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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<sub>2</sub> and 138.4 mt CO<sub>2</sub> 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<sub>2</sub> hydrogenation were shown outperform conventional petroleum based fuels, reducing greenhouse gas emissions 82–86%, minimizing other criteria pollutants (SO<sub>x</sub>, NO<sub>x</sub>, 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.

**Keywords:** Alternative fuels, CO<sub>2</sub> capture and utilization, Electrolytic hydrogen, Wind power, Methanol production, Dimethyl ether production, Life-cycle assessment

## 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<sub>2</sub> 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<sub>2</sub> emissions and ambient CO<sub>2</sub> levels; reduce the amount of CO<sub>2</sub> produced, store or sequester CO<sub>2</sub>, or use CO<sub>2</sub> as a chemical feedstock. CO<sub>2</sub> 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<sub>2</sub>. Generally, high energy processes or feedstocks are required for its conversion. As these techniques can be costly, the current use of CO<sub>2</sub> 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<sub>2</sub> with H<sub>2</sub> (Tremel et al., 2015). Our previous work proposed a method of producing methanol from renewably derived H<sub>2</sub> and CO<sub>2</sub> (Matzen et al., 2015). While there are many methods for producing renewable H<sub>2</sub> this work focused on electrolysis, specifically powered by wind energy. CO<sub>2</sub> can also come from various sources but this paper used CO<sub>2</sub> captured and compressed from an ethanol fermentation process. The direct use of CO<sub>2</sub> and H<sub>2</sub> 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 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  $\text{NO}_x$  and  $\text{SO}_x$  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).

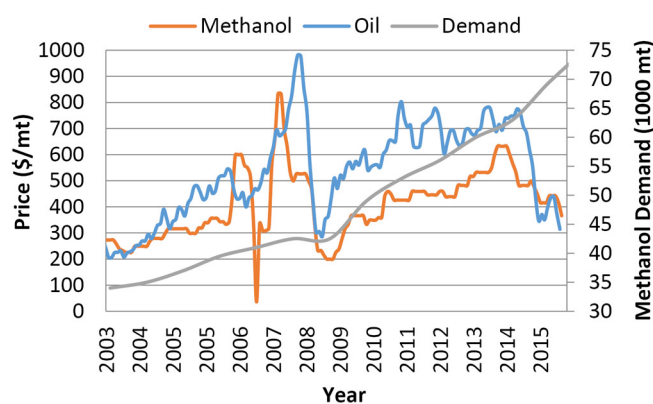
It is important to note that both the production and utilization of fuels causes detrimental environmental emissions. It is estimated that 23% of  $\text{CO}_2$  emissions comes from the transportation sector. With the increase in demand for personal transport vehicles this value is expected to rise. A main opportunity for reducing  $\text{CO}_2$  emissions is the switching of fuel sources used in the transportation sector. Potential fuels would be biofuels, hydrogen, renewable electricity, or less  $\text{CO}_2$  intensive fossil fuels (Kobayashi et al., 2007). The use of bio-based fuels ultimately recycles  $\text{CO}_2$ , as the original carbon

source in these cases is atmospheric  $\text{CO}_2$ . Hence, the  $\text{CO}_2$  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 switch-grass gasification to produce liquid fuels, including methanol and DME. ASPEN Plus was used to model biofuels production and Argonne's GREET (Greenhouse 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  $\text{CO}_2$  hydrogenation. In fact, there seems to be a substantial lack of life-cycle assessments in direct  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{H}_2$ , liquefied  $\text{CO}_2$  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 ( $\text{CO}$ ,  $\text{NO}_x$ ,  $\text{SO}_x$ , 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.

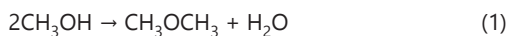


**Fig. 1.** Methanol price and demand in recent history (Methanex, 2015; U.S. Energy Information Administration, 2015; Semelsberger et al., 2006).

## 2. Methods and data

### 2.1. Dimethyl ether simulation

The production of DME from methanol follows a simple dehydration reaction between two methanol molecules.



This reaction is usually catalyzed by alumina based catalysts in a fixed bed reactor (Tokay et al., 2012). Typical reactor temperatures are around 250–400 °C while pressure values can vary from 10 to 25 bar. At these conditions methanol conversions can approach 70–85% (mol basis), nearing equilibrium values. Selectivity is also usually high with a small amount of formaldehyde being produced (Zhu et al., 2011; Farsi et al., 2011; Fazlollahnejad et al., 2009).

We modeled DME production in ASPEN Plus using a continuation of the methanol process described in previous work (Matzen et al., 2015). The process utilizes 96.2 mt/day of methanol which is produced from 138.4 mt CO<sub>2</sub>/day and 18.6 mt H<sub>2</sub>/day. The facility produces 68.5 mt/day of 99.6 wt% DME. This simulation uses the NRTL-RK property method to properly model vapor-liquid equilibrium between methanol, water and dimethyl ether. The DME process flow diagram can be seen in Fig. 2. The methanol production facility is encapsulated in the MEOHPROD block; this hierarchy block contains the full process flow diagram produced in our previous work (Matzen et al., 2015). The remainder of the process flow diagram is associated with DME production.

The product methanol (S1) is first mixed with a recycle stream (S8) containing unreacted methanol separated in column T202. This stream is then brought up to reactor conditions with a pump (P201) and a series of heat exchangers. The heat exchangers capture process heat from the waste water stream (HX201), from the reactor effluent (HX202) and the combusted flue gas (HX203). The heat exchangers are modeled as fixed tube shell and tube heat exchangers. Associated parameters for all of the heat exchangers can be seen in the Appendix. A rigorous modeling approach was taken in modeling these heat exchangers which calculates the pressure drop for both streams. High pressure steam is used to bring the stream to final conditions of 17 bar and 275 °C in E201.

