



Full Length Article

Thermodynamic assessment of the novel concept of the energy storage system using compressed carbon dioxide, methanation and hydrogen generator

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ABSTRACT

The main aim of this paper is to characterize the concept of a novel energy storage system, based on compressed CO₂ storage installation, that uses an infrastructure of depleted coal mines to provide required volume of tanks, and, additionally, hydrogen generators, and a methanation installation to generate synthetic natural gas that can be used within the system or taken out of it, e.g., to a gas grid. A detailed mathematical model of the proposed solution was built using own codes and Aspen Plus software. Thermodynamic evaluation, aiming at determining parameters, composition and streams in all the most important nodes of the system for the nominal point and when changing a defined decision variable δ (in the range from 0.1 to 0.9) was made. The evaluation was made based on the storage efficiency, volume of the tanks and flows of energy within the system. The storage efficiency in the nominal point reached 45.08%, but was changing in the range from 35.06% (for $\delta = 0.1$) to 63.93% (for $\delta = 0.9$). For the nominal value of δ , equal to 0.5, volume of the low-pressure tank (LPT) was equal to 132,869 m³, while of the high pressure tank (HPT) to 1219 m³. When changing δ these volumes were changing from 101,900 m³ to 190,878 m³ (for LPT), and from 935 to 1751 m³ (for HPT), respectively. Detailed results are presented in the paper and indicate high storage potential of the proposed solution in regions with underground mine infrastructure.

1. Introduction

Increasing share of renewable energy sources (RES) in energy generation entails additional challenges to existing electricity distribution networks [1]. This is mainly due to the stochastic nature of wind and solar energy, which is characterized by the production depending on the current weather conditions, which causes problems with power quality, voltage stability, reliability [2], etc., requiring additional flexibility from the power system [3]. One of the possibilities of stabilizing the work of energy systems is the use of energy storage that allows the storage of surplus amounts of energy at the time of its overproduction and transfer of stored energy to the network during its high demand [4]. However, this requires the use of large scale electricity storage solutions [5]. Apart from helping to balance the grids, they allow improving energy efficiency and increasing energy security. Thus, energy storage has

a key role to play in the transition towards a carbon-neutral economy.

There are many types of energy storage technologies, including mechanical, electrochemical, chemical, thermal and electrical energy storage methods [6]. The technologies designed for large-scale systems are dominated by solutions using chemical and mechanical methods [7]. One of the representatives of the group of mechanical methods is a compressed air energy storage (CAES) technology, which is currently being developed by many entities around the world [8]. Among the systems using chemical methods, a technology in which electricity undergoes an indirect conversion into chemical energy of hydrogen in the electrolysis process can be distinguished (the so-called Power to Gas (PtG) technology). It allows the transformation of electricity (primarily based on the energy coming from RES) into the chemical energy of gaseous fuel [9]. Recovering the electricity requires the use of fuel cells [10] or heat engines [11] driving electricity generators. A classical PtG can be converted to a system where synthetic natural gas (SNG) is

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Nomenclature	
CB	circulating blower
CCH	combustion chamber
CO2-C1	single-stage CO ₂ compressor
CO2-C2	multi-stage CO ₂ compressor
CO2-C3	CO ₂ compressor of MSs
CO ₂ -C4	CO ₂ compressor of SNGOCs
CO2-CL	CO ₂ cooler
CO2-Ex1	CO ₂ expander of compression unit
CO2-Ex2	CO ₂ expander of methanation unit
E	energy, kWh (MWh)
E1	electric engine of CO2-C1
E2	electric engine of CO2-C2
E3	electric engine of CO2-C3
E4	electric engine of SNG-C
E5	electric engine of CO2-C4
FG/WS	flue gases/water separator
FGC	flue gases cooler
FGDC	flue gases deep-cooling cooler
FG-Ex	flue gases expander
G1	electricity generator of CO2-Ex1
G2	electricity generator of CO2-Ex2
G4	electricity generator of FG-Ex
H ₂ O-T	H ₂ O tank
H ₂ -T	hydrogen tank
HG	hydrogen generator
HPT	high-pressure tank
LPT	low-pressure tank
m	mass, kg
MU	methanation unit
MUC	methanation coolers
O ₂ -T	oxygen tank
P1	water pump of hydrogen generator
P2	water pump of SNG/water separator
P3	water pump of flue gases/water separator
SNG/WS	SNG/water separator
SNG-C	SNG compressor
SNGDC	SNG deep-cooling cooler
SNG-T	SNG tank
TES-CU	thermal energy storage system of compression unit
TES-MU	thermal energy storage system of methanation unit
WTI	water treatment installation
η	efficiency

produced (PtSNG) by the use of an additional methanation process to convert hydrogen with the use of carbon dioxide into synthetic natural gas or other useful products (e.g. for chemical industry) [12]. Various sources of carbon dioxide can be used here, mostly including CO₂ separated from flue/process gas resulting from combustion of fossil fuels and biomass [13,14]. The main advantage of SNG over hydrogen as a fuel is its easier storage, transport and use for energy generation purposes.

Another option, being the basis of the system proposed in this paper, is energy storage in compressed carbon dioxide. Energy storage in this type of technology is carried out in a similar way as it is in the case of classic compressed air energy storage systems. For these solutions, atmospheric air is used as the energy carrier, which is compressed at the charging stage by a compressor driven by an electric motor. The compressed air is collected in a pressure tank and then, during the system discharge stage, the high-pressure gas is heated and expanded in the expander driving the electricity generator [15].

The big advantage of energy storage in compressed air is that such systems use commonly available gas as the energy carrier, of which natural reservoir is the Earth's atmosphere. The main disadvantage of the solution is low density of the energy carrier after compression, even under very high pressures, which for applications directed at high storage capacities requires the use of very large, high-pressure tanks. Another drawback is that the process of compressing air to high pressures is accompanied by a high temperature rise, which requires the use of machines with interstage cooling. Currently, the main problem for the popularization of energy storage systems in compressed air, in many regions of the world, is the lack of potential for organization of large-size tanks enabling storage of air at high pressures.

Instead of air, carbon dioxide can be used as energy carrier. Energy storage systems using CO₂ in gaseous (subcritical or supercritical) and liquid states have been analyzed in the literature. In [16] a hybrid thermal-compressed supercritical carbon dioxide energy storage system is proposed, combined with a stratified water thermal energy storage (TES), to store both released heat of compression and high-frequency reluctant power of a wind farm using electrical heaters. In [17] the authors propose to use liquid carbon dioxide energy storage system which allows to limit the dependence of the system on large caverns (thus, to overcome the drawbacks of traditional CAES technology). In [18] a solar-assisted liquid CO₂ energy storage system (LCES) based on

Rankine cycle is proposed. In each case, the systems assume the use of two storage tanks, i.e., a high-pressure tank and a low-pressure tank, which is required due to the need to close the process loop of the energy carrier that is used.

