

## Integrated combustion flue gas separation and Methanation

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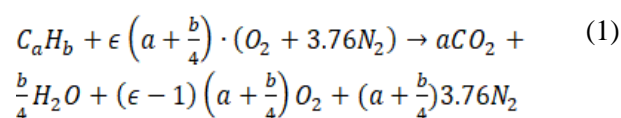
Chemical energy storage is a potential process for balancing supply and demand in energy production based on renewable energy. The objective of this paper is firstly to review characteristics of conventional exhaust treatments and methane formation and secondly to propose a combustion flue gas methanation model that will be able to achieve an alternative energy storage solution. An initial description and technical analysis of its key features are presented. This research demonstrates a scalable process that integrates the abundance of renewable energy and the dispatchability of fossil fuels by using wind/Solar electricity to convert carbon dioxide into methane. As a result, an existing fossil-fuel-fired combustion appliance may be turned into a 100% carbon neutral system that maintains a closed-loop on carbon. The process includes the following critical steps: Capture of combustion exhaust, separation of water from the exhaust, Separation of nitrogen from the exhaust, a distillation of the water produced, electrolysis of the water to produce hydrogen, mixing of carbon dioxide and hydrogen in a Sabatier reactor to produce methane.

**Keywords:** Methanation, CO<sub>2</sub> capture, power to methane

### INTRODUCTION

Reducing CO<sub>2</sub> emissions produced via combustion is an essential goal to achieve the economical and climate change objectives defined by the COP-21 in Paris in 2015, when 194 states and the European Union signed the Paris Agreement, in order to reduce global emissions and limit the temperature increase to 1.5 °C above pre- industrial levels [1]. The fact that these goals have significant economic implications created difficulties resulting in the USA announcement to withdraw from the Paris agreement [2]. Chemical energy generated from renewable sources such as PV solar and wind can meet the gap created between economic and climate goals and thus enable detractor of the Paris Climate Agreement such as the USA to rejoin the accord. The primary challenge is fluctuations of wind and sunlight. Development economic baseload renewable electricity production requires the implementation of energy storage technologies to address overproduction periods and distribute it during underproduction periods. Based on the Power To Gas (PtG) concept [3], The suggested system will capture the CO<sub>2</sub> from combustion exhaust gas and use PV solar energy to convert it to natural gas which has already existing infrastructure for storage and distribution. This innovative system integrates within a single device all of the core processes required to

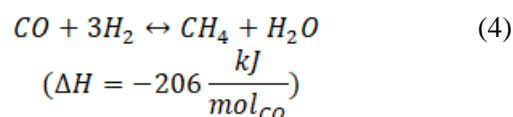
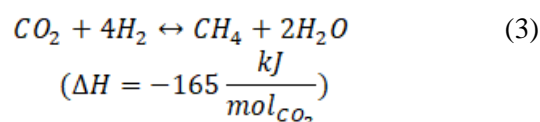
seamlessly convert the combustion exhaust of any system into renewable natural gas. These processes include but are not limited to the following: CO<sub>2</sub> post-combustion capture, electrolysis of water entrained in both the combustion and methanation exhaust to generate hydrogen, and a methanation (Sabatier) reaction for the desired conversion of CO<sub>2</sub> to methane. The combustion reaction can be described according to Eq.(1):