The reactor (R201) is modeled as an RGIBBS reactor which calculates the minimum free energy of the products at the specified temperature and pressure. The choice of this reactor assumes that the

reaction reaches equilibrium at these operating conditions. A sensitivity analysis was run to ensure consistent conversions and selectivities with literature data (Zhu et al., 2011). The effluent contains an equilibrium mixture of methanol, dimethyl ether, formaldehyde and water. Methanol conversion reaches 87.2% while selectivity to DME is 99.5%.

The effluent is brought down to 10 bar in a turbine (J201) to recover energy from this stream before product separation. The turbine collects 71.8 kW of energy which can help power the reactor feed pump. After the turbine, the reactor effluent is cooled in HX202 and fed to the first distillation column. The first column separates out the product DME. It operates at 9.5 bar to facilitate DME separation while maintaining an achievable condenser temperature. Lower pressure columns result in negative condenser temps which cannot feasibly be done. Internal column design specifications were set so that the vapor distillate reaches a purity of 99.6 wt% DME and the column recovers 99% of the DME in this stream. This was done by varying the reflux ratio and the distillate to feed ratio. The product DME stream is cooled to 30 °C in E202 which liquefies the compressed DME for transport and sale.

The bottoms is fed to a second column (T202) to recover unreacted methanol. This column operates at 7 bar. The methanol recovered in the distillate is sent back to the beginning of the process. Some of this stream (0.5 mol %) is bled and mixed with the flue stream from the methanol facility. The bottoms is mixed with the waste water from the methanol facility and sent for conditioning. We have assumed that this waste treatment step reduces the formaldehyde concentration to 0.1%. The design specs for column T202 were set to recover 99.5% of H<sub>2</sub>O in the bottoms and 95% of the methanol in the distillate. As in column T201, the reflux ratio and distillate to feed ratio were varied to accomplish this. Column operating conditions and specifications for both columns can be seen in the Appendix. Values used for the columns were found to be within common operating heuristics (Turton et al., 2012).

The combined flue streams are mixed with a fresh air supply and combusted in a thermal oxidizer, R202. This is done to prevent the

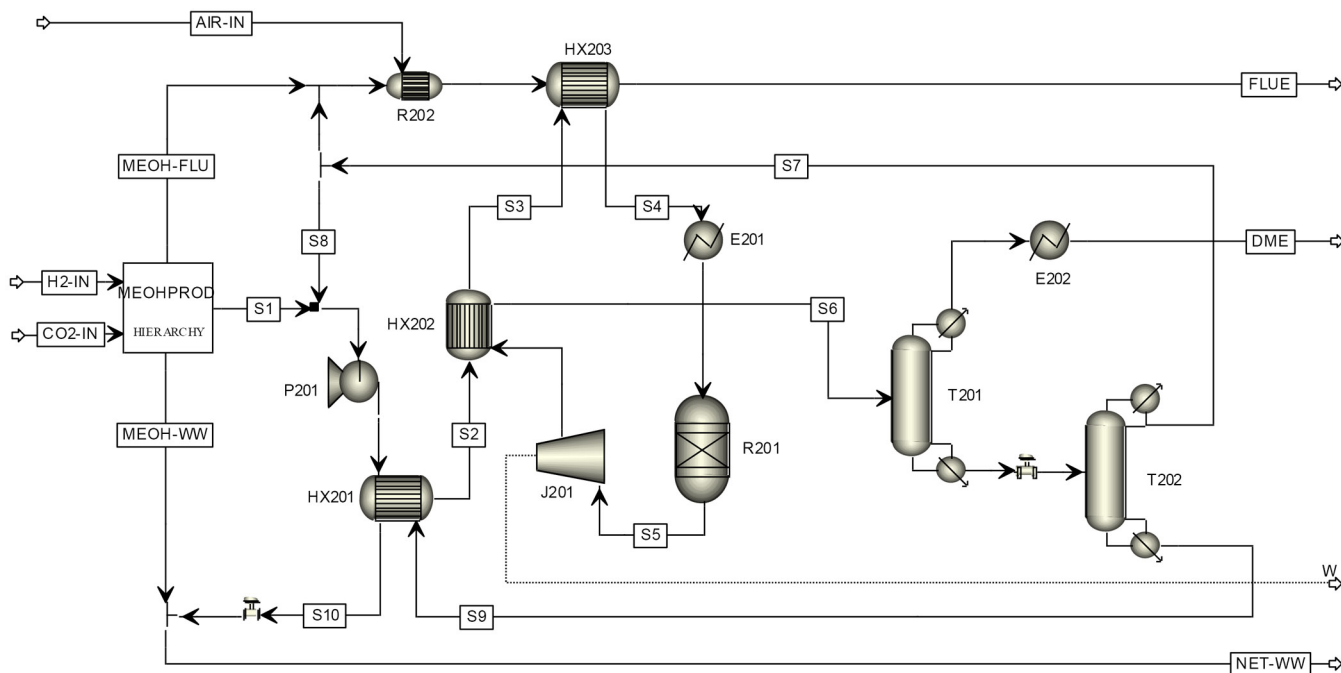


Fig. 2. Process flow diagram for the backend DME facility.

emission of volatile organic compounds and has an added benefit of recovering some process heat. The combustion is simulated in R202 which is modeled as another RGIBBS reactor operating adiabatically and at atmospheric pressure. This succeeds in removing all of the methanol and DME from the flue gas. The gas exits at a temperature of 800 °C and is sent to HX203 to further preheat the reactor feed. The results of this simulation are in line with the technologies of industrial scale production studied by Pontzen et al. (2011). They also reported a good stability of the catalytic system and a good capability for a CO<sub>2</sub> emission reduction with simultaneous production of MeOH or dimethyl ether (DME) as bulk chemicals or alternative fuels.

