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Process Development for Conversion of Carbon Dioxide to Dimethyl Ether

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A B S T R A C T

Carbon dioxide emissions have been increased into the atmosphere recently and consequently carbon content in atmosphere increases and contributing to global warming. Captured CO_2 may become a profitable income, besides controlling the carbon content in the atmosphere. A process development to produce clean and economic fuel-grade dimethyl ether (DME) from captured CO_2 which recently attract the attention of industry is achieved in this work, and also methods used according to the use of raw material as each direct or indirect process have a different operating condition with specified catalyst and kinetic models for synthesis process. A process simulated program has been used in this work. The heat integration has been used in the development of the process and energy saving reached 40% as it reaches 50 MW_{th} energy saving between the actual energy must use before any integration process and after integration in whole utility streams. As the total Energy capacity for factory to produce 44.2 t/h of DME is 125 MW and after process of Energy saving which include inserting heat exchangers the energy capacity reaches 75 MW. The plant capacity handles 88 t/h of CO2 with 12.1 t/h of H2 to produce 63.5 t/h of methanol and finally production of main product is 44.2 t/h of DME so it requires nearly 2 t/h of CO2 per ton of dimethyl ether produced.

Keywords:

Dimethyl ether, Process design, Hydrogenation, Carbon dioxide.

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1. Introduction

Carbon dioxide emissions from many industries and transportation, for instance cement industry, affect the environment negatively because it increases carbon content in the environment [1]. Therefore, it enhances global warming, i.e., the temperature of atmosphere increases from 2 to 4 ^{o}C. To minimize the carbon content in atmosphere, carbon dioxide may be used as a raw material for allied chemicals [1-6]. Carbon dioxide may be converted to many useful chemicals through process of carbon capture and storage [7-10], for instance methanol, ethanol, dimethyl carbonate, acetic acid, formaldehyde and dimethyl ether [11-15].

Dimethyl ether (DME) is considered as useful chemical may be produced from carbon dioxide hydrogenation as it may be used as a fuel for transportation [16, 17].

DME may be produced by two methods, namely conventional method as it uses methanol as a raw material feed stoke and direct method which uses carbon dioxide as

Nomenclature and the symbol list

Symbol	Definition	unit
DME	Di-methyl ether	
MEOH	Methanol	
ΔH_0	Enthalpy change	(kJ/mol)
r	Rate of reaction	(mol/$Kg_{cat}S$)
K	Reaction rate constant	
K_s	Kinetic parameter	
K_{eq}	Thermodynamic equilibrium constant	
A_i	Arrhenius equation constants	
B_i	Arrhenius equation constants	
R	Gas constant = 8.314	(J/mol K)
T	Temperature	(K)
P_i	Partial pressure of component i	(bar)
A	Kinetic model constant	
B	Kinetic model constant	
C_i	Concentration	(mol/kg)

raw material feed stokes. So the direct process is very important than conventional method as it considered as promising technology for carbon dioxide conversion, cost of producing DME is lower than conventional and promoting biogas gasification process [18-20].

Ishag et al. [21] provided new technique for DME production from CO_2 and H_2 The synthesis of methanol undergoes a strongly exothermic reaction at high temperature (225–300 ^oC) and high pressure (50–150 bar). The mixed gas stream is then fed to the distillation tower to separate the synthetic methanol from the water.

The separated methanol is then fed into the DME fusion reactor, which undergoes high temperature (250–400 ^oC) and high pressure (18 bar). The mixed gas stream is then routed to the distillation columns to separate the synthetic DME from the water.

Catizzone et al. [22] used zeolites at 260 ^oC and 30 bar to convert CO_2 to DME yields high amount of water and Zeolites are more resistant to water. Michailos et al. [23] used Aspen Plus V10 to simulate DME synthesis process and Simulation done by mixing CO_2 with hydrogen and then compress to 75 bar and 210 ^oC to methanol reactor using catalyst $Cu/ZnO/Al_2O_3$, then methanol produced fed to packed bed reactor for dehydration process to synthesis DME.