In the storage solutions considered in the literature heat (and cold) accumulators are used. The main disadvantage of such solutions is relatively small energy capacity of the storage systems in relation to the required volume of pressure tanks. One of the solutions that allows to increase storage capacity without the need to adapt pressure tanks with correspondingly larger volumes is hybridization focused on the integration of storage in compressed gases with energy storage systems, using the electrolysis and methanation processes. An example of such a hybrid system, presented in the literature, is a solution integrating the energy storage in compressed air and the energy storage system in hydrogen subjected to additional conversion to synthetic natural gas [19].

This paper aims to characterize and make the assessment of a concept of the novel hybrid energy storage system based on the use of the compressed CO₂ storage installation and the volume of underground storage spaces in the form of mining shafts. The main novelty of this paper lies in the detailed thermodynamic analysis of the proposed concept of the energy storage system that allows not only to store surplus energy in the energy demand valleys but also to utilize additional amount of carbon dioxide, coming, e.g., from the industry. The system is using post-mining infrastructure, thus, may be applied for reclamation of post-mining areas. The energy storage system may also be integrated into industrial clusters and utilize CO₂ that is produced in the industry to generate electricity, heat or fuels.

2. Methodology

2.1. Description of the proposed energy storage system

Fig. 1 presents the structure of the proposed energy storage system. It consists of two sealed pressure tanks for carbon dioxide storage, a high-pressure tank (HPT) and a large-volume low-pressure tank (LPT), which is a post-mining excavation. In both tanks, carbon dioxide is stored in the gas state. The systems includes also a hydrogen generator powered with electricity from the grid, a methanation unit, two thermal energy storage tanks, a water treatment installation, carbon dioxide and flue gas

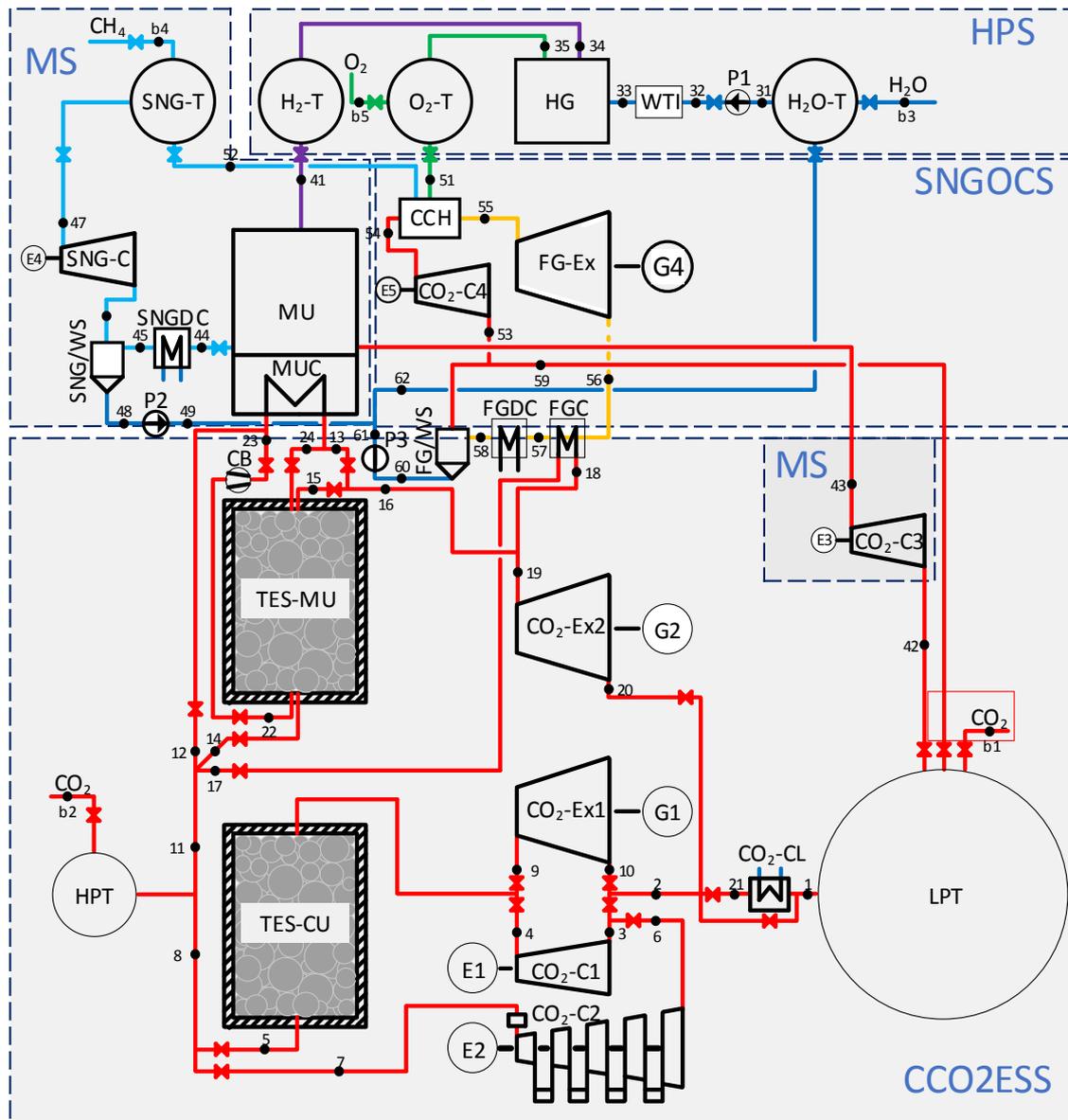


Fig. 1. Schematic diagram of the proposed energy storage system, consisting of four main installations: Compressed CO₂ Energy Storage Subsystem (CCO₂ESS), Methanation Subsystem (MS), Hydrogen Production Subsystem (HPS) and SNG-Oxy combustion Subsystem (SNGOCS).

expanders, carbon dioxide and SNG compressors, a combustion chamber, phase separators, heat exchangers, pumps and hydrogen, oxygen, SNG and water tanks. The concept of the system was submitted to the patent application [20].

In the system's operation cycle, three stages can be distinguished: (i) charging stage, (ii) storage stage and (iii) discharging stage.

