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Novel process technologies for conversion of carbon dioxide from industrial flue gas streams into methanol

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ABSTRACT

This research aims to develop efficient process technologies that are capable of converting/utilising CO_2 streams into energy-rich liquid products (fuels). This would result in better solutions with near-zero-carbon-emissions level. From an energetic and economic point of view, methanol synthesis from CO_2 is a competitive alternate to methanol production from biomass. Our work considers the CO_2 balance for the technologies proposed, taking into account all CO_2 flows from/to the environment. Flue gas CO_2 streams released from electric power stations, steel industry, petroleum industry, and cement industry are good candidates for the developed technologies. Three new processes are developed and modelled for converting CO_2 streams into liquid methanol. The total cost of equipment and utility for all process scenarios are evaluated and compared. The energy targets as well as the CO_2 emissions (balance) are determined. Heat integration is performed on the best selected process technology. The case study employed for the present work is a power station plant burning natural gas for electricity production with a capacity of 112 MW, releasing 328 t/h flue gases to the atmosphere, of which CO_2 gas accounts for 14%; hydrogen required for CO_2 conversion comes from the chlor-alkali industry. The optimum process technology reached in this contribution results in methanol production of 0.625 t-per-tonne of CO_2 waste gas supply, leading to an annual production of 222,507 tons methanol with a profit of 56.55 M$/y. Thus, the CO_2 release to the environment is cut by about 62%.

1. Introduction

The 20th century can be considered as the century of rapid escalation in energy consumption. The large dependence on fossil fuels and their presence in limited amounts necessitates finding new alternatives. Also, the need for protecting the environment from the greenhouse gases (GHGs) that result from burning the carbon-based fuels urges us to search for suitable solutions in order to decrease their concentrations in the atmosphere. As a GHG, carbon dioxide (CO_2) accords more than 60% to climatic changes due to its high emissions to the atmosphere, where in the period between 2004 and 2013 global CO_2 emissions have had continued intense rise of about 2.5% per annum [1].

CO_2 is a naturally occurring gas, emitted as a side gaseous product during burning biomass and fossil fuels, and produced as a side-product in some industrial processes. Combustion of various types of fuels in different mobile and stationary energy systems results in emission of, not only pollutants like NO_x, SO_x, and solid particulates, but also to GHGs like CO_2 and CH_4. The natural carbon cycle can recycle 203 Gt of CO_2 each year, whereas the anthropogenic CO_2 is emitted at an approximate rate of 7 Gt every year, representing about 3.4% of the total CO_2 converted in the natural cycle [2]. Although the manmade CO_2 represents a small amount, the natural carbon cycle cannot recycle this excess CO_2, so it accumulates in the atmosphere leading to an increase in the greenhouse effect and hence a strong impact on climate change. Actually, CO_2 is blamed to be the most important factor causing the greenhouse effect, since it is the main influential anthropogenic GHG. It is believed that, the annual increase of the CO_2 emissions is 1.2%, and climate models predict that the CO_2 concentration in the atmosphere will reach about (540–970) ppm by 2100 [3]. The increase in the CO_2 concentration in the atmosphere has resulted in global warming, however, the carbon-level increase is not only anthropogenic, but it is also due to other natural processes such as the changes in the CO_2

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solubility in the oceans [4].

At present, the atmospheric concentration of CO_2 is about to surpass the 400 ppm mark. So we can say that, the current CO_2 concentration is higher than that of the pre-industrial period (280 ppm) by over than 100 ppm [5]. In order to mitigate the global warming, the Kyoto Protocol forced the European Union and some other 37 industrial nations to decrease their emissions on average to a level of 5.2%; this target is lower than that of year 1990, within 2008 to 2012 time period. In this framework, the Kyoto targets were peculiarly easy for Europe to achieve [6]. The Copenhagen Accord seeks in addition to restrict the global temperature increase to 2 °C by the year 2100, above the pre-industrial level [6]. Moreover and as pointed out by the International Energy Agency (IEA), in order to successfully accomplish the ± 2 °C target, carbon capture and storage (CCS) advanced technologies are needed; in this case the contribution of the total emissions reductions shall rather be 19% by 2050 [7].

In principle, three well-defined technical options are used to mitigate the CO_2 emissions; these approaches are basically energy efficiency, energy choices, and carbon capture. The captured CO_2 can then be subject to sequestration or utilisation. The former option requires switching between the different energy forms seeking to a less carbon intensive energy source. The latter option, on the other hand, requires developing the chemical processes towards increasing the energy efficiency by different methods like choosing more selective catalyst, selecting a more efficient process, or by performing a suitable energy integration over the whole process in order to maximise heat recovery and hence minimise the demand for fuels [8]. Controlling CO_2 concentration in the atmosphere by the capture technology is costly and energy intensive option. CO_2 utilisation as a feedstock for chemicals production is an excellent option since it does not only contribute to attenuate the world climatic changes generated by the increased CO_2 emissions, but also presents a great challenge in exploring novel concepts and chances for catalytic, process-wise, and industrial development.

