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Methanol and dimethyl ether from renewable hydrogen and carbon dioxide: Alternative fuels production and life-cycle assessment

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ABSTRACT

In this work we investigate two renewably based alternative fuels; methanol and dimethyl ether. The ultimate feedstocks for production are wind-based electrolytic hydrogen and carbon dioxide captured from an ethanol fermentation process. Dimethyl ether production was modeled in ASPEN Plus using a previously simulated methanol production facility. The facilities use 18.6 metric tons (mt) of H_2 and 138.4 mt CO_2 per day. Methanol is produced at a rate 96.7 mt/day (99.5 wt%) and dimethyl ether is produced at a rate of 68.5 mt/day (99.6 wt%). A full comparative life-cycle assessment (cradle-to-grave) of both fuels was conducted to investigate their feasibility and sustainability. Renewable methanol and dimethyl ether results were independently compared and this renewable process was also compared to conventional production routes. Results show that production of dimethyl ether impacts the environment more than methanol production. However the combustion of methanol fuel evens out many of the emissions metrics compared to dimethyl ether. The largest environmental impact was found to be related to the fuel production stage for both fuels. Both biofuels were shown to be comparable to biomass-based gasification fuel production routes. Methanol and dimethyl ether from CO_2 hydrogenation were shown outperform conventional petroleum based fuels, reducing greenhouse gas emissions 82−86%, minimizing other criteria pollutants (SO_x, NO_x, etc.) and reducing fossil fuel depletion by 82−91%. The inclusion of environmental impacts in feasibility analyses is of great importance in order to improve sustainable living practices. The results found here highlight the favorable feasibility of renewably produced methanol and dimethyl ether as alternative fuels.

1. Introduction

The use of fossil fuels in the industrial era has led us to unprecedented success in terms of technology and quality of life. However, with reserves being depleted and rising levels of CO_2 in the atmosphere, it is important that we not only develop sources of non-fossil based energy but also find ways to reduce carbon emissions. There are three proposed methods of lowering CO_2 emissions and ambient CO_2 levels; reduce the amount of CO_2 produced, store or sequester CO_2, or use CO_2 as a chemical feedstock. CO_2 conversion is of interest due to the economic gains that can potentially be made through its development. This is a difficult process due to the inherent thermodynamic stability of CO_2. Generally, high energy processes or feedstocks are required for its conversion. As these techniques can be costly, the current use of CO_2 industrially is mainly limited to the production of urea, salicylic acid and various carbonates (Saeidi et al., 2014). Hydrogen is one high energy feedstock that can react with carbon dioxide. The result of these reactions is dependent on the catalyst, operating conditions and reaction time. The products of carbon dioxide hydrogenation can include; hydrocarbon fuels, formamides, carboxylic acids, methanol and more (Jessop et al., 2004; Gnanamani et al., 2015; Jadhav et al., 2014). Due to its low production costs, well established infrastructure and advanced processing technology, methanol is an ideal candidate for the conversion of CO_2 with H_2 (Tremel et al., 2015). Our previous work proposed a method of producing methanol from renewably derived H_2 and CO_2 (Matzen et al., 2015). While there a many methods for producing renewable H_2 this work focused on electrolysis, specifically powered by wind energy. CO_2 can also come from various sources but this paper used CO_2 captured and compressed from an ethanol fermentation process. The direct use of CO_2 and H_2 avoids many of the complications and variabilities dealt with in using syngas, especially when it is produced via biomass gasification. As well, this feedstock is

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chemically similar to syngas and relies on the same technology as conventional methanol production.

Recently, the demand for methanol has shown a substantial increasing trend. The emergence of large scale methanol production facilities have been able to meet this demand. These plants typically use natural gas (NG) as the source of syngas for methanol production. There is logically an economic correlation between natural gas prices and oil prices and consequently oil prices and methanol prices (see Fig. 1). As fossil fuel sources are depleted, prices of natural gas (and other fossil fuels) will continue to increase, ultimately leading to an increased methanol production cost (Singh and Singh, 2012; Shafiee and Topal, 2009). The use of renewables in the production of methanol would not only avoid the issues associated with an increase in fossil fuel cost but would eliminate methanol's dependency on fossil fuel feedstocks. Since methanol can be used as a fuel source itself, its production from renewables would help to reduce the reliance of our energy and transportation sectors on fossil fuels. Olah (2005), Olah et al. (2009) presents this idea in a very concise term called the "Methanol Economy". Put short, this concept purveys the idea that methanol can be used as an alternative way for storing, transporting and using energy.

We previously recognized that inexpensive backend processes for methanol conversion should be investigated to increase the economic potential of the facility. Methanol can readily be converted to dimethyl ether (DME) via catalytic dehydration. Due to the simplicity of this conversion process, its industrial maturity and the potential of DME as an alternative fuel; we have also chosen to investigate DME production. This process can handle any feedstock or methanol production technology that gives reasonably pure methanol as an output. Dimethyl ether has recently gained attention for its potential use as an alternative transportation fuel. DME has a higher cetane number than diesel (55–60 versus 40–55 for diesel) and its combustion also results in lower NO_x and SO_x emissions. While DME is a volatile organic compound (VOC) it is non-toxic, non-carcinogenic, non-teratogenic and non-mutagenic. It has also been shown to be environmentally benign (Semelsberger et al., 2006).

