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The agricultural Waste of Tatarstan Republic in Russia is Effective Biogas Potential.

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ABSTRACT

The article adduces a short observation of the existing situation in the production of methane from biomass, estimates industrial potential of processing of organic part of agricultural waste into biogas, fertilizers, electrical and thermal energy. In the article are shown perspectives of using biogas technologies in Russia and especially in Tatarstan Republic.

Keywords: Bioenergetics, methanogenesis, biogas, waste, agriculture, organic fertilizers, energy potential.

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INTRODUCTION

The shortage and dearness of the traditional power resources (the electric power and natural gas), which are necessary for the ability to live of mankind, create for use practically a perennial spring is conditions of a solar energy. Is perspective to use such solar energy, which is accumulated in a biomass of plants due to their photosynthetic activity. This energy is liberated at the destruction of biomass by microbes. But if at aerobic splitting the significant part of the reserved energy dissipates in an environment and is irrevocably lost, an anaerobic decomposition promotes its translation in ecologically pure energy carrier, i.e. biofuel or biopower.

It is necessary to add, that today an anaerobic process of organic substances of a biological origin the increasing attention in many countries owing to the interest in the renewable energy sources is paid.

Thus the important problem is solved: 1) reduction of volume agricultural and household large-tonnage waste, 2) manufacture of the energy carrier, i.e. biogas and 3) decrease in emissions in an atmosphere of the strongest hotbed gases of methane CH_4 and nitrogen monoxide N_2O . These gases render stronger influence on an atmosphere (23 and 296 times accordingly) in comparison with carbon dioxide CO_2 [1, 2].

The emissions of the greenhouse gases from the manure can be reduced by 25 % by means of biogas plants [3]. The reduction of emissions of greenhouse gases on 20 % by 2020 and increase in a share of renewable energy at 20 % corresponds to the purposes of the European Union [4].

THE MODERN POSITION IN BIOPOWER BRANCH

Raw material for biogas

The biological energy can develop in Tatarstan Republic only under condition of high economic utility of biological fuel technologies. Such plants can be useful at power deficiency of traditional carriers of energy in remote or sparsely populated regions.

The large manufacturers of energy do not require alternative sources, but the small agricultural enterprises can improve considerably the economic and ecological position. They can reduce a share of expenses on electric and thermal energy of production owing to transition to independent provision of energy from own sources, i.e. inexhaustible biological fuel.

The biomass shares on two parts. The first is a large organic material, all is direct or indirectly made by photosynthesis, i.e. kinds of substances of a vegetative both animal origin; the second it is the products of an ability to live of organisms and the organic waste, which are formed in processes of manufacture, consumption of production and at stages of a work cycle of waste. The primary and secondary biomass is raw material in the biological energetic. It or biological resources: a) the agricultural crops specially grown up for these purposes such as rape, corn, etc., b) the waste, containing organic agricultural substances

(vegetative and cattle-breeding) or c) the waste of a timber industry complex (the cabin of trees, the processing of wood and reception of a commodity output), waste food, textile and a pulp and paper industry, household waste and deposits of sewage.

The power cultures (corn, silphium, rape etc.) give in 2-3 times a greater output of biogas, than waste. However for reproduction of bio-resources (a primary biomass) as energy source the significant financial, power and working expenses, which increase the cost price of biogas manufacture on the average twice are required. Besides, the allocation of the areas under the crops in the overwhelming majority intended for reception of food agricultural production is necessary, therefore here it is complex to speak about ecological benefit from ecological fuel. The reproduction of the waste (a secondary biomass) has a tendency to steady growth.

We shall pay attention to agricultural both household waste and deposits of sewage also. So, on the clearing constructions of cities and large settlements the quantity of a deposit (the organic from technological process organic and mineral substances and a complex of the microorganisms allocated at upholding and biological sewage treatment) makes 0.5-1.0 % of the cleared sewage volume usually [5]. The quantity of household sewage in Russia has been grown from 1 977 up to 2 160 million meter³/year with 2005 on 2009 [6].

The transition of the animal industries to an the industrial basis and the concentration of animals, connected with this process to large-scale farms and complexes, have caused the sharp increase in quantity of manure and manure drains, which should be utilized not polluting an environment [7].