2.1.1. Operation of the system during charging phase

During the charging phase, carbon dioxide that is accumulated in the low-pressure tank (LPT), flows through a bypass of the expanded carbon dioxide cooler (CO₂-CL) to two carbon dioxide compressors, i.e., the first – basic single-stage carbon dioxide compressor (CO₂-C1) and the second – multi-stage carbon dioxide (CO₂-C2) compressor. The compressors are driven by electric motors using electricity drawn from the electricity distribution network. After compression in a single-stage compressor (CO₂-C1) CO₂ is directed to the thermally insulated heat accumulator of the compression system (TES-CU), in which the gas is cooled by transferring heat to the material of the accumulator. In the case of a multi-stage carbon dioxide (CO₂-C2) compressor, the

compressed carbon dioxide is cooled in the coolers built-in between the compressor stages and at the compressor outlet, resulting in lower value of the unit work, than in the case of a single-stage compressor. After cooling, compressed carbon dioxide streams are introduced into the high-pressure tank (HPT) and stored there until beginning of the discharging stage. At the charging stage, in addition to carbon dioxide compressors, a hydrogen generator (HG) operates in the system, in which hydrogen and oxygen are obtained through the water electrolysis. The hydrogen generator is powered by electricity drawn from the power system. It is supplied with water prepared (cleaned) in the water treatment plant installation (WTI), previously taken from the water tank (H₂O-T). The products of the electrolysis process are collected in two tanks, whereby hydrogen is stored in a hydrogen tank (H₂-T), from which, in the full cycle of the energy storage system, it is supplied into the methanation process taking place in a methanation reactor (MU), while oxygen is stored in the oxygen tank (O₂-T). In addition to hydrogen, the methanation reactor is supplied with CO₂, which is taken from the low-pressure carbon dioxide tank (LPC) and is compressed to the required pressure by the carbon dioxide compressor (CO₂-C3). Due

to the fact that methanation is an exothermic process, the methanation reactor is cooled. Heat from this process is extracted through the methanation system's heat exchanger (MUC) by carbon dioxide heating, which, apart from the discharging stage of the energy storage system, circulates in a loop between the heat exchanger and the methanation system's heat accumulator (TES-MU), heating the accumulator storage material. The methane obtained in the methanation reactor is compressed in a methane compressor (SNG-C) and then stored in a SNG tank (SNG-T).

2.1.2. Operation of the system during discharging phase

At the phase of discharging the energy storage system, the basic single-stage and multi-stage carbon dioxide compressor and the hydrogen generator are not working. At this stage, the compressed carbon dioxide leaves the high-pressure tank (HPC), wherein the stream is divided into four streams. The respective streams' flows are determined by the available amount of heat in respective subsystems which can be used for heating CO₂ stream before its expansion. One of the CO₂ streams is directed to the heat accumulator of the compression system (TES-CU), where it absorbs heat from the accumulation material and goes to the carbon dioxide expander of the compression system (CO₂-EX1), in which it performs work. The second stream of carbon dioxide is directed to the diaphragm exhaust gas cooler (FGC), where it is heated, and then, as a high-temperature gas, it is introduced into carbon dioxide expander (CO₂-EX2). The two remaining streams of carbon dioxide, before they are fed to the carbon dioxide expander of the methanation system (CO₂-EX1), receive the cooling heat of the methanation process. One of the streams receives heat directly in the heat exchanger of the methanation system (MUC), while the other from the accumulation material, flowing through the heat accumulator of the methanation system (TES-MU).

The carbon dioxide streams expanded in the CO₂-EX1 and CO₂-EX2 expanders are merged in a collector. At the discharging stage of the energy storage system, the methane tank (SNG-T) is emptied and the gaseous fuel is directed to the combustion chamber (CCH), to which oxygen is also supplied from the oxygen tank (O₂-T) and carbon dioxide from the low-pressure tank (LPT), after being compressed in a recirculated carbon dioxide (CO₂-C4) compressor. High-temperature flue gases (a mixture of carbon dioxide and water vapor) are directed to the flue gas expander (FG-Ex). After expansion, the flue gas is flowing to the exhaust gas cooler (FGC), giving off heat to CO₂ stream, and then is additionally cooled in the supplementary cooler (FGDS). Next, it goes to the moisture separator (FG/WS), where the condensed water is separated from the stream. The separated condensate is directed to the water tank (H₂O-T) through the moisture separation system pump (P3). Carbon dioxide is directed to the collector, from which, together with carbon dioxide expanded in CO₂ expanders (CO₂-EX1 and CO₂-EX2), is supplied to the cooler (CO₂-CL), where the gas is reaching temperature in the range of 30–40 °C, and is directed to the low-pressure tank.

The proposed storage system enables additionally utilization of CO₂ directed to the energy storage system (by conversion to gaseous fuel) from external sources, such as, for example, carbon dioxide separation from flue gases generated in electricity production systems or industry. In this case, carbon dioxide to be utilized, depending on the pressure, is fed to the system via a stub pipe fitted in a high-pressure (b2) or low-pressure (b1) tank. Carbon dioxide utilization takes place as part of the methanation process, the product of which is additionally the amount of methane that can be discharged into the gas network.

2.2. Assumptions for the analyzed case

The system, as shown in Fig. 1, for the modelling purpose, is divided into four main subsystems:

- Compressed CO₂ Energy Storage Subsystem (CCO₂ESS),
- Methanation Subsystem (MS).

- Hydrogen Production Subsystem (HPS),
- SNG-Oxy Combustion Subsystem (SNGOCS).

Mathematical models of all the installations were built in the in-house computational code in the MS Excel environment and Aspen Plus software [21]. It was assumed that the duration of individual phases (charging, storage and discharging) in the daily work cycle are the same, so each lasts 8 h. The main characteristics and assumptions for the conducted analysis are presented in this section.

2.2.1. Compressed CO₂ energy storage subsystem

The first subsystem consists of high- and low-pressure CO₂ tanks, two carbon dioxide expanders operating in a discharging phase, two CO₂ compressors (single-stage and multi-stage), operating in charging phase, thermal energy storage system of the compression and methanation unit, CO₂ cooler and circulating fan.

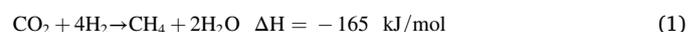
In the analysis it was assumed that the LPT is a large volume reservoir, which in this case is a post-mining excavation. Carbon dioxide is stored at the pressure of 200 kPa. The high-pressure tank is placed underground, and the pressure in the tank is kept at 10 MPa. In both tanks carbon dioxide is stored in the gas state. Thermal energy storages were assumed to be specially designed heat accumulators allowing to store heat between charging and discharging phases. However, technical construction details of the equipment used was not considered here.

