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METHODS OF CO_2 ACQUISITION AND COSTS REDUCTION IN SHALE ROCKS FRACTURING TECHNOLOGY

1. INTRODUCTION

The innovative method of shale gas recovery with the use of subcritical CO_2 is currently developed within the project titled "Development of guidelines for design of innovative technology of shale gas recovery with the use of liquid CO_2 on the base of numerical and experimental research –DIOX4SHELL", supported by the National Centre for Research and Development (NCBR). The project is carried out by Polish company PGNiG and by academics from WAT, AGH and PW (Military University of Technology, AGH University of Science and Technology, and Warsaw University of Technology). Finding the best business model, in which costs of CO_2 production or acquisition are negligible is one of the most important factors influencing the economical effectiveness of the technology. The main part of known CO_2 acquisition methods is based on fuel purchase and its combustion, what is very expensive process. It results with the high CO_2 price, when purchasing from producer, about 300 zl/ton. This price is quite high, considering current low prices of natural gas. In the paper basic aspects of CO_2 acquisition from CO_2 producers, exhaust gases treatment plants or plasma gasification methods will be presented.

2. SHALE GAS EXTRACTION METHODS BASICS

Shale is characterized by its dual porosity: it contains both primary (micro pores and meso pores) and secondary (macro pores and natural fractures) porosity systems.

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The primary porosity systems contains the vast majority of the gas-in-place, while the secondary porosity system provides the conduit for mass transfer to the wellbore. Primary porosity gas storage is dominated by adsorption. Primary porosity is relatively impermeable due to its small pore size. Mass transfer for each gas molecular species is dominated by diffusion that is driven by the concentration gradient. Flow through the secondary porosity system is dominated by Darcy flow that relates flow rate to permeability and pressure gradient [1].

When the pressure of natural fracture system in shale drops below the critical desorption pressure, methane starts to desorb from the primary porosity and is released into the secondary porosity system near the natural fractures is reduced. This reduction creates a concentration gradient that results in mass transfer by diffusion through the micro and meso porosity. Adsorbed gas continues to be released as the pressure is reduced [2].

On the base of research carried out in the coal – mining gases configurations through last twenty years it is commonly accepted that CO_2 is preferably adsorbed than methane in coal, and the amount of adsorbed CO_2 is greater than of adsorbed CH_4, and the ratio of the coal adsorptiveness for those gases is 2:1. Although it depends on many different factors, such as coal viscosity, pressure, temperature, humidity.

On the base of those mechanisms analyses a new innovative method of gas shale fracturing and gas recovery coupled with carbon dioxide storage was developed in Department of Mechanics and Applied Computer Science of Military University of Technology.

Fracturing has been widely used since the 1970s to increase production from formations with low permeability or wellbore damage. Unlike conventional hydraulic and acid fracturing techniques, CO_2-sand fracturing stimulates the flow of hydrocarbons without the risk of formation damage and without producing wastes for disposal. A mixture of sand proppants and liquid CO_2 is pumped downhole, where it creates and enlarges fractures. Then the CO_2 vaporizes, leaving only the sand to hold the fracture open – no liquids, gels, or chemicals are used that could create waste or damage the reservoir. Any reservoir that is water-sensitive or susceptible to damage from invading fluids.

Carbon dioxide (CO_2) is injected into the underground rock for a variety of purposes. It is often used for miscible flooding to enhance oil recovery in depleted petroleum reservoirs, and the use of CO_2 as a fracturing fluid for well stimulation has been considered because it eliminates formation damage and residual fracturing fluid [5]. Using CO_2 for fracturing and as a circulating fluid has also been proposed in hot dry rock geothermal energy extraction, because it reduces the circulating pumping power requirements and eliminates scaling in the surface piping due to the inability of CO_2 to dissolve mineral species [6].

For all of these purposes it is necessary to understand the behavior of CO_2 in rock. It is also important to know how injected CO_2 will infiltrate into the surrounding rock mass in CO_2 capture and storage projects [7].