The prospect absence in the field of bio-energetic field as a whole, is connected with the no-purpose use of agricultural places, i.e. the biological raw material is used not as food, and as power.

Therefore by searches alternative powers it is not necessary to mention the manufacture of food stuffs and the basic attention to concentrate to a perspective biomass as an organic part of the waste.

Bioconversion processes

Anaerobic process is the controllable microbic splitting of liquid organic substances for the lack of oxygen with reception of methane (40-70%) and oxygen dioxide (30-60%). Methane is a collateral power product, which the microbes made in oxidation-reduction reactions. Usually the final electron acceptor is not oxygen but carbon [8]. Practically all classes of organic compounds of the industrial and agricultural waste can be converted in biological gas, and methane is the most valuable component in it.

M. Sobotka and co-authors [9] have offered for organic substance of cattle-breeding waste the empirically deduced integrated molecular formulas: (manure cattle) a) cow/except for cow they are $\text{CH}_{1.773}\text{O}_{0.830}\text{N}_{0.056}/\text{CH}_{1.820}\text{O}_{0.880}\text{N}_{0.042}$, b) manure pork they are $\text{CH}_{1.655}\text{O}_{0.767}\text{N}_{0.063}$, c) bird's dung they are $\text{CH}_{1.864}\text{O}_{0.909}\text{N}_{0.113}$.

The theoretical output of methane makes of three basic classes of bioorganic substances: 0.41 – 0.48 m³/kg for carbohydrates, 0.44 – 0.53 m³/kg for proteins and 1.0 m³/kg for lipids [1].

The quantity and parity of proteins, fats and carbohydrates are the most important parameters of quality of the waste applied to manufacture of biogas. A parity of these biopolymers in the structure of organic substance of the waste change and depends from a source in the following limits:

- The manure of the cattle consists from the 71-75% of carbohydrates, 22-26% of proteins and 3% lipids;
- The manure of pigs consists from the 70% of carbohydrates, 24% of proteins and 6% of lipids;
- The bird's dung consists from the 55% of carbohydrates, 41% of proteins and 3% of lipids [10];
- The municipal solid waste (MSW) consists from the 59-71% of carbohydrates (easily and difficultly processed), 12-15% of proteins and 1-2% of lipids [11];
- A sewage sludge consists from the 3-4% of carbohydrates, 27-28% of proteins and 35-36% of lipids [12].

The fluctuations of the listed above components in the structure of waste influence on the speed of process and the yield of biogas. The time of splitting varies from the infinitely large (degradation of lignin) until to several weeks (cellulose) and the some days (hemicelluloses, fats, proteins) and hours (the low molecular sugar, volatile fatty acids, alcohols). Therefore the wood biomass without preliminary preparation does not approach for manufacture of biogas because of the high maintenance lignin, which practically is not exposed to conversion in anaerobic conditions [13, 14].

The methane yield is directly proportional to a degree of destruction of organic substance. As a whole the process of bioconversion of natural biopolymers in low-molecular compounds can be presented as follows: the biomass + H₂O → CH₄ + CO₂ + H₂ + NH₃ + H₂S + the fermented organic. Hydrogen and hydrogen sulphide in the composition of biogas it can be formed up to 1 and 3% respectively.

This chain of biological processes is carried out consistently through a number of the trophic communications of the mixed microflora, such as Methanobacterium, Methanobrevibacter, Methanosphaera, Methanothermus etc. Owing to the such significant specific variety of the bioprocesses it is possible to use practically all kinds of liquid and solid organic waste for reception of biogas. The duration of all processes is limited by the most long first stage, i.e. the hydrolytic splitting of biopolymers under the action of exo-ferments, allocated in an environment by aerobic microorganisms. Anaerobic conditions are created owing to consumption of oxygen by acid-forming bacteria at the subsequent stages of fermentation. Water is necessary not only as the full participant of biochemical reactions, but also for reproduction of microorganisms and their distribution on a surface of firm substance.

