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ENVIRONMENTAL FRIENDLY TECHNOLOGIES OF WASTES PROCESSING IN RAW MATERIALS FOR ENERGY PRODUCTION

EKOLOGICZNIE CZYSTE TECHNOLOGIE PRZETWARZANIA ODPADÓW W SUROWCE DLA PRODUKCJI ENERGII

A b s t r a c t

The acting model of biological waste utilizer with the complex using of solar energy and heat accumulation on the phase transitional materials is considered. The analysis of the elaboration of the thermal and chemical utilization of heavy oil residues in the mixture with oil shale's is conducted. This elaboration is connected with two problems: heavy oil residues utilization that as a rule is realized on the base of enough expensive technologies with using of the greatly hydrogen quantity for hydrogenation and special catalysts in enough hard conditions.

Keywords: biological waste utilization, heavy oil residues utilization, solar energy

S t r e s z c z e n i e

Przeanalizowano warunki pracy instalacji do utylizacji biologicznych odpadów, w której jako źródło ciepła wykorzystano energię słoneczną. W instalacji tej zastosowano akumulację ciepła w układzie wykorzystującym ciepło przemiany fazowej. Przeanalizowano również proces termicznej i chemicznej utylizacji ciężkich pozostałości naftowych w mieszaninie z łupkami palnymi. Zaproponowano modyfikację drogich technologii przerobu ciężkich pozostałości naftowych, które realizowane są dotychczas z zastosowaniem wysokich koncentracji wodoru niezbędnego dla procesu uwodornienia i odpowiednich katalizatorów dla warunków tego procesu.

Słowa kluczowe: utylizacja odpadów biologicznych, utylizacja ciężkich pozostałości naftowych, energia słoneczna

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1. Preface

Technical progress of XIX–XXI centuries was accompanied not only with various attributes of civilization – modern transport systems, today class of household units, information technologies we are using – to say: all we can't imagine the everyday human life but also the very serious problems of global ecological crisis. People had resolutely intervened to natural life looking for special preferences never thinking about the possible consequences.

The result of such an activity was followed with symptoms of global ecological crisis that are arousing a serious worry of scientific, technical and political community.

Among the main symptoms of the ecological crisis it's possible to mark the following:
– change of climate,
– exhaust of some non-renewable natural sources, particularly some types of natural fuels,
– pollution of the terrain by wastes and degradation of the terrain,
– acid rains,
and many other negative effects.

This is so indeed that just two branches of applied science were found the most adequate to solve ecological problems: chemical technology and chemical engineering. Let's examine certain examples of engineering decision for the problems named above that were elaborated in co-operation between Moscow State University of Environmental Engineering, Cracow University of Technology, Russian Academy of Sciences Institute of High Temperatures and its branch in Makhachkala, Institute of Fossil Fuels, Gubkin University of Oil and Gas and other. In realization of this work had participated a set of specialists in various spheres. Among them are: prof. S.I. Vainshtein, prof. E.E. Shpilrain, prof. A.M. Amadziev, dr. S.E. Gorlova and other.

2. Mobile unit for biological waste recovery with usage of solar energy and heat accumulator based on phase transition materials

This research effort is directly coordinate with problem of climate change as a result of possible change of greenhouse effect magnitude.

Greenhouse effect is the effect of bottom layer heating resulting the fact some gases (CO_2, water steam, ethane, nitric oxides, Freon) have the adsorption bands near wave length of heat emission from Earth surface (8–28 mcm). The magnitude of greenhouse effect is determined by radiative balance of short-wave irradiation intake to Earth and return of infrared irradiation. For Earth it's over 40°.

Of course the magnitude of greenhouse effect is influenced by hothouse gases content in atmosphere and first of all CO_2 that is the main participant of carbon circulation. Ecologists are segregating two types of carbon cycles – short, natural (CO_2 – glucose – organic materials – organic mass oxidation in food chains – CO_2) and long cycle that is seriously interconnected with man's activity (CO_2 – biomass – necrosis of organic refuse – accumulation in Earth strata with formation of fossil fuel – burning of fossil fuel – CO_2). The short cycle provides an approximate persistence of carbon dioxide content in atmosphere and had practically no influence to the change of greenhouse effect magnitude. Biomass participates the short cycle. Under burning the biomass (wood, for example) to get energy or under burning of new types of fuels produced from biomass including the organic wastes of man's activity (for example, biogas got by biochemical methods) there will not be any influence to the magnitude of greenhouse effect and climate change. The increase of carbon dioxide content in atmosphere following with the change of greenhouse effect magnitude is realized first of all cause of burning of fossil fuel that participates long carbon circulation.

