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Equilibrium thermodynamic analyses of methanol production via a novel Chemical Looping Carbon Arrestor process

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ABSTRACT

Methanol economy is considered as an alternative to hydrogen economy due to the better handling and storage characteristics of methanol fuel than liquid hydrogen. This paper is concerned about a comprehensive equilibrium thermodynamic analysis carried out on methanol production via an innovative Chemical Looping Carbon Arrestor/Reforming process being developed at the University of Newcastle in order to reduce both energy consumption and carbon emissions. The detailed simulation revealed thermodynamic limitations within the Chemical Looping Carbon Reforming process however on the other hand it also confirmed that the new concept is a low energy requirement and low emission option compared to other methanol production technologies. Specifically, the mass and energy balance study showed that the Chemical Looping Carbon Reforming process typically consumes approximately 0.76–0.77 mole methane, 0.25–0.27 mole carbon dioxide, 0.49–0.50 mole water, and 0.51 mole iron oxide (in a chemical looping manner) per mole of methanol production. Moreover, the energy efficiency of Chemical Looping Carbon Reforming process was found to be ~64–70% and its emission profile was found as low as 0.14 mole carbon dioxide per mole of methanol, which is about 82–88% less than the conventional methanol production process and well below the emission levels of other emerging methanol production technologies.

1. Introduction

Hydrogen is considered as the key element of the sustainable energy scenarios of the future. Hydrogen is a clean fuel, has a very high energy density (≈120 MJ/kg), and can be utilised efficiently in fuel-cells to produce heat and power. However, success of hydrogen based energy systems/hydrogen economy greatly depends on the availability of suitable methods for efficient production and storage of hydrogen [1]. Safe storage of hydrogen remains an unresolved technical challenge and as such has been the subject of numerous studies [2].

Techniques for storing hydrogen include compression, liquefaction, physio-sorption (e.g. in carbon nano-tubes), metallic hydrides, and complex hydrides. However, all of them suffer from a combination of high cost, high energy demand, technical difficulty and inefficiency [1]. There are, however, more suitable methods of hydrogen storage which have been overlooked, for example, the use of hydrocarbon-based H_2 carries – methanol (CH_3OH). The use of methanol as energy carrier offers an alternative to hydrogen economy – methanol economy.

Methanol has a relatively high hydrogen storage capacity and possesses higher energy density than that of hydrogen. At room temperatures and pressures methanol is in its liquid form and, hence, can readily be stored and transported, making it an excellent transportation fuel. Methanol can also be blended with gasoline (e.g. M15 and M85), and for its application in automobile sector only limited modifications to the existing gasoline based engine systems are required [3].

The application of methanol in transportation sector is especially important for Australia, where oil security becomes a key issue due to its relative isolation and reliance on transportation fuels. The growing import dependence also leaves Australia more vulnerable to potential disruptions in overseas crude oil and petroleum products supply chains. According to a recent IEA report, net-oil imports for Australia have increased from 12,000 bpd in 2000 to 519,000 bpd in 2011, the highest on record [4]. In contrast, in 2011 Australia's oil production stood at 484,000 barrels per day (bpd) which is a drop of 41% from the peak of 819,000 bpd in 2000 [4]. Such a rapid transformation in the structure of country's oil supply–demand is quite alarming.

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Nomenclature

CLCR	Chemical Looping Carbon Arrestor/Reforming
CRM, SRM	CO_2/steam reforming of methane
E_p	the energy content of the product (i.e. methanol)
E_f	the energy in the feedstock
E_a	auxiliary energy requirement in the process
GHG	greenhouse gasses
ΔH_c°	the low heat of combustion of fuels
m_{CO_2}	CO_2 emission
m_{CH_3OH}	methanol production
S_R	syngas (molar) ratio
S_R'	alternative/revised syngas (molar) ratio
Subscript	
p	product
a	auxiliary
f	feedstock

Methanol blended gasoline may offer an excellent solution. Methanol is a clean burning, high octane blending component processed from alternative non-petroleum energy sources such as natural gas, coal and biomass [3]. It has been commercially blended into gasoline at various times and locations since 1980 in United States, China, New Zealand and parts of the Europe [5]. Because carburetted fuel systems were most prevalent in the road vehicle fleet at that time and such vehicles had limited ability to handle high oxygen levels in the fuel, methanol concentrations were generally limited to 3–5 volume percent of the gasoline blend [6]. However, with today's modern pressurised fuel injector systems with computerised feedback control loops, blends with as high as 15 volume percent methanol (M15) can now be successfully used in the modern vehicles that are on the road today [7].

