Production and Cost Analysis of Dimethyl Ether for Transportation

Rev 5: June 19, 2017

Business Objectives

The use of dimethyl ether (DME) as a transportation fuel has been called a path towards near zero particulate emission diesel cars [2], and vehicles. DME can be produced from a variety of sources such as sustainable biomass, municipal solid waste, [3] or CO2 and sustainable energy supplies [2], as well as natural gas and methanol making it a flexible and unique product with potentially improved environmental and human health impacts.

This project asks that you to determine the production cost of DME, and if necessary, the required incentives to motivate transportation users to switch from low sulfur diesel to DME. Your recommendations should include a risk analysis of technical, business and safety. Key validation tests of your assumptions can be recommended if they cannot be completed as part of this study.

The plant should be capable of supporting a high volume shipping region of 2000 trucks (6 mi/gal x 12 hr/day), or 250,000 US gal/day of DME. Where possible in the design, innovative technologies should be used to avoid intellectual property licensing costs.

Methanol should be considered the feed material for the process and will be delivered by railcar. Methanol transportation costs from the Lake Charles MeOH plant, or another, should be considered to be (0.02 \$/ gal), unless you can find a more accurate value. Methanol pricing will subject to market prices throughout the life of the project and [4] historical prices be found on websites such as www.Methanex.com.

Please consider the following when designing the system:

1. Production of DME should meet 250,000 US gal/day, with turn down to 50% of that.
2. Capital Costs and Operational Costs (including operating labour) should be included in the economic analysis.
3. You can consider that part of the facility will be a truck filling station, but CAPEX/OPEX costs for the filling station can be excluded from your analysis.
4. The produced DME must meet the ISO DME Fuel Plant Gate Standard (ASTM D7901.144734) (see details below).
5. Lubrication additives for DME are required. The exact requirements are unclear at this time, but somewhere around 900 ppm (mass) can be assumed [5]. A bulk cost of \$1.65/lb, plus shipping (same as methanol shipping costs), for the lubricant can be used.
6. The process must have as small a carbon footprint as possible. Please make recommendations on how this can be achieved.
7. Please provide recommendations on ways to monetize any waste products.
8. For the purposes of your economic analysis assume the system will have a 20-year plant life, and a Minimum Acceptable Rate of Return (discount rate) of 8%.
9. Safety and Environmental aspects are considered in decisions and recommendations.

Technical Objectives and Data

DME Fuel Standard composition requirements: (ref ASTM ASTM D7901.144734)

Property	Requirement
DME, mass % (min.	98.5
Methanol, mass %, max.	0.05%
Water, mass %, max.	0.03%
Methyl Formate , mass %	report

Production Methods:

You may choose to use any process you wish, and the following information should be considered as only one possible starting point. Clearly explain the rational for the process you have selected.

DME can be produced by a gas phase condensation reaction of methanol using an acid catalyst. The reaction of Methanol to DME is as follows:

$$2 \text{ MeOH} <-> \text{DME} + H_2O$$

It is an exothermic equilibrium reaction catalyzed by an acid. There are numerous options for the catalyst, but typically solid (heterogeneous) catalysts are suggested in the literature. A literature search shows that a high temperature process using a gama alumina oxide catalyst is [6] [7] possible. Alternatively, a low temperature liquid process using a super-acid polymer resin has been examined [8]. Other catalysts options are possible, including a gas phase dual function catalyst that combines both methanol synthesis and DME formation steps from syngas. The DME formation reaction equilibrium favours low temperature, but kinetics favour high temperature. You should explain your justification for the reaction catalyst and conditions you choose.

Turton [9] describes the use of a gas phase reaction (above 250 and below 400 °C) for producing DME with the following data by Bondiera and Naccache:

$$-Rate\ methanol = Ae^{-Ea/RT} \times [PMethanol]$$

Where:

$$A = 1.21 \times 10^6 \left(\frac{kmol}{m^3 reactor\ hr\ kPa}\right)$$

$$Ea = 80.48 \frac{kJ}{mol}$$

$$[PMethanol] = Partial\ Pressure\ of\ Methanol\ (kPa)$$

The equilibrium constant can be calculated from the equation presented by Aguayo [10] and can be used to determine the reverse reaction. Values produced from the equilibrium equation below are relatively consistent with those obtained using a Gibbs Free Energy method.

$$\text{Ln Kp} = -9.76 + 3200/T + 1.07 \times \ln(T) - 6.57 \times 10^{-4} \times T + 4.9 \times 10^{-8} \times T^2 + 6050/T^2$$

Where T, is in Kelvin (between 240 and 340 °C).