It is important to note that both the production and utilization of fuels causes detrimental environmental emissions. It is estimated that 23% of CO_2 emissions comes from the transportation sector. With the increase in demand for personal transport vehicles this value is expected to rise. A main opportunity for reducing CO_2 emissions is the switching of fuel sources used in the transportation sector. Potential fuels would be biofuels, hydrogen, renewable electricity, or less CO_2 intensive fossil fuels (Kobayashi et al., 2007).

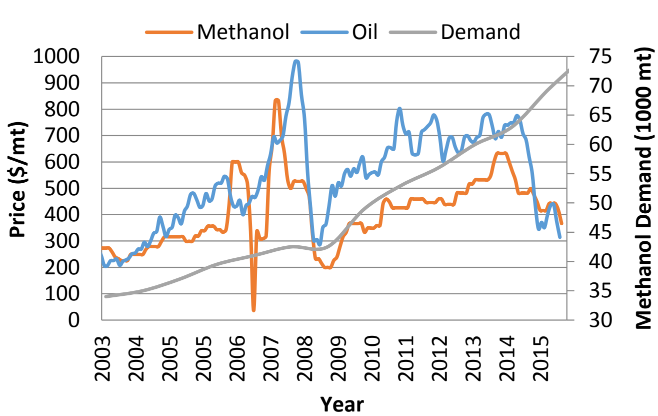

Fig. 1. Methanol price and demand in recent history (Methanex, 2015; U.S. Energy Information Administration, 2015; Semelsberger et al., 2006).

The use of bio-based fuels ultimately recycles CO_2, as the original carbon source in these cases is atmospheric CO_2. Hence, the CO_2 released in the combustion of methanol/DME produced in this study would be recycled back into the atmosphere.

In order to more definitively compare the impact fuels have on the environment, additional studies are required. Life-cycle assessment (LCA) has been a technique to fully evaluate the environmental impact a product has from "cradle-to-grave". That is, LCA looks at all of the activities in the course of a product's life, from the production of raw materials for its manufacture to the products ultimate disposal. This helps assess the total environmental burden a product might have and avoids shifting environmental problems from one output to another (e.g. air emissions for solid wastes) or from one cycle stage to another. This "problem shifting" is common, as environmental concerns are generally bounded by the fences of the production facility. Energy requirements and emissions for processes like transportation or raw material production are usually ignored in less rigorous assessments. A cradle-to-grave analysis is a holistic process as it shows the interconnectedness of the whole life-cycle of a chemical to the environmental burdens it entails (de Bruijn et al., 2004).

A number of articles have been published based on the life-cycle analysis of methanol production. However, the renewable based processes mainly focus on gasification of biomass as the ultimate chemical feedstock. A substantial review of current literature work can be found in Quek and Balasubramanian (2014). Wu et al. (2006) have conducted a well-to-wheels investigation into using switchgrass gasification to produce liquid fuels, including methanol and DME. ASPEN Plus was used to model biofuels production and Argonne's GREET (Greenhous gases, Regulated Emissions, and Energy use in Transportation) model was used to estimate environmental impacts. An extensive report on DME production, use and life-cycle can also be found in work prepared by the University of California Davis and Berkeley (The University of California, 2014). Together, renewable methanol and DME show exciting promise in the light of sustainability of processes and technological feasibility. However, most work in methanol and DME production focuses on biomass gasification routes rather than direct CO_2 hydrogenation. In fact, there seems to be a substantial lack of life-cycle assessments in direct CO_2 conversion into fuels (Cuellar-Franca and Azapagic, 2015).

The purpose of this study is to conduct a life-cycle assessment for novel methanol and DME production for use as alternative fuels. Production routes use wind-based electrolytic hydrogen and CO_2 captured and compressed from an ethanol fermentation process. We use a combinatory technique of process simulation using ASPEN Plus and LCA formulation using GREET to produce a full life-cycle assessment. Cradle to gate metrics are produced for wind-based H_2, liquefied CO_2 from ethanol fermentation, methanol and dimethyl ether. Life cycle emissions are tabulated and a life-cycle impact assessment is conducted. A cradle-to-grave analysis is also conducted and compared to other methanol/DME production techniques (biomass and natural gas gasification) as well as petroleum based fuels. Data produced includes greenhouse gas emissions, criteria pollutant (CO, NO_x, SO_x, etc.) emissions and energy use. Collectively this work highlights the importance of LCA in fuel use and the potential reduction in environmental impact that could be realized through the use of renewably produced methanol and dimethyl ether.

2. Methods and data

2.1. Dimethyl ether simulation

The production of DME from methanol follows a simple