It's necessary to take into account one more aspect. Biomass reproduction to get new types of fuel also needs energy. So in case technological processes of biomass reproduction need the large quantity of energy got by traditional methods under burning of fossil fuel the summary effect in decrease of damage to atmosphere may become equal to zero. The consumption of energy is permanently increasing and now is more than 10 billion tones of coal equivalent for all the planet annually. Tremendous and growing scales of energy production and consumption are providing by permanently growing quantity of non--renewable energy sources (oil, gas, coal, uranium) recovery but the reserve is limited.

So, it makes sense to solve several problems in power engineering:
- step-by-step replacement of non-renewable energy sources by the renewables (biomass energy, solar energy etc.),
- increase of industrial process energy efficiency with decrease of energy specific consumption,

usage of wastes as possible energy source.

Table 1

Composition and features of biogas

Features	Biogas components and its content				Biogas mixture:60 [%] CH_4 and 40 [%] CO_2
	CH_4	CO_2	H_2	H_2S	
Fraction by volume, [%]	55—80	20–45	<1,0	<3,0	100,0
Heat of combustion, [Ccal/m^3]	8000,0	-	2300,0	5000,0	6000,0
Inflammability limit (content in air), [%]	5—15	-	4—80	4—45	6—12
Ignition temperature, [°C]	650—750	-	585	-	650—750
Critical pressure	4,7	7,5	1,3	8,9	7,5—8,9
Critical temperature, [°C]	-82,5	31		100	-2,5
Standard density, [g/l]	0,72	1,98	0,09	1,54	1,2
Critical density, [g/l]	102	468	31	349	320
Density in relation to air	0,55	2,5	0,7	1,2	0,83

The research made is just close to the said situation. There was elaborated biological unit for recovery of agricultural and stock-raising industry wastes with usage of new scientific and technological decisions that permit:
- to conduct anaerobic fermentation of agricultural and stock-raising production with usage of phase transition materials and solar energy based heat accumulators (without application of other fuel-energy resources),

– to direct the process of anaerobic fermentation, temperature conditions and thermostatic process that permits to increase the quality and quantity of final biogas in a most effective way,
– to use the phase transition based heat accumulator (various eutectic compositions) that provides anaerobic fermentation under fixed temperature round-the-clock,
– to use the water heat accumulator that apply low-potential heat of heat-carrying agent (water in this case) cause of reprocessing of solar irradiation in solar collector that provides anaerobic fermentation under fixed temperatures round-the-clock.

The resulted biogas is a really competitive product. Some of it's features are shown in Table 1.

Table 2 represent the comparison of biogas with traditional types of fuels by energy characteristics.

Table 2

Comparison energy characteristic of biogas and traditional fuels

Source of energy	Quantity of fuel equivalent to 1[m^3] of biogas
Biogas	1 [m^3]
Electric power	2 [KW·h]
Kerosene	0,62 [l]
Coal	1,4 [kg]
Wood fuel	1,8 [kg]
Butane	0,43 [kg]
Manure briquettes	3,0 [kg]

The additional task that is solved by such the utilization units is the fact that in line with organic waste fermentation in methane-tanks there is presumed the cancellation of pesticides traditionally accompanying agricultural wastes as a result of reaction catalyzed under fermentation by feeding the vessels for mixing with the nets covered with titanium dioxide TiO_2.

To utilize the pesticides there is applied a combined two-stage technology:
– photo-catalytic decomposition of organic compounds at the cover of semiconductors under influence of intensive solar irradiation,
– anaerobic biological fermentation in methane-tanks of the prepared mix with agricultural wastes (manure, food and wine industry wastes).

Figure 1 shows the operative example of biological utilizing unit now placed at Institute of High Temperatures and MSUIE UNESCO chair polygon in Makhachkala.

The casing of methane-tank is made as double one. The space between the main case and outer jacket for thermo-stating of fermentation process under cold temperature is filled with heat accumulators (loaded by solar energy or biogas) based on phase transition materials – paraffin wastes of oil refineries with necessary additives to regulate the phase period temperature and to increase the cycling of heat accumulator loading and unloading processes. During the summertime it's presumed the application of solar water-heating units with solar collectors using various heat agents that invert solar irradiation into low-potential heat.

So, there was elaborated the effective system for maintenance of necessary temperature conditions to realize the reaction of thermophile methane fermentation in dependence of climate particularly by biogas (up to 20%) extracting during the fermentation process and/or solar water heater and or heat accumulator based on phase transition materials.

Fig. 1. Operative biological unit for utilization of organic wastes with usage of solar energy and heat accumulators based on phase transition materials

Rys. 1. Aparat do biologicznej utylizacji organicznych odpadów z wykorzystaniem energii słonecznej i akumulacji ciepła w układzie wykorzystującym ciepło przemiany fazowej

As the result of anaerobic stock-raising wastes fermentation process in methane-tanks there is produced the organic fertilizer applicable for application in agriculture.