An important part of the storage system are the installations of CO₂ compressors and expanders. In the charging stage the CO₂ is directed from LPT to HPT either through the main single-stage compressor (CO₂-C1) or through the multi-stage compressor with inter-stage cooling (CO₂-C2). The division of the stream into these two paths is the main decision variable in the calculations presented in this article (see the following sections). The smaller the stream of CO₂ supplied to the single-stage compressor, the larger the hydrogen production system, as this installation is responsible for providing proper amount of heat, which at the stage of discharging the system heats carbon dioxide before it is introduced into the expanders. After the single-stage compressor carbon dioxide temperature typically exceeds 400 °C and is cooled to 50 °C in heat storage tank (TES-CU). In the case of multi-stage compressor the interstage cooling allows to cool down the CO₂ stream to 50 °C. It was assumed that the internal efficiency of each compressor stage is 88% and the electromechanical efficiency of the compressor assembly is 98%.

At the discharging phase the stream of CO₂ is heated to a level of several hundred degrees in the compression unit storage tanks, methanation unit storage tank, methanation coolers or flue gas cooler, and is expanded in two CO₂ expanders. The internal efficiency of each group of expander stages was assumed at 90%, while their electromechanical efficiency at 98%. After expansion the CO₂ streams are merged together with a stream of CO₂ coming from flue gas phase separator in SNG oxy-combustion subsystem and directed to LPT through the carbon dioxide cooler where it is cooled to 30 °C.

2.2.2. Methanation subsystem

The aim of the methanation subsystem is to produce synthetic natural gas from hydrogen and carbon dioxide, based on the so-called methanation (Sabatier) reaction:



Hydrogen is supplied from the hydrogen tank, while carbon dioxide is supplied from the low-pressure storage tank (after compression to the required pressure in the CO₂-C3 compressor). The mathematical model of the methanation process built for the purposes of this work consists of two isothermal reactors [22,23] that reach equilibrium composition at the operational conditions and the heat from cooling of the reactor is usefully utilized or dispersed in the environment. Such approach, although simplified (compared to e.g. the detailed design of a multistage plug flow reactor presented in [24]) is met in the literature, e.g. [25–27], and shows results similar to the adiabatic approach. It was assumed that

isothermal operation is performed in a heat exchanger multi-tubular reactor [22]. Temperature and pressure were assumed equal to 200 °C and 500 kPa, respectively.

Stoichiometric streams of CO₂ and H₂ were assumed in the process. The kinetics of the reactions were not included in the analysis. For the calculations of thermodynamic parameters, built-in Aspen Plus method was used, i.e. Peng-Robinson [28]. In order to determine the equilibrium composition of the products, depending on the temperature and pressure of the process, the method of minimizing Gibbs free enthalpy was adapted [29].

The methanation reactors are cooled by carbon dioxide which, beyond the discharging phase of the energy storage system, circulates in a loop between the heat exchanger and the methanation system heat accumulator, heating the accumulator storage material. Heat capacity of CO₂ is relatively small, thus, a special design of heat exchanger (e.g., with intermediate energy carrier) would be required to transfer heat from methanation process to CO₂. An interesting option can be the use of a TES system with thermal oil as the energy storage carrier instead of the TES system with solid material. In such case, the thermal oil could also be an intermediary medium in the heat transfer between CO₂ and the methanation unit. However, in this paper the heat exchanger was not modelled in details, but the amount of heat that can be usefully utilized was estimated based on the simplified model.

Pressure loss in the methanation unit was assumed at 150 kPa. After leaving methanation reactor rich methane gas is cooled and dried in SNG/WS phase separator. Separated water is pumped to the H₂O tank in hydrogen production subsystem and prepared for the use in hydrogen generator or for other processes. It should be mentioned that contamination of water with organic compounds or carboxyl groups may require additional treatment. SNG is compressed to the pressure of 3 MPa and stored in SNG tank. Efficiency of the compressor was assumed at 88% (internal) and 98% (electromechanical). Synthetic natural gas in the discharging stage is supplied to the combustion chamber of the SNG oxy-combustion subsystem. If excess amount is produced, it is sent to the natural gas grid.

2.2.3. Hydrogen production subsystem

Hydrogen production subsystem operates during charging phase. It consists of a hydrogen generator operating based on the electrolysis process, water preparation installation, in which water is cleaned to the requirements of the electrolysis process, water pump and water, hydrogen and oxygen tanks. Hydrogen generators are supplied with renewable energy, such as wind or solar, in the energy demand valleys. Here no specific type of source was adopted, however, it was assumed that sufficient amount of electricity can be supplied to the generators to produce required amount of hydrogen. It was assumed that the demand valleys last 8 h during the day, from 10 p.m. to 6 a.m.

The main element of hydrogen generator is an electrolyzer responsible for the water electrolysis process. For proper operation it needs a number of auxiliary devices, such as power supplies, air or water coolers, feed water pumps and, depending on the type of electrolyzer, pumps, heaters and electrolyte tanks, as well as filter sets, responsible for the purification process of the gas generated in the electrolysis. Due to the fact that these auxiliary devices operate within the hydrogen generator, the efficiency of the generator is lower than the efficiency of the electrolyzers installed in it. In this paper it was assumed that hydrogen generator's efficiency is equal to 70% (calculated in relation to HHV) [19]. The electrolysis process is conducted at the pressure of 4 MPa, which allows to store resulting gases without further compression. The purity of products (H₂ and O₂) was assumed at 100%. When needed, hydrogen is supplied to the methanation reactor, while oxygen is delivered to the combustion chamber in the SNG-oxy combustion subsystem and partially brought out of the system (and, e.g., sold) if there is an excess amount produced.

2.2.4. SNG-oxy combustion subsystem

The SNG-oxy combustion subsystem is operating in the discharging period, allowing to produce additional amount of electricity. Synthetic natural gas, produced in the methanation installation, is burned in the combustion chamber in the atmosphere of oxygen, being a product of electrolysis process. Oxygen and SNG are supplied from tanks at the pressure of 3 MPa. It was assumed that complete combustion of these components takes place and the amount of oxygen supplied to the combustion chamber results from the need of stoichiometric combustion; thus, there is no oxygen in flue gases. Resulting flue gas, consisting of CO₂ and H₂O, is expanded and cooled down in two heat exchangers. Heat from the first heat exchanger (FGC) is used for heating part of the CO₂ stream that is directed from the high-pressure tank to the low-pressure tank. Heat from the second heat exchanger (FGDC) is not separately utilized and serves for cooling of the flue gas before phase separator, where it is separated into a stream of carbon dioxide and water.