Since the reaction is commonly done using a heterogeneous catalyst, and it has been found that water inhibits the reaction, other forms of the reaction equation could be used and some typical values are shown in the table below. The low temperature heterogeneous catalyst equation was found to have a constant initial reaction rate at Methanol concentrations that vary from pure methanol down to 5 mol/litre. The reverse direction is not considered, and thus a chemical equilibrium is not predicted by this correlation. You should use caution in using the correlation at MeOH concentrations below 5 mol/litre.

An equilibrium constant (Kc) for liquid molar concentrations was derived from Gibbs Free Energy and is follows:

$$\text{Ln(Kc)} = 787.64/\text{Temperature (K)} + 1.4937$$

Based on this Kc relationship, at equilibrium, the liquid methanol conversion from pure methanol follows the following correlation.

$$\text{MeOH Conversion (\%)} = -0.0363 \times \text{Temperature (°C)} + 95.881$$

Range of data fit by this equation is from 90 to 140 °C.

Other Kinetic Data

Reaction equation (ref Aspen HYSYS)and heterogeneous catalyst parameters for Methanol Dehydration:

$$Rate\left(\frac{kgmole}{m^3\,s}\right)=\frac{k\times[MeOH]^m-k'\times[H2O][DME]}{(1+K1\times[Methanol]^{(f1\_Methanol\_exp)}\times[H2O]^{(f1\_H2O\_\mathrm{exp})}+K2\times[H2O]^{(f2\_H2O\_\mathrm{exp})})^n}$$

