhouses provided for this purpose with hot water and carbon dioxide.

Thus, the products of IPOW include products of greenhouses, provided with heat of hot water and with carbon dioxide to implement technology of intensive cultivation; fuel gas; hot water; absorptive dry inorganic residue.

The inorganic residue is shown to have a well-developed inner surface (60 m^2/g). Inorganic residue of waste treatment facilities product of petrochemical enterprise has the following composition, mass %: SiO_2 32.5–43.0, CaO 11.4–18.0, Na_2O 2.0–2.8, K_2O 12.0–14.6, MgO 2.0–2.4, Fe_2O_3 18.0–25.6, Ni 0.0034, Zn 0.077, V 0.07, Mo 0.07, P 0.39. The presence of heavy metal compounds (mainly in the form of oxides) in the inorganic residue is apparently due to the corrosion of the equipment used in the process of production and to the sewage treat-

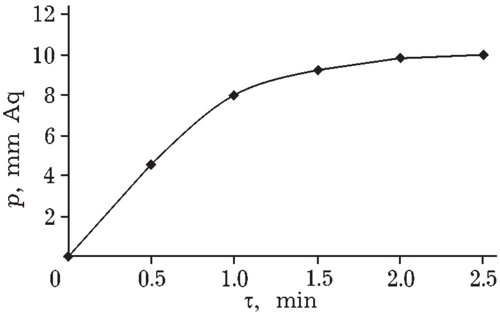

Fig. 1. Pressure change (vacuum) in the holder during adsorption at 35 °C.

ment technology. It should be noted that the bulk density of the inorganic residue, its sorption characteristics and the inner surface strongly depend on the method of its isolation. Thus, the sorption properties of the inorganic residue obtained in the fluidized bed reactor with IPOW at 500–550 °C, were much higher than those for the inorganic residue obtained by baking in a thin layer in a muffle furnace at 700–750 °C. The properties of inorganic residue of waste treatment facilities as a sorbent for the adsorption of carbon dioxide were studied as well.

As is shown in [1–3], methanogenic stage of IPOW has a positive effect during the stage of dehydration, pyrolysis and oxidative thermal decomposition. In particular, waste dewatering increases, pyrogas composition improves, its calorie increases, temperature of oxidative thermal decomposition reduces.

As is known biogas consists of 50 mass % of carbon dioxide, which cannot be significant in biogas as fuel. In this regard, it seems advisable to minimize its content in biogas. At the same time, pure carbon dioxide has a wide application in industry. There are various methods for removal of carbon dioxide from biogas [6].

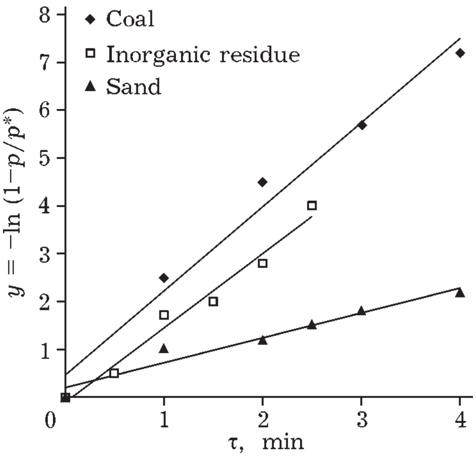

Fig. 2. Sorption time dependence of $-\ln(1 - p/p^*)$ value.

We investigated the sorption method of carbon dioxide removal from biogas using inorganic residue of IPOW as adsorbent. The method of evaluation of adsorption kinetics by the pressure drop in a sealed thermostatically controlled holder, the adsorbent is put there and gas to be absorbed is fed.

Before starting the experiment the system was thoroughly checked for leaks. Then the holder was blown out into the atmosphere with certain amount of carbon dioxide for a few seconds, and then the system disconnected from the atmosphere and the beginning of the experiment was fixed.