## 2.2. Life-cycle assessment

The methods behind LCA have been internationally standardized in ISO 14040 and ISO 14044 (ISO/IEC, 2006a; ISO/IEC, 2006b). These standards layout requirements and guidelines for the definition of the goal and scope, the life-cycle inventory analysis phase, life-cycle impact assessment phase, interpretation phase and reporting and critical review of the LCA. The first step in an LCA is goal definition and scoping and the production of a system boundary. It is important to clarify what will be studied as well as the depth that will be considered. It is clear that the impact of methanol production from CO<sub>2</sub> and H<sub>2</sub> will be investigated. CO<sub>2</sub> will be produced from biomass fermentation

and H<sub>2</sub> will be supplied by wind powered water electrolysis. Methanol will either be converted into DME or used directly as a fuel. By tracing process inputs back to their source and investigating the required raw materials for these steps we can establish an LCA map (Fig. 3).

This map will be broken into pieces and individually addressed in subsequent sections. Data that was not produced in the simulations above was gathered from published data or found using the GREET database.

The next phase is the life-cycle inventory analysis. This phase of the work is in which the energy and materials uses are calculated along with the environmental releases. This data is then analyzed in the impact assessment phase and are usually translated into direct potential human and ecological effects (e.g. NO<sub>x</sub> compounds emitted create acid rain which acidifies ponds causing large fish death). In the last phase the results of the inventory analysis are evaluated and a decision based on the environmental impact of the product can be made. It is also at this time that the uncertainty of the analysis is addressed. Uncertainty in an LCA comes from the assumptions made in the scope, the data (or lack thereof) and characterization factors in the impact assessment phase (Scientific Applications International Corporation, 2006; von der Assen et al., 2014). More detailed descriptions of the LCA process can be found in relevant literature (de Bruijn et al., 2004; Scientific Applications International Corporation, 2006; Owens, 1997).

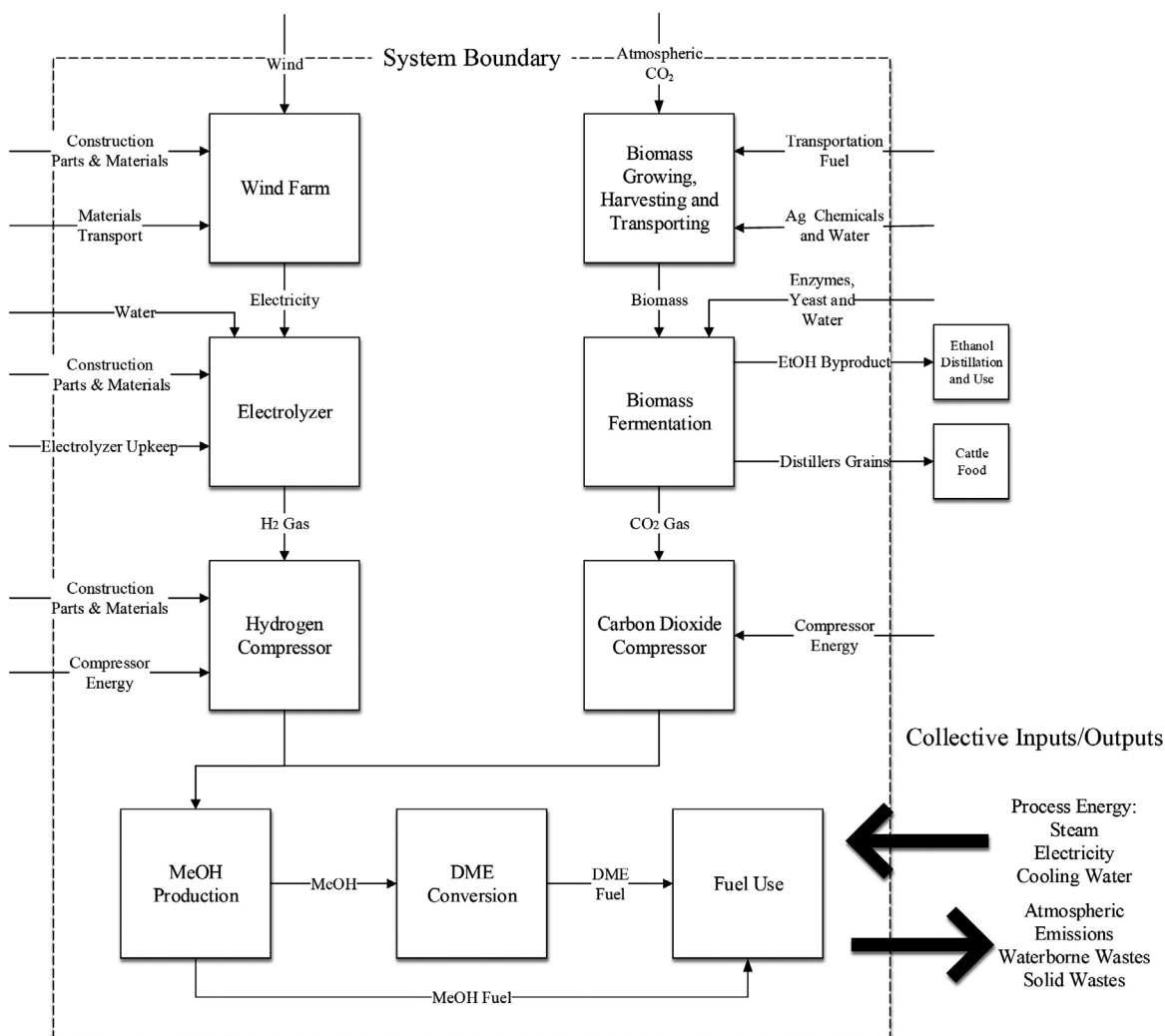


Fig. 3. A map detailing the system boundary of the LCA and the inputs/outputs and processes investigated.