Kartohardjono et al. [24] produced DME via simulation using Unisim Design R390.1 as a simulation program via two way direct and in direct process using hydrogen and acid gas which consider to be CO_2, Indirect process produced methanol in single bed reactor with purity 99% conversion of CO_2 to methanol then methanol sent to another single bed reactor to produce DME, conversion is 0.87. Direct process to produce DME via single bed reactor by producing methanol then conversion process from methanol to DME in the same reactor at 40 bar and 276 ^oC, DME produced with purity 99%, catalyst used was Cu-ZnO.

De França Lopes et al. [25] produced dimethyl ether via direct process from CO_2 and using Aspen HYSYS simulation program. DME produced in plug flow reactor using ($CuO-ZnO-Al_2O_3$) for methanol production and γ-Al_2O_3 as solid acid for DME production. Produced DME with purity 99.9% and 1 kg of DME produced from 1.6 Kg of syngas. CO_2 captured from industries flue gases for instances cement industry [5-8], while H_2 produced by water electrolysis [23, 26, 27].

Salomone et. al. [28] developed the effect of CeO_2 and

ZrO_2 on In_2O_3-based catalysts in this study, testing samples occured in a fixed bed reactor under different reaction conditions. CO adsorption was amplified by adding Ce or Zr from 1.8 $mmol_{CO2 \cdot gcat}^{-1}$ of pure In_{100} up to 10.6 $mmol_{CO2 \cdot gcat}^{-1}$ of $In_{40}Ce_{60}$ or 6.6 $mmol_{CO2 \cdot gcat}^{-1}$ of $In_{40}Zr_{60}$. Results suggest that the higher specific activity (168 mg $_{CH3OH.gIn2O3}^{-1.}{}_{h}^{-1}$ at 300 °C and 2.5 MPa $In_{40}Zr_{60}$) is due to the electron promotion of Zr.

Salomone et. al. [29] study the activity of variously prepared CuZnZr furrieries-based hybrid catalysts has been investigated in light of the physicochemical changes that occur during the direct conversion of carbon dioxide to dimethyl ether. The experiments occurred in a fixed bed reactor at a pressure of 2.5 MPa and a stoichiometric H_2/CO_2 molar ratio, whereby both the reaction temperature (200–300 °C) and the reaction temperature (200–300 °C) were changed, Activity assays showed higher catalyst activity at higher oxide-to-zeolite mass ratios, With maximum DME efficiencies as high as 4.5%. At lower oxide/zeolite ratios, the catalysts showed comparable DME yields, while mixed sample showed high CO hydrogenation activity but low selectivity for methanol and DME.

Guzmán et. al. [30] developed a new catalyst for CO_2 conversion to methanol and found that during the hydrogenation of CO_2, a methanol selectivity of close to 100% was achieved with the Cu/ZnO catalyst at 200 °C, a value that decreases at higher temperatures (i.e. 23% at 300°C) due to the thermodynamic limit. Cu/ZnO composite catalysts were prepared using commercial copper and zinc oxide nanoparticles. The size of zinc is about 20-25 nm. Samples were prepared by pre-oxidizing Cu/ZnO at 150 °C for two hours in still air, followed by manual mixing with ZnO and 65/35 is molar ratio between Cu/ZnO.

The objective of this work is to develop a process for conversion of carbon dioxide to dimethyl ether and economical study for the process will be achieved. DME is produced using catalytic hydrogenation, which contains compression, methanol synthesis, methanol dehydration, energy generation and optimization and DME purification. Process simulation and design were done using Aspen Plus V10 process simulator. Also, to obtain mass and energy integration to perform the best operating parameters and cost minimization.

2. Process Simulation of carbon dioxide conversion

Production of DME may be performed using either direct method or indirect method, direct method includes conversion of carbon dioxide directly to DME in packed bed reactor over bi-functional catalyst. Indirect method includes production of methanol through dehydrogenation of carbon dioxide then methanol dehydration to DME [13, 31, 32].