However the number of bacteria in different groups should be balanced for the greatest methane generation speed. Microorganisms require both nitrogen, and in the carbon, assimilating in their cellular structure. Therefore one of the most important factors influencing methane fermentation and allocation of biogas, the parity of carbon and nitrogen in processed raw material is.

If the parity Carbon/Nitrogen (C/N) is excessively great, lack of nitrogen will serve as the limiting factor for methane genesis. If this parity is not enough, such plenty of ammonia is formed, that it becomes toxic for bacteria. The most optimum condition is when the parity of is C/N equal 10-30. A plenty of nitrogen contains in the majority of food waste, a juicy biomass of grassy plants, manure and bird's dung.

The surplus of carbon contains in wood waste, a paper, parts of weeds, straw, a potato and tomato tops of vegetable. For the achievement of optimum parity C/N and, accordingly, the high production of biogas mixing raw material as a manure from different kinds of animals, or a manure with vegetative waste often use. Thus there is an increase in an output of biogas at 5-11%. For each kind of a substratum or a mix of substrata it is necessary to settle an invoice parities of substances. The biggest output of biogas is given with waste in structure of which fats dominate. But thus for support methane generation in a reactor nutrients and microcells are dosed out. It is necessary to remember, that besides of the fat acids formed as by-products at decomposition of fats and oils, can interfere with all process of decomposition because of downturn pH to a mix.

The temperature is one of key factors of quality and quantity of gas produced by microorganisms. Microorganisms should live, first, secondly, to be made multiple copies, and thirdly, actively to function. At 5-15° C the microorganisms survive but do not function. At rise in temperature fermentation begins. Too the heat leads to destruction and destroy of microorganisms. Metabolic activity and reproductive ability of bacteria are in direct functional dependence on temperature. The best output of biogas with high enough maintenance of methane is reached, if the temperature in fermented organic chemistry is in a range 32-35° C (mesophilic mode), at lower and higher values of temperature (psychrophilic and thermophilic modes, accordingly) the maintenance of dioxide of carbon in total amount of allocated gases increases due to reduction of a share of methane, and quality of biogas falls.

For the consumer of biogas the greatest interest represent the mesophilic and thermophilic bacteria, fermenting organic substances at a greater output of gas.

The mesophilic fermentation is less sensitive to the changes of a temperature mode on some of degrees from an optimum range and demands a smaller expense of energy for the heating of an organic material in a bioreactor. Its minuses, in comparison with thermophilic fermentation, is in a smaller output of gas, greater term of full processing of an organic substratum (about 25 days), the organic material spread out as a result can contain nocuous flora since the low temperature in a bioreactor does not provide 100%-th destruction of pathogenic microorganisms and the loss germination seeds of weeds.

The opportunities of manufacture of biogas are now investigated also at low temperatures [15], that is actual for climatic conditions of an average strip of Russia and Tatarstan in particular.

Potential of biogas technologies in Tatarstan Republic

To estimate a resource of biogas technologies for manufacture of energy and biofertilizers from waste of animal industries, we have lead the analysis of the potential of a raw-material base on an example of Russia as a whole and its separate region Tatarstan Republic. For this purpose we used the official (statistical departments of the Ministries of natural resources and ecologies of the Russian Federation and the Ministry of ecology and natural resources Tatarstan Republic) and the help information on the manufacture and consumption of fuel, the electric power and fertilizers and formation of organic waste, and at insufficiency of the information (settlement data).

The output of excrement depends on a kind of animals and their age and gender structures, parities solid and liquid excretions, technologies of the maintenance of animals (covering, without covering) and manure removal systems (hydro-washout or in another way). We defined the annual accumulation of manure Q (total raw potential of region) under the equation (1):

$$Q = \sum Q_i = [\sum (N_i \cdot q_{mi} \cdot D_i)] / 1000 \quad (1),$$

Where Q_i is an output of manure for a year from i^{th} kind of animals, million tons; N_i is a livestock of animals of each kind, million head;

q_{mi} is the daily norm of an output of manure (dung) from one animal; kg/(head daily). It is established on the zoo-technical data and norms of formation of organic waste;