In the calculations it was assumed that the nominal temperature of the flue gas after combustion is equal to 900 °C, which is mainly due to the thermal resistance of the materials used for the production of expander blades. Since the adiabatic temperature in the combustion chamber is much higher than the assumed one, in order to keep the temperature at the desired level, a stream of CO₂ is supplied to the combustion chamber from the low-pressure tank, after being compressed to 2 MPa. It was also assumed that the pressure losses in the combustion chamber are equal to 3%.

2.3. Evaluation indices

Efficiency of an energy storage system (η_{ESS}) is usually defined as the ratio of energy that is taken out of the system in a discharging stage (E_{out}) to the energy put into the storage in a charging stage (E_{in}), according to the equation:

$$\eta_{\text{ESS}} = \frac{E_{\text{out}}}{E_{\text{in}}} \quad (2)$$

It is typically calculated for a certain period of time (e.g. a year), thus, annual amounts of energy are considered. Depending on the type of the storage system, heat, electricity or chemical energy of fuels can be substituted into the equation. In this paper, the efficiency is defined by the following relationship (according to the electricity flows as shown in Fig. 1):

$$\eta_{\text{ESS}} = \frac{E_{\text{CO}_2\text{-EX1}} + E_{\text{CO}_2\text{-EX2}} + E_{\text{FG-EX}} - E_{\text{Aux,dch}}}{E_{\text{CO}_2\text{-C1}} + E_{\text{CO}_2\text{-C2}} + E_{\text{HG}} + E_{\text{Aux,ch}} + E_{\text{Aux,st}}} \quad (3)$$

where: $E_{\text{CO}_2\text{-EX1}}$, $E_{\text{CO}_2\text{-EX2}}$ – the electricity produced in CO₂ expanders, $E_{\text{FG-EX1}}$ – the electricity produced in flue gas expander, $E_{\text{Aux,dch}}$ – the electricity consumption of the main auxiliary machines operating during discharging stage, $E_{\text{CO}_2\text{-C1}}$, $E_{\text{CO}_2\text{-C2}}$ – the electricity consumed in CO₂ compressors, E_{HG} – the electricity consumed in hydrogen generator, $E_{\text{Aux,ch}}$ – the electricity consumption of the main auxiliary machines operating during charging stages, $E_{\text{Aux,st}}$ – the electricity consumption at storage stages.

Auxiliary consumption of energy is calculated from the following relationships:

$$\eta_{\text{Aux,dch}} = E_{\text{CB}} + E_{\text{P3}} + E_{\text{P2,dch}} \quad (4)$$

$$\eta_{\text{Aux,st}} = E_{\text{CO}_2\text{-C3}} + E_{\text{SNG-C,st}} + E_{\text{CB,st}} + E_{\text{P2,st}} \quad (5)$$

where: E_{CB} – the electricity consumed by the circulating blower, E_{P3} – electricity consumed by the water pump P3, E_{P2} – electricity consumed by the water pump P2, $E_{\text{CO}_2\text{-C3}}$ – electricity consumed by the compressor C3 during storage phase, $E_{\text{SNG-C}}$ – electricity consumed by the SNG compressor; denotation dch relates to the discharging period while st to the storage period.

Table 1
Parameters of the streams in the main points of the analysed storage system (streams denotations according to Fig. 1).

	Charging			Storage			Discharging			Charging			Storage			Discharging			
	m, kg/s	p, kPa	t, °C	m, kg/s	p, kPa	t, °C	m, kg/s	p, kPa	t, °C	m, kg/s	p, kPa	t, °C	m, kg/s	p, kPa	t, °C	m, kg/s	p, kPa	t, °C	
Compressed CO ₂ Energy Storage Subsystem									Methanation Subsystem										
1	16.265	200	30	–	–	–	16.264	200	30	41	0.011	500	25	0.011	500	25	0.011	500	25
2	16.265	200	30	–	–	–	7.709	200	119.7	42	0.06	200	30	0.06	200	30	0.06	200	30
3	8.132	200	30	–	–	–	–	–	–	43	0.06	500	106.9	0.06	500	106.9	0.06	500	106.9
4	8.132	10,526	461.6	–	–	–	–	–	–	44	0.071	350	78.7	0.071	350	78.7	0.071	350	78.7
5	8.132	10,000	50	–	–	–	7.709	10,000	50	45	0.071	343	25	0.071	343	25	0.071	343	25
6	8.132	200	30	–	–	–	–	–	–	46	0.023	190	25	0.023	190	25	0.023	190	25
7	8.132	10,000	50	–	–	–	–	–	–	47	0.023	3,000	286.5	0.023	3,000	286.5	0.023	3,000	286.5
8	16.265	10,000	50	–	–	–	7.709	10,000	50	48	0.048	326	25	0.048	326	25	0.048	326	25
9	–	–	–	–	–	–	7.709	9,500	461.6	49	0.048	500	25	0.048	500	25	0.048	500	25
10	–	–	–	–	–	–	7.709	200	119.7	b4	–	–	–	–	–	–	–	–	–
11	–	–	–	–	–	–	8.556	10,000	50	SNG-Oxy combustion Subsystem									
12	–	–	–	–	–	–	1.642	10,000	50	51	–	–	–	–	–	–	0.263	3,000	25
13	–	–	–	–	–	–	1.642	9,800	160	52	–	–	–	–	–	–	0.068	3,000	25
14	–	–	–	–	–	–	3.143	10,000	50	53	–	–	–	–	–	–	3.566	200	24.5
15	–	–	–	–	–	–	3.143	9,500	160	54	–	–	–	–	–	–	3.566	2,000	233.6
16	–	–	–	–	–	–	4.784	9,500	159.6	55	–	–	–	–	–	–	3.897	1,940	899.9
17	–	–	–	–	–	–	3.771	10,000	50	56	–	–	–	–	–	–	3.897	215	599.2
18	–	–	–	–	–	–	3.771	9,800	499.2	57	–	–	–	–	–	–	3.897	213	69
19	–	–	–	–	–	–	8.556	9,500	309.8	58	–	–	–	–	–	–	3.897	211	25
20	–	–	–	–	–	–	8.556	204	18.3	59	–	–	–	–	–	–	0.182	200	24.5
21	–	–	–	–	–	–	16.264	200	67.6	60	–	–	–	–	–	–	0.149	200	24.5
22	1.863	9310	50	1.863	9310	50	–	–	–	61	–	–	–	–	–	–	0.149	500	24.6
23	1.863	10,000	55	1.863	10,000	55	–	–	–	62	–	–	–	–	–	–	0.197	500	24.7
24	1.863	9,800	160	1.863	9,800	160	–	–	–	b5	–	–	–	–	–	–	–	–	–
b1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
b2	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Hydrogen Production Subsystem																			
31	0.296	3,500	25	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
32	0.296	3,500	25	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
33	0.296	3,500	25	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
34	0.033	3,500	25	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
35	0.263	3,500	25	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
b3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

Table 2
Main energy flows in all the most important points of the analysed system.