$$\text{Where:}$$

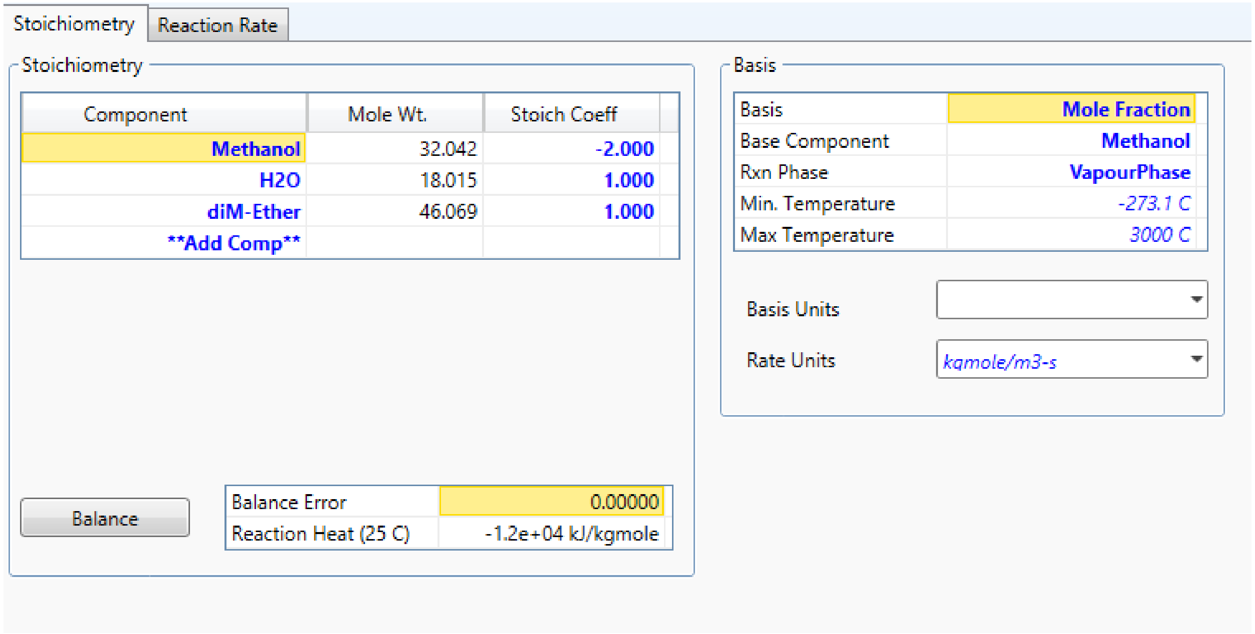
$$k,k'=A\times e^{-\frac{E}{RT}}$$

$$K1,K2,\ldots=A1\times e^{-\frac{E1}{RT}}$$

$$[Methanol]\,,\ [H2O],\ [DME]=mole\ fraction\ of\ material$$

Catalyst Reaction Kinetic Parameters and Data	High Temperature Gas Phase (Gamma Alumina catalyst) [6]	Low temperature Liquid Phase (high acid resin i.e. Amberlyst 35)
Heat Of Reaction, kJ/kgmole	-11712.0	-11712.0
A forward, kgmole/m3-s	1.0626×10^6	1.2457×10^{11}
E forward, kJ/kgmole	65633.0	98000.
m Forward Reaction Order	2	0
A' reverse, kgmole/m3-s	1.4677×10^7	(no reverse rxn data)
E' reverse, kJ/kgmole	88994.0	(Correlation limited from pure to 5mol/litre MeOH)
A1	0.5366	1.565×10^{-3}