In the projects mentioned above, CO_2 is usually injected into rocks at a depth of more than 1000 m. Temperature and pressure at that depth usually makes CO_2 a supercritical state, while the lower temperatures in special geological conditions create a liquid state. Viscosity of liquid CO_2 is one order lower than that of normal liquid water, while that of the supercritical state is much lower still. To clarify fracture behavior induced with injection of the low viscosity fluid, the scientists conducted hydraulic fracturing experiments using supercritical CO_2 (SC-CO_2) and liquid CO_2 (L-CO_2) using 17 cm cubic granite blocks. In the paper [8] the authors discussed the breakdown pressure and distribution of located acoustic emission (AE) sources of the experiments in comparison with those with water and viscous oil injections in the previous similar experiments [9]. They concluded that AE sources with the SC- and L-CO_2 injections tend to distribute in a larger area than those with water injection, and furthermore, SC-CO_2 tended to generate cracks extending more three dimensionally rather than along a flat plane than L-CO_2. It was also found that the breakdown pressures for SC- and L-CO_2 injections are expected to be considerably lower than for water.

Thus, under the same condition of in situ rock stress and flow rate, the breakdown pressure with CO_2 injection is expected to be considerably lower than with usual water injection due to its lower viscosity.

Concerns about global warming generated interest in reducing the emissions of the main greenhouse gas – carbon dioxide (CO_2). Large quantities of CO_2 are produced during the combustion of fossil fuels. Methods intended to reduce CO_2 emission include its storage in geological formations, e.g., saline aquifers and (depleted) gas reservoirs. One of the options is CO_2 injection into underground coal in combination with the production of CH_4 originally present in coal seams. Another idea is to inject flue gas, i.e. a mixture of N_2 and CO_2 [10]. In these cases N_2 acts as a stripping agent. This technology is known as flue gas-Enhanced Coalbed Methane (flue gas-ECBM) recovery [11].

3. METHOD OF SHALE GAS RECOVERY WITH THE USE OF CO_2 DESCRIPTION AND ADVANTAGES

The object of the invention (Polish patent acquired on 22nd on September 2015) offered by WAT is the method of extraction of gaseous hydrocarbons coupled with CO_2 storage; gas is extracted from horizontal small-diameter wellbores in a single vertical wellbore. The definition of a "method for extraction of gaseous hydrocarbons (shale gas) from horizontal small-diameter wellbores produced in a single vertical wellbore, coupled with CO_2 storage" will be understood as the process of gas hydrocarbon (shale gas) recovery by means of injection of compressed and cooled-down liquid CO_2 into the said horizontal wellbores, with resultant penetration of CO_2 into the rock and its phase transition under the influence of temperature inside the reservoir, intensive rock fracturing, as well as adsorption of CO_2 and simultaneous desorption of gaseous hydrocarbon (shale gas). The fracturing medium will take the energy required to produce the fracturing effect, directly from the rock mass. Hence, the fracturing process will partially proceed intrinsically, i.e. by means of natural forces, which will ensure cost reduction and natural environment protection.

In addition if CO_2 can be taken from the industry facilities (e.g. power plants) which emit it to the atmosphere and bear costs of limits (Kyoto protocol).

Development of a method for shale gas recovery has become feasible thanks to reduction in the costs of technologies of drilling horizontal wellbores and hydraulic fracturing.

The method of horizontal wellbore consists in pre-drilling of a wellbore vertical section followed by the change in the pathway from vertical to horizontal and further drilling into selected rock stratum once the preset depth is achieved [12].

Hydraulic fracturing consists in injection of a very high-pressure fluid into a selected section of the wellbore, the fluid containing the carrier (mainly water) and two types of additives: mechanical additives which fill up the slits (mainly proppant featuring applicable grain size and mechanical strength) and chemical additives (mainly in order to improve the viscosity). Pressurized liquid will produce slits in the rock structure whereas the sand will fill up and maintain the slits and produce new pathways of gas migration into the well. In average, 7.5 through 11.3 million of liters of fracturing liquid and 450 through 680 tons of proppant are injected into a single wellbore during the fracturing operation [12].

Underground extraction is another method of natural gas recovery from the reservoirs. Methane gas may be evacuated from underground mines, e.g. prior to and during coal mining [13].

Another method of natural gas recovery from the reservoirs goes together with open mining. Generally, methane is discharged into the atmosphere during the removal of rock strata cover; regrettably, no methods of emission control are used today in this case [13].

Rock permeability is the key element of evaluation of performance of methane recovery from coal beds. Usually, coal or gas-bearing shale rocks feature low permeability, mostly because of the fractures such as e.g. cleavage planes and junctions. There are two types of cleavage planes: back and front planes, located almost at the right angle to each other. In the main, front planes are continuous and ensure pathways featuring higher permeability whereas back planes are discrete and terminate in the front plane area [13].

