**LCA Module - Case Study**

**Life Cycle Assessment for Comparing Methanol Production Routes from Carbon Dioxide**

**Problem Definition**

Methanol is traditionally produced from natural gas via steam reforming of methane. Methanol can also be produced via catalytic hydrogenation of carbon dioxide. Carbon dioxide is a greenhouse gas and its consumption promises a sustainable option compared to fossil fuel based natural gas feedstock.

This problem will compare the various processes for the production of methanol using life cycle assessment methodology, and determine which process is the best for the production of methanol.

This case has been built upon the work by Mukherjee et al., 2015.

***Conventional Process for Methanol Production via Steam Reforming of Methane:***

*Synthesis Gas Preparation*

CH4 + H2O = CO + 3H2  (1)

The reaction is very endothermic, favored by high temperature and low pressure. This reaction produces 1:3 ratio of CO to H2 instead of the 1:2 needed for methanol synthesis.

Water-gas shift reaction produces CO.

CO2 + H2 = CO + H2O (2)

From Equation (1) and (2), we get:

3CH4 + 2H2O + CO2 = 4CO + 8H2  (3)

*Methanol Synthesis in Catalytic Converter*

Methanol synthesis occurs in a converter using Lurgi technology

CO + 2H2 = CH3OH (4)

***New Processes for Methanol Production via Catalytic Conversion of CO2:***

* Methanol from CO2 Hydrogenation over Cu(100) Catalyst (Nerlov and Chorkendorff, 1999)

CO2 + 3H2 → CH3OH + H2O ΔHo = -49 kJ/mol, ΔGo = 3 kJ/mol (5)

* Methanol from CO2 Hydrogenation over Cu - Zr Catalyst (Toyir et al., 1998)

CO2 + 3 H2 → CH3OH + H2O ΔHo = -49 kJ/mol, ΔGo = 3 kJ/mol (6)

CO2 + H2 → CO + H2O ΔHo = 41 kJ/mol, ΔGo = 29 kJ/mol (7)

* Methanol from CO2 Hydrogenation over Cu/ZnO/ZrO2/Al2O3/Ga2O3 Catalyst (Ushikoshi et al., 1998)

CO2 + 3 H2 → CH3OH + H2O ΔHo = -49 kJ/mol, ΔGo = 3 kJ/mol (8)

CO2 + H2 → CO + H2O ΔHo = 41 kJ/mol, ΔGo = 29 kJ/mol (9)

CO + 2H2 → CH3OH ΔHo = -90.5 kJ/mol, ΔGo = -25 kJ/mol (10)

* Methanol from Hydrogenation over Cu/ZnO/Cr2O3 and CuNaY Zeolite Catalyst (Jun et al., 1998)

CO2 + H2 → CO + H2O ΔHo = 41 kJ/mol, ΔGo = 29 kJ/mol (11)

CO + 2H2 → CH3OH ΔHo = -90.5 kJ/mol, ΔGo = -25 kJ/mol (12)

2CH3OH → CH3OCH3 + H2O ΔHo = -24 kJ/mol, ΔGo = -17 kJ/mol (13)

* Methanol from Hydrogenation over Pd/SiO2 Catalyst (Bonivardi et al., 1998)

CO2 + H2 → CO + H2O ΔHo = 41 kJ/mol, ΔGo = 29 kJ/mol (14)

CO + 2H2 → CH3OH ΔHo = -90.5 kJ/mol, ΔGo = -25 kJ/mol (15)

Conduct a Life Cycle Assessment study to determine whether any of the new processes from CO2 is better than the existing route for production of methanol. Assume that cost is not a factor for bringing the technology to the market.