E1, kJ/kgmole	-3450.0	-24642.7
f1_Methanol _exp	0.5	-1
f1_H2O_exp	0	1
A2	4.50×10^{-2}	n/a
E2, kJ/kgmole	-9395.0	n/a
f2_H2O_exp,	1	n/a
n, Denominator Exponent	4	2
Maximum Temp, °C	400 (catalyst deactivation), Ref: Turton	150 (catalyst limit) ref: DOW data sheet
Price	\$4.65/lb - \$5.25/lb.	\$15 / lb in large quantities
Bulk Density (typical), gm/cm^3	0.882	0.607
Material Density (typical), gm/cm3	1.47	1.504
Void Fraction	0.40	0.60
Life	9 to 12 months	unknown

i.e, High temperature reaction kinetic parameters (for heterogeneous catalysts) in Aspen HYSYS are:



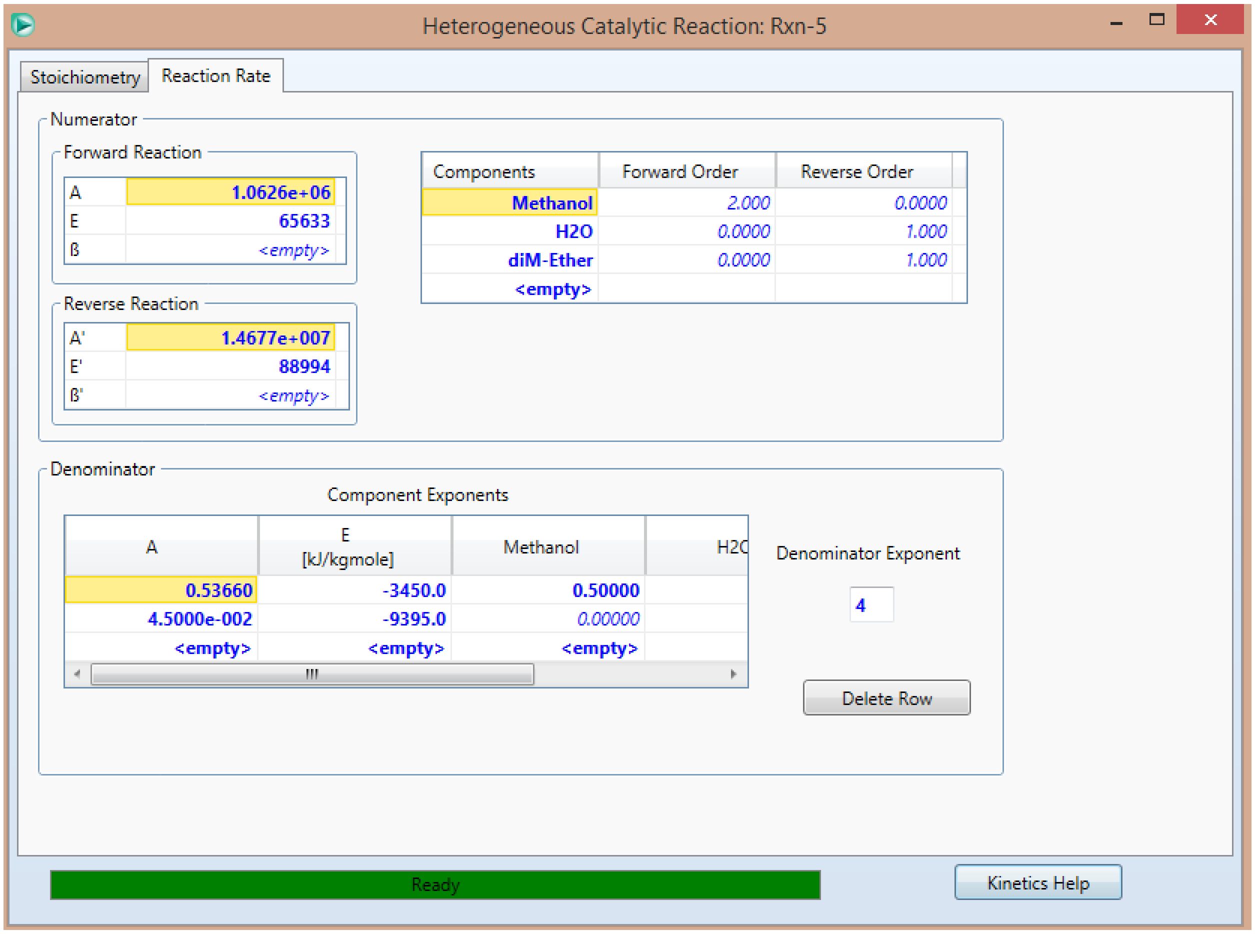
Component	Mole Wt.	Stoich Coeff
Methanol	32.042	-2.000
H2O	18.015	1.000
diM-Ether	46.069	1.000
Add Comp		