D_i is duration of accumulation of manure for a day. For birds and pigs D_i is equal 365 days, for the cattle D_i depend on time of the stall maintenance as at pasture the manure is irrevocably lost. In Tatarstan Republic for cattle basically the stall-pasturable system is applied, and the pasturable season in conditions of Tatarstan Republik lasts from the third decade of May up to the end of September - October, that is the duration of the stall period over 220 days. Therefore the total amount of the manure accumulation for a year can be calculated or on tabulated values of an output of the manure for different duration of the stall period, or to count quantity separately for stall and separately for the pasturable period, when summarize only 1/3 outputs of the animals excrement, or easier to subtract 30% because of the losses on pastures [5]. We have applied last way to the integrated estimation of an output of manure cattle, i.e. for cattle $D_i = 365 \cdot 0.7$; 1000 is the coefficient of translation of kg in ton.

The initial information for calculation of D_i , q_{mi} and q_{bi} is presented in Table 1 (here q_{mi} is the daily norm of an output of biogas from one animal, liter/(head·day). From all agricultural animals we considered only large horned livestock, pigs, birds and did not take in calculation of a facilities of the population as on literary data biogas plants become profitable at the size of herd not less than 20 conditional heads [16]. To translation of a

physical livestock of the animals in conditional heads of cattle apply following coefficients: cows, bulls, horses are 1.0, the others cattle are 0.6, pigs are 0.3, sheeps and goats are 0.1, birds are 0.02 [17]. Also the livestock of the adult birds, that is the hens, was considered only. Other birds and young growth (and it makes 2/3 from the general livestock of a birds) were excluded from calculations. So, the general livestock of all birds in Russia in 2012 in facilities of all categories was 495 million heads, we have taken only adult hens and cocks and only in the agricultural organizations is 113 million heads [18].

In Table 1 we result the data for 2011 and 2012 years to illustrate the fluctuations in a number of animals. At the further calculations we took data for 2011 for the correct comparison with the consumption of fuel and the electric power, because the last official statistical information is presented for this year.

Table 1. The initial data for calculation of the waste of animal industries

Animals	The livestock (N_i), one million goals ^[18]				Yield	
	Region, year				Manure (q_{mi}), kg/ head · day ^[21]	Biogas (q_{bi}), m ³ /t a fresh substratum
	Russia		Tatarstan			
	2011	2012	2011	2012		
Cattle	10.86	10.99	0.80	0.78	55	60
Pigs	12.10	14.24	0.53	0.57	4.5	65
Birds	113 ^[19]	114.8	3.04 ^[20]	2.81	0.25	130

Potential of an output of biogas P_b counted under the Eq. (2):

$$P_b = [\sum (Q_i \cdot q_{bi} \cdot E_{cal})] / 1000, \text{ million tons of equivalent fuel} \quad (2),$$

Where E_{cal} is a high-calorie equivalent for translation of the separate kinds of the fuel and energy in tons of the conditional fuel. Usually it is resulted in normative documents [22] or reference books. For biogas it is calculated by us and 0.672 (Table 2) is equal.

The Table 2 has been made for the simplification of mutual translation of units of measure of energy and reduction conformity of the energy units and gaseous and conditional fuel. The equivalent fuel (EF) is the concept, serving for the comparison of thermal value of various kinds of natural fuel. In Russia for unit of EF is accepted the heat ability (the lowest heat of combustion) 1 kg of coal, i.e. 7000 kcal [22].

An equivalent of the one cubic meter methane is 35.808 mega joules (i.e. $J \times 10^6$) [23] and the 1 m³ of the natural gas corresponds on the average 1.154 kg of EF [22]. The further calculations spent all at the rate of maintenances of methane: in natural gas is 95% (in the Russian gas makes quantity about of 92-98%), in biogas is 55% (the least output of methane in structure of biogas at processing manure). As in various references data on the fuel and its a heat abilities, including biogas, in different units and multiple by it sizes as J, gigaJ (GJ), kcal, gigacal (Gcal), kWh, megaWh, EF are resulted as cubic meter we, for simplification of comparison, result in Table 2 all these values.