**­­*Notes to Instructor:*** *The solution for this case can be administered in accordance to the stages of the LCA method. The accompanying slides can be used to guide the students into identifying the requirements for Goal and Scope Definition, LCI and LCIA. Based on these results, the students will be required to submit a report to complete the Step 4 of LCA which contains their critical evaluation of which process should be selected. The report should also explicitly state the goal and scope, include the LCIA results in main text, and the LCI in appendix or documented in Excel®.*

*Optional Addition to Problem (Depends on discretion of Instructor): The instructor may choose to expand the scope of this problem by asking the class to divide into groups and design each new process in process flowsheet software. Then the information from the design results can be extracted and used for Life Cycle Inventory creation. These designs have not been provided in this case study.*

**Activity for Goal and Scope Definition**

* From the problem statement above, what is the goal? How does the goal help in being sustainable?
* Identify the stages in the production of Methanol via steam reforming of methane. Make a list of raw materials, emissions and co-products if any. *(Use a standard process industries book, like Shreve, Randolph Norris, and Nicholas Basta. Shreve's Chemical Process Industries Handbook. McGraw, 1993.)*
* For each input and output from the process, track the upstream preparation and downstream use. Using this information, prepare a diagram which shows the entire life cycle of methanol.
* Choose the functional unit for the proposed study. Explain why one kg of methanol is a good function to compare the processes.
* Justify why only studying the boundary of methanol production process is sufficient for this LCA study.

**Solution**

**Goal:** To determine whether a new methanol process which utilizes carbon dioxide as a raw material is better than existing methanol process from steam reforming of natural gas. *(Guide the students to explore the sustainable aspects which make the process better. Hint on economic, environmental and social issues associated with the production through one route and compare to others.)*

**Scope:** The complete life cycle for methanol production needs to study the feedstock extraction, methanol production, methanol use and final disposal. In this case, we only need to study the process within the scope of gate-to-gate for methanol production.

For comparing the production routes for methanol, the changes are anticipated only in the methanol production phase. For this reason, a gate to gate analysis of the methanol production life cycle phase will be sufficient to make a judgment on the acceptability of the process. Thus, we consider the system boundary to include the conventional methanol production, and the methanol production from carbon dioxide.

The function of the LCA is to compare the methanol production processes. So, the functional unit of 1 kg methanol is chosen.

**Activity for Life Cycle Inventory**

*Use Microsoft Excel® for preparing the Life Cycle Inventory for the processes. You can use the data table provided in this exercise, or prepare your own tables from process flowsheet software.*

* Prepare a life cycle inventory of the inputs and outputs from the processes. Include the material and energy flows.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Process | Input Streams | Flow Rate (Kg/hr) | Output Streams | Flow Rate (Kg/hr) |
| Nerlov and Chokendorff, 1999 | Carbon Dioxide | 75,540 | Methanol | 54,760 |
| Hydrogen | 10,380 |  |  |
| Cooling Water | 18,160,000 |  |  |
| HP Steam | 776,000 |  |  |
| Toyir et al., 1998 | Carbon Dioxide | 151,400 | Methanol | 54,870 |
| Hydrogen | 13,870 | Carbon Monoxide | 48,180 |
| Cooling Water | 26,740,000 |  |  |
| HP Steam | 1,205,000 |  |  |
| Ushikoshi, 2002 | Carbon Dioxide | 76,450 | Methanol | 54,730 |
| Hydrogen | 10,420 | Carbon Monoxide | 585 |
| Cooling Water | 16,510,000 |  |  |
| HP Steam | 693,000 |  |  |
| Jun, et al., 1998 | Carbon Dioxide | 79,740 | Methanol | 54,700 |
| Hydrogen | 10,940 | Dimethyl Ether (DME) | 2,102 |
| Cooling Water | 148,000,000 |  |  |
| HP Steam | 602,000 |  |  |
| Bonivardi, et al., 1998 | Carbon Dioxide | 79,590 | Methanol | 54,800 |
| Hydrogen | 10,570 | Carbon Monoxide | 2,527 |
| Cooling Water | 13,180,000 |  |  |
| HP Steam | 525,000 |  |  |
| Conventional Process | Carbon Dioxide | 7,177 | Methanol | 20,698 |
| Methane | 7,782 | Carbon Monoxide | 13.57 |
| Cooling Water | 2,498,850 | Carbon Dioxide | 71.76 |
| LP Steam | 5,828 | Hydrogen | 2.97 |

**Solution**

*See Table. The new methanol processes were designed as industrial scale methanol plants in ASPEN HYSYS. The capacity for each new methanol plant was set to 160 million gallons per year (480,846 metric tons/year). The capacity for the existing methanol process design was 200,000 metric tons/year.*

**Activity for Life Cycle Impact Assessment (LCIA)**

*The aim of this exercise is to explain impact as an expression for combining several flows. The instructor can explain mid-point and end-point impact categories for this section as an additional exercise.*

* Prepare one paragraph review of the following indicators:
  + Energy Intensity
  + Water Intensity
  + Material Intensity
  + Global Warming Potential
  + Smog Formation Potential
  + Human Health Impacts Particulate Matter
* Which flows are anticipated to have an environmental impact? Color code the inputs as green where environmental pollutants are utilized, and outputs as red where environmental pollutants are released. For the Energy Intensity indicator, color the Steam requirement. For the Water Intensity, color the cooling water requirement.