3. Thermochemical reproduction of oil heavy residual stocks in mix with pyroshales

This research concerns two problems:

– utilization of oil heavy residual stocks that are traditionally realized on the base of comparatively expensive technologies with usage of significant amount of hydrogen for hydrogenation and special catalytic agents under serious conditions (pressure 60–250 atm, temperature 450–480°C),
– possibility to get the additional amount of motor fuel without new consumption of oil.

Application of the processes of deep catalytic reproduction of oil heavy residual stocks (masut, goudron) into white products is based on the usage of special catalytic agents operating in hydrogen mixture.

Such the processes are characterized with high flexibility and high quality of the result products. But it's necessary to mark among the other significant defects the necessity of high-scale investments, the necessity in hydrogen plant and limitation of condition for operation: pressure 6–25 MPa, temperature 450–480 °C, high amount of hydrogen using for operation.

At the same time it's possible to organize thermochemical reproduction of oil heavy residual stocks under presence of activator without entering of gaseous hydrogen under pressure 0,5–2,0 MPa and temperature 400–430°C.

It's suggested to use for activating the following natural sapropelic substances: pyroshales, sapropelites etc.) that content ≥ 7 mass% of hydrogen of organic mass. The pyroshales reserve, for example in Russia and CIS countries, is over 120 billion tones of oil equivalent.

Common thermochemical reproduction of oil residuals and sapropelites is possible because of their organic base is too similar by component and group content to heavy oils and natural bitumen.

As the result of conducted researches there was elaborated the technology of thermochemical reproduction of heavy oil residual stocks (goudron, pyrolytic resin, masut) in combination with shales and production of refined oil (boiling temperature up to 360 °C) and cracked residuals with the features of binding material in according with hygienic and ecological requirements to be used as materials for highway engineering.

There were determined the optimal technological conditions, optimal concentration of shales in mix with heavy oil residuals (10–13%), optimal temperatures for process and contact period.

It's interesting to mark the incidental result of the research: detection of the mechanics of autocatalytic effect of minimal shale content to the process of thermal cracking to say the process transforms into thermo-catalytic cracking. It's possible to say about the special type of autocatalytic effect. The presence of micro amount of molybdenum, nickel, cobalt and other hydrogenising metals (Mo – 13 ppm, Ni, Li, Co – 3 ppm) in mineral part of pyroshales in combination with macro amount of iron compounds (5,9–6,2 mass%) and aluminum silicates (39,2–53,6 mass%) is resulting in a specific catalytic influence to the process of thermal cracking of oil heavy residual stocks.

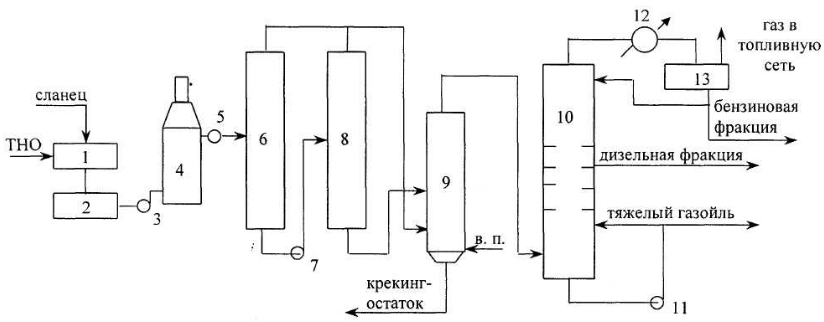

Fig. 2. Process flow sheet of unit for thermochemical reprocessing of heavy black oil in combination with piroshales:
1 – blender; 2 – homogenizer; 3, 11 – pumps; 4 – oven; 5, 7 – disintegrators; 6, 8 – reactors; 9 – separator; 10 – rectifier; 12 – condenser; 13 – reservoir-separator

Rys. 2. Schemat technologiczny instalacji dla procesu cieplno-chemicznej regeneracji ciężkich pozostałości naftowych z wykorzystaniem łupków palnych:
1 – mieszarka; 2 – homogenizator; 3, 11 – pompy; 4 – piec; 5, 7 – dezyntegratory; 6, 8 – reaktory; 9 – separator; 10 – kolumna rektyfikacyjna; 13 – zbiornik-separator

Basing the results of the research work conducted there was elaborated the principal technological scheme and technological operation conditions for thermochemical reproduction of oil heavy residual stocks in mixture with shales. The technological decisions are using for design of experimental industrial unit for masut reproduction with 50 tones annual capacity. Figure 2 represents the technological scheme of this process.

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