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Equilibrium and kinetic aspects for catalytic methanation focusing on CO_2 derived Substitute Natural Gas (SNG)

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ABSTRACT

The production of Substitute Natural Gas (SNG) can be a key component of indigenous energy supply towards a low carbon future. In the present work, state of the art catalytic processes for SNG production based on CO and CO_2 methanation are presented. Equilibrium based simulations are performed for both CO and CO_2 methanation in order to define the optimum process parameters. A special focus is given on SNG derived from CO_2 and hydrogen via power to gas process, which combines energy storage, Carbon Capture and Utilisation (CCU) with SNG production. Three kinetic models for CO_2 methanation at 10 atm, 17 atm and 20 atm from the literature are compared. The quality of SNG produced is evaluated depending on the different operating pressure and temperature of CO_2 derived SNG process. Low pressure bulk methanation (< 20 atm) cannot meet today's grid specifications without any additional measures taken such as blending with fossil natural gas or additional process equipment. Although heating value and Wobbe Index can be fulfilled, the maximum allowed hydrogen content remains a critical issue. Optimum process scheme and conditions for a dry hydrogen mole fraction lower than 2%vol in the final SNG are presented.

1. Introduction

Methane (CH_4) is the main component of natural gas, which is found abundant on Earth in gaseous state below ground and under the sea. Natural gas resources are abundant in the world but not equally distributed. Limited oil and natural gas resources in Europe increase the dependencies on energy imports and highly influence the economics of countries. Gas imports have the second share among presented fuels. The dependency from non-European sources reaches for example approximately 100% for Greece and 78.6–85.7% for Germany over the years, which also imports from Scandinavian countries [1,2]. Natural gas has developed as a key component of indigenous energy supply due to its wide use, its lower carbon footprint compared to other fossil fuels, its well-established infrastructure but also due to the recently low prices raising from the remarkable speed and scale of shale gas development in US. Natural gas is also considered nowadays as key fuel for the energy transition via its use in highly efficient combined cycle plants, for combined heat and power plants as well as in co combustion applications with solid fuels, but also as a feedstock for fuel and chemical production. In the present work, the synthesis of natural gas is being investigated with so called Synthetic Natural Gas (SNG) derived from CO_2 and hydrogen via power to fuel concept. A literature review is presented based on existing catalytic processes. Equilibrium simulations, reaction kinetics for the CO_2 derived SNG and process design aspects are assessed according to the final end product quality and design parameters.

2. Feedstock for synthetic natural gas production

Synthetic Natural Gas can be produced over a wide range of feedstock and processes. Primary feedstock rich in hydrogen and carbon sources is required for its synthesis. In general, SNG can be produced from the gases derived from solid fuels, industrial gases from process industry but also via the use of power to fuel technology. Among solid fuel utilisation technologies, combustion, gasification and pyrolysis process are known for many years as thermochemical processes. Although combustion is only used for electricity production and does not primarily allow a polygeneration scheme, in combination with

Abbreviations: AEL, Alkaline Electrolysis; BTX, Benzene-toluene-xylene; CFE, Cold Fuel Efficiency; COG, Coke Oven Gas; EU, European Union;; GSV, Gas Space Velocity; HHV, Higher Heating Value; HT, High Temperature; IGCC, Integrated Gasification Combined Cycle; LHV, Lower Heating Value; LPM, Liquid Phase Methanation; NGL, Natural Gas Liquids; PEM, Polymer Exchange Membranes; PL, Power Law; RES, Renewable Energy Sources; RK-SOAVE, Redlich-Kwong-Soave; RWGS, Reverse Water Gas Shift; S, Sulphur; SNG, Substitute Natural Gas; SOEC, Solid Oxide Electrolyser Cell; US, United States of America

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Nomenclature

Symbols

C	Conversion (%)
P	Pressure
R/F	Recycle to Feed mole flow ratio
R	Gas constant
S	Selectivity (%)
T	Temperature
Y	Yield (%)
ΔH	Molar enthalpy