In this paper indirect method will be used to produce DME

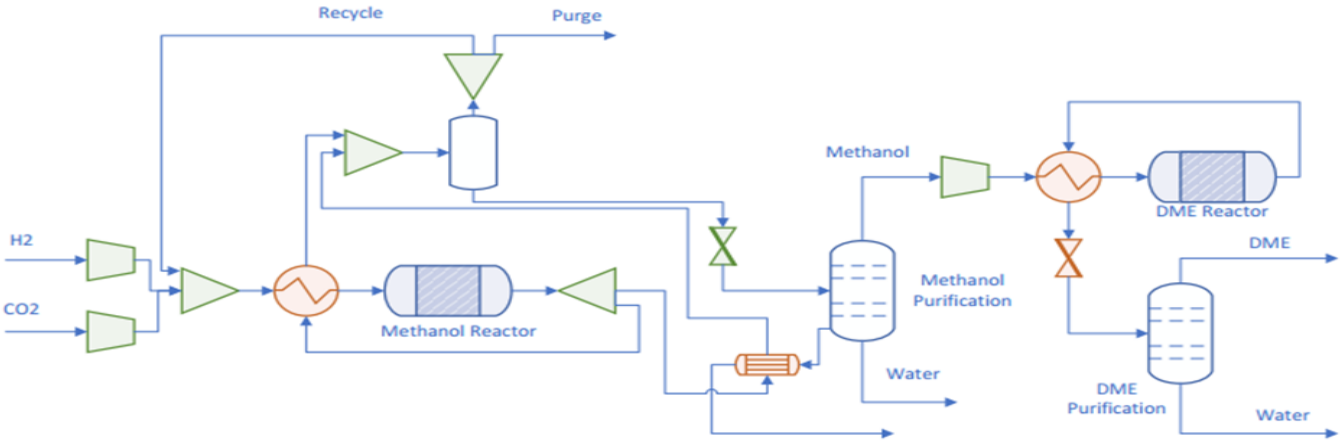


Figure 1 Process flow diagram using Visio Microsoft office for production of DME from CO_2

from CO_2, as shown in Figure 1. Figure 1 illustrates process flow diagram using Visio Microsoft office for production of DME from CO_2.

Production of methanol from CO_2 and reverse water gas shift reaction then dehydration of methanol to DME are shown below in equations 1 to 4:

CO hydrogenation: $CO + 2H_2 \leftrightarrow CH_3OH + H_2O$

$\Delta H_0 = -128$ kJ/mol (1)

CO2 hydrogenation: $CO_2 + 3H_2 \leftrightarrow CH_3OH$

$\Delta H_0 = -49.5$ kJ/mol (2)

Reverse water gas shift: $CO_2 + H_2 \leftrightarrow CO + H_2O$

$\Delta H_0 = +41.2$ kJ/mol (3)

Methanol dehydration: $2CH_3OH \leftrightarrow CH_3OCH_3 + H_2$

$\Delta H_0 = -23.4$ kJ/mol (4)

2.1. Process modeling

Aspen Plus simulation program V10 was used for process simulation and optimization. Two property methods used in this simulation first one for high pressures more than 10 bars which is RKSMHV2 and second method for low pressures less than 10 bars which is NRTL-RK. For pumps efficiencies are set at 70% and for compressors and turbine efficiencies are set at 95% and 90% for both mechanical and isentropic respectively [33].

The pressure drop in heat exchangers is typically phase dependent. Usually, the Gases stream fed to fixed bed reactor with specified temperature profile.

2.2. Flow sheet description

Carbon dioxide used in plant as recommended captured and storage from flue gases of industries for instance cement industry, it delivered to plant with 88 t/hr. with pressure 1 bar and 25 ^oC. The required H_2 (3:1 H_2: CO2 molar ratio for methanol synthesis) delivered with 30 bar and 25 ^oC. The first to do is to prepare inlet streams to pressure and temperature of methanol reactor. CO_2 is fed to multistage compressor consisting of 4 stages with intercooler streams. Figure 2 shows all process equipment and appendix a contain material stream Tables (7- 9).