### 2.2.1. $H_2$ production

A single electrolyzer can operate at a  $H_2$  flow rate of 485  $Nm^3/hr$  and would require 4.1  $kWh/Nm^3$  (NEL Hydrogen). A single large scale industrial electrolyzer maxes out around these production values. In order to produce methanol at the quantity specified above we would require 18 of these large electrolyzers operating together in series. As well, the energy demand to power this array of electrolyzers is around 35.8 MW which would require 12 turbines, each producing 3 MW, for complete operation.

Spath and Mann (2004) have presented a detailed report on the total life-cycle analysis of hydrogen production via wind-based electrolysis. They show the influence of the manufacture, transport and installation of wind turbines as well as electrolysis and compression/storage. These aspects represent the major technologies that go into the production of electrolytic hydrogen and are what our LCA on wind-based  $H_2$  will be focused on.

The manufacture of a wind turbine starts with the production of its individual components; the tower, generator, gearbox, nacelle, rotor and blades. These components are then shipped to the final location and installed. Installation requires the pouring of a reinforced concrete foundation. Materials required for the production of a 3 MW, horizontal axis, 3 blade wind turbine were found in literature (Crawford, 2009). While materials are known, individual production techniques and associated emissions are site specific and typically considered small enough to be irrelevant (Martinez et al., 2009). It is also important to note that the decommissioning of these wind turbines is not addressed in this assessment.

The individual components were submitted into GREET along with their materials of construction. Shipment from production facilities was also simulated, using transport data found in literature (Haapala and Prempreeda, 2014). We have assumed the model 2 suppliers in the associated literature and assumed these turbines would be located in southeast Nebraska. A collection of transport data can be found in the Appendix. We assumed heavy-duty trucks would be used to transport the pieces of the turbines.

At this stage the addition of a reinforced concrete foundation was also applied. The assembly of the turbine was assumed to have a negligible effect on analysis. The turbines were assumed to have a net annual output of 29,743 MWh and to operate for 20 years (Crawford, 2009). The environmental outputs from the simulation were normalized to a functional unit of MWh based on the turbines total life. The emissions for the production of electricity for electrolysis was calculated based on these normalized values and attributed to the turbine section of the assessment.

Data for the components of an electrolyzer were found in literature (Maack, 2008). We have investigated the production of the electrolyzer and compressor units in the scope of this LCA. The literature values were taken and entered into the GREET platform to establish emissions and material requirements. We have assumed that transportation is negligible when compared to production and use costs of the electrolyzer (Spath and Mann, 2004). The energy required to compress the production hydrogen from the outlet conditions to 30 bar was calculated in ASPEN Plus and used as an input for the hydrogen production process in the GREET simulation. The results of all the hydrogen production steps were compiled and use the functional unit of 1 mt of  $H_2$ .

### 2.2.2. $CO_2$ production

$CO_2$  is produced as a byproduct of the fermentation of sugars into ethanol. Ethanol production is a widely studied technology in GREET due to its nationwide use as a fuel. As our main focus is the byproduct  $CO_2$  we have chosen to forgo a full analysis into the production of ethanol and to use data provided by the GREET database. Due its industrial maturity, we have chosen to base our analysis on a

dry milling, corn ethanol production facility. The total ethanol process includes corn farming, corn transportation to the plant and then ethanol production. A brief description of this process will be described below however a more detailed description can be found in literature (Wang et al., 2007).

The GREET model for corn farming includes; production of fertilizers (e.g.  $NH_3$ , urea,  $K_2O$ ,  $P_2O_5$ ,  $CaCO_3$ , etc.), pesticides, herbicides, water use, and fossil energy (required for farm equipment, kernel drying, water pumping, etc.). All of these inputs are added in proportion to the output corn amount according to current farming statistics (Wang et al., 2014). Transportation includes shipment by truck from farm to distribution facility and ultimately to the biorefinery. The ethanol production facility takes in this corn along with additional alpha and glucoamylase, yeast and water. The process requires fossil fuel inputs of coal, natural gas, and electricity. For every one gallon of ethanol produced 2.556 kg of distiller grains and solubles (DGS) and 3.08 kg of  $CO_2$  are produced. The amount of DGS was provided in the GREET analysis while the value for  $CO_2$  was found in literature (Lorenz and Morris, 1995). The produced ethanol and DGS are then shipped but this is beyond the scope of our LCA.

As ethanol is the main product of the fermentation process we must determine how to fairly assign the emissions between ethanol and the byproducts. As we focus on the further conversion of  $CO_2$  into value added products we must assume that  $CO_2$  has some economic value. This allows us to use economic allocation to assess the environmental impacts of  $CO_2$  production from the ethanol process (von der Assen et al., 2013). Assuming a value of \$40/mt  $CO_2$  (GoDec, 2014), \$1.43/gal ethanol (OPIS, 2015) and \$180/mt DGS (U.S. Grains Council, 2015) we can create an allocation factor to scale the results to account for the different co-products that are produced. These calculations can be seen in Appendix. The total well-to-product emissions for ethanol production are scaled by multiplication by the allocation factor. This effectively allocates the emissions to the byproduct  $CO_2$  according to the economic value it has compared to the other products.