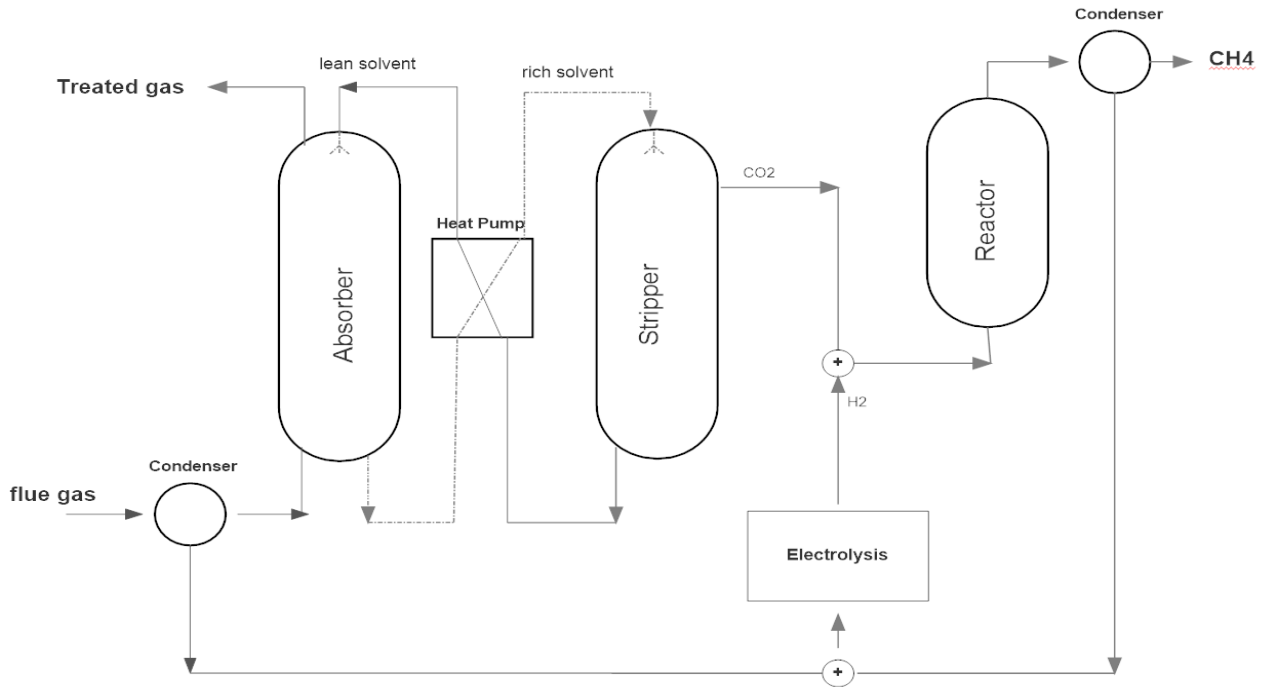
where  $a$  and  $b$  are defined as  $C_aH_b$ , and  $\epsilon$  represents the added amount of air to the burner system which is more than the amount required for perfect stoichiometric combustion and is defined as Eq.(2).

$$\epsilon = 1 + \frac{\% \text{ Excess Air}}{100} \quad (2)$$

The two key reactions of methane production are:



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**Fig 1.** Process flow diagram for CO<sub>2</sub> capture and methanation reaction

The exhaust gas characteristics in the simulation of the processes is shown in Tab.1, as in ideal combustion with 20% excess air.

**Table 1.** Typical characteristics of flue gas

Flue Gas Specification	Composition
CO <sub>2</sub> (mol %)	6.7
N <sub>2</sub> (mol %)	75.8
O <sub>2</sub> (mol %)	4.1
H <sub>2</sub> O (mol %)	13.4

Methanation reactions are thermodynamically favorable, yet a catalyst is necessary to obtain an appropriate conversion rate, with reported efficiencies of up to 80% CO<sub>2</sub> due to the high-water content produced in the process, and up to 89% in three phase reactors [3]. However, all research is done on pure gases without contaminants and therefore lower values are to be expected. The main effect on CO<sub>2</sub> conversion is reaction temperature, catalyst activity, and H<sub>2</sub>/CO<sub>2</sub> ratio. It has been reported that a molar ratio of 4 which is higher than the stoichiometric ratio is favored for this reaction as well as a temperature range of 300-350 °C, as for catalysts, research is still being done on the field of methanation. Ni-based catalysts are reported to produce good results, and 80% CO<sub>2</sub> conversion is expected to be achievable. The scope of our study is to demonstrate the integration of combustion exhaust

gas capture, treatment, and conversion into a single system that may economically be deployed on existing appliances. The threefold research aims include a) separation of CO<sub>2</sub> from generator exhaust, b) ensure negligible emissions of greenhouse gases to the atmosphere c) to demonstrate high CO<sub>2</sub> conversion (>70%) with the proposed system.