		Amount of energy	Phase of operation			
			charging	Storage	Discharging	
Consumption	Main	E_{HG} , kWh	53,520.75	0	0	
		E_{CO2-C1} , kWh	28,356.80	0	0	
		E_{CO2-C2} , kWh	18,122.45	0	0	
		Auxiliary	E_{CO2-C3} , kWh	32.78	32.78	32.78
			E_{CO2-C4} , kWh	0	0	5,586.06
			E_{SNG-C} , kWh	166.75	166.75	166.75
	E_{CB} , kWh	38.74	38.74	0		
	E_{P1} , kWh	0.06	0	0		
	E_{P2} , kWh	0.09	0.09	0.09		
	E_{P3} , kWh	0	0	0.43		
	Production	$E_{CO2-Ex1}$, kWh	0	0	21,002.02	
		$E_{CO2-Ex2}$, kWh	0	0	18,262.01	
E_{FG-Ex} , kWh		0	0	11,819.28		

In the analysis presented in this paper, as the main decision variable, a parameter defined as δ was used. It describes the division of carbon dioxide stream during charging stage into the stream directed to the single-stage compressor and multi-stage compressor, and is calculated according to the following equation (streams number correspond to denotations in Fig. 1):

$$\delta = \frac{(m_{CO2})_3}{(m_{CO2})_2} = \frac{(m_{CO2})_2 - (m_{CO2})_6}{(m_{CO2})_2} = 1 - \frac{(m_{CO2})_6}{(m_{CO2})_2} \quad (6)$$

The division of streams primarily affects the amount of electricity that is consumed in CO₂ compressors CO₂-C1 and CO₂-C2. Unit energy consumption (per kg/s of CO₂) is lower in case of the multi-stage compressor as the stream of compressed CO₂ is cooled after each stage to 50 °C. It also affects the amount of heat that is stored in the storage tank TES-CU, because heat from compressor cooling is dissipated in the environment, thus, is not utilized. In the calculations it was assumed that nominal value of this decision variable is 0.5 and it is changed within the range from 0.1 to 0.9. In the calculations the system was designed to store (i.e. consume in the charging period) 100 MWh of electricity.

3. Results and discussion

The main aim of the analysis presented in this paper was to determine the thermodynamic parameters of streams in the main points of the proposed storage system, as well as the energy flows and storage efficiency. The volume of low-pressure and high-pressure tanks, and the amount of CO₂ stored in the system were also determined as they provide valuable information on technical possibility of adopting the system into a real infrastructure.

Nominal point for the calculation was assumed for a value of the decision variable (calculated according to the equation (6)) $\delta = 0.5$. For this assumption the efficiency of the system was equal to 0.4508. Calculated volume of the low-pressure tank was equal to 132,868 m³, which would require the use of 2–3 individual mine shafts in a coal mine (as typically an individual shaft reaches a volume of 50,000 m³ [30]). Volume of the high pressure tank was equal to 1219 m³ and the stream of CO₂ circulating between the tanks was 468,417 kg. Table 1 presents main thermodynamic parameters of the streams in all the most important points of the system while Table 2 the energy flows for the nominal case. Moreover, composition of streams is shown in Appendix 1.

Total energy delivered to the machines during charging phase was equal to 100,238.43 kWh. The highest energy demand is required for hydrogen generator (53,520.75 kWh), which constitutes 53% of all the

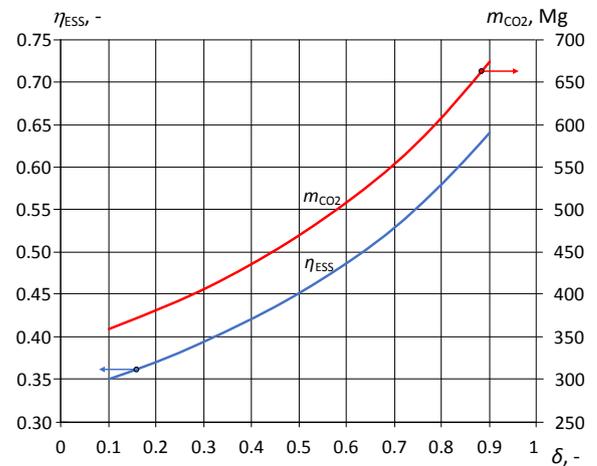


Fig. 2. Energy storage efficiency and mass of CO₂ stored as a function of parameter δ .

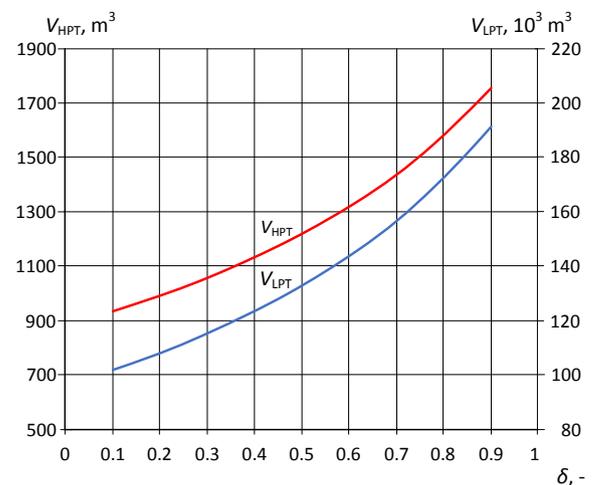


Fig. 3. Volume of low and high-pressure tanks as a function of parameter δ .

energy consumed in this period. During discharging 51,083.31 kWh of electricity can be produced, with first CO₂ expander (CO₂-Ex1) being responsible for the production of around 41% of this amount, second (CO₂-Ex2) for around 36% and flue gas expander (FG-Ex) for the rest, i. e. 23%.

As mentioned before, the main decision variable in the calculations was parameter δ , determining the share of CO₂ stream directed to the single-stage CO₂ compressor (CO₂-C1). The analysis was made for the δ value between 0.1 and 0.9 with a step of 0.1. Fig. 2 presents the characteristic of the storage efficiency (determined according to the equation (3)) and CO₂ mass circulating in the system, while Fig. 3 presents volume of CO₂ tanks as a function of parameter δ .