Compared with the prior art, the option to use a single vertical wellbore only (the existing wellbores may be used, either) with horizontal wells for the purpose of the entire extraction process seems another beneficial feature of the new method. In relation to other methods, a large area of rock crushing inside the reservoir is produced and consequently, the economic productivity of a single wellbore will increase.

The method of shale gas displacement is very effective, the process of absorption and desorption occurring at the gas molecular level.

In volumetric units, gas-bearing rocks may adsorb twice more CO_2 than methane. This feature may be used to obtain a "clean energy" (produced in a closed loop), e.g. methane burning close to the reservoir, in order to manufacture e.g. electric energy, with subsequent re-pumping CO_2 produced in this process into the shale rock stratum. Hence, we can state that the new domestic solution of shale gas recovery from horizontal wellbores by means of liquid CO_2 in a single wellbore is beneficial both in terms of economy and protection of natural environment.

The new technology will considerably reduce CO_2 storage costs and emissions into the atmosphere as well as ensure the maximum performance of extraction of the shale gas from its reservoirs.

Fracturing efficiency depends on many parameters, such as e.g. rock composition; accordingly, the characteristics of our reservoirs are different from American resources given that Polish shales are not uniform. In our country, projects must account for dissimilar geological conditions which may pose prospecting and working problems. The statement made by the President of ExxonMobil pointed out the need to carry out additional laboratory studies and analyses of the reservoirs in order to set up better fracturing operations [14, 15].

Consequently, works on development of a national technology of extracting shale gas or other gaseous hydrocarbons from domestic reservoirs as well as of environment-friendly and cost-effective methods seem essential. More importantly, the technology should help extracting the gas from gas-bearing reservoirs in actual Polish geological conditions.

Summarizing, the technology will employ carbon dioxide as a fracturing fluid. This solution will allow avoiding the objections raised by the ecologists against the process of rock hydraulic fracturing. Additionally, storage of the greenhouse gas deep under the ground may reduce CO_2 emissions into the atmosphere and hence, help meeting the requirements set out by the European Union in connection with the phenomena connected with greenhouse effect.

4. CO_2 ACQUISITION METHODS

Carbon dioxide that can be used for shale rock fracturing and gas recovery may have natural or anthropologic origin. In summary, CO_2 can be acquired from the following processes:

- in thermal decomposition of $CaCO_3$ in CaO production,
- as a by-product in trisodium phosphate production,
- as a by-product in factories producing ammonia and hydrogen, where methane is transformed into CO_2,
- as a by-product in sugar fermentation process,
- directly from carbon dioxide natural resources, where it is produced as a result of acid water and limestone interaction.

There are no natural resources of CO_2 in Poland and carbon dioxide for fracturing purposes should be acquired from anthropological sources, it means that it has to be taken from the manufacturers that produce or emit this gas.

The methods of CO_2 acquisition mentioned above can be widen with technologies that use wastes to CO_2 production. Also technologies of CO_2 capture and storage from the out coming gases that are developed in existing power plants supplied with conventional fuel (e.g. coal, methane) should be mentioned. For example the biggest research center for carbon capture and storage (CCS) technology was built in Norway.

Carbon Capture is the process of capturing waste carbon dioxide (CO_2) from large point sources, such as fossil fuel power plants. The CC technologies can be divided into three groups:

- CO_2 and waste gases from power plants emission separation with the use of special absorber and separation system (amine absorption).
- CO_2 is captured from fuel before combustion in power plant. Gasified coal may be treated as such fuel and then be refined in the purpose of synthesis gas acquisition (H_2, CO/CO_2). CO_2 is captured from such a high-hydrogenous fuel before its combustion e.g. in gas turbine.
- Natural gas or coal is combusted in clean oxygen ("oxy-fuel"). It means that waste gases consist only of CO_2 and water steam, what allows to apply less complicated capture equipment. Although oxygen must be separated from air in highly energy absorbing separators.

Currently, CO_2 capture processes based on amine absorption are mature technologies and can be practically used in large scale installations. For example Norway government and StatoilHydro agreed to build the CO_2 installation based on amine sorption. The installation was designed to capture 100 000 ton CO_2 per year. The currently developed project covers the commercial facility capturing CO_2 from power plant and refinery building in Bergen city [16]. The scheme of the installation is presented in Figure 1.