It is found that kinetic curve (Fig. 1) has an exponential form and is satisfactory described by the equation

$$p = p^*(1 - e^{-\mathrm{Ko}}) \qquad (1)$$

where p is the current pressure in the cartridge, p^* is ultimate pressure in the holder; Ko is adsorption contact criterion [7, 8], defined as

$$\mathrm{Ko} = \int K \frac{V_{\mathrm{ads}} p_0}{N_0}\, \mathrm{d}\tau \qquad (2)$$

where K is sorption constant; V_{ads} – adsorbent volume; p_0 is initial pressure; N_0 is the number of moles of the adsorbed substance.

Equation (1) can be linearized:

$$-\ln(1 - p/p^*) = \mathrm{Ko} \sim \tau \qquad (1a)$$

According to the linearized curve the kinetic parameters can be determined (Fig. 2). For comparison prepared charcoal Medisorb (Russia) and river sand were used as adsorbents.

Table 1 shows the kinetic parameters for the sorption of test materials.

The kinetic adsorption constants for inorganic residue of IPOW waste at temperature of 25, 35 and 45 °C are found. The experimental

TABLE 1

Data on the adsorption constant (K) and ultimate pressure (p^*) for the investigated adsorbents

Sorbents	T, °C	K	p^*
Activated charcoal	35	0.94	17.7
Sand	35	0.72	2.53
Inorganic residue	25	1.2	7.07
	35	1.52	12.5
	45	2.14	15.5

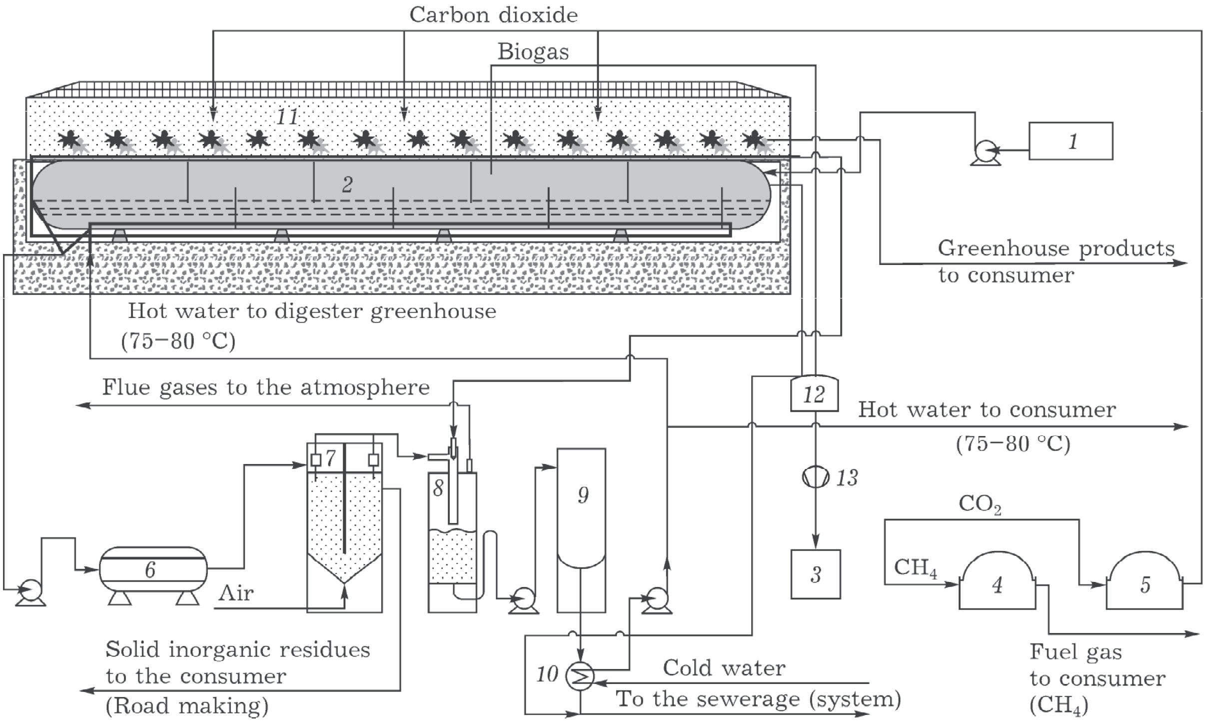

Fig. 3. Flow sheet of the pilot plant for complex processing of organic waste: *1* – waste pre treatment unit, *2* – digester, *3* – gas separation unit, *4* – CH_4 receiver, *5* – CO_2 receiver, *6* – screw filter press, *7* – thermal decomposition reactor, *8* – jet absorber, *9* – hot water storage, *10* – heat exchanger, *11* – greenhouse, *12* – gas tank for biogas, *13* – compressor.