With the increasing share of CO₂ stream directed to the single-stage compressor, the efficiency is increasing from around 0.35 for $\delta = 0.1$ to 0.64 for $\delta = 0.9$. In the same time an increase of the mass of CO₂ circulating in the system can be observed by almost 90% (from 359 Mg to 673 Mg). Thus, the volume of low-pressure tank and high-pressure tank is also increasing. In case of LPT the volume is changing from 101,900 m³ to 190,878 m³. The volume of high-pressure tank is increasing from 935 to 1751 m³. The required volume of LPT and HPT should not constitute a technical problem for the proposed installation.

In Fig. 4 the energy consumed in the main machines operating in the system is shown. Left graph shows the energy consumed in three machines responsible for the highest use of energy, i.e., hydrogen generator

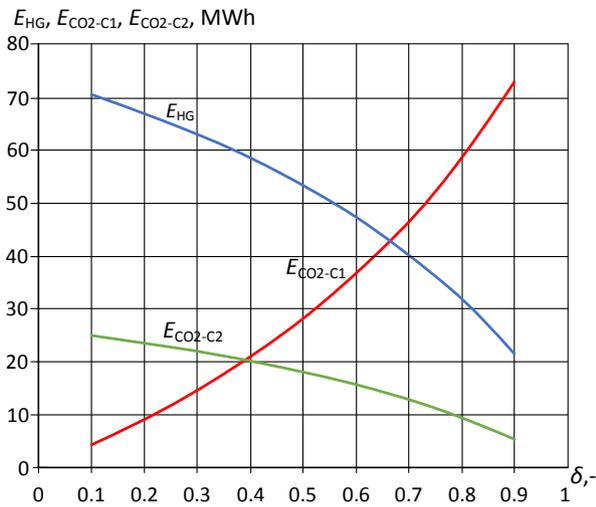


Fig. 4. Energy delivered to: hydrogen generator (E_{HG}), CO₂ compressors (E_{CO2-C1} , E_{CO2-C2} and E_{CO2-C3}), circulating blower (E_{CB}) and SNG compressor (E_{SNG-C}).

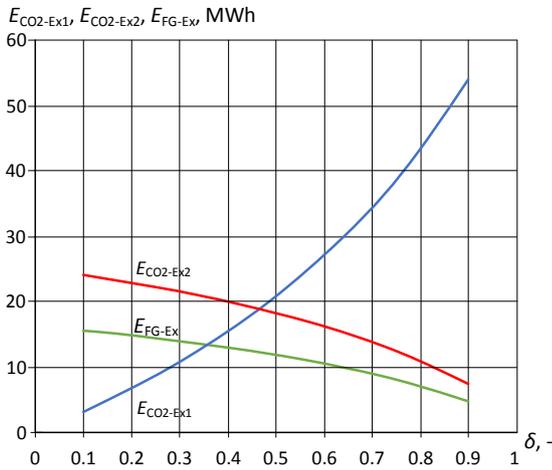


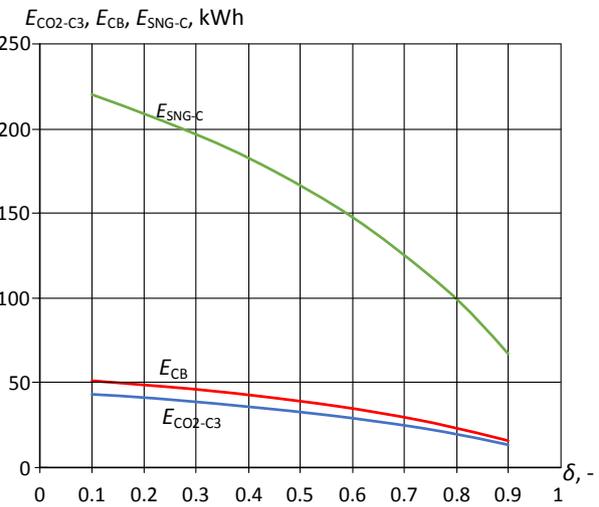
Fig. 5. Energy produced in: CO₂ expanders ($E_{CO2-Ex1}$ and $E_{CO2-Ex2}$) and flue gas expander (E_{FG-Ex}).

and two CO₂ compressors (single-stage CO₂-C1 and multi-stage CO₂-C2). These machines operate only during charging phase. According to the definition of δ , the higher the CO₂ stream flowing through CO₂-C1, the lower the stream flowing through CO₂-C2. Thus, the higher consumption of the first, the lower of the second. With increasing δ the energy delivered to hydrogen generator is significantly decreasing; thus, the size of this installation is decreasing. Energy delivered to auxiliary machines (right graph in Fig. 4) is significantly lower than in case of the three main compressors.

Fig. 5 presents the energy delivered as a result of operation of the expanders in the discharging period as a function of δ . With increasing value of δ energy produced in the first CO₂ expander is significantly increasing and, around the nominal point, becomes the main source of electricity produced within the system. In the same time, energy delivered from flue gas expander is decreasing, which is the result of decreasing required size of this subsystem.

4. Conclusions

In this paper the detailed description of the novel energy storage system is presented. The system is based on the use of compressed carbon dioxide, hydrogen generators and methanation process. The system can use, for instance, the storage volume of post-mine excavations, thus,



allows to use the infrastructure that is not utilized any more. Perfect example of a region that has a high potential of such infrastructure is Upper Silesia region in Poland, where there is a lot of coal mines and the industry, that can provide CO₂ that is used as the energy carrier, and also that can be utilized (converted into SNG) within the system.

The proposed system is designed mainly for energy storage, thus, carbon dioxide that is used in the system circulates between low- and high-pressure tank. The system may additionally utilize CO₂ that is coming from the power or other industries. However, an important advantage of the system is that the CO₂ utilization process is not obligatory, but may result from the current market situation. This feature of the system minimizes the investment risk for the methanation subsystem, which will be able to work effectively regardless the current demand for the CO₂ utilization process. In further studies economic assessment of the proposed solution under various business conditions will be made, which will consider also source of carbon dioxide.

For the nominal point of operation the proposed system reaches energy storage efficiency equal to 45.08%. The higher the value of decision variable δ (the share of the CO₂ stream flowing through the single-stage compressor), the higher efficiency of the storage system, no matter the fact that unit work is higher than in case when the CO₂ is flowing through the multi-stage compressor. In the best solution, for the value of decision variable $\delta = 0.9$, the storage efficiency can reach 63.93%; thus, is comparable to other energy storage technologies. With increasing value of δ , the energy delivered to the hydrogen generators is decreasing (thus, the size of this installation is decreasing).