Considering the amount of acquired CO_2 in comparison to traditional methods of its acquisition, the best methods are those, which uses amine absorption coupled with CO_2/CO separation from so called synthesis gas.

CO_2 acquired from this gas producers

The main producers of CO_2 in Poland are ACP Włocławek, Zakłady Azotowe Puławy, Air Products. On the base of the offer from ACP company from 2014 the price of liquid cooled down to –31°C temperature and in balanced pressure CO_2 is 300 zl/ton.

The production facilities which in example combust mine fuels and emit waste gases to atmosphere are CO_2 emitters. The nitrogenous fertilizers producers are the biggest emitters. Some of them, such as Zakłady Azotowe mentioned above, became CO_2 producers with the application of capture technologies.

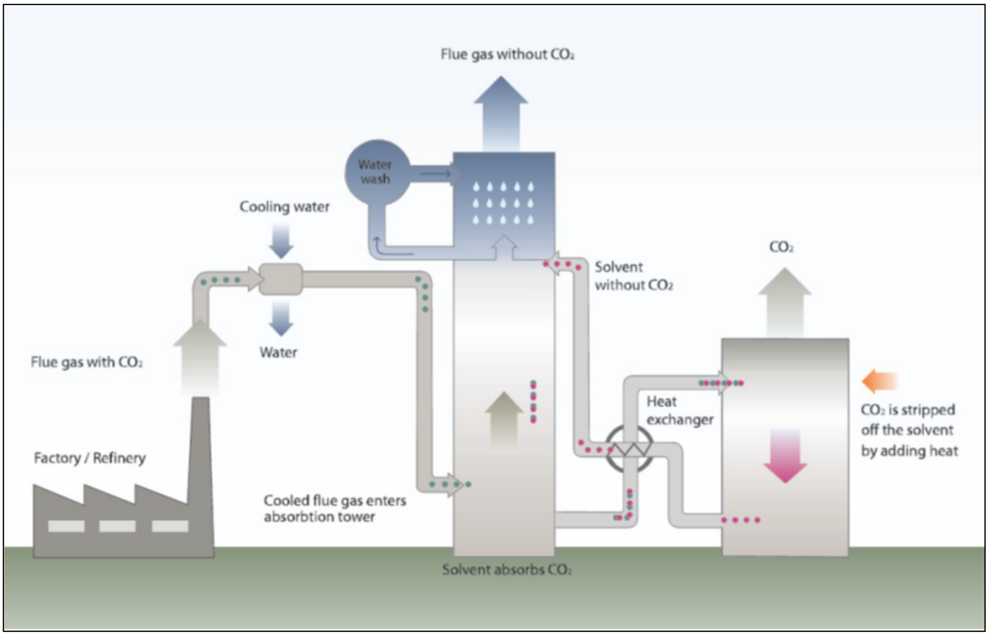

Fig. 1. Scheme of CO_2 capture installation developed in Norway [16]

CO_2 acquired from exhaust gases separation

In this area of CO_2 acquisition the innovative method developed by The Institute for Chemical Processing of Coal (ICHPW) in cooperation with TAURON group amine absorption demonstration utility is the most interesting idea. The installation was built in 2013 and tested in Łaziska power plant. It was developed within the project "Development of a technology for highly efficient zero-emission coal-fired power units integrated with CO_2 capture", which object was to demonstrate the post combustion process in pilot plant connected to coal-fired power plant. It was co-financed by National Research and Development Center.

The pilot amine-based CO_2 capture plant is able to capture 1 tone of CO_2 per day from real flue gases that contain different types of pollutants such as SO_x, NO_x and other particles. The plant consists of flue gas pre-treatment unit (with deep desulfurization) and CO_2 capture unit – consisting of absorber and desorber columns. The pilot plant operates 24 h per day, 5 days per week. The conducted research in this installation allows for extended evaluation of chosen solvents (MEA -monoethanolamine), and the capture process efficiency. Over 500 h, 81 tests and more than 20 t of separated CO_2 were achieved during the operation in 2013. The unique design of the installation allowed for the evaluation of various process modifications such as split stream and heat recuperation.

The scheme of the amine absorption installation was presented in Figure 2.