**Solution**

* For each input and output stream, express it in terms of the functional unit. This should give you results in terms of kg/kg methanol.
* *Material Intensity:* To compute the material intensity, for each process, sum the total process inputs and divide by the methanol production. *(This will not include the cooling water or steam, as they do not directly take part in the process. They are the utility streams.)*
* *Energy Intensity:* To compute the energy intensity, we use the Steam Input. Using the values in the table below compute the energy required in the processes. Assume a temperature drop of 1 oC. (*Source: ASPEN HYSYS Utility Properties)*

|  |  |
| --- | --- |
| Steam Type | Enthalpy (kJ/kg-C) |
| LP Steam | 2196.4 |
| MP Steam | 1981.4 |
| HP Steam | 1703.1 |

* *Water Intensity:* To compute the water intensity, we use the Cooling Water Input. NOTE: *The water requirement for Cooling is assumed to be non-recyclable, and the water for Steam generation to be recyclable. The solution gives the water intensity only for cooling water used, but the instructor may choose to include water use in steam (i.e. non-recyclable) to calculate the indicator.*
* Use the following method for the next three indicators: *Global Warming Potential, Smog Formation Potential, Human Health Impacts Particulate Matter*

For each of the compounds, multiply the inputs or outputs with the impact characterization factor. The impact of input or output is given according to the following equation:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Process** | **Input Streams** | **Flow Rate (Kg/hr)** | **Flow Rate (kg/kg methanol)** | **Output Streams** | **Flow Rate (Kg/hr)** | **Flow Rate (kg/kg methanol)** |
| Nerlov and Chokendorff, 1999 | Carbon Dioxide | 75,540 | 1.38E+00 | Methanol | 54,760 | 1.00E+00 |
| Hydrogen | 10,380 | 1.90E-01 |  |  |  |
| Cooling Water | 18,160,000 | 3.32E+02 |  |  |  |
| HP Steam | 776,000 | 1.42E+01 |  |  |  |
| Toyir et al., 1998 | Carbon Dioxide | 151,400 | 2.76E+00 | Methanol | 54,870 | 1.00E+00 |
| Hydrogen | 13,870 | 2.53E-01 | Carbon Monoxide | 48,180 | 8.78E-01 |
| Cooling Water | 26,740,000 | 4.87E+02 |  |  |  |
| HP Steam | 1,205,000 | 2.20E+01 |  |  |  |
| Ushikoshi, 2002 | Carbon Dioxide | 76,450 | 1.40E+00 | Methanol | 54,730 | 1.00E+00 |
| Hydrogen | 10,420 | 1.90E-01 | Carbon Monoxide | 585 | 1.07E-02 |
| Cooling Water | 16,510,000 | 3.02E+02 |  |  |  |
| HP Steam | 693,000 | 1.27E+01 |  |  |  |
| Jun, et al., 1998 | Carbon Dioxide | 79,740 | 1.46E+00 | Methanol | 54,700 | 1.00E+00 |
| Hydrogen | 10,940 | 2.00E-01 | Dimethyl Ether (DME) | 2,102 | 3.84E-02 |
| Cooling Water | 148,000,000 | 2.71E+03 |  |  |  |
| HP Steam | 602,000 | 1.10E+01 |  |  |  |
| Bonivardi, et al., 1998 | Carbon Dioxide | 79,590 | 1.45E+00 | Methanol | 54,800 | 1.00E+00 |
| Hydrogen | 10,570 | 1.93E-01 | Carbon Monoxide | 2,527 | 4.61E-02 |
| Cooling Water | 13,180,000 | 2.41E+02 |  |  |  |
| HP Steam | 525,000 | 9.58E+00 |  |  |  |
| Conventional Process | Carbon Dioxide | 7,177 | 3.47E-01 | Methanol | 20,698 | 1.00E+00 |
| Methane | 7,782 | 3.76E-01 | Carbon Monoxide | 13.57 | 6.56E-04 |
| Cooling Water | 2,498,850 | 1.21E+02 | Carbon Dioxide | 71.76 | 3.47E-03 |
| LP Steam | 95,567 | 4.62E+00 | Hydrogen | 2.97 | 1.43E-04 |