Basis	Mole Fraction
Base Component	Methanol
Rxn Phase	VapourPhase
Min. Temperature	-273.1 C
Max Temperature	3000 C

Basis Units:

Rate Units: kgmole/m3-s

Balance Error	0.00000
Reaction Heat (25 C)	-1.2e+04 kJ/kgmole



Forward Reaction

A	1.0626e+06
E	65633
ß	<empty>

Reverse Reaction

A'	1.4677e+007
E'	88994
ß'	<empty>

Components	Forward Order	Reverse Order
Methanol	2.000	0.0000
H2O	0.0000	1.000
diM-Ether	0.0000	1.000
<empty>		

A	E [kJ/kgmole]	Methanol	H2C
0.53660	-3450.0	0.50000	
4.5000e-002	-9395.0	0.00000	
<empty>	<empty>	<empty>	

Denominator Exponent: 4

Catalyst Limitations:

Low Temperature Catalyst:

The low temperature catalyst is superacid polymeric material. Although it will not soften at higher temperatures, it will desulfonate in a way that releases SO_3 groups forming H_2SO_4 in aqueous solutions. Kinetics of the degradation reaction can be assumed negligible at temperatures less than 120°C, and the catalyst weight loss due to lost SO_3 is 15.9% weight at 160°C [11].

Reactor designs for this catalyst (for large) are usually no more than 30 ft in height, with a preferred pressure drop of less than 15 psi (max 30psi). The Ergun equation is a reasonable method to estimate the pressure drops. Larger pressure drops tend to compress the beads and cause fines that can blind screens in a reactor.

Further vendor information for the catalyst can be found at: http://cheedesign.net/AICHE2018/

Thermodynamics:

The published properties of Methanol/DME/Water Systems are such that DME and Water will form two liquid phases when MeOH concentrations are low [9] [12]. Separation methods should consider the effects of a possible three phase mixture in this region.