## SYSTEM DESCRIPTION

The model in Fig.1, consists of two spray towers, a heat pump, a tubular reactor, an electrolysis machine, and gas supply lines of O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, and water. The system consists of four sections: feed, absorption, desorption and methanation. The approach adopted in this study Fig.1 is to remove the water before capturing the CO<sub>2</sub> and flue with the cyclic aqueous amine absorber, heating the rich solvent to release the desired CO<sub>2</sub> on the stripper column and adding hydrogen from electrolysis machine to satisfy high H<sub>2</sub>/CO<sub>2</sub> ratio in the reactor. All water produced in this process (exhaust gas and reaction products condensation) is to be distilled to prevent electrolyte contaminations [4], and feed the electrolysis machine.

### Condenser

Condensation is made using two tanks and the same principle is considered on both exhaust water and reaction product, the first tank is held at room

temperature to cool the gases and condense the water, the second contains silica gel to fully condense the vapor formed in the exhaust and the reaction to prevent it from reaching the system sensors, analyzers and dilute the liquid amine absorber. Silica gel has recorded adsorption capacity towards both  $CO_2$  and  $H_2O$  but favors the second [5]. Note the condenser will produce water not suitable for electrolysis due to sulfur solubility in water and absorption of other gases in it, therefore distillation is required before feeding the excess water to the electrolysis process. The amount of water produced in the process varies at about four moles as both exhaust feed and Sabatier reaction products contains two moles of  $H_2O$ .

### Absorption

Aqueous solutions of Alkanolamines are frequently used for the removal of acid gases from a variety of gas streams. Acid gas absorption-desorption cycle of the acid gas is presented in Fig.1, the  $CO_2$  contents of the exhaust gas are chemically absorbed by the basic liquid absorbent and are released at elevated temperatures or low-pressure conditions. The absorber is designed to capture 90% of  $CO_2$  emitted from the generator. The desired temperatures for the operation of the absorber are room temperature for the acid gas capture and elevated temperature (about 120 °C) on the stripper. The temperature regime and amine transfer between the two tanks are made using a heat pump. The gas and liquid are moving in opposite direction both on absorber and stripper, the flue gas is injected at the bottom and removed as exhaust at the top while the solvent is injected at the top and removed at the bottom. In this flow consideration [6] the concentration of the  $CO_2$  in the flue gas will decrease as a function of the height in the column. The concentration of  $CO_2$  in the solvent is the lowest at the top and highest on the bottom of the absorber tank making it easier for the acid gas to be absorbed due to the high difference between actual concentration and the equilibrium concentration and opposite for the stripper. This approach ensures high mass transfer efficiency. The application of a spray tower promises substantial advantages in comparison with a packed dry adsorption tower, due to expensive packing, insignificant pressure drop, and the ability to use precipitating solvents. in the stripper. The consequent reduction in operating costs and investment is are expected to also reduce the size for the facility as the absorber height depends on amine concentration. Absorber efficiency can be determined

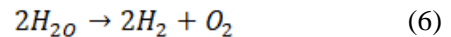
as  $\eta_{abs}$  and equals the amount of  $CO_2$  moles exiting the stripper exhaust times moles of  $CO_2$  in the absorber flue gas as shown in Eq.(5). High power efficiency is expected on the absorption-desorption section since the absorber vents the majority of the flue gases to the atmosphere without requiring additional electricity investment in the process. The desorption temperature serves as Sabatier reactor pre-heater. The amine solution is determined according to its selectivity towards  $CO_2$  according to its partial pressure. Absorber efficiency sets the amount of hydrogen needed to be produced as well as the amount of excess water accumulated in the condensers. The efficiency of the absorber is defined based on the solvent temperature and flow rate.

$$\eta_{abs} = \frac{y_{CO_2 \text{ inlet}} - y_{CO_2 \text{ outlet}}}{y_{CO_2 \text{ inlet}}} \cdot 100\% \quad (5)$$

The absorber efficiency in turn determines the tower dimensions [7]. The minimum energy required to separate the  $CO_2$  from flue gas can be easily calculated relative to the gas mixture entropy [8] and is dependent on the acid gas concentration, the lower the initial concentration of the  $CO_2$  in the flue gas, and the higher the minimum work required to separate it. Thus, high concentrations of  $CO_2$  in flue gas are preferred and will produce more methane as well as reduce separation costs.

