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Modeling and simulation of CO methanation process for renewable electricity storage

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ABSTRACT

In this paper, a new approach of converting renewable electricity into methane via syngas (a mixture of CO and H_2) and CO methanation is presented. Surplus of electricity is used to electrolyze H_2O and CO_2 to H_2 and CO by using a SOEC (Solid Oxide Electrolysis Cell). Syngas produced is then converted into methane. When high consumption peaks appear, methane is used to produce electricity. The main conversion step in this process is CO methanation. A modeling of catalytic fixed bed methanation reactor and a design of methanation unit composed of multistage adiabatic reactors are carried out using Aspen plus™ software. The model was validated by comparing the simulated results of gas composition (CH_4, CO, CO_2 and H_2) with industrial data. In addition, the effects of recycle ratio on adiabatic reactor stages, outlet temperature, and H_2 and CO conversions are carefully investigated. It is found that for storing 10 MW of renewable electricity, methanation unit is composed of three adiabatic reactors with recycle loop and intermediate cooling at 553 K and 1.5 MPa. The methanation unit generates 3778.6 kg/h of steam at 523.2 K and 1 MPa (13.67 MW).

1. Introduction

The climate change has been caused by anthropogenic activities like excessive combustion of fossil fuels, industrial processes, deforestation and GHG (greenhouse gases) released into the atmosphere [1]. Potential policies, legislation, and regulation are expected to have an impact on the way, energy is generated, delivered, and used, whether by specific measures or through pricing incentives or disincentives [2]. Therefore, it is imperative to develop and promote alternative sources of energy that can lead to sustainability of energy and the environment system. Indeed, renewable electricity contributes to global sustainability through GHG reduction [3].

However, many renewable sources of energy, such as wind power and solar energy provide energy in a fluctuating manner [4]. EES (Electrical energy storage) is one solution. EES can potentially smooth the variability in power flow from renewable generation and store renewable energy in order to decrease the cost of integrating renewable power with the electricity grid, increase market penetration of renewable energy, and lead to GHG reductions [5,6].

A new approach to seasonal storage of renewable energy is based on using excess electricity produced from a renewable source to co-electrolyze at high temperature (1073 K) steam and CO_2 into syngas via RSOC (Reversible Solid Oxide Cell) in SOEC (Solid Oxide Electrolysis Cell) mode. The syngas produced ($H_2 + CO$) is fed into a methanation reactor where it is converted into CH_4. This gas is then injected into the natural gas network [7]. When high consumption peaks appear, the RSOC is switched to SOFC (Solid Oxide Fuel Cell) mode fed by syngas. This latter is produced by tri-reforming of methane. The global diagram of this process is described in Fig. 1 and detailed in the reference [8].

In this way, renewable electrical energy is stored as chemical energy in existing storage capacities. Storage and power conversion technologies for natural gas are state-of-the-art and commercial unlike hydrogen technologies [9,10] . A further advantage for storage is the higher energy density of methane. Besides conversion of SNG (Synthetic Natural Gas) to electricity in large power plants, the SNG can also be used in decentralized CHP (combined heat and power) units or as a transportation fuel in the mobility sector [11].

The main conversion step in such process is the methanation. The principle of catalytic synthetic production of methane from

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carbon monoxide and hydrogen was discovered in 1902 by Sabatier and Senderens [12]. It can be described by the CO methanation reaction:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H = -206.28\ kJ/mol \tag{1}$$

Another reaction called WGS (Water Gas Shift) occurs simultaneously whenever active catalysts are used:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -41.16\ kJ/mol \tag{2}$$

The heterogeneously catalyzed methanation is important in two main applications: Removal of traces of CO in hydrogen rich gases for the ammonia synthesis and conversion of syngas to methane rich fuel [13,14]. This reaction was performed on various catalysts: Ruthenium (Ru), Rhodium (Rh), Platinum (Pt), Iron (Fe), Nickel (Ni) and Cobalt (Co) [15]. Nickel catalyst is the most appropriate due to its selectivity, activity and its price.

Unfortunately, the commercial deployment of technologies for the production of SNG is constrained by economic and technical barriers. The main issue of methanation is the strong exothermicity of the methane formation reactions. The temperature increase may cause catalyst sintering and possibly leads to carbon particle formation [16]. One pilot plant was designed by Lurgi and Sasol in Sasolburg (South Africa) and another pilot plant, developed by Lurgi and El Paso Natural gas Corporation in Austria [17]. Based on the results of lurgi and sasol, the first and only commercial unit has been developed in the USA (North Dakota) in 1984, producing 1.53 billion Nm^3/y [12,18]. This process is composed of an isothermal reactor and two adiabatic fixed bed reactors with recycling [19].