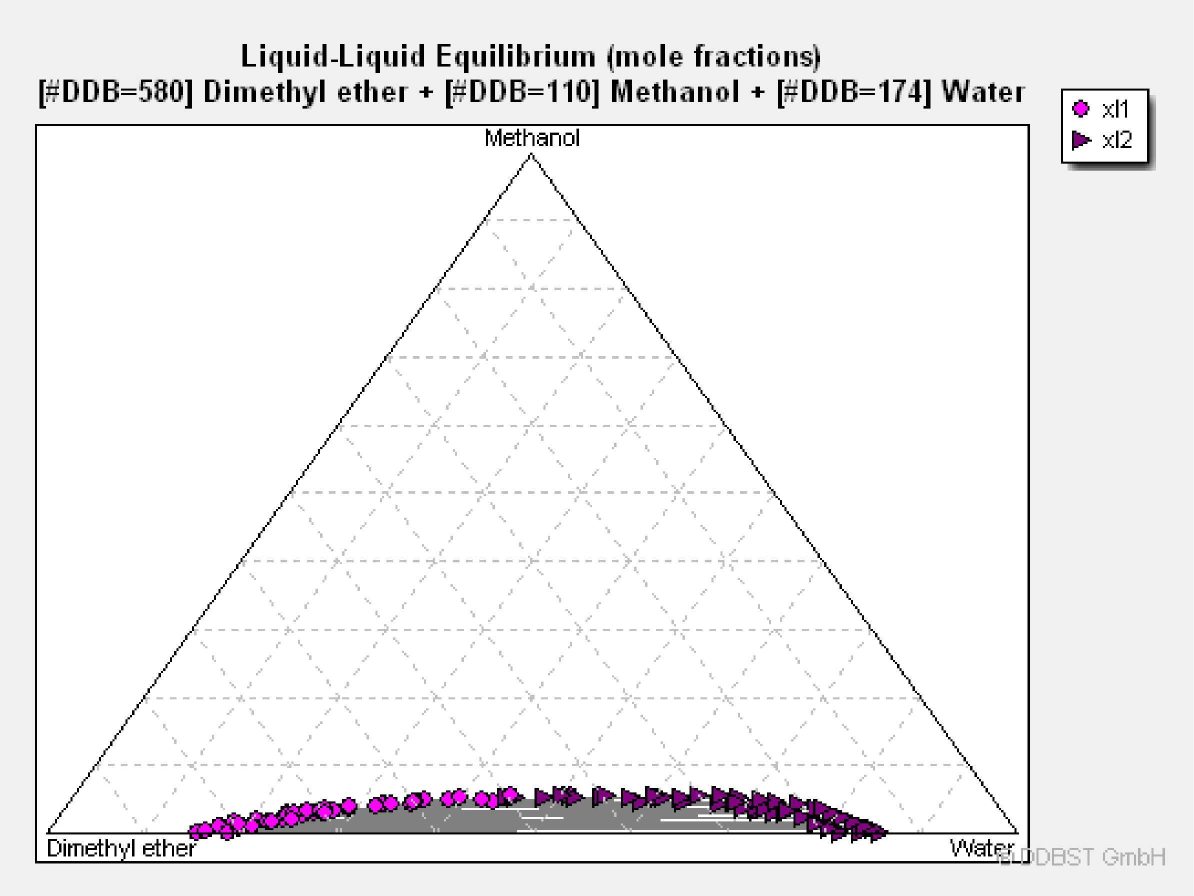


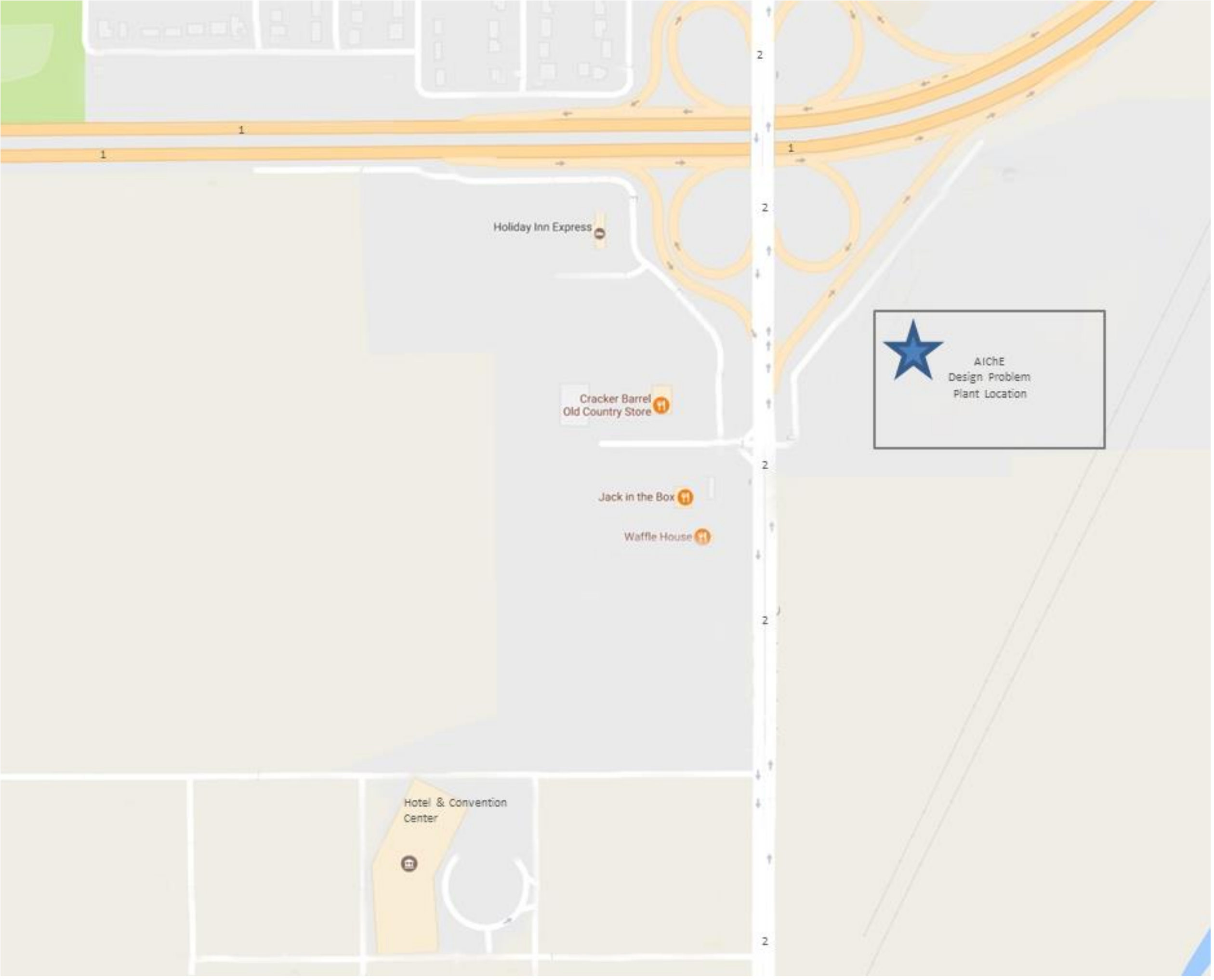
Fig 1: Liquid-Liquid Equilibrium of DME/Water/Methanol, Courtesy of DDBST

Intellectual Property (IP)

Currently there are a variety of processes being proposed for the production of DME from a variety of feedstocks. The process proposed by you should consider the cost of licensing the IP, or attempt to develop a process that would avoid IP issues.

Plant Location, Safety and Environmental Information:

For consideration of safety and environmental review, assume the plant could be located at the following location: https://www.google.ca/maps/place/Lake+Charles,+LA,+USA/@30.2123853,-93.3240263,16.74z Note: this location has been arbitrarily chosen so that it is close the Lake Charles Methanol Plant project and for its proximity to highways, and access to rail and pipelines. Permission of the actual owners of the land has not been discussed, or asked for this purely academic contest. Justified recommendations for relocation are acceptable. You can consider that part of the facility would be a truck filling station. Consequences Analysis [13] [14] may be used to support statements. You may use the following spreadsheet to screen for offsite consequences [15] http://www.cheedesign.net/consequence/default.html .



