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Design and simulation of a methanol production plant from CO_2 hydrogenation

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ABSTRACT

There has been a large increase in anthropogenic emissions of CO_2 over the past century. The use of captured CO_2 can become a profitable business, in addition to controlling CO_2 concentration in the atmosphere. A process for producing fuel grade methanol from captured CO_2 is proposed in this paper. The process is designed and simulated with Aspen Plus. The CO_2 is captured by chemical absorption from the flue gases of a thermal power plant. The hydrogen is produced by water electrolysis using carbon-free electricity. The methanol plant provides 36% of the thermal energy required for CO_2 capture, reducing considerably the costs of the capture. The CO_2 balance of the process showed that it is possible to abate 1.6 t of CO_2 per tonne of methanol produced if oxygen by-product is sold, or 1.2 t if it is not.

1. Introduction

Anthropogenic emissions of carbon dioxide have increased vertiginously in the last century. Despite the uncertainty about the consequences of this phenomenon in the long term, great part of the scientific community believes that increasing the CO_2 concentration in the atmosphere is closely linked to the recent global temperature increase. Thus, great efforts have been made to capture CO_2 (Rivera-Tinoco and Bouallou, 2010) and re-inject it in the underground (Câmara et al., 2013), so as to minimise the increase of its concentration in the atmosphere.

Approximately 40% of anthropogenic CO_2 emissions originate from coal or natural gas power plants (Amann, 2007). Therefore, the capture of CO_2 emitted by thermal power plants is of major importance. However, the costs of capture are still high since the reduction on the power plant efficiency caused by the CO_2 capture unit is still considerable (Harkin et al., 2012).

If the captured CO_2 were used as raw material in the production of a marketable product, its capture and sale could become not only economically viable but also a profitable business. Another major challenge of this century is to substitute fossil fuels by renewable ones. Thus, the recycling of CO_2 as a feedstock for the production of hydrocarbons substituents presents great economic and environmental interests.

Methanol is widely used in the chemical industry, mainly in the production of formaldehyde, MTBE (methyl tert-butyl ether) and acetic acid. Moreover, methanol has excellent combustion properties, which allows its use as a fuel in vehicles, although it has only about half the energy density of gasoline. Furthermore, methanol is less polluting than conventional fossil fuels (Olah et al., 2008).

Methanol can be used in a wide range of concentrations mixed with gasoline, from small concentrations where it is an additive up to high concentrations such as the M85 (15% gasoline and 85% methanol). Vehicles fuelled by pure methanol (M100) are also viable and even more efficient (Olah et al., 2008). However, the toxicity of methanol is often cited as restriction for its use as fuel. Methanol is extremely toxic when ingested in large quantities, causing blindness and possibly death.

DME (dimethyl ether), which is a possible substitute for conventional diesel, can be synthesized from the dehydration of methanol. Therefore, the production of methanol from captured CO_2 may cause a reduction in the consumption of fossil fuels and enable CO_2 recycling.

The main objective of this study is to evaluate and quantify the abatement of CO_2 through the production of fuel grade methanol by the process proposed in this paper.

1.1. Conventional methanol production process

Most of the methanol produced industrially today is derived from the catalytic conversion of synthesis gas (gaseous mixture of

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CO, CO_2 and H_2). Although it may be produced from various carbonaceous components, most of the synthesis gas currently produced is derived from natural gas.

The commercial catalyst $Cu/ZnO/Al_2O_3$ is commonly employed in the production of methanol from synthesis gas. It allows the production of methanol under relatively “soft” conditions (210–270 °C and 50–100 bar), with a selectivity of 99% in relation to CO_x (Ullmann, 2002). By-products produced are mainly higher alcohols, methane, methyl formate and DME.

Considering the natural gas used as reagent and fuel, a typical plant consumes between 29 and 33 GJ of natural gas per metric ton of methanol produced (Uhde).

1.2. CO_2 to methanol process

1.2.1. Overview

Methanol can be produced from CO_2 in two different ways: in one step or in two steps. The one step conversion is the direct hydrogenation of CO_2 to methanol. In two steps conversion, CO_2 is first converted into CO through the Reverse Water Gas Shift (RWGS) reaction and then hydrogenated to methanol. In this paper, the conversion of CO_2 in one step was employed. Some routes of conversion of CO_2 to produce fuels are shown in Fig. 1.

The source of CO_2 may be the flue gases from thermal power plants (e.g. coal, natural gas) or factories producing steel, cement and other major emitters of CO_2. Hydrogen must be produced in a carbon-free way, such as biological production from algae or the electrolysis of water using carbon-free electricity (Demirci and Miele, 2013).