studies carried out demonstrate comparability of sorption properties of the inorganic residue of IPOW and universally accepted adsorbent – activated carbon. We examined the hydrogen unit at Naftan OJSC (Novopolotsk, Belarus), where hydrogen is produced by steam reforming of methane and separated from the reaction mixture by the PSA method, and composition of the reaction gas mixture is close to that of biogas. During investigation of the blowing stage, we found that reaction gases during desorption evolve in strict order according to their molecular weight (from more light ones to carbon dioxide). This allowed us to offer a process flowsheet of IPOW with carbon dioxide evolving from biogas by adsorption method using inorganic residue of IPOW as a sorbent.

Figure 3 shows a process flowsheet of the IPOW experimental industrial plant (for more detailed description, see, for example, [4]) with a capacity of biogas 500 t/year, which involves two-step oxidation thermal destruction. Biogas released from the digester is sent to gas tank, and then with the help of compressor – to the gas separation unit (Fig. 4), where inorganic residue of IPOW is used as adsorbent.

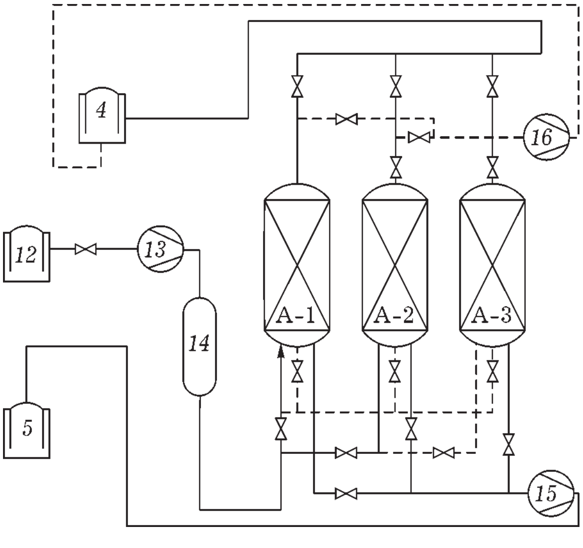

Fig. 4. Scheme of gas separation unit: *4* – methane receiver; *5* – carbonic acid receiver; *12* – biogas gasholder; *13*, *15*, *16* – compressors; *14* – moisture trap tank; A-1, A -2, A-3 – adsorbers.

PSA adsorption method is applied at a pressure of 10–20 atm for 10–16 min. This is followed by blow-off stage when the light part of biogas (mainly methane) is blown into the receiver of fuel gas, and carbon dioxide at the end of blow-off stage goes to carbon dioxide receiver. Prior to the next stage of biogas adsorption adsorber is blown by fuel gas. Then the cycle adsorption – blow-off – fuel gas blow is repeated; as resulting biogas is separated into clean fuel gas and carbon dioxide which are in different receivers. In the scheme of adsorption separation three adsorbers are used. When adsorption step takes place in one of them, blow-off and fuel gas blow take place in other two ones, respectively. Each gas from two receivers is used for its intended purpose. Such a scheme of the adsorption gas separation by PSA method is implemented in the industry in the production of pure hydrogen gas from contact gases of steam reforming of methane. According to the results of studying the sorption kinetics the size of adsorbers for IPOW plant with capacity of 500 t of biogas a year is estimated. The estimated volume of the adsorber for given capacity is about 5–10 m^3, but these data should be defined more precisely at the experimental industrial plant.

CONCLUSION

Thus, not biogas itself, but carbon dioxide and fuel gas may be the product of methanogenic stage of IPOW. The inorganic residue of IPOW can be used to separate the components of biogas.

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