### Electrolysis

Electrolysis demands relatively high amounts of energy for separation of water molecules at ambient temperature and is, the highest power consumer in the system. The equilibrium voltage of a water molecule is approximately 1.23V, which and is needed to break the water molecules into hydrogen and oxygen as noted in Eq.(6). The hydrogen production rate depends on the stable  $CO_2$  flow out of the stripper on maintaining a high  $CO_2/H_2$  ratio.



### Sabatier Reaction

Synthesis of hydrocarbons from  $H_2/CO_2$  mixtures via thermos catalytic processes are favored over group VIII metals (Fe, Co, Ni, Ru, Rh, Pd, Ir, Pt) dispersed on metal oxide supports. Preferred catalysts for the methanation reaction are Nickel and Ruthenium [9] due to their high catalytic activity and selectivity, while Ni is more efficient on the temperature range of 300-350 °C and Ru can produce

methane on a lower temperature. There still exist some problems, such as carbon deposition, and sulfur poisoning during SNG production [10] [11]. Sulfur deactivates carbon dioxide absorption. Carbon

deposition mainly affects the activity, reducing the performance and impacts the amount of catalyst needed in the reactor.

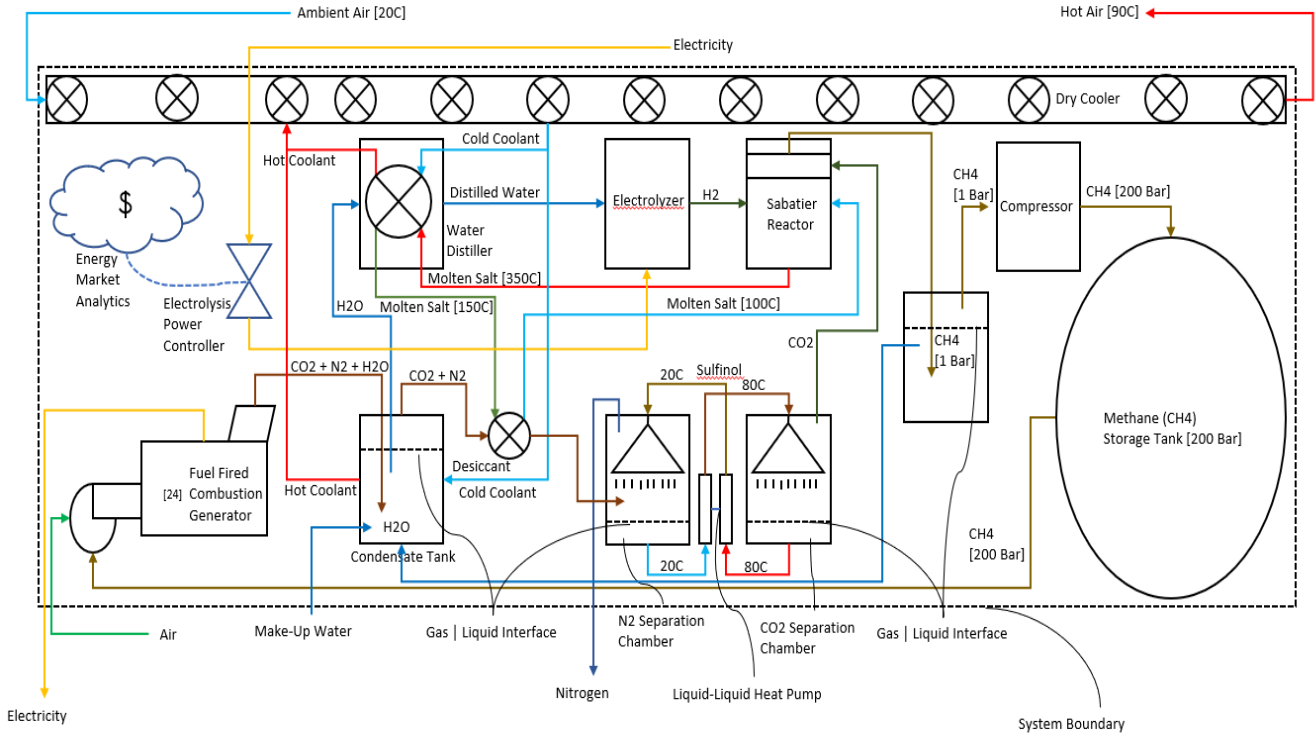


Fig.2. Proposed process for shipping container scale  $CH_4$  production and storage of exhaust gas

