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Development of the experimental scheme for methanation process

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Abstract

The aim of this study is to develop an experimental scheme for realization of methanation reaction ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) realization. The existing experimental stands show that there are many factors and reaction parameters that may negatively act on CO_2 conversion. The highest CO_2 conversion rates are achieved at the temperature range of 300–400 °C. Methane production efficiency also depends on reactor's space velocity, reaction's stoichiometry, catalyst's surface area and type. Nickel and Ruthenium are the most popular catalysts. Gas contaminants (like NO_2, O_2 and SO_2) which may be in exhaust flow, act negatively on the reaction. According to this great amount of aspects acting on methanation process positive outcome special scheme was developed. It combines not only inlet gas properties, proper catalyst or reactor design selection, but also technical aspects such as preheating/mixing chamber and condensing unit design. This summarizing scheme will be used for real methnation reactor design in the future studies.

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Keywords: CO_2 recycling; Sabatier reaction; renewable methane; methanation system design

1. Introduction

Nowadays one of the most significant environmental problems is fossil fuel usage and, as a result, increasing carbon dioxide (CO_2) concentration in the atmosphere [1, 2]. Also, technology progress and ever increasing economic activity has stimulated release of CO_2 emissions inducing global warming. Today, large effort is made towards finding sustainable solutions for solving this problem without interrupting the economic development.

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Most occurring activity is fossil fuel replacement with renewable energy sources (RES), such as wind, solar and biomass energy. The European Union (EU) has set the target to achieve 20 % of renewables in the primary energy supply by 2020. It means that installed capacities of RES will grow in the EU. The tendency of increasing RES share is observed also on the global scale. In 2012, the total global operating capacity of solar PVs reached 100 GW, while the total installed wind capacity was 283 GW. Between 2007 and 2012, the average annual growth rates of solar PV and wind energy capacities were 60 % and 25 %, respectively [3]. The rapid increase has been driven by price decrease, technology development, competition between manufacturers and governmental support.

Despite this positive tendency there is an existing storage problem of stochastic electricity from wind and solar PV energy sources: misbalance between generation and consumption can lead to severe consequences or even to blackout of power system [4]. At the present time, one of the options for RES energy storage is to accumulate it by producing hydrogen (H_2) through water electrolysis. Due to the shortage of renewable H2 infrastructure, methanation where H_2 is combined with CO_2 to produce synthetic methane can be possible solution for recycling of increasing CO_2 and accumulation of non-continuous electricity. Synthetic methane (CH_4) production is convenient because of existing natural gas pipe system. CH_4 can also be burned in an existing power generation stations recovering CO_2 (which should be captured and used in the next cycle). Specific energy of CH_4 is also higher than H2: 40.0 MJ/m^3 versus 12.7 MJ/m^3 [5]. Thus, methanizing H_2 has several preferences.

The aim of this study is to develop an experimental scheme for testing the methanation reaction.

2. Methanation

Although, the methanation reaction was discovered in far 1910s, only in recent years it has attracted more attention, as the depletion of fossil fuels and air pollution problems have become more acute [6]. In the methanation reaction, H_2 reacts with carbon oxides (CO and CO_2) to produce methane (see reactions (1) and (2)). Both reactions are highly exothermic [7, 8].

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \Delta H = -165kJ/mol \tag{1}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad \Delta H = -206kJ/mol \tag{2}$$

Although, the methanation reaction theoretically looks simple, in reality there are many factors and reaction parameters that may negatively act on H_2 and CO_2 conversion, and methane production. The most important aspects affecting the process are discussed below.

2.1. Catalysts

A catalyst is necessary to initiate the reactions (1) and (2). A wide variety of catalysts exist. For methanation, both noble and non-noble metals are used, e.g. Rhodium (Rh), Ruthenium (Ru), Cobalt (Co), Manganese (Mn) and Nickel (Ni) [9]. Some catalysts, especially noble metals, have high costs (e.g. Silver-Ag, platinum-Pt and gold-Au); hence it would not be economically feasible to utilise these metals in pure form. In such cases, it is suitable to use a support material – a less costly material than the catalyst itself, but with a high contact area relative to its size [10]. Various oxide supports exist, e.g. TiO_2, SiO_2, $Al2O_3$, CeO_2, ZrO_2, CuO [11]. Despite the large variety, Nickel and Ruthenium catalysts are the most used and explored [12–16].

2.2. Temperature

Depending on the specific application and catalyst type, the methanation reaction is typically conducted at temperatures between 250–400 °C [17]. The reverse reaction is generally conducted at temperatures higher than 500 °C [7, 10].