The TREMP process (Topsoe's Recycle Energy-efficient Methanation Process), was developed by Haldor Topsoe's laboratory. Due to the unique MCR-2X methanation catalyst, TREMP can operate at high temperature, up to 973 K. This catalyst allows reaction heat recovery in the form of high pressure superheated steam and low recycle ratio to ensure energy saving [20]. The CO methanation takes place in adiabatic fixed bed reactors. The reaction exothermicity results in a high temperature increase. Recycling is used to control this temperature rise in the first methanation reactor. No industrial facility has been developed because of the political problems and the price of energy. However, within the last five years, the interest in substitute natural gas has become strong. Efforts have been reinitiated in the technology, and the knowledge gained over the years has been used to refine the tried and tested technology and catalyst [21]. As a result, an updated version with improved efficiencies and lower investment cost is now being offered to the market [22].

In Scotland, a demonstration plant (Westfield coal gasification plant) was built producing 59 Million Nm^3/d of SNG from coal. The methanation unit composed of fixed bed reactors with gas recycle was added to an existing Lurgi-Rectisol purification unit [17]. A further development of the British Gas Corporation was the HICOM process in which shift and methanation are combined. The syngas is passed through a series of fixed bed reactors with recycling of reacted gas and steam dilution [12,17].

All processes described above use fixed bed reactors with recycling the cooled product gas and/or adding steam to limit the strong exothermicity of the reaction. Monitoring temperature increase can be ensured by recycling of reacted gas or steam dilution, or by special technologies such as isothermal reactors or fluidized beds, each with indirect cooling by evaporating water [20].

The aim of this study is to design a methanation unit for renewable electricity storage. The methanation reactor model incorporates the catalytic reaction kinetics. The simulation results will be compared with industrial data for model validation. Then, adiabatic multistage reactors with intermediate cooling and recycling will be designed. The calculation of the recycle ratio, the outlet temperatures and the number of adiabatic reactors will be carefully detailed.

2. Methodology

2.1. Catalytic fixed bed reactor modeling

The methanation reactor model is implemented in Aspen plus™ software. The used physical properties of the following compounds are provided by Aspen Plus™: Water (H_2O), carbon dioxide (CO_2), methane (CH_4), hydrogen (H_2) and carbon monoxide (CO). For the thermodynamic model, the RKSMHV2 property method based on the Redlich – Kwong – Soave equation of state with modified Huron–Vidal mixing rules is used. This model is used for mixtures of non-polar and polar compounds, in combination with light gases [23]. All the binary interaction parameter values needed for this model were provided by Aspen Plus™ library.

The kinetic models used in this paper is that of Kopyscinski [17] over a commercial catalyst Ni/Al_2O_3 (50 wt% Ni/Al_2O_3, BET surface area = 183 m^2/g) in fixed bed reactor (Eqs. (3) and (4) in which pressures are expressed in bar and temperature in K). The reactor is

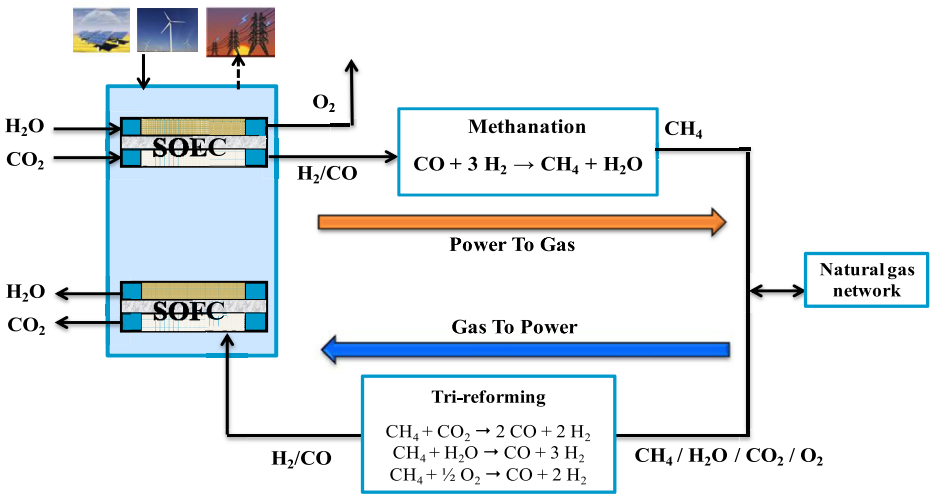

Fig. 1. Reversible power to gas process.