H_2 stream pressurized using compressor to 75 bars. Both streams are fed to two mixers (B5, B6) as second one for

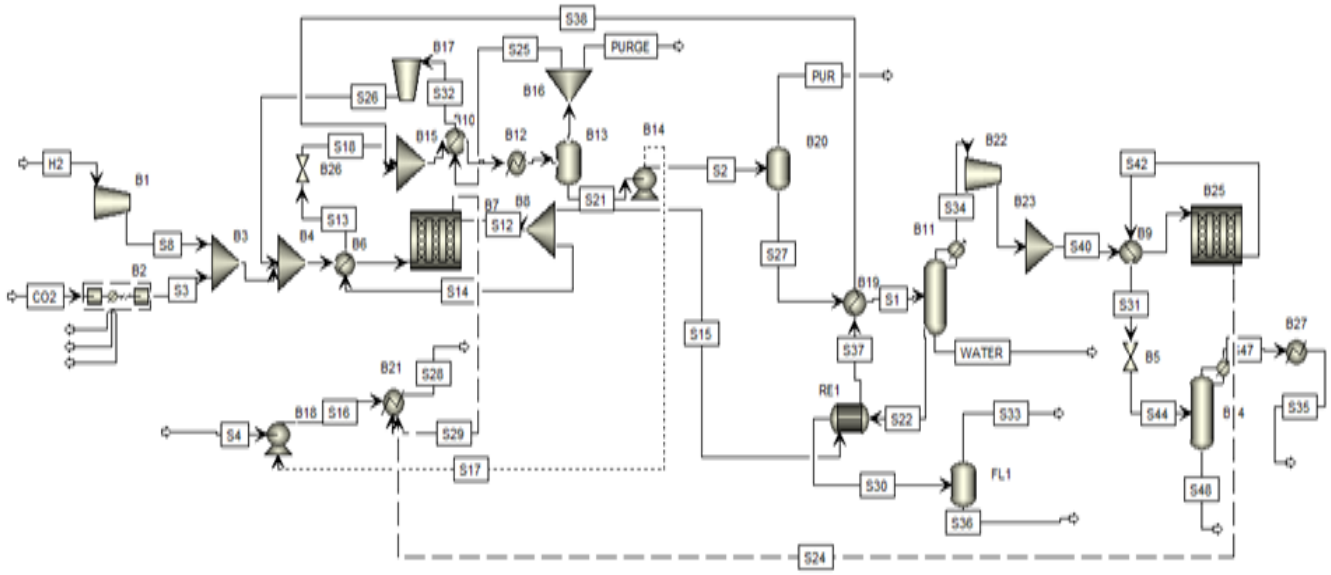


Figure 2 – Process simulation using Aspen Plus for production of DME from CO_2

convergence with recycled, stream then fed to heat exchanger to raise stream temperature to 220 ^{o}C inlet reactor temperature,

then flow the outlet stream from the reactor split into two streams first on to heat exchanger before the reactor to heat up inlet flow to reactor, second stream to reboiler of distillation column to make best heat integration and then to heat up distillation feed. The Two split streams remixed again in a mixer then fed to heat exchanger to heat up recycled stream from flash first flash drum, after heat exchanger the stream fed to cooler to reduce its temperature to 35 ^{o}C, then fed to flash drum to separate unreacted gases and then to splitter to recycle, most of unreacted flue gases and vent purge to atmosphere. After first flash drum, bottom product fed to pump turbine to reduce its pressure to 1 atm and to generate electricity then fed to second flash drum also to recycle most of unreacted gases and then to heat exchanger before distillation column then fed to distillation column to separate water from methanol and obtain a purified methanol with purity 99.99% which will be used as a raw material. Second step in this plant to synthesis DME as a final product from carbon dioxide.

Purified methanol fed to compressor to increase its pressure to 5 bar then to heat exchanger to raise its temperature to 250 ^{o}C then fed to DME fixed bed reactor which convert most of methanol to DME, reactor outlet stream send to heat exchanger before the reactor then to valve to reduce its pressure to 3 bar, then final stream sends to distillation column to separate DME with purity 99.99 % and from bottom stream to separate water produced in the reactor.

2.3. Process Kinetics and Design

There are two kinetic models in this work first one for synthesis of methanol from carbon dioxide and this model was developed by Vanden Bussche [34] and parameters were adjusted by Mignard [35] where pressures in bar and temperatures are in K. Kinetic parameters shown in Table 1 and also follow Arrhenius law. Graaf et al. [36] illustrated thermodynamic constants.