The requirements for compression were taken from literature (Finely, 2006). This source accounts for compression and water removal from fermentation based  $CO_2$ . The  $CO_2$  stream out of the fermenter is nearly pure (~96 mol%) and at atmospheric conditions with a temperature of 27 °C. The stream leaves the compression stage as liquefied  $CO_2$  at 16.4 bar. The electricity requirement was entered into the GREET platform to determine the environmental impacts for the compression stage. This data was then compiled with the other  $CO_2$  capture and compression data, normalized to the production of 1 metric ton of  $CO_2$ . Emissions data was not calculated for the production of the unit operations for the  $CO_2$  compression as the utility requirements over the life time of the plant largely outweigh the impact their production generates (Shi et al., 2015). Transportation of the  $CO_2$  is also assumed to be negligible.

### 2.2.3. Methanol/DME production

Methanol and DME production facilities were simulated in ASPEN Plus. The data concerning direct  $CO_2$  emissions, waste streams and utilities use were taken from these simulations. The total steam and electrical energy demand for the plants were calculated in ASPEN. GREET was used to model steam production using natural gas as a fuel. Electricity required for the facility is assumed to come from the wind turbines and the emissions on an energy basis were used to calculate the electricity demand data. Direct  $CO_2$  emissions in the flue gas of the plants were also added to the utility emissions data to provide a complete analysis.

We have also collected data for product storage and transportation to fueling stations as would be required for the use of these products as fuels. The data for this is built into the GREET software.

The data estimated for methanol/DME production and transportation were normalized on a per mt product basis. That is, data was compiled using 1 mt of methanol or 1 mt of DME as the functional unit for the methanol and DME plants, respectively.

Conventional production of methanol and DME were also investigated using the GREET software. Raw materials, transport, production and distribution are all accounted for in these simulations. The only change made was an erroneous data value for CO<sub>2</sub> emissions in the DME production pathway. The original negative value was converted to 78.96 g/kWh which was taken from a report compiled by Argonne (Wang and Huang, 1999).

#### 2.2.4. Fuel utilization

GREET analysis also allows us to investigate the utilization of different fuels in a variety of different vehicles. A comparison between our renewably based methanol and dimethyl ether was made to conventional (fossil fuel based) methanol and dimethyl ether. The data collected for the conventional processes was taken from the GREET platform. Using this method we were able to detail the emissions and energy from utilizing the fuel in order to more directly compare methanol and DME on a per energy basis. With this we were able to compare the results of our simulations to conventional methanol and DME production routes as well as other renewable production methods. Three simulations were compared in all, two renewable options and one based on natural gas feedstock. The two renewable options are; our process using CO<sub>2</sub> from ethanol fermentation and wind-based electrolytic H<sub>2</sub> while the other is a process simulated in GREET based on the gasification of biomass. We chose corn as the biomass for gasification to allow for a more direct comparison between the different processes. We also compared these values to petroleum based fuels on a per energy basis. Methanol was compared to reformulated gasoline (RFG) and dimethyl ether was compared to ultra-low sulfur diesel (ULSD). Liquefied natural gas (LNG) was also chosen as a comparative fuel.

Until this point we have strictly focused on CO<sub>2</sub> produced during the production of our fuels. However the biogenic CO<sub>2</sub> used in this process has not yet been accounted for. CO<sub>2</sub> emissions from fermentation processes are typically neglected as the CO<sub>2</sub> produced was originally captured by the biomass feedstock. Therefore these emissions show a net zero effect on the overall CO<sub>2</sub> emissions for the total process. For this reason we have calculated the fixed CO<sub>2</sub> in our fuels (by stoichiometric ratio) and subtracted this from the total CO<sub>2</sub> emissions (and consequently GHG emissions) for our fuels. This allows us to directly compare our emissions values to the simulated GREET fuels.

For the fuel utilization we chose to use the spark ignited direct injection (SIDI) dedicated methanol car in GREET for the methanol fueled car. We changed the fuel in this model to be 100% methanol to allow for a direct comparison between this and our DME model. Although current technology does not utilize a 100% methanol fuel this was required for accurate data comparison. The DME car was chosen to be a compression ignited direct injection (CID) vehicle running on 100% DME. Similar vehicle choices were made for the RFG, ULSD and LNG cars.

#### 2.2.5. Process environmental impact indicators

Two primary indicators of environmental impact in fuels production are the fossil fuel energy ratio (FER) and life-cycle efficiency (LCE). The FER is defined as the ratio of the energy content of the fuel to the fossil energy required to produce this fuel (Equation (2)). The LCE is the overall energy produced in methanol over the total energy consumed (shown as the ratio in Equation (3)).  $E_{\text{primary}}$  is any form of energy used that has not undergone any conversion processes (e.g. natural gas, wind energy, etc.).

$$\text{FER} = \frac{E_{\text{fuel}}}{E_{\text{fossil}}} \quad (2)$$

$$\text{LCE} = \frac{E_{\text{fuel}}}{E_{\text{primary}} + E_{\text{fuel}}} \quad (3)$$

Another environmental indicator would be the amount of CO<sub>2</sub> that has been fixed into the chemical compared to the emissions of CO<sub>2</sub> required to make said chemical. We have defined this metric as the carbon fixation fraction (CFF), defined in Equation (4).

$$\text{CFF} = \frac{\text{CO}_2 \text{ fixed} - \text{CO}_2 \text{e emission}}{\text{CO}_2 \text{ fixed}} \quad (4)$$

#### 2.2.6. Normalization to midpoint level

To accurately compare impacts of different emission sources normalization is typically conducted. We chose to utilize ReCiPe 2008 as the database for characterization factors and normalization constants. Characterization factors are used to convert pollutants into a single base unit based on their individual environmental impact. This allows different pollutants to be summed into a single category based on environmental impact (i.e. global warming potential or acidification potential). Normalization then converts these totals into direct environmental impact factors that can be compared across different impact categories. We chose to use the Midpoint Hierarchist World normalization factors found in ReCiPe and Hierarchist values for the characterization as well (Goedkoop et al., 2013). Example calculations can be found in Equations (A1) and (A2) in the appendix.

