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Research paper

Methanation potential: Suitable catalyst and optimized process conditions for upgrading biogas to reach gas grid requirements

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A B S T R A C T

Increasing CO_2 and greenhouse gas emissions are decreasing the living conditions all around the world and considerable damage is inflicted on our planet. Creating solutions for clean energy, air, water and food is becoming inevitable and urgent. This paper focuses on upgrading biogas to high quality biofuel to meet German gas grid requirements. The Sabatier process has proven that carbon dioxide present in biogas can be converted to methane (>96% -Vol) by adding hydrogen in a stoichiometric ratio. High quality methane yield 98.9%, with CO_2 conversion 99.6% is achieved with a Nickel catalyst and with process conditions of temperature (473.15 K), pressure (1000 kpa), H_2/CO_2 ratio (6), CH_4/CO_2 ratio (1.52), a flow rate of 1.11×10^{-6} m^3 s^{-1} for the reactor dimensions of a diameter of 0.1 m, a catalyst bed height of 0.14 m, a catalyst amount of 0.01 kg and a reactor volume of 1.099×10^{-3} m^3. These experimental laboratory parameters are beneficial as a reference for upscaling Methanation reactors.

1. Introduction

Political goals, regarding the energy system in Germany have led to an increased use of renewable energies in the energy mix, which is currently still based on fossil fuel (coal and gas) fired power plants. In 2018, about 59,313 MW of wind powered energy production was installed which make up 20.4% of the German electricity production. However, in 2017 5518 GW h of wind energy was unused hence, utilizing surplus energy seems beneficial [5].

The Power-to-Gas system is one approach, which can be a possible solution for using surplus energy. The concept is based on the conversion of electrical energy to chemical energy in the form of hydrogen, where the gas could be stored in Germany's natural gas grid. Based on the requirements for injecting gas into the H-gas grid a minimum of less than 2%- Vol of hydrogen and the methane concentration above 96%- Vol is required [7].

The hydrogen can be produced by classical electrolysis where the electrical energy is used for a redox-reaction which follows $2H_2O \rightarrow 2H_2 + O_2$. The produced oxygen is released into the environment and the hydrogen is collected and stored for further usage in the methanation process. The required carbon source for the Sabatier process can be acquired from either the carbon dioxide from exhaust gas from biogas plants or the released CO_2 from biomethane upgrading plants or the produced biogas directly, which contains about 50% - Vol of CO_2. The trace components from the biogas like hydrogen sulphide and siloxanes have to be removed by prior gas cleaning for the methanation plant to prevent deactivation of the catalyst [27].

The necessary heat for the methanation plant can be supplied by the exhaust gas from the CHP plant (Temperatures about 723 K). The electrolysis must begin quickly when using fluctuating wind power; these demands are covered by PEM electrolysers of the newest generation, which have a starting time of several minutes. Furthermore, the methanation plant also has to start up from stand-by within a few minutes. This can potentially be solved by operating the methanation plant in partial load mode and then increase the methane production in times of surplus energy production. Temperatures about 593 K are necessary to achieve full activation of the Nickel Catalyst but these temperatures are not thermodynamically beneficial so that methane yields above 95%- Vol are not possible [27].

However, this research is about optimal process designs and conditions for Nickel and Ruthenium based catalysts. For this, different pathways of the syngas are proposed in the fixed bed reactor and different catalyst amounts and mixtures are tested. In addition, a statistical program, STAVEX, was used for the design of experiments.

2. Sabatier process

Originally, CO and CO_2 Methanation process were first discovered by Sabatier and Senderens in 1902 [4]. In the presence of metal catalysts, Methanation process produces methane from hydrogen and carbon oxides.

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$$CO + 3H_2 \leftrightarrow CH_4 + H_2O\ (g)\ -\ 206\ kJ\ mol^{-1}\ (at\ 298K) \quad (1)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O\ (g)\ -\ 164\ kJ\ mol^{-1}\ (at\ 298K) \quad (2)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O\ (g)\ 41\ kJ\ mol^{-1}\ (at\ 298K) \quad (3)$$

Both (Eq. (1)), (Eq. (2)) reactions are exothermic. CO_2 Methanation is a linear combination of CO Methanation and reverse water-gas shift reaction (Eq. (3)), which always accompanies the CO Methanation reaction in practical operation until certain threshold levels [22].

Power-to-Gas applications have seen extended use during the last ten years due to the global demand for renewable energies. Methanation of carbon dioxide (CO_2) via Sabatier process is increasingly gaining attention for its 100 years of research background and process development.

Throughout the history of the Sabatier process, constant improvements have been made to reactor design, the dynamic behaviour of the reactors and the catalysts used in the process. During the 1970s and 80s, the first developments using syngas from coal gasification were focused on fixed and fluidized bed technologies. Later, more advanced reactors like micro reactors, three-phase, two-phase and modifications to the structural catalysts were developed aiming to improve heat management and to simplify the overall process [22].

The problems of the high-heat of the reaction and sensitive catalysts made the methanation process history long. The first application was the removal of carbon monoxide from syngases, for example, - in ammonia production process and later proton-exchange membrane fuel cells [22]. During the oil crisis in the 1970s, SNG production by CO Methanation lead to the idea to produce natural gas from coal gasification [14]. Over the years many Methanation concepts have been developed like Coal-to-Gas, Coke oven gas (CO_2-meth) and PtG applications.