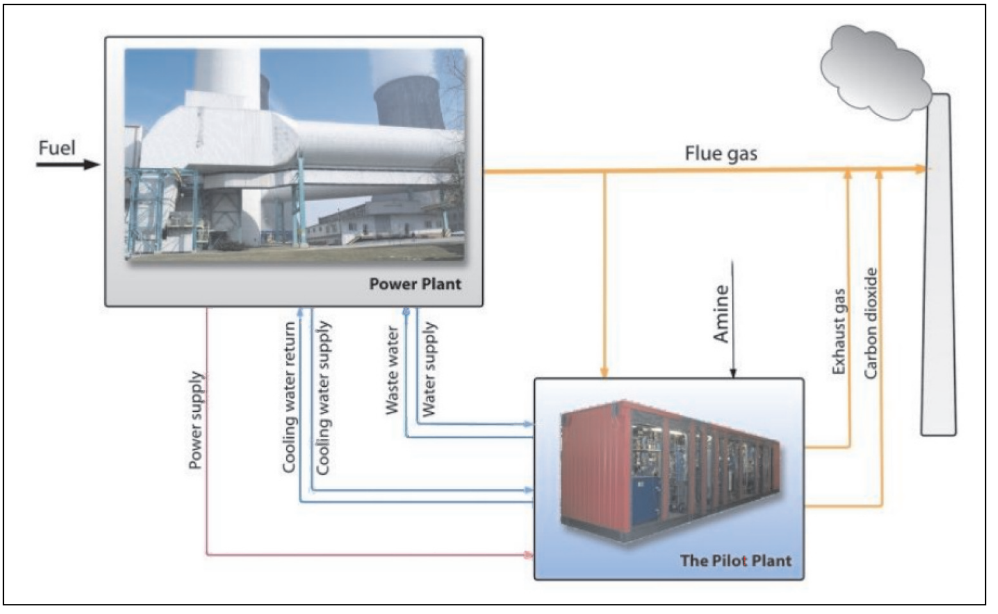

Fig. 2. The pilot plant connection diagram [17]

CO_2 captured in this installation can be successfully used in shale gas recovery process. It is said that it is twice cheaper than gas purchased from the producer. Coupling two Polish innovative technologies also is very interesting and good for Polish economy development.

Plasma gasification technology for CO_2 acquisition

However, "Waste to energy" (Fig. 3) installations which use plasma gasification technology seem to be the best model to acquire CO_2. Gasification is a process of organic and fossil compounds consisting of coal conversion into carbon oxide (37%), hydrogen (36%) and carbon dioxide (17%). The process is carried out by transformation those compounds in 700°C temperature, with no combustion, but withy controlled amount of oxygen and/or water steam presence in the special equipment called gasificator. The gas mixture, so called high energetic syngas, with large share of hydrogen is a result of gasification and can be used as a fuel.

Two methods applying gasification and plasma to waste transformation to syngas are known worldwide. First of them uses single device (some kind of gasificator equipped with plasma burners). Acquired syngas needs cleaning from solid particles with the use of special equipment.

Second method implements gasificator e.g. with fluidal bed and loaded with water steam mixed with oxygen, where organic material is gasified, and non-organic one is driven to further processing as dust. Acquired syngas is driven to the special device where plasma arc is generated and reacts with syngas and pollution particles in it. All pitchy substances and other substances are damaged and non-organic ones are vitrified. It is said that in this method plasma is used for destruction of dangerous substances.