#### 2.2.7. Assumptions

It should be noted that by changing the assumptions made in producing this life-cycle assessment, the results of this LCA can be drastically altered. A very key assumption is that economic allocation is used account for CO<sub>2</sub> emissions. Changing product costs or to exergy-based allocation would give different results. Below is a collective list of assumptions used in the collection and assembly of data for the life-cycle assessment. As well the choice of normalization factors will ultimately affect the normalized results. A different normalization method will alter results. Below is a list of assumptions made in the production of this LCA.

- Site specific turbine part production is negligible
- Decommissioning of the turbines, compressors, electrolyzers and plant equipment is beyond the scope of this work
- The integrated plant will be located in Southeast Nebraska due to the proximity to ethanol production facilities and abundance of wind energy
- Wind turbine assembly has negligible environmental effects
- Transportation of the electrolyzer and compressors is negligible
- Ethanol production is taken from GREET system
- Every gallon of ethanol produced also forms 3.08 kg CO<sub>2</sub> and 2.56 kg of DGS
- An economic allocation for CO<sub>2</sub> production from ethanol is used
- Production of CO<sub>2</sub> compression and purification unit operations negligible
- Production of unit operations for the ethanol facility, CO<sub>2</sub> compression and purification facility and methanol/DME production facility are negligible when compared to lifetime use
- Conventional and gasification based methanol and DME data were taken from the GREET platform
- Fuel use was simulated in GREET
- ReCiPe Midpoint Hierarchist World factors are used for characterization and normalization (Goedkoop et al., 2013)

### 3. Results and analysis

#### 3.1. Cradle-to-gate analysis

##### 3.1.1. Impact indicators

The environmental impact indicators for the methanol and DME processes can be seen in Table 1. Methanol shows higher metrics in FER and CFF due to the heating requirements of the DME columns in the production stage of this process. Both processes show similar LCE. However these efficiencies are low when compared to other methanol production LCA results (Reno et al., 2011) and even lower when compared to general energy efficiencies for methanol production (Matzen et al., 2015). This is due to the low energy efficiency of wind based electrolysis. Since wind is considered a primary energy source, it is included in LCE calculations and leads to a lower efficiency.

##### 3.1.2. Normalized results

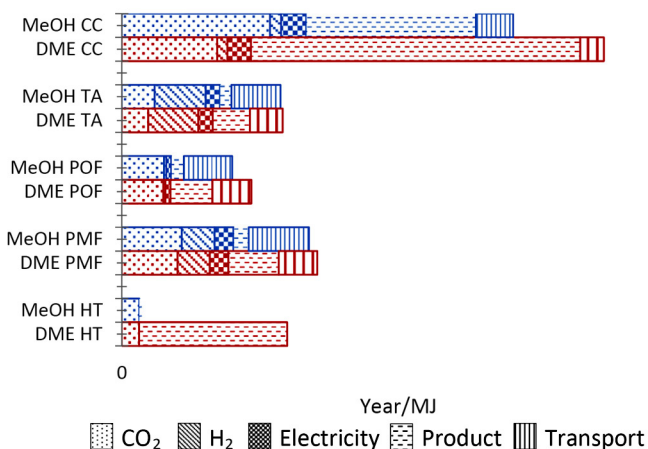
After normalization we were able directly compare methanol and dimethyl ether production in terms of specific impact factors. We have chosen to use impact factors of human toxicity (HT), particulate matter formation (PMF), photochemical oxidant formation (POF), terrestrial acidification/acidification potential (TA) and climate change (CC) to compare our two processes. The results of this normalization can be found in Fig. 4.

This figure was prepared using a functional unit of 1 MJ of energy, based on the lower heating value of the fuel. Both methanol (red) and dimethyl ether (blue) values are shown in Fig. 4. As well, we have shown how the different production stages influence the economic results (shown as different textures). This figure shows

**Table 1.** Comparative indicators for methanol and dimethyl ether facilities.

	Methanol	Dimethyl ether
FER	9.00	4.69
LCE	0.45	0.43
CFF	0.78	0.70

FER: Fossil Fuel Energy Ratio; LCE: Life Cycle Efficiency; CFF: Carbon Fixation Fraction.



**Fig. 4.** Normalized midpoint indicators for both DME (blue) and methanol (red) production processes. Impacts from individual process sections are shown as different textures; HT: Human Toxicity, PMF: Particulate Matter Formation, POF: Photochemical Oxidant Formation, TA: Terrestrial Acidification, CC: Climate Change.

that methanol slightly outperforms dimethyl ether in most of the environmental considerations. The deciding factor for this difference is the product production stage. Again, the amount of natural gas burned for process heat in the DME process is the likely cause of this. As well the large difference in toxicity values comes from the production stage. Formaldehyde is a known carcinogen and is by-product of the DME production facility. Even after waste treatment the effect of formaldehyde release is substantial.

Non-normalized indicators for the entire processes can be found in Table 2. It should be noted that these values are strictly for the production stages of these chemicals (cradle-to-gate). Fuel combustion and the influence of using biogenic CO<sub>2</sub> are not accounted for.