I = Impact (or Potential Impact)

*CFi* = Characterization Factor of *ith* species

*Ei* = Elementary Flow, *ith* species in Life Cycle Inventory

To compute the overall impact, use the following equation:

Overall Impact = *IOutput - IInput*

TRACI Impact Characterization Factors have been given for the relevant compounds. For a full list of the most recent TRACI Characterization Factors, please email [bare.jane@epa.gov](mailto:bare.jane@epa.gov). The user manual for TRACI 2.1 and a list of factors from 2014 is provided in the supporting document (Bare, 2014).

|  |  |  |  |
| --- | --- | --- | --- |
| Compound | Global Warming Air (kg CO2 eq / kg substance) | HH Particulate Air (PM2.5 eq / kg substance) | Smog Air (kg O3 eq / kg substance) |
| Carbon Dioxide | 1 | - | - |
| Methane | 25 | - | - |
| Carbon Monoxide | - | 3.56E-04 | 5.56E-02 |
| Methanol | - | - | 6.72E-01 |

*Bonus Question:* For the Global Warming Potential, it can be noted that there is a net negative value, denoting a positive impact. However, this does not account for the emissions due to energy generation, i.e. steam. Only the energy intensity of the processes has been compared. The system boundary can be expanded to include the emissions due to energy generation, and the energy production process can be considered. This will increase the carbon dioxide release into the atmosphere by burning a fossil fuel (natural gas, petroleum or coal). Compute the overall GWP as a result of this expansion of the system boundary, and report your results.

Do you think the Energy Intensity indicator should be discarded if you are using the natural gas as input and CO2 as output from the energy generation process? Justify.

**Activity for LCA Report**

*The LCA report typically includes a GOAL and SCOPE Definition, the inventory results as given in Tables above, and LCIA results with explanation. Sample LCIA results are given here.*

The material intensity for Toyir et al. 1998 is the highest, thus making it the “worst process”. This means that the process uses more materials per unit of ethanol produced. A closer look at the process reveals that it uses more carbon dioxide than the other processes. Thus, carbon dioxide use intensity will give a better assessment of whether this process is better than the others in terms of removing the GHG from the atmosphere. Thus in this case, having a high material intensity is good because it uses CO2. The Conventional process has the least material intensity.

The water intensity for Jun et al. 1998 is significantly higher than the rest of the processes. Because only cooling water is considered in the water intensity, this means that a high amount of energy is liberated in the process that needs to be removed by the cooling water. The conventional process has the lowest water intensity.

Toyir et al., 1998 has high energy intensity, denoting the high use of external energy in the processes. The conventional process has the lowest energy intensity. From this, it can be anticipated that the Toyir et al. 1998 process will have higher GHG emissions due to energy generation compared to the rest of the processes.

The global warming potential for all the processes are negative, because carbon dioxide or methane are consumed in the processes. The conventional process consumes both CO2 and CH4 and has the lowest GWP.

Toyir et al., 1998 has the highest smog formation potential. This is due to the high amount of carbon monoxide produced with methanol, both of which have SFP. The conventional process has the least SFP.

Toyir et al., 1998 had high CO production, which caused the Human Health impacts to be high. Bonivardi et al., 1998 had CO production, as well as the conventional process, but these were negligible compared to the Toyir et al., 1998 process.

Based on the results, the conventional process is best in all the categories on a relative scale. It will possibly be beneficial to keep the conventional process. Improvement of the other processes based on these results is desired to make them acceptable.

**References:**

Mukherjee R, Sengupta D, Sikdar SK, “Selection of Sustainable Processes using Sustainability Footprint Method: A Case Study of Methanol Production from Carbon Dioxide” in “Sustainability of Products, Processes and Supply Chains”; edited by Fengqi You, Elsevier, expected publication June 2015.

Bare J, 2014, TRACI 2.1, personal communication on May 7th, 2014.