During the past years, direct CO_2 hydrogenation to methanol (MeOH) involving process design activities has evidently attracted the attention [9–11]. Here, it is worthy to point out the important role of incorporating rigorous and robust simulation models in the decision making process regarding such technologies as in the gas processing industry [12–16]. Finding innovative ways of producing MeOH from these spent sources, subsequently upgrades the economic value of the off-gases and reduces the specific CO_2 emissions of industrial plants [17]. According to literature studies and as a CO_2 reduction measure, CO_2 gas can react with hydrogen (H_2) to produce MeOH directly that could be easily transported and is considered to be a future renewable energy carrier [18]. In this way, MeOH can be produced at a lower reaction temperature with higher selectivity.

Methanol (CH_3OH) is an industrially important substrate that can be used to produce several important chemicals, like acetic acid and formaldehyde, in addition to being a solvent on its own. This longer-chain liquid petrochemical is in big demand, due to the ease in its storage and transportation; it was anticipated for instance that the global methanol consumption will reach up to 58.6 million metric tons (MMT) by 2012 [19]. According to the Methanol Institute (MI), the demand for MeOH production is now increasing and expected to boost to well over 100 million tons by 2020, where the current emerging energy applications only represent about 40% of methanol demand and are responsible for much of that market growth [20]. As pointed out by Olah in his state-of-the-art essay on the methanol economy, recycling of CO_2 into MeOH generation can be attributed as a feasible approach to tackle our carbon conundrum, diminishing the dependence on fossil fuels while at the same time helping in mitigating the matters associated with excessive CO_2 emissions [21]. The strong demand of MeOH is not only to be used as a fuel, but also as an alternative starting raw materials for petrochemicals production [22].

The combustion of MeOH will result in neither NO_x nor SO_x to exhaust gases, turning it into a less polluting option in comparison to conventional fossil fuels [23]. Fossil fuels are burned at higher temperatures than that required for burning MeOH, thus the MeOH combustion unit design is simpler [24]. To efficiently replace fossil energy sources and oil-derived transportation fuels, it is necessary to develop highly profitable and sustainable technologies for producing MeOH and other alternative synthetic fuels. The utilisation of CO_2 in MeOH synthesis can reduce the intake from natural resources, because the fate of CO_2 from flue gas will eventually be emitted after a while by MeOH combustion. More specific, the sustainability aspect of CO_2 blending/valorisation in MeOH synthesis emerges from the chaining of the carbon atom in the MeOH molecule for longer time and also because of the reduction in the resource intake, i.e. CH_4, caused by such blending. This approach carry a great potential as one of the possible/promising transition strategies towards the *methanol economy* concept, mitigating large amounts of CO_2 and reducing the reliance on carbon-based feeds, like natural gas and coal [25]. Such MeOH will then be a feedstock for the key products of chemical and petrochemical synthesis and environmentally clean motor fuels [26].

The present contribution throws the light on the environmental problems caused by CO_2 accumulation in the atmosphere, together with the energy crisis and the rapid depletion of the fossil fuels. In this paper, solutions for both the aforementioned problems are introduced by presenting new approaches for capturing/converting flue gas CO_2 streams generated from power stations into liquid fuel methanol. The introduced concepts seek to reduce both the fossil fuel consumption and the atmospheric emissions by recycling the secondary CO_2 as a carbon source instead of using natural gas. Three chemical conversion process technologies are developed for CO_2 utilisation in MeOH synthesis and modelling/simulation tasks are performed, employing the Aspen HYSYS® commercial software platform. Economic and environmental implications are further assessed for the different proposed process scenarios. Heat integration studies are also conducted for achieving energy efficiency in the process schemes. Results attained in this work will shed light on the further development of diverse GTL processes.

2. Methods

The conventional way for MeOH production relies on the use of natural gas as a source for synthesis gas (syngas) production. The first step includes desulphurisation of natural gas before introducing it to the syngas production step to prevent the catalyst poisoning. After its production, syngas is fed to the reactor at a certain temperature and pressure. The effluent of the reactor consists of MeOH product and water, in addition to unconverted syngas. The reactor outlet is then directed to a distillation tower to separate MeOH as a main product, and recycle the unconverted syngas back to the MeOH convertor.

In this work, methanol is produced via the CO_2 hydrogenation route. The products of CO_2 hydrogenation like MeOH and hydrocarbons are excellent fuels in internal combustion engines, and are easily stored and transported. Methanol is a raw material which feeds several chemical industries, however, a suitable source for H_2 production should be selected in order to support the chemical recycling of CO_2 to MeOH through an economic process. Most researchers suggested H_2 generation either by using significant sources of remaining fossil fuels, mainly natural gas, or from splitting water (by electrolysis or other cleavage). But our research proposes H_2 generation through chlor-alkali industry. The H_2, in this context, is available at no cost since it is a by-product from the chlor-alkali industry of an existing local plant. Thus, this approach is considered as a by-product valorisation option for an efficient utilisation of H_2 by-product streams of the aforementioned technology. The H_2 figure, which is available at such local industry, is assigned according to the requirement of our developed processes (typically less than the available H_2 amount generated at the local facility). Also, as pointed out earlier, most of research efforts preferred to produce MeOH starting from natural gas, emitting large amounts of CO_2 and