Methanol synthesis:

$$r_{CH_3OH} = \frac{K_1 P_{CO_2} P_{H_2} (1 - \frac{1}{K_{eq1}} \frac{P_{H_2O} P_{CH_3OH}}{P_{H_2}^3 P_{CO_2}})}{(1 + k_2 \frac{P_{H_2O}}{P_{H_2}} + K_3 P_{H_2}^{0.5} + K_4 P_{H_2O})^3} \quad [\frac{mol}{Kg_{cat} S}] \quad (5)$$

Water gas (RWGS) shift reaction:

$$r_{RWGS} = \frac{K_5 P_{CO_2} (1 - K_{eq2} \frac{P_{H_2O} P_{CO}}{P_{CO_2} P_{H_2}})}{(1 + k_2 \frac{P_{H_2O}}{P_{H_2}} + K_3 P_{H_2}^{0.5} + K_4 P_{H_2O})} \quad [\frac{mol}{Kg_{cat} S}] \quad (6)$$

$$K_i = A_i \exp(\frac{B_i}{RT}), \quad (7)$$

$$log_{10} k_{eq1} = \frac{3066}{T} - 10.592, \quad (8)$$

$$log_{10} \frac{1}{K_{eq2}} = -\frac{2073}{T} + 2.029 \quad (9)$$

Table 1- Parameters kinetic model [37]

K_1	A_1	1.07
	B_1	40,000
K_2	A_2	3453.38
	B_2	-
K_3	A_3	0.499
	B_3	17,197
K_4	A_4	$6.62*10^{-11}$
	B_4	124,119
K_5	A_5	$1.22*10^{10}$
	B_5	-98,084

Aspen Plus can't deal directly with these equation so, thermodynamic equations rearranged and illustrated in new equation and parameters in Table 2 [37], As Aspen Plus deal with certain types of data, the rearranged data appears in next equations and also Table 2 shows kinetic parameters that also follow Arrhenius equations.

$$r_{CH_3OH} = \frac{K_1 P_{CO_2} P_{H_2} - K_6 P_{H_2O} P_{CH_3OH} P_{H_2}^{-2}}{(1 + k_2 P_{H_2O} P_{H_2}^{-1} + K_3 P_{H_2}^{0.5} + K_4 P_{H_2O})^3} \quad [\frac{mol}{Kg_{cat} S}] \quad (10)$$

$$r_{RWGS} = \frac{K_5 P_{CO_2} - K_7 P_{H_2O} P_{CO} P_{H_2}^{-1}}{(1 + k_2 P_{H_2O} P_{H_2}^{-1} + K_3 P_{H_2}^{0.5} + K_4 P_{H_2O})} \quad [\frac{mol}{Kg_{cat} S}] \quad (11)$$

$$\ln K_i = A_i + \frac{B_i}{T} \quad (12)$$

Table 2 – Rearranged parameters kinetic model

K_1	A_1	-29.87
	B_1	4811.2
K_2	A_2	8.147
	B_2	0
K_3	A_3	-6.452
	B_3	2068.4
K_4	A_4	-34.95
	B_4	14,928.9
K_5	A_5	4.804
	B_5	-11,797.5
K_6	A_6	17.55
	B_6	-2249.8
K_7	A_7	0.1310
	B_7	-7023.5

Second kinetic model is for DME synthesis and was described by Langmuir –Hinshelwood mechanism provided by Berčič and Levec [38]. In this model the kinetic rate directly used in Aspen Plus and it is given as follow:

$$r_{DME} = \frac{K_s K_{MeOH}^2 (C_{MeOH}^2 - \frac{C_{Water} C_{DME}}{K_{eq}})}{(1 + 2\sqrt{K_{MeOH} C_{MeOH}} + K_{water} C_{water})^4} \quad (13)$$

$$K_s = 6.6 \times 10^8 \exp(\frac{-10800}{T}), \quad (14)$$

$$K_{MeOH} = 0.0072 \exp(\frac{830}{T}), \quad (15)$$

$$K_{Water} = 0.0045 \exp(\frac{1130}{T}) \quad (16)$$

$$lnK_{eq} = \frac{4019}{T} + 3.707lnT - 2.783 \times 10^{-3}T + 3.8 \times 10^{-7}T^2 - 6.561 \times \frac{10^4}{T^3} - 26.64 \quad (17)$$

As C_i is concentration, k_s kinetic parameter, K_i are adsorption constants, Pi are pressures and K_{eq} the equilibrium constant [23].