Reaction efficiency can be determined as:

$$\eta_{reactor} = \frac{y_{CO_2\ inlet} - y_{CO_2\ outlet}}{y_{CO_2\ inlet}} \cdot 100\% \quad (7)$$

And therefore, overall methane yield in the process is:

$$\mathfrak{R} = \eta_{abs} \cdot \eta_{reactor} \quad (8)$$

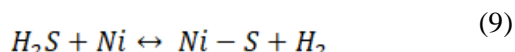
$\mathfrak{R}$  is the  $CH_4$  yield and is depends on both absorber and reaction efficiencies. The desired  $CO_2$  capture and solvent flow rate determines the spray tower dimensions. The Sabatier reaction is a highly exothermic reaction, and thus harvesting heat generated during the reaction can be used to reduce cost. Fig.2 is a suggested model for the integration of all four sections. Real time analysis of electricity prices triggers the electrolysis process, which in turn feeds hydrogen to the methanation reactor. Electrolysis is the system's highest power consumer. Distillation is used to purify the condensed water and

feed the electrolysis machine. Molten salt transfers additional heat from the reactor to boil pre-electrolysis distilled water. At the process end, the resultant  $CH_4$  is compressed to pressure at which it can be stored. All pressures and temperatures noted were designed around achieving a minimum power consumption, amine solvents (sulfinol – manufactured by Shell), and a  $(NiAlO_3)$  reaction catalyst.

#### Gas Impurities

The combustion reaction described in Eq.(1) is somewhat idealized. For typical gaseous fuel, N forms  $NO_x$  and S forms  $SO_x$  with traces metals. The major pollutants resulting from combustion are carbon monoxide (CO) and Nitrogen dioxide ( $NO_x$ ), generally including nitrogen monoxide also known as nitric oxide (NO) and nitrogen dioxide ( $NO_2$ ), the majority of the  $NO_x$  exiting the exhaust stack is in the form of NO. According to Eq.(4) CO reacts as carbon dioxide to produce methane and does not require pretreatments. Sulfur on the other hand is poisonous and reduces the catalyst activity drastically [12] by switching the reaction mechanism at the

Catalysts surface to produce Hydrogen-Sulfide, which adsorbs strongly and reduces its active sites.



Sulfur containing components must be cleaned ahead a time to ppb levels [12]. Impurities in the exhaust gas set the requirements for the system with respect to impurity removal. Selection of the ideal amine absorbant should be based on its selectivity towards Sulfur, in order to reduce the sulfur content and prevent catalyast poisoning. The linear dependency between catalyst lifetime, and  $S, H_2$  adsorption capacities described in detail in [12] predicted a lifetime for *NiAlO* catalyst on constant flow of 20 ppb Sulfur of 350 days.

### CONCLUSIONS

Producing synthetic renewable methane from combustion exhaust gas and feeding it into the existing natural gas distribution infrastructure will reduce greenhouse gases and will allow for the establishment of energy storage to overcome the disadvantages of intermittent renewable energies (e.g., solar or wind). The proposed system will overcome current challenges making the methanation technology truly commercially viable. The main characteristics of this system will be as follows:

- Power Quality – in terms of supporting the electric grid for voltage stability, availability, and resiliency.
- Energy Storage - the ability to store energy on the grid on a varied timescale from hours to months
- Energy Sink – the ability to capture overproduction of renewable energy through the generation of methane.

The main disadvantage of such a system is periodic replacement/ regeneration of the catalyst after the activity is reduced.

### ACKNOWLEDGEMENT

We thank the Israel Ministry of science and technology for funding our work.

### NOMENCLATURE

$\eta_{abs}$  - absorption efficiency, %;  
 $y_{CO_2 inlet}$  - CO<sub>2</sub> inlet mole ratio, mol%;

$y_{CO_2 outlet}$  - CO<sub>2</sub> outlet mole ratio, mol%;  
 $\eta_{reactor}$  – reactor efficiency, %;  
 $\mathfrak{R}$  - overall methane yield, %;

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