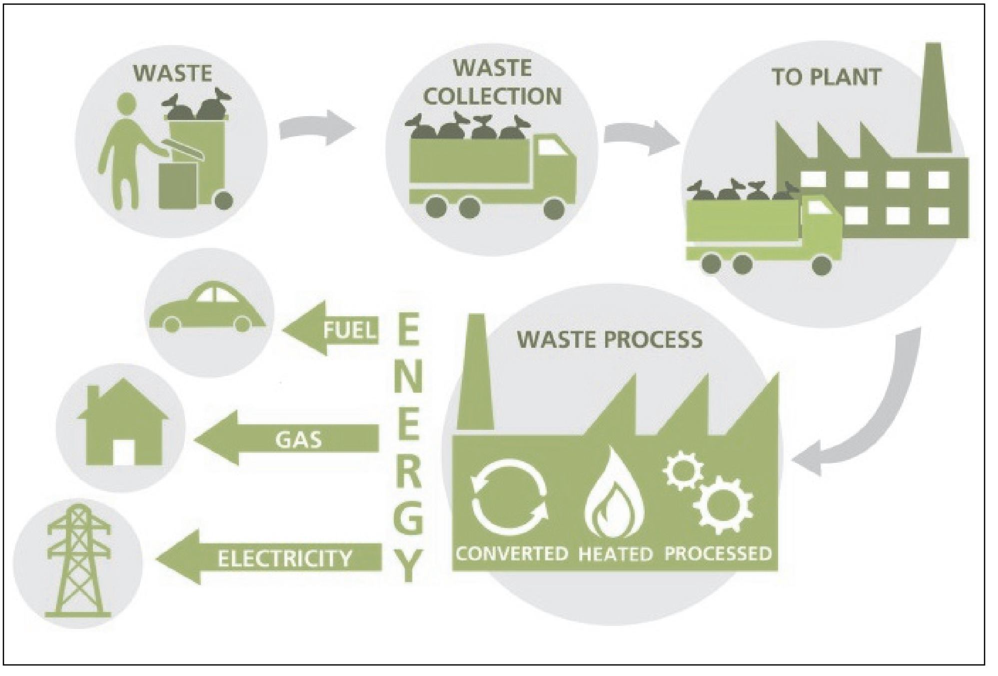

Fig. 3. "Waste to energy" process idea

As it was mentioned the "waste to energy" based on plasma gasification technology for CO_2 acquisition implementation is the best business model for shale gas recovery method. Such business model has a lot of advantages, such as:

– fuel for energy production is cost free, even more: waste utilization is paid special fees,
– two methods of CO_2 capture can be used – from produced syngas or after its combustion (waste gasification technology),
– "waste to energy" based on plasma gasification technology allows to get clean syngas,
– nitrogen content is lower than in e.g. natural gas.

Data for installation of 90 000 ton of Refuse Derived Fuel (RDF) productivity using waste gasification with separated gasificator and plasma device for syngas cleaning was presented in Table 1.

Acquired clean syngas consists of only H_2, CO, CO_2, CH_4, N_2. CO_2 can be captured with the use of special membranes e.g. after syngas combustion in internal combustion engine. As it was shown in Table 1, we can get 128 000 tone of CO_2, and cost of it consists only of purchase and usage of special capture equipment (membranes, compressors, tanks, water separators, filters for nitrogen).

Table 1

Data for installation of 90 000 ton of Refuse Derived Fuel (RDF) productivity using waste gasification with separated gasificator and plasma device for syngas cleaning

Input (MSW*/RDF) [kta]	Syngas amount [kg/h]	Amount of CO_2 before plasma device [kg/h]	Amount of CO before plasma device [kg/h]	Amount of CO_2 after syngas combustion [kg/h]	Year amount of CO_2 to capture when 8000 RDF [ton]
150/90	14 000	5 300	6 800	16 000	128 000

*MSW – Municipal Solid Waste

It must be also mentioned, that "waste to energy" based on plasma gasification technology is characterized with larger productivity in comparison to traditional methods, like waste incinerators with grill heart, and allows to utilize dangerous waste (solid, gaseous and liquid ones). It is caused especially by special plasma property – high temperature from 5000 to 10 000°C and very strong UV radiation. Those factors cause destruction of connections between particles. Organic substances are gasified and non-organic ones are vitrified to so called slag, which is like marble rock.

Waste utilization with the use of plasma technologies allows to get economically effective solution for waste economy problems in accordance to new rules for waste--yards and emission, together with natural resources protection.

Examples of wastes that can be processed with this technology are as follows:

- materials with asbestos content,
- solid organic contamination with polychlorinated biphenyl, contaminated soil,
- thermal treatment remains, also from Air Pollution Control systems,
- used linings from stoves producing aluminum, which contain cyanides and fluorides that with water gives poisoned gases,
- chemical and biological military agents,
- nuclear wastes (stabilization by virtification).

5. CONCLUSIONS

Different methods of CO_2 acquisition were presented in the paper. Large amount of CO_2 (comparable to amount of water used during hydraulic fracturing) will be used in shale gas recovery method, currently developed in Military University, for rock fracturing and methane gaining. The price of CO_2 is one of the most important factors influencing economical effectiveness of the method.

Summarizing, acquiring cheap (almost costless) carbon dioxide from “waste to energy: installations is the best solution for gaining the highest economical effectiveness of shale gas recovery.

Till now, there is no such installation in Poland. But as it is known Polish company ORLEN finalizes specification document for the plasma plant, which is planned to be built in Płock. The productivity of this installation will be 150 tone of wastes per year coupled with syngas production.

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