2.4. Reactor and Catalyst

Two reactors used in this plant, first fixed bed reactor for methanol synthesis which deal with equations (1-3) and also used rearranged kinetic model and parameters in Table 2, Fixed bed reactor designed with temperature profile as temperature increased with length, tubes length and diameter designed for best performance and also pressure drop calculations done by Ergun equation in Aspen Plus. 44,500 kg of commercial catalyst $Cu/ZnO/Al_2O_3$ used in the reactor with particle density 1775 kg/m^3 and bed void age 0.5 [37]. $Cu/ZnO/ Al_2O_3$ considered as best commercial catalyst based on studies done by Centi et al. [39].

Second Fixed bed reactor for DME synthesis from methanol which deal with equation (4) and also has kinetic model developed by Berčič et al. [38]. Fixed bed reactor designed with temperature profile increase also with tube length which show great performance tubes length and diameter designed for best performance and also pressure drop calculations done by Ergun equation in Aspen Plus. Commercial γ- Al_2O_3 catalyst [40] show best performance towards DME synthesis from methanol with particle density 1470 kg/m^3 and bed void age 0.4.

2.5. Distillation Columns and Heat Exchangers

Two distillation columns designed with rigorous model RADFRAC in Aspen Plus first one to purify methanol with 44 stages and feed stage in stage number 13 from top, second distillation column used to purify DME with 22 stages and 14 stripping stages.

Heat Exchangers in general designed to make the best use of heat to reduce heat losses and by the way to reduce plant costs, Pinch analysis method used in heat integration devolved by Linnhoff [41].

Coolers used cooling water at ambient temperatures and heat exchangers implemented in the simulation designed with minimum temperature approach 10 ^oC.

3. Results and Discussion

Methanol and DME conversion in the two fixed bed reactor along with reactor length are shown in Figures 3 and 4. Figure 3 shows methanol conversion along with reactor length and Figure 4 shows the conversion of both methanol and DME along with reactor length, and a fixed temperature profile show best conversion that considered to be more valuable in obtaining methanol from carbon dioxide in first fixed bed reactor and DME from methanol in second bed reactor as it was obtained, for methanol 0.71 kg methanol / kg of CO_2 and for DME considering CO_2 as a raw material, it was obtained 0.5 kg DME / Kg of CO_2 and these conversions and the produced amounts are more than other conventional amounts.

Figure 5 – Sensitivity analysis of amount of methanol Vs. catalyst diameter

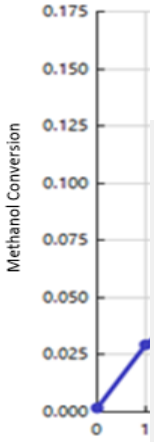
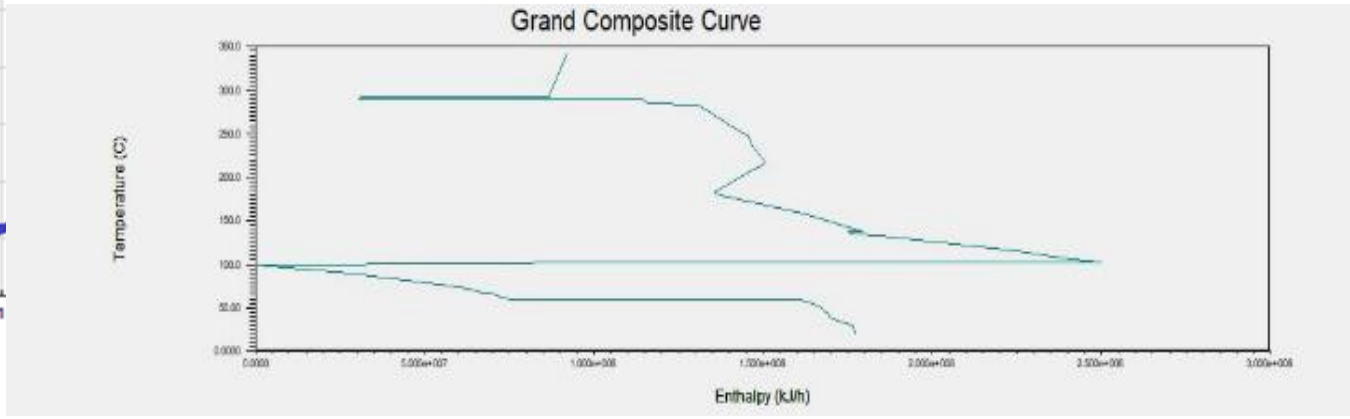