An important indicator that can decide on the technical feasibility of the proposed solution are volumes of the low- and high-pressure tanks in the system. For the analysed nominal case, a volume of the first tank was calculated at 132,869 m³, which typically would require 3 mine shafts. With increasing δ , the volume of the tank is increasing, reaching for the highest value 190,878 m³. These values, although significant, should not constitute a technical problem because typically, a single coal mine would provide the required volume. For the high-pressure tank, the volume is changing from 935 m³ (for $\delta = 0.1$) to 1751 m³ ($\delta = 0.9$), with volume of 1219 m³ for the nominal case. This tank can be placed either over- or underground.

The proposed storage system can potentially be implemented into the existing infrastructure, making the use of exploited coal mines. The proposed solution can be further optimized, especially with economic criterion and taking into account various business criteria. Such works will be performed by the authors in further steps of analysis.

CRedit authorship contribution statement

Anna Skorek-Osikowska: . : Conceptualization, Methodology, Investigation, Writing - original draft, Supervision, Funding acquisition. **Łukasz Bartela:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft. **Daria Katla:** Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **Sebastian Waniczek:** Conceptualization, Validation, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix 1

Composition of streams in the most important points of the system (see Fig. 1) for parameter $\delta = 0.5$.

	CHARGING STAGE					STORAGE STAGE					DISCHARGING STAGE				
	H ₂	CH ₄	H ₂ O	O ₂	CO ₂	H ₂	CH ₄	H ₂ O	O ₂	CO ₂	H ₂	CH ₄	H ₂ O	O ₂	CO ₂
Compressed CO₂ Energy Storage Subsystem															
1	0	0	0	0	1	0	0	0	0	1	0	0	0	0	1
2	0	0	0	0	1	0	0	0	0	1	0	0	0	0	1
3	0	0	0	0	1	0	0	0	0	1	-	-	-	-	-
4	0	0	0	0	1	0	0	0	0	1	-	-	-	-	-
5	0	0	0	0	1	0	0	0	0	1	0	0	0	0	1
6	0	0	0	0	1	0	0	0	0	1	-	-	-	-	-
7	0	0	0	0	1	0	0	0	0	1	-	-	-	-	-
8	0	0	0	0	1	0	0	0	0	1	0	0	0	0	1
9	-	-	-	-	-	-	-	-	-	-	0	0	0	0	1
10	-	-	-	-	-	-	-	-	-	-	0	0	0	0	1
11	-	-	-	-	-	-	-	-	-	-	0	0	0	0	1
12	-	-	-	-	-	-	-	-	-	-	0	0	0	0	1
13	-	-	-	-	-	-	-	-	-	-	0	0	0	0	1
14	-	-	-	-	-	-	-	-	-	-	0	0	0	0	1
15	-	-	-	-	-	-	-	-	-	-	0	0	0	0	1
16	-	-	-	-	-	-	-	-	-	-	0	0	0	0	1
17	-	-	-	-	-	-	-	-	-	-	0	0	0	0	1
18	-	-	-	-	-	-	-	-	-	-	0	0	0	0	1
19	-	-	-	-	-	-	-	-	-	-	0	0	0	0	1
20	-	-	-	-	-	-	-	-	-	-	0	0	0	0	1
21	-	-	-	-	-	-	-	-	-	-	0	0	0	0	1
22	0	0	0	0	1	0	0	0	0	1	-	-	-	-	-
23	0	0	0	0	1	0	0	0	0	1	-	-	-	-	-
24	0	0	0	0	1	0	0	0	0	1	-	-	-	-	-
b1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
b2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Hydrogen Production Subsystem															
31	0	0	1	0	0	-	-	-	-	-	-	-	-	-	-
32	0	0	1	0	0	-	-	-	-	-	-	-	-	-	-
33	0	0	1	0	0	-	-	-	-	-	-	-	-	-	-
34	1	0	0	0	0	-	-	-	-	-	-	-	-	-	-
35	0	0	0	1	0	-	-	-	-	-	-	-	-	-	-
b3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Methanation Subsystem															
41	1	0	0	0	0	1	0	0	0	0	1	0	0	0	0
42	0	0	0	0	1	0	0	0	0	1	0	0	0	0	1
43	0	0	0	0	1	0	0	0	0	1	0	0	0	0	1
44	0.0091	0.3296	0.6591	0	0.0023	0.0091	0.3296	0.6591	0	0.0023	0.0091	0.3296	0.6591	0	0.0023
45	0.0091	0.3296	0.6591	0	0.0023	0.0091	0.3296	0.6591	0	0.0023	0.0091	0.3296	0.6591	0	0.0023
46	0.0262	0.9533	0.0139	0	0.0066	0.0262	0.9533	0.0139	0	0.0066	0.0262	0.9533	0.0139	0	0.0066
47	0.0262	0.9533	0.0139	0	0.0066	0.0262	0.9533	0.0139	0	0.0066	0.0262	0.9533	0.0139	0	0.0066
48	0	0	1	0	0	0	0	1	0	0	0	0	1	0	0
49	0	0	1	0	0	0	0	1	0	0	0	0	1	0	0
b4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SNG-Oxy combustion Subsystem															
51	-	-	-	-	-	-	-	-	-	-	0	0	0	1	0
52	-	-	-	-	-	-	-	-	-	-	0.0262	0.9533	0.0139	0	0.0066
53	-	-	-	-	-	-	-	-	-	-	0	0	0.0154	0.0003	0.9843

(continued on next page)

(continued)

	CHARGING STAGE					STORAGE STAGE					DISCHARGING STAGE				
	H ₂	CH ₄	H ₂ O	O ₂	CO ₂	H ₂	CH ₄	H ₂ O	O ₂	CO ₂	H ₂	CH ₄	H ₂ O	O ₂	CO ₂
54	-	-	-	-	-	-	-	-	-	-	0	0	0.0154	0.0003	0.9843
55	-	-	-	-	-	-	-	-	-	-	0	0	0.1017	0.0003	0.8980
56	-	-	-	-	-	-	-	-	-	-	0	0	0.1017	0.0003	0.8980
57	-	-	-	-	-	-	-	-	-	-	0	0	0.1017	0.0003	0.8980
58	-	-	-	-	-	-	-	-	-	-	0	0	0.1017	0.0003	0.8980
59	-	-	-	-	-	-	-	-	-	-	0	0	0.0154	0.0003	0.9843
60	-	-	-	-	-	-	-	-	-	-	0	0	1	0	0
61	-	-	-	-	-	-	-	-	-	-	0	0	1	0	0
62	-	-	-	-	-	-	-	-	-	-	0	0	1	0	0
b5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

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