#### 3.2. Cradle-to-grave analysis

Three different processes for both methanol and DME production were compared including our CO<sub>2</sub> hydrogenation process, a biomass gasification process, and conventional natural gas reforming process. Combustion analyses of these product fuels were compared with petroleum based fuels on a per energy basis. Methanol is compared to gasoline and dimethyl ether is compared to ultra-low sulfur diesel. Liquefied natural gas was also used as a comparison fuel as its use is becoming increasingly favored over methanol or dimethyl ether fuels. Cradle-to-grave results for wind-based electrolytic H<sub>2</sub>, captured and compressed CO<sub>2</sub> from ethanol fermentation, methanol production and dimethyl ether production can be found in the Appendix. The results shown in Table A5 were included to allow the extension of these results to the use of these products as chemical feedstocks.

Fig. 5 shows the emissions after combustion of all of these fuels. The results were compared on a per energy basis and then normalized to the largest emission value. The figure shows emissions of criteria pollutants (VOC, CO, NO<sub>x</sub> and SO<sub>x</sub>) as well as greenhouse gas emissions (GHG) and fossil fuel use (FF). Interestingly unlike the production stage DME now outperforms methanol in terms of fuel use emissions. This is due to the high emissions results for using methanol directly as a combustion fuel as well as the lower heating value that methanol has compared to dimethyl ether. The CO emissions for methanol are similar between all of the processes and this is because of the large emissions of CO during fuel use. However methanol does emit less greenhouse gasses and use less fossil fuel than DME on a per energy basis.

Our process based on CO<sub>2</sub> hydrogenation is comparable to the biomass-based gasification process in GREET. The major difference between the two renewable processes is SO<sub>x</sub> emissions. The majority of the SO<sub>x</sub> in the CO<sub>2</sub> hydrogenation process results from the electrolyzer production stage. This is likely due to the processing emissions for the metals required for electrolysis. NO<sub>x</sub> emissions for the renewable processes are also high. This is because of the nitrogen fertilizer used in the farming of biomass. This fertilizer readily converts to gaseous NO<sub>x</sub> compounds and is emitted during biomass growth (Wang et al., 2014).

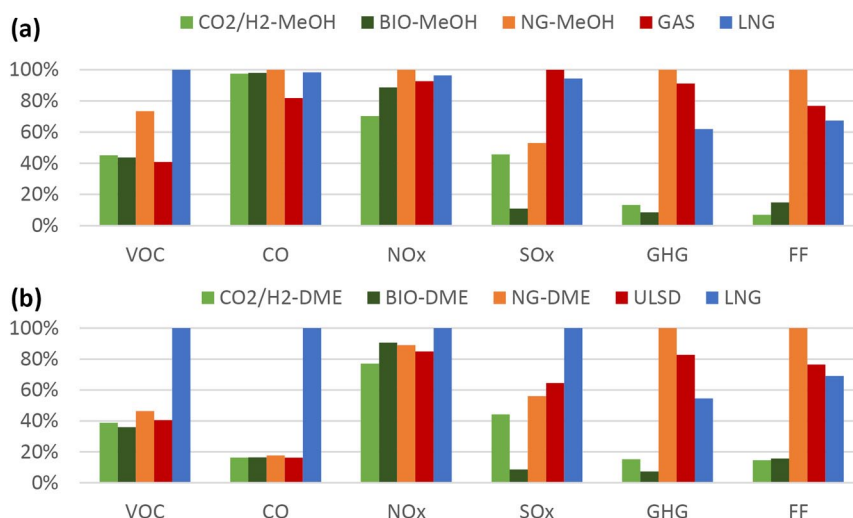
**Table 2.** Non-normalized environmental impacts for energy produced in MJ.

Indicator	MeOH	DME	Unit/MJ product
Global Warming Potential	0.30	0.50	mt CO <sub>2</sub> eq
Acidification Potential	0.67	0.95	kg SO <sub>2</sub> eq
Photochemical Oxidant Formation	0.69	1.13	kg NMVOC eq <sup>a</sup>
Particulate Matter Formation	0.29	0.43	kg PM <sub>10</sub> eq
Human Toxicity	0.10	7.68	kg 1,4-DB eq <sup>b</sup>

a. NMVOC: Non-Methane Volatile Organic Compound.

b. 1,4-DM: 1,4 dichlorobenzene.





**Fig. 5.** Cradle-to-grave emissions for methanol (a) and dimethyl ether (b); shown for comparison are emissions from biomass gasification based methanol and DME (BIO-MeOH/ BIO-DME), natural gas based methanol and DME (NG-MeOH/NG-DME), gasoline (GAS), ultra-low sulfur diesel (ULSD) and liquefied natural gas (LNG).

However, both of the renewable options largely outperform the natural gas facility and the petroleum based fuels. Criteria pollutant levels would decrease by implementing these renewable fuels over petroleum based reformulated gasoline and ultra-low sulfur diesel. By implementing a CO<sub>2</sub> hydrogenation process for methanol and DME alternative fuels, greenhouse gas emissions alone can be reduced 86% and 82% over conventional petroleum based fuels, respectively. The use of our renewable methanol and DME also reduces fossil fuel depletion by 91% and 82% when compared to conventional petroleum based fuels.

#### 4. Conclusions

This study presents a life-cycle assessment of the production of renewable methanol and dimethyl ether. The renewable processes presented show comparable results to other renewable production methods and are more sustainable than petroleum based fuels. However, using both methanol and DME as transportation fuels would require some modifications before practical implementation is realized. Both fuels have lower energy densities than typical petroleum fuels which would require minor changes to combustion engines. As well, direct fuel use of DME requires pressurization due to low vapor pressure and methanol is slightly corrosive and more toxic than gasoline. However, the minor modifications required would be built from the existing infrastructure and would be cheaper and more feasible than building from the ground up (Zhu et al., 2011). As well, when determining process feasibility it is important to weigh societal, economic and environmental factors together. While the economics behind alternative renewable fuels are still weak, peak oil and increasing petroleum prices will push the market towards more sustainable fuels. Future work should include a full comparative techno economic analysis based on these processes to aid in determining true feasibility.