Figure 3 –



Methanol conversion

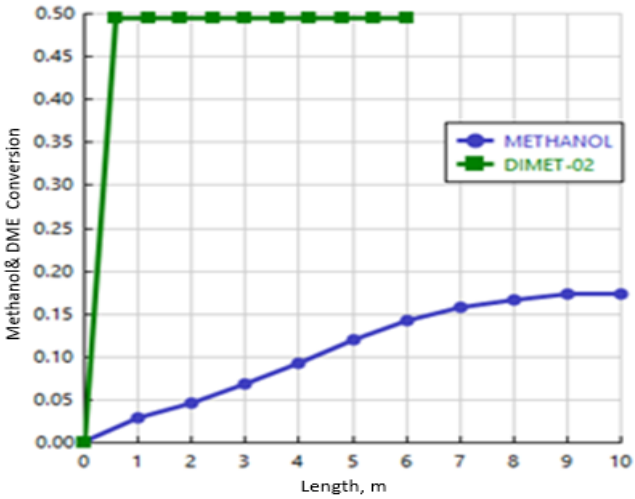


Figure 4 – Methanol and DME conversion

Sensitivity analysis have been done on catalyst diameter to maximize the MEOH mass flow which appear in Figure 5 – and found that max mass flow for methanol after first reactor obtained at 6.5 mm.

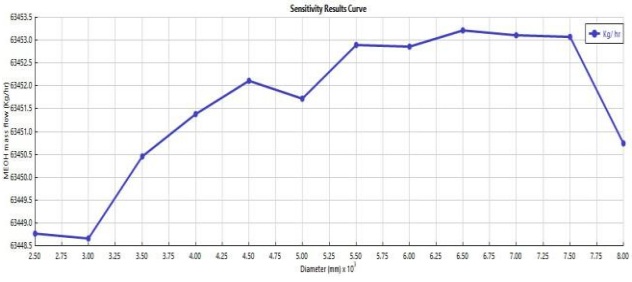


Figure 6 – Grand composite curve

3.1. Energy and Mass Integration

As mentioned and designed in process simulation recycle stream after first reactor for unreacted CO_2 and H_2 considered as mass integration as it isn't acceptable to vent unreacted gases which costs money to atmosphere and based on this mass integration 16.8 ton of CO_2 recycled again to process plant.

Energy integration and pinch analysis method applied to this process and Table 3 - illustrates heat exchangers and amount of energy integrated within.

Table 3 – Energy integration within Process stream

Heat exchanger equipment	Heat duty (MW_{th})	Utility
HX1	5.1	Integrated
HX2	5.9	Integrated
HX3	28.8	Cooling water
HX4	3.7	Integrated
HX5	1.3	Integrated
RE1	29.1	Integrated

After Applying pinch analysis method to the process, Figure 6 illustrates the grand composite curve and may represent the excess of heat which was integrated within the process for energy saving.

Two Fixed bed reactors includes exothermic reaction, heat generated within fixed bed reactors used to generate low pressure steam used in hole process with 27.4 $MW_{th,}$ Also pump turbine used to reduce pressure as mentioned in process description and generated 156 KW.

Also, Aspen Energy Analyzer AEA used to study the process and results shown that in all process streams we have 50 MW_{th} energy saving between the actual energy must use before any integration process and after integration in whole utility streams, about 40% energy saving resulting from that the total energy required for Process operation as illustrated in Figure 7 - is 125 MW, and after applying energy integration by adding heat exchangers to get the best performance and safe energy which will affect directly cost of production of DME, we found the energy required reduced to 75 MW.

