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Investigation of technical and economic aspects for methanol production through CO_2 hydrogenation

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ABSTRACT

This study investigates various design and operating aspects for the valorization of industrially captured CO_2 towards methanol production and the circumstances under of which this concept can be economically viable. Cost breakdown in various Power-to-Fuel concepts confirm that hydrogen cost is the most crucial factor. Several power delivery options for hydrogen production through electrolysis are compared for their economics. The use of cheap electricity in conjunction with adequate time coverage throughout the annum is of high importance for lowering the overall H_2 production costs. Also, a Power-to-Fuel system integrated with a coal fired power plant can be an interesting option for excess power transformation when the electricity sell is not profitable. The economic analysis on the H_2 production scheme revealed that each of the three main parameters for the determination of the H_2 cost (electrolyzer capital cost, electricity cost and storage cost) can play the key role in the feasibility of the plant depending on the concept each time. A considerable effort is needed in order the CO_2 derived fuels to reach a competitive level in the global market.

Introduction

The control of the Greenhouse Gas (GHG) emissions is one of the most challenging environmental issues that should be faced in the 21st century. The increase of CO_2 concentration from 280 ppm at the beginning of the Industrial Revolution to 370 ppm up-to-date is proved that a great part of it comes from anthropogenic factors and has disastrous effects on the global weather, the climate, and the average temperature [1,2]. According to IEA Blue Map Scenario for reducing CO_2 emissions, the Carbon Capture and Storage (CCS) is considered among the major measurements that should be addressed in large scale worldwide [1,3]. However, several

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obstacles such as high capital and operational cost, the several social and technical issues that should be addressed for the CO_2 safe storage in conjunction to the low carbon pricing policy, hinder the adoption of this option for CO_2 footprint mitigation.

A more feasible option to mitigate CO_2 emissions is to transform it into valuable compounds, like fuel organic and inorganic chemicals, namely as 'the CO_2 Capture and Utilization (CCU) concept'. The majority of CO_2 use in industry is for urea production, which accounts for more than half of the global annual usage [4]. Alternatively, CO_2 is utilized also physically in various applications such as refrigerant medium, in fire extinguishers and in the petroleum and NG industry for Enhanced Oil Recovery (EOR) and Enhanced Gas Recovery (EGR), respectively [3,5]. Even though CO_2 is a thermodynamically and kinetically stable molecule, various ways have been developed for CO_2 reduction, mainly based on the fact that the central carbon of the CO_2 molecule is electrophilic and can be easily attacked by nucleophiles [6]. The methods for CO_2 transformation can be sorted in six categories [4,7]: chemical reduction (i.e. Boudouard), electrochemical reduction [8], photochemical reduction (i.e. artificial photosynthesis), thermochemical conversion (i.e. dry reforming and hydrogenation), biological (i.e. photosynthesis, anaerobic conversion) [9] and inorganic transformation. This study focuses on synthesis of methanol from CO_2 through catalytic hydrogenation. Hence, the main feedstock apart from CO_2 that is required is pure hydrogen.

Since the H_2/CO_2 ratio for CO_2 hydrogenation towards hydrocarbons synthesis should be four (4) for methane and three (3) for methanol synthesis, the required amounts of hydrogen are very large. There are three routes for non-fossil derived hydrogen production: water electrolysis, biomass conversion and solar conversion [10,11]. Electrolysis is based on the water splitting into H_2 and O_2, the energy for this reaction is given in the form of electricity derived from Renewable Energy Source (RES) i.e. photovoltaic panels (PV), wind farms hydropower and geothermal plants. The second category consists of thermochemical (i.e. gasification, pyrolysis) or biochemical conversion of biomass, the intermediate products of which process are properly converted into rich H_2 fuel. Through solar conversion, either via thermolysis or photolysis, heat or photons are respectively used for hydrogen synthesis [12,13]. Biomass gasification and separation of H_2 from the produced product gas is not commercially available at large scales while thermolysis and photolysis processes are just beginning to be explored for their potential use by research projects in the EU [14,15]. In the present study, the hydrogen is considered to be derived from electrolysis, since this is the most mature and well-established technology even in industrial scale [16] and also it is not relied on carbon-contained source like biomass.

Several electricity sources have been proposed in the literature, including cheap grid electricity [17], surplus electricity from power plants [18,19], renewable electricity [20,21], etc. In the case of RES one of the major issues that should be addressed is the stochastic nature of the renewable power production and the extreme load fluctuations that require a highly flexible system for an efficient operation. Besides, the CCU unit cannot operate with maintain high performances under these variable throughputs conditions as it incorporates, according to the existing technology, since components such unit operations that have lower efficiencies at part load, such as compressors, steam production cycle and the CO_2 capture system itself. A technical solution to this issue is the intermediate storage of the produced H_2 in order to secure the constant hydrogen delivery to the CCU unit with the negative effect of the increase in the investment cost. Methanol is considered as one of the most valuable chemicals with a series of uses in various sectors (power, transport, steel, chemical industry) either as fuel or as block for the synthesis of other chemicals (dimethyl ether, formaldehyde, methyl tert-butyl ether, acetic acid, gasoline, etc). Moreover, since methanol has the lowest production cost to market price ratio among the fuels that can be potentially produced from CO_2, it is the most representative product of the so called "Power-to-Fuel" concept. In Iceland, a demonstration plant with capacity 4000 tons of renewable methanol per year is operating since 2011 and a larger plant with capacity 40,000 t/y is planned to be constructed by Carbon Recycling International (CRI) [22]. In Canada, Blue Fuel Energy will built a methanol plant with capacity 400,000 t/y of methanol, powered by renewable electricity [23].

The scope of this study is the investigation of various aspects for the valorization of CO_2 towards the production of liquid fuel (methanol), in large scale applications. These aspects are related to the power source for the hydrogen production through electrolysis (grid electricity, renewable energy source), the CO_2 capture scheme (selection of the proper capture technique) and the input gas (H_2 and CO_2) transportation options (pipeline, truck or trailer). The assessment is made in terms of minimization of methanol production cost by performing the economic evaluation, determining the boundary conditions and the next steps that should be done so that the proposed concept can be profitable.

Process description

The concept for liquid fuel (methanol) synthesis through CO_2 hydrogenation is shown in Fig. 1. The pure CO_2 stream is fossil derived and comes from separation and purification from combustion gases of a power plant or other intensive carbon emission industry (e.g. cement plant, steel industry).

The concept that is presented in this study is not based on a total utilization of the produced CO_2 from fossil fuel combustion (power plant or intensive industry). In case that the total amount of the CO_2 captured from the flue gases of a typical 300 MW_e coal fired power plant undergoes to hydrogenation, the required power duty for water electrolysis is estimated at 1.77GW_e which is technically infeasible and economically unprofitable.

Several studies dedicated to the techno-economic investigation of this concept can be found in the literature [17,19,24–29]. Among the major conclusions that are extracted from them is that the hydrogen production cost is most significant factor that affects the economics of this methanol-from-CO_2 concept.