Because of the increasing demand for energy storing caused by the high amounts of surplus energy produced from wind and solar, CO_2 Methanation has been investigated for its potential in this application [11,12].

3. Potential applications

Creation of SNG: coal or wood undergo gasification which creates a producer gas that can be utilized in the methanation reaction to produce useful gas (methane) but only after it has undergone a purification step. The first commercial synthetic gas plant opened in 1984 in North Dakota, which presently, still operates and produces 1500 MW worth of SNG using coal as the carbon source [22].

In a renewable-energy-dominated energy system, hydrogen, produced by electrolysers from the excess electricity generated by but not limited to wind, solar, photovoltaic, etc., can be subsequently be utilized in the Sabatier reaction to produce methane. The advantage of this method is that the methane produced can be either stored, used in the transportation sector or can be injected into the gas grid (power-to-gas) [1].

Ammonia synthesis: In ammonia production, the by-products CO and CO_2 damage the catalysts. Therefore, methanation catalysts are added after several hydrogen producing steps to prevent carbon oxides build-up in the ammonia synthesis loop, as methane does not have any adverse effects on the catalysts [13].

Sabatier reaction in space: The biggest potential for future application today lies in space exploration. Methane is more stable than hydrogen, as it does not cause metal embrittlement, has a boiling point similar to that of oxygen and does not need highly insulated cryogenic tanks. Methane is lighter than kerosene and does not form coking. Mostly it can be produced from CO_2 through the Sabatier process, revealing its promising future for space exploration [26].

Table 1
Biogas impurities & effects.

Impurities	Impacts/Effects
CO_2	Reduces overall calorific value; promotes corrosion of metallic parts by formation of weak carbonic acid.
H_2S	Acts as corrosive in pipelines; causes SO_2 emissions after combustion or H_2S emissions in case of incomplete combustions; poisons the catalytic convertor.
H_2O	A major contributor to corrosion by forming acid with other compounds; formation of condensation leading to the damage of instruments; freezing of accumulated water in high-pressure low temperature conditions.
NH_3	Leads to an increase in antiknock properties of engines; causes formation of NOx.
N_2	Leads to an increase in antiknock properties of engines; leads to a reduction in calorific value as well.
Siloxanes	They are mainly present in biogas formed out of landfill or sewage gas. These hydrocarbon acts as quartz of silica, grinding motor parts.
Dust	Damages vents and exhaust by clogging.

4. Catalysts

Many noble metal catalysts, like Rhodium, Ruthenium, Palladium, Nickel etc. [8], have been investigated for the Methanation process. Amongst them, Nickel is the most widely used catalyst for Methanation process, due to its high activity and selectivity towards methane production and its low cost. However one of the disadvantages of nickel is, that nickel has a problem with the formation of free carbon and Nickel carbide (Ni_3C), which deactivates the catalyst. This can be easily solved by maintaining appropriate process conditions such as temperature and pressure [21]. To obtain high quality methane (>96%- Vol) through the Methanation process, there are however many open research questions about the right catalyst electron supporters and promoters.

Al_2O_3, TiO_2, ZrO_2 and CeO_2 are main supports used so far. But however, Ni/SiO_2 and Ni/Al_2O_3 have been commonly used because of their activities [24]. The improvement of catalytic properties like reducibility, active metal dispersion and stability, CO_2 conversion and selectivity increasing the attention of using complex composite support with metal oxides [24]. The supports have special characteristics, which influences the properties of catalysts like variation of the dispersion of the active phase. This can modify the reducibility of the oxide precursors by influencing the binding between the active phase and support [8].

Firstly, even though Alumina-supported catalysts performed with good reactivity and good conversion, there are issues with resistance towards high reaction temperature [16]. To test this temperature resistance profile, Nickel catalysts (20%) supported on nanocrystalline γ-Al_2O_3 with a high surface area (13×10^4–177×10^3 $m^2\ kg^{-1}$) was tested on CO_2 conversion and CH_4 selectivity. It showed good stability in between 473.15 K and 623.15 K [19]. CH_4 selectivity of 100% and CO_2 conversion of 82% is achieved at 623.15 K with a combination of Nickel and strong basic support (Ni–Al hydrotalcite-derived catalyst) [25]. With additional supporter (23 wt% $Ni/CaO/Al_2O_3$) 81% CO_2 conversion at 673.15 K has been achieved [17]. From the studies, yield and conversion can be increased by modifying the structural and electronic properties through addition of promoters. Mainly, promoters help in increasing the thermal stability, dispersion of the metal onto the support and improvement of metal-support interaction.

Compared to many potential promoters, CeO_2 notably satisfied the properties [8]. 2 wt% cerium oxide exhibited the highest activity at 623.15 K [20]. Other supporters like Zirconia, ceria, hydrotalcite, Iron based, nickel catalysts exhibited good activity, but with a smaller yield or with less conversion. There are many references available on Methanation catalysts, but in this paper only recently published papers are mentioned as an overview on the different supporters and promoters is given in the supplementary material in form of a table.

Morphology of the active phase, adsorption ability and improving the catalytic features are the essential qualities of supporter for effective Methanation process. Nickel on Silica-Alumina have high thermal stability, a high surface area (166×10^3 $m^2\ kg^{-1}$) and good CO_2 conversion (82.38%) capabilities even at high temperatures [15,29]. With this inspiration, 66% Ni on Silica-Alumina is adopted for our experiments.