Table 2: The factors of the translation of energy units and fuel

Unit	Equivalent						
	GJ	Gcal	kWh	kg of EF	m ³ of CH ₄	m ³ of natural gas	m ³ of biogas (55% of methane)
1 GJ = 10 ⁹ J	1	0.239	0.278·10 ³	34.144	27.926	29.568	50.775
1 Gcal = 10 ⁹ cal	4.187	1	1.163·10 ³	0.149·10 ³	0.117·10 ³	0.124·10 ³	0.322·10 ³
1 kWh	3.6·10 ⁻³	0.860·10 ⁻³	1	0.123	0.1005	0.1064	0.1827
kg of EF = 7000 kcal	29.308·10 ⁻³	7·10 ⁻³	8.136	1	0.818	0.867	1.487
1 m ³ of methane	35.808·10 ⁻³	8.553·10 ⁻³	9.947	1.222	1	1.05	1.818
1 m ³ of natural gas	33.82·10 ⁻³	8.078·10 ⁻³	9.395	1.154	0.95	1	1.727
1 m ³ of biogas (55% methane)	19.694·10 ⁻³	4.704·10 ⁻³	5.471	0.672	0.55	0.578	1

The potential of manufacture of electric power (P_e) at the use of biogas technologies was calculated under the Eq. (3):

$$P_e = P_b \cdot E_e \cdot 1000, \text{ million kWh} \quad (3),$$

Where E_e is a factor of translation of the equivalent fuel in the units of the electric power is kWh; E_e is equal 8.136 (Table 2).

The potential of manufacture of heat P_t at use of biogas technologies was calculated under the Eq. (4):

$$P_t = P_b \cdot E_t \cdot 1000, \text{ million GJ (Gcal)} \quad (4),$$

Where E_t is a factor of translation of the equivalent fuel in units of thermal energy (Gcal); E_t equal $29.288 \cdot 10^{-3}$ GJ; ($7 \cdot 10^{-3}$ Gcal) (Table 2).

The potential of manufacture of organic fertilizers P_y at use of biogas technologies counted under the Eq. (5):

$$P_y = Q \cdot 0.9, \text{ million ton} \quad (5),$$

Here 0.9 is an average share of an output of the effluent from total of the waste, usually laying in a range 0.79 [24] – 0.95 [25]. The results of calculations are presented in Table 3.

Thus, by the most approximate and meaningfully underestimated estimations (kinds of pets planted in Russia, not all livestock of cattle and a bird, not all the facilities having cattle were considered not all, and the charge of a laying on the maintenance of the cattle was not considered, increasing by 10-15% of the formed manure [5]). A resource only cattle-breeding waste can cover quantity on 70% need of an agriculture for gas supply (and in Tatarstan completely) and in electro-supply even to block in some times (Table 3).

Table 3: The cattle-breeding waste as a raw material for biogas technologies

Parameter	Russia	Tatarstan
Consumption of natural fuel; million ton EF	1043.1 ^[26]	14.08 ^[27]
Consumption of natural gas; million ton EF	543.7 ^[26]	13.68 ^[27]
Consumption of natural gas in an agriculture, million ton EF	11.16 ^[26]	0.26 ^[27]
Quantity of cattle-breeding waste, million ton (the formula 1)	182.8*	12.39*
Quantity of vegetative waste, million ton	126.527 ^[28]	5.075 ^[28]
Potential of manufacture of biogas from cattle-breeding waste, million ton (Eq. 2)	7.922*	0.516*
It is consumed the electric power in an agriculture in 2011, million kWh	15500 ^[26]	607 ^[20]
Potential of manufacture of the electric power, million kWh (Eq. 3)	64451*	4194*
Potential of manufacture of heat, million of GJ/Gcal (Eq. 4)	<u>23.18*</u> 55.45	<u>15.11*</u> 3.61
Consumption of organic fertilizers, million ton	52.6 ^[19]	3.9433 ^[20]
Potential of manufacture of fertilizers, million ton (Eq. 5)	164.52*	11.151*

*The calculated data (excepting household)

The technical potential of energy, the prisoner in a biomass of cattle-breeding waste, corresponds total as all at modern technical opportunities can be processed these waste in energy.