Exothermic reactions (Eqs. (1) and (2)) produce methanol. The RWGS reaction (Eq. (3)) occurs in parallel.

$$CO_{(g)} + 2H_{2(g)} \Leftrightarrow CH_3OH_{(l)} \quad \Delta H = -128\ \text{kJ/mol}(298\ \text{K}) \tag{1}$$

$$CO_{2(g)} + 3H_{2(g)} \Leftrightarrow CH_3OH_{(l)} + H_2O_{(g)} \quad \Delta H = -87\ \text{kJ/mol}(298\ \text{K}) \tag{2}$$

$$CO_{2(g)} + H_{2(g)} \Leftrightarrow CO_{(g)} + H_2O_{(g)} \quad \Delta H = +41\ \text{kJ/mol}(298\ \text{K}) \tag{3}$$

The production of methanol from CO_2 hydrogenation has been the subject of many recent studies. Joo et al. (1999) studied the production of methanol in two steps and concluded that it has a higher yield than the process in one step. Mignard et al. (2003) proposed a methanol synthesis process from CO_2 captured from flue gas of a coal power plant and electrolytic hydrogen. The process depends on availability of waste heat in the power plant to provide thermal energy to the process in order to have a significant abate of CO_2. In the absence of these thermal sources, CO_2 abatement is almost null. Mignard and Pritchard (2006) compared the energy efficiencies of production processes of methanol, ethanol and gasoline from the CO_2 hydrogenation. The methanol process showed the highest efficiency. Pontzen et al. (2011) carried out experiments to compare methanol from CO_2 production over $Cu/ZnO/Al_2O_3$ catalyst with the conventional syngas production process. The CO_2-based process showed lower productivities when compared to the conventional one. Soltanieh et al. (2012) studied and analysed economically the co-production of methanol and electricity from captured CO_2 and carbon-free hydrogen. Van Der Ham et al. (2012) designed a CO_2 to methanol process using a fluidised-bed membrane reactor. The process provided significant CO_2 abatement, but did not present economic viability.

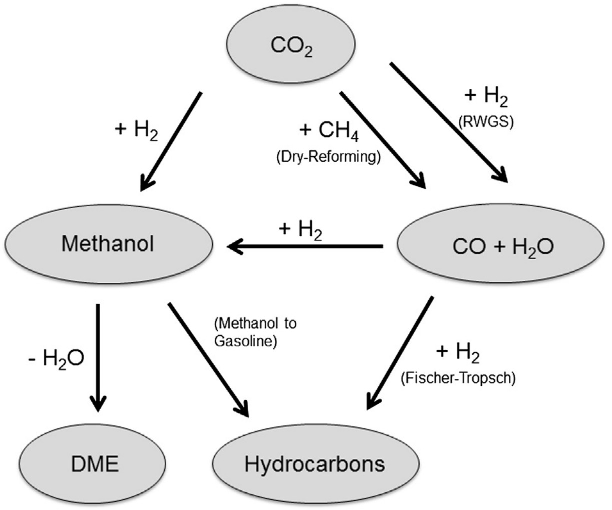

Fig. 1. CO_2 utilisation diagram.

1.2.2. Catalysts

The commercial catalyst $Cu/ZnO/Al_2O_3$ has been studied by several authors (Mignard and Pritchard, 2006; Mignard et al., 2003; Pontzen et al., 2011; Sahibzada et al., 1998) for the production of methanol from CO_2, although it is less efficient with supply of CO_2 than CO/CO_2 (ADEME, 2010).

Catalysts better adapted to CO_2 feed have been extensively studied. In many cases, the proposed catalysts are based on Cu–Zn oxides containing additives such as ZrO_2, GaO_3 and SiO_2 over alumina. Guo et al. (2011) investigated the effects of the procedure of preparation on the performance of a $Cu/ZnO/ZrO_2$ catalyst. Zhang et al. (2006) studied the effect of zirconia addition on γ-Al_2O_3 support of a Cu based catalyst. Raudaskoski et al. (2009) reviewed papers about copper-based zirconia-containing catalysts. Chiavassa et al. (2009) studied the synthesis from Ga_2O_3–Pd/silica catalyst. Sahibzada (2000) reviewed kinetic results of Pd-promoted Cu/ZnO catalyst.

1.2.3. Installations

Carbon Recycling International installed at the end of 2010 a unit capable of producing 3000 t/y of methanol in Iceland (ADEME, 2010). This unit have a capacity of about 10 t of methanol from 18 t of CO_2 (Carbon Recycling International, 2009). The CO_2 used comes from the Svartsengi geothermal plant and an aluminium production plant. Hydrogen is generated from the electrolysis of water using a renewable source of electricity.

Mitsui Chemicals Inc. has a pilot unit in Japan capable of producing 100 t of methanol per year. CO_2 used comes from an ethylene production plant of Osaka Works Petrochemical Complex (ADEME, 2010).

The economic viability of plants depends on several factors, such as the price of a barrel of oil, electricity price, CO_2 price and use of by-products.

2. Methods

This paper proposes an enhancement of the process proposed by Van-Dal and Bouallou (2012), and also provides greater detail on the calculations as well as a deeper analysis. CO_2 captured from flue gases of a coal power plant and hydrogen generated from water electrolysis are fed into a methanol plant. An overview of the process is presented on Fig. 2.

Electrolysis of water is carried out using carbon-free electricity source, such as renewable (e.g. hydraulic, eolic, solar or biomass) or nuclear. However, the CO_2 capture unit and methanol unit are supplied with electricity from the coal power plant. Thus, hydrogen can be imported from somewhere where carbon-free energy is available and used in methanol plants installed in places where only fossil