Subscripts

e	electric
R	reaction

power to fuel technology and Renewable Energy Sources (RES) electricity can commute the process emissions to valuable SNG production. Among the solid fuel feedstocks, biomass and wastes are also being treated in biological and biochemical processes for polygeneration. However, thermochemical processes have higher scales and efficiencies compared to long reaction times of biological processes. The introduction of biowaste collection (EU Landfill regulation) and the incentives for production of renewable energy have resulted in a remarkable increase of biomass and waste treatment plants via aerobic or anaerobic digestion and waste to energy plants. In pyrolysis process ranging from fast to intermediate or to slow biomass pyrolysis, the content of the produced gas can be 13–35% of the fuel input and can have significantly different gas compositions depending on the process and on the feedstock [3,4]. On the other hand, gasification contributes to the reduction of carbon chain, providing a higher heating value gas mainly composed of H_2, CO, CO_2, H_2O and CH_4 and lower tar content which depending on the carbon conversion can vary from 80% to 99% of the fuel input. Except from the end product and configuration of gasification processes, they have also considerable differences in the technology used and in the thermochemical reactions mainly driven by the different temperature, pressure conditions and agent used [5]. These technologies allow a multi generation of chemicals, heat and electricity and the feasibility for pre-combustion capture of CO_2. Worldwide and in Europe, there are a number of gasification projects in pilot and commercial scale [6]. Technical challenges for the broad application of gasification technology include gas cleaning steps and technologies, increase of operational hours and minimisation of maintenance time as well as efficiency optimisation. Among industrial residues, there are different kinds of by product or waste gases in chemical sites, such as the coke oven gas in coke plants, hydrogen gases in chloro-alkali electrolysers or propylene plants, and in general high energetic gases from refinery and chemical processes. The composition, quality and heating value of these gases are considerably different and many intermediate gas cleaning, conditioning and scavenging processes are required for the treatment of the feed gas. [6–8].

Power to Fuel as a process refers to the use of power via the -electrolysis technology towards hydrogen production initially, but also towards SNG (also known as power to gas) and other chemical production, when combined with CO_2. Power to fuel enables energy storage and grid balancing required in inherent RES electricity production but also enables the production of chemicals via the use and reaction of carbon dioxide. Water electrolysis can be achieved via alkaline (AEL), polymer exchange membranes (PEM), and solid oxide fuel electrolysers (SOEC). AEL is commercialised, while PEM and SOEC electrolysers have not yet found a large commercial application [9]. Carbon dioxide is abundant in all combustion processes and within power to fuel concept, technologies for its separation from flue gases or from biogenous gases are required. A production of 1000 metric tons CO_2 derived SNG is achieved in the E-Gas Project by Audi, located in Wertle, Germany [10].

The production of synthetic natural gas (SNG) is known for many years, where methane is produced via catalytic processes, known as methanation, but also via biological processes. Among the biological processes, two different categories can be considered. The first one includes the biological treatment of biomass and wastes towards a methane and carbon dioxide gas, which in subsequent step requires only the removal of carbon dioxide and feed to the grid. The second category is known as biological methanation referring to enzymes which can treat hydrogen, carbon dioxide and/or carbon monoxide towards the production of methane [11]. In the present work, no further investigation on biological processes is presented. The prerequisite for methanation process is the composition of feeding gas, which has to meet the stoichiometric ratios and not to contain impurities that poison the catalysts. For power to fuel cases such as pre-combustion capture of landfill gas or post combustion capture from flue gases, almost 99% purity of carbon dioxide and hydrogen can be achieved. The ratio can be adapted according to the availability of CO_2 and installed capacity of

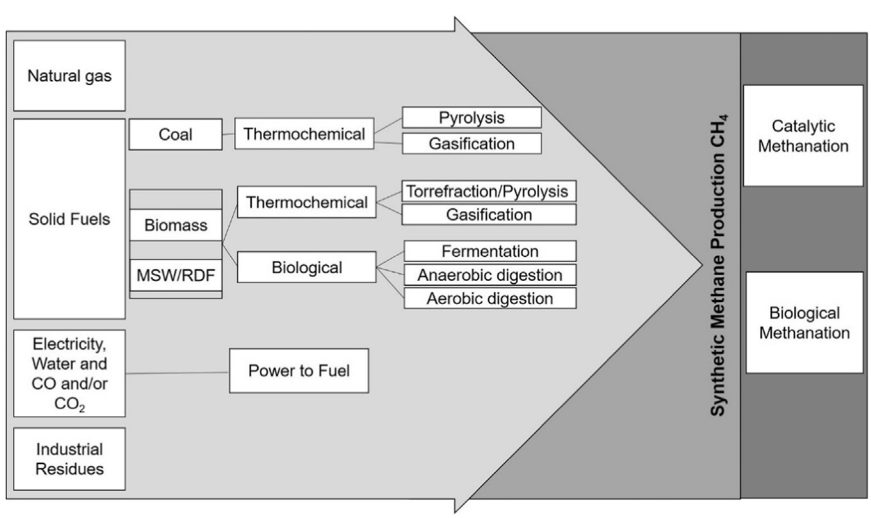

Fig. 1. Feedstock and processes for SNG production.