Nonetheless, the inclusion of environmental metrics through life-cycle assessment in process feasibility analyses is a comprehensive way to monitor and compare the sustainability of processes. The use of fermentation based CO<sub>2</sub> and wind powered water electrolysis for H<sub>2</sub> production present a sustainable and environmentally friendly way to produce transportation fuels of methanol and DME,

with minimal fossil energy requirements. The life-cycle assessment presented shows the total environmental impacts of this production approach from well-to-wheels. Environmental costs are compared between our production processes, a biomass-based gasification process, a conventional (natural gas) based process, and petroleum based fuels. Emissions are compared and a normalized life-cycle impact analysis was conducted. Our renewable methanol and dimethyl ether outperform conventional petroleum based fuels, relying on less fossil based energy and reducing greenhouse gas emissions by 82–86%, minimizing other criteria pollutants (SO<sub>x</sub>, NO<sub>x</sub> etc.), and reducing fossil fuel depletion by 82–91%. While practical implementation and economic constraints of renewable fuels would be a minor challenge, the reduction in environmental burdens shown increase the feasibility of this renewable process.

#### Appendix

**Table A1.** Operating conditions and results for the three heat exchangers.

	HX201	HX202	HX203
Specified UA <sup>a</sup> (cal/s K)	471.1	1695.2	335.4
Specified area (m <sup>2</sup> )	2.05	4.19	6.78
Heat transfer (kW)	117	378	338

a. UA: the product of overall heat transfer coefficient and heat transfer area of the heat exchanger.

**Table A2.** Column specifications and results for the DME process towers.

Column specifications/results	T201	T202
Pressure (bar)	9.5	7
Stages	15	25
Feed stage	6	17
Height (m)	10.5	17.5
Diameter (m)	0.66	0.7
Reflux ratio (molar)	3.30	1.94
D:F <sup>a</sup> (molar)	0.43	0.22

a. D:F = Distillate to Feed ratio.

**Table A3.** Transportation data collected and used for the transport of individual turbine components.

Component	Mass (mt)	Location	Distance (km)	Mass-distance (tkm)
Blades	20.07	Windsor, CO	761.5	1.528E+04
Rotor	19.93	Brighton, CO	753.0	1.501E+04
Gearbox	24.06	Lake Zurich, IL	848.6	2.042E+04
Generator	7.14	Raleigh, NC	2037.9	1.455E+04
Yaw/Pitch system	11.82	Hebron, KY	1246.1	1.473E+04
Tower	160	Pueblo, CO	969.6	1.551E+05
Nacelle	24.98	Brighton, CO	753.0	1.881E+04

**Table A4.** Calculation of allocation factors for the ethanol production facility.

Compound	Flow	Cost	Cost flow (\$/mt CO <sub>2</sub> )	Allocation factor (%)
CO <sub>2</sub>	3.08 kg	\$40/mt	40	6.1
Ethanol	1 gallon	\$1.43/gal	463.45	71.0
DGS	2.56 kg	\$180/mt	149.16	22.9

**Table A5.** Total cradle-to-gate emissions and energy use for producing a metric ton of CO<sub>2</sub>, H<sub>2</sub>, methanol and dimethyl ether. A negative GHG result implies biogenic CO<sub>2</sub> is captured in the product

	CO <sub>2</sub>	H <sub>2</sub>	MeOH	DME	Unit per mt product
<b>Criteria Pollutants</b>					
VOC	43.7	25	90	196.8	g
CO	43	227.7	208.6	399.8	g
NO <sub>x</sub>	138	197.3	589.8	906.3	g
PM <sub>10</sub>	22.6	72.4	61	88.9	g
PM <sub>2.5</sub>	7.9	35.8	32	47.8	g
SO <sub>x</sub>	18.9	1321.5	338.8	444.8	g
CH <sub>4</sub>	4.9	224.8	229.9	855.1	g
N <sub>2</sub> O	96.4	1.3	283.5	401.7	g
CO <sub>2</sub>	51.4	134.8	-1240.1	-1527	kg
SF <sub>6</sub>	0	4.4	2	0.6	mg
C <sub>2</sub> F <sub>6</sub>	0	0.5	0.1	0.1	mg
Black carbon	1.4	1.2	2.9	6.5	g
POC	1.3	2.1	5.2	11.5	g
<b>Greenhouse Gas</b>	<b>78.4</b>	<b>142.5</b>	<b>-1128.5</b>	<b>-1443.6</b>	<b>kg</b>
<b>Energy Use</b>					
Fossil Fuel	148.4	615.3	619.5	1709.3	kWh
Renewable Fuel	2149.2	26.5	3096.3	4378.2	kWh

$$\text{Normalized Emission} = m_j = \sum_{i=1}^n a_i^j m^i \quad (\text{A1})$$

$$\text{Normalized Impact} = \frac{m_j}{\beta} \quad (\text{A2})$$

Equation (A1) shows how the emissions of different components are normalized to a single emission value. In this equation  $m_j$  is the normalized emission value (e.g. kg SO<sub>2</sub> for acidification potential, kg CO<sub>2</sub> for global warming potential, etc.),  $m^i$  is the mass of component  $i$  that is emitted from the process and  $a_i^j$  is the characterization factor of component  $i$  as it relates to the normalized emission compound  $j$ .

Equation (A2) takes the normalized emission value ( $m_j$ ) and normalizes it to its environmental impact by dividing by the normalization factor,  $\beta$ . Both characterization factors and normalization factors were taken from ReCiPe.

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