The major impediment in realising methanol economy, and in particular, the large-scale deployment of methanol-gasoline blends, is the high energy costs associated with generating hydrogen/syngas needed to synthesise methanol. Conventional steam reforming (SRM), dry/CO_2 reforming, partial oxidation, oxy reforming and auto-thermal reforming of methane, as well as coal/biomass gasification are the most common processes used for the production of syngas for methanol production [8]. Among them, SRM is the predominant technology used at present for methanol production and accounts for approximately 75% of global methanol production [9]. In general, the energy required to drive the syngas production using the above-mentioned conventional processes is quite high and typically constitutes about 50% of the total energy demand of the methanol production process [10]. This invariably results in high GHG emissions during the production phase. In addition to large energy and GHG footprints, significant operational/production costs and considerable capital investment required for conventional syngas production processes are among the major barriers against their widespread deployment for methanol production.

A number of new syngas production methods have been proposed in recent years, including the use of plasma and catalytic type reactors. Yao et al. [11] examined the approach of methane selective oxidation to syngas and finally methanol fuel using non-thermal pulsed plasma. Aasberg-Petersen et al. [12] reviewed the catalytic conversion of natural gas into syngas using various catalysts and catalytic processes. Yet, these methods have largely failed to make any major attraction primarily because of the low yields and selectivity of the product streams, as well as complex hardware and hence high capital costs. It is, therefore, time to consider an entirely new strategy that firstly meets the essential requirement of inexpensive capital, operation and production costs, while offering the prospect of higher product yields, lower energy demands and smaller GHG footprint.

As a respond to the above technology bottleneck, an alternative methanol synthesis process based on chemical looping concept was proposed and developed at the University of Newcastle, Australia. It is also part of a larger programme being carried out at the University of Newcastle in which chemical looping concept has been applied to a number of areas other than combustion. Moghtaderi et al. [13] applied chemical looping concept for oxygen production. The working principle behind the chemical looping air separation (CLAS) process for oxygen production involves the cyclic oxidation and reduction reactions of metallic oxide particles in two separate reactors as a means of separating oxygen from air [14]. The process can be used for either high purity oxygen production [15] or can be integrated to oxy-fuel combustion and gasification plant to suffice their need for oxygen by eliminating nitrogen from air stream in the air reactor [16]. In the advanced version of the CLAS-oxy-fuel integration proposed by Shah et al. [17], efforts have been made to provide coal-natural gas based hybrid power plant called chemical looping oxy-combustor (CLOC). Moghtaderi et al. [18] also applied chemical looping concept for biomass gasification using construction demolition waste material. The process can produce hydrogen rich synthesis gas by capturing CO_2 via construction demolition waste material. Also, the research team has successfully applied chemical looping concept for ventilation air methane abatement. The two processes being developed in this area are called chemical looping VAM abatement unit [19] and stone dust looping VAM abatement unit [20]. The former one utilises metal oxide oxygen carriers while the later one uses stone dust (limestone). The novel chemical looping based Chemical Looping Carbon Reforming (CLCR) process proposed in this work utilises natural gas and CO_2 as the feedstock and can produce synthesis gas with a CO/H_2 ratio suitable for methanol synthesis and/or other Fischer–Tropsch processes.

The novelty of the CLCR process lies in its ability to minimise carbon losses throughout the process by converting CO_2 into intermediates (CO and carbon) then methanol via a chemical looping route followed by carbon gasification. The CLCR process features carbon gasification for achieving higher yields and greater utilisation of CO_2 (i.e. if deployed at commercial scales the CLCR process can offer a large sink for CO_2 sequestration). In this way, methanol may be produced with less energy requirement and theoretically negative CO_2 emission. The CLCR process also eliminates the need for an expensive air separation unit (i.e. oxygen plant) as required in other conventional processes. Apart from lower energy requirement and greater utilisation of CO_2, CLCR process employs a compact multi-loop-seal modular design to ensure better oxygen carrier circulation, more efficient heat transfer and a smaller process plant footprint.

Use of natural gas as the feedstock for CLCR process is also considered quite suitable for Australia where natural gas resources are abundant. If CO_2 is sourced from ambient, the process may become even more attractive by mimicking nature's photosynthesis process allowing for the chemical recycling of global CO_2 emission. To the best of our knowledge, no equilibrium thermodynamic study or process simulation has been performed for CLCR process. The only relevant work is the one published by Zeman and Castaldi [9] who solely performed the calculations for a process similar to