Safety Data for Methanol and DME are available. The lubricant has the following properties:

Lubricant Additive Properties	Value
Specific Gravity	0.898
Flash Point, °C	200 °C, closed cup
Maximum Temperature for long term storage,	27°C, degradation occurs at 40°C
Viscosity, cST	24 @ 80°F

ENVIRONMENTAL Criteria:

Assume the waste water could be sent to a municipal waste treatment plant. Methanol does not have an absolute limit; it's based on available technology to remove the methanol for pre-treatment prior to discharging to receiving waters. One criterion that would be evaluated by the regulator is to examine the breakeven cost of purifying the methanol. The breakeven cost means when the dollar value of methanol lost is equal to the dollar value of energy required to purify the methanol. An assumption around the cost of Methanol ($420/MT) can be used for this analysis. Other criteria include ensuring the discharge water is below the Lower Explosive limit, and does not present a toxicity hazard. The regulator might consider the trade-off of higher allowable MeOH concentrations in the waste water with the positive effects on improved air quality due to adoption of DME vehicles, and the reduction in CO2 emissions to provide a less restrictive separation.

Bibliography:

[1] W. D. Seider, Product and Process Design Principles: Synthesis, Analysis and Evaluation, Wiley, 2008.

[2] Ford Motor Company, "Ford Leads Project to Develop Near Zero Particulate Emission Diesel Cars That Could Run on Converted CO2," 11 9 2015. [Online]. Available: https://media.ford.com/content/fordmedia/feu/en/news/2015/09/11/ford-leads-project-to-develop-near-zero-particulate-emission-die.html. [Accessed 9 5 2017].

[3] International DME association, "Recent Headlines: First Customer Demonstration of DME-Powered Mack Truck Begins in New York City," 12 1 2017. [Online]. Available: https://www.aboutdme.org/index.asp?sid=97. [Accessed 5 5 2017].

[4] Methanex, "Current Posted Prices," Methanex, [Online]. Available: https://www.methanex.com/our-business/pricing.

[5] National Research Council Canada, "Dimethyl ether fuel literature review," 18 06 2015. [Online]. Available: http://nparc.cisti-icist.nrc-cnrc.gc.ca/eng/view/object/?id=b22a2fd1-f2fc-40d9-a6f4-cf109f3ea344. [Accessed 04 05 2017].

[6] Bercic, "Catalystic Dehydration of Methanol to Dimethyl Ether. Kinetic Investigation and Reactor Simulation," *Ind Eng Chem Res ,* Vols. 32, , pp. 2478-2484, 1993, .

[7] Bercic, "Intrinsic and global reaction rate of methanol dehydration over g-Al2O3 pellets," *Ind Eng Chem Res,* vol. 31, pp. 1035-1040, 1992.

[8] H. Hosseininejad, "Catalytic and kinetic study of methanol dehydration to dimethyl ether," *Chem Eng Res Design,* 2012.

[9] Turton, Analysis Synthesis and Design Of Chemical Proceses, Prentice Hall, 1998.

[10] J. E. D. M. J. M. A. M. O. a. J. B. Andre´s T. Aguayo, "Kinetic Modeling of Dimethyl Ether Synthesis in a Single Step on a CuO-ZnO-Al2O3/γ-Al2O3 Catalys," *Ind. Eng. Chem. Res. ,* vol. 46, pp. 5522-5530, 2007.

[11] D. Chemical, Dow Chemical, 2015. [Online]. Available: http://cheedesign.net/AICHE2018/default.html. [Accessed 5 Sept 2017].

[12] D. Database, " http://www.ddbst.com/," DDBST GmbH (Oldenburg). [Online].

[13] Crowl, Chemical Process Safety Fundamentals with Applications, Prentice Hall, 2011.

[14] U. S. E. P. Agency, "RMP Guidance for Offsite Consequence Analysis," 31 May 2017. [Online]. Available: https://www.epa.gov/rmp/rmp-guidance-offsite-consequence-analysis. [Accessed 31 may 2017].

[15] D. Mody, "Consequence Analyzer for 2018 AIChE Design Problem," [Online]. Available: http://www.cheedesign.net/consequence/ConsequenceAnalyser.xls. [Accessed 1 5 2017].

[16] Chemical & Engineering News, "Gulf methanol plant gets $2 billion loan," 27 12 2016. [Online]. Available: http://cen.acs.org/articles/94/web/2016/12/Gulf-methanol-plant-2-billion.html?type=paidArticleContent. [Accessed 4 5 2017].