The calculated by us potential of energy corresponds to economic potential. The produced waste is economically justified to process in energy (at the existing prices for energy carriers, their transportation and consumption) on-line, at the cattle-breeding enterprises and integrated poultry farms where the enormous quantity of not demanded waste, first, is formed, and, secondly, which are the basic energy-compiled branches of an agricultural production (on them it is necessary up to 68 % from the general consumption of energy carriers by stationary objects in an agriculture of Russia [29]).

Consequently, large agricultural enterprises can focus on their own generation of electricity and heat, as the economic efficiency of biogas plants is especially high when processing large continuous flow of waste. According to REN21 [30] in 2013 the capital costs of energy production in biogas power plants (capacity of 1-20 MW) on average in the world are 500-6500 \$ / kW (at an conversion efficiency of anaerobic digestion of 25-40% and Capacity factor of 50 - 90 %) and operating costs - 6-19 cents / kWh. Small businesses are also lossless with adequate technical solution.

The other product of biogas plants is the re-fermentation mass, representing a mix of liquid and firm products of processing of bio-waste in methane-tanker, other words as effluent. An effluent it is possible to use in the further as ecologically pure organic fertilizers. It fit of all concerns to the vegetative and cattle-breeding waste. From them on an output from biogas plants the mass without a smell, bio-safe turns out; it is considered, that entering of the crude preliminary raw manure on fields in general should be forbidden, and to be brought mass should only after biogas plants. Moreover, in such the re-fermentation waste raise the maintenance of bio-effective nitrogen, which is not allocated in an atmosphere as from pure manure and remains in the form acquired by plants.

The twenty years' researches of the leading ecologo-soil Centers of Russia have shown that practical application of organic fertilizers on the basis of biogas technologies in a number of regions of the country considerably increases productivity of various agricultural crops, raises stability of plants to adverse influences of an environment [31]. Feature of the bio-fertilizers received anaerobic re-fermentation, by virtue of their high activity rather low norm of entering (up to 1 ton/hectares) against 20-40 ton/hectares of pure manure [5], and in Tatarstan even 60-80 ton/hectares is [32].

Apparently from Table 3, the potential of the manufacture of fertilizers at anaerobic re-fermentation cattle-breeding waste three times exceeds quantity of the organic fertilizers brought on fields, both in Russia, and in Tatarstan. The use of vegetative waste will even more increase this value. Certainly, for the manufacture of fertilizers the agricultural waste, which have been not polluted by extraneous impurity because otherwise at anaerobic digestion other organic waste, in particular MSW, there is an allocation or formation of toxic substances approach basically only, as well as at decomposition of waste on ranges.

Thus will be polluted also biogas and re-fermentation biomass. Hence, at entering re-fermentation biomass of waste as fertilizer, it is necessary to proceed not only from the fertilization values of the useful components. For the observance of the obligatory requirements to safety of the fertilizers for a life, health of the population, property, a condition of an environment it is required to consider the maintenance the effluent the dangerous substances, that there was no their above permitted standard accumulation in the ground and they did not get in the cultures, which are going on a forage by an animal and in a food.

This re-fermentation biomass it is possible to apply for the cultivation of the degraded, urbanized grounds of not agricultural purpose, dumps of the firm household waste, under the landings of the wood-bushes vegetation, in the nursery of wood and decorative cultures, in parks, floriculture, if it does not meet all requirements shown to "pure ground" agricultural fields and recreational territories. The use of the effluent will mean also the absence of the technological waste, leading to the pollution of objects of an environment.

CONCLUSIONS

Thus, the anaerobic processing of organic waste with the reception of biogas, energy and fertilizers relates to resources and energy saving technologies. Now the energy saving in Russia is based on the reduction of the consumption of primary power resources in a fuel and energy complex of the country on the transport, the reduction of the consumption electric and thermal energy in all spheres of a national economy and the liquidation of the losses of resources and energy. In the long term for the further reduction of the use of mineral energy sources and energy saving it is necessary, in addition to traditional, to apply the renewed energy source. The optimum parity of the traditional and alternative energy sources, on the basis of a biomass, will allow to improve considerably an ecological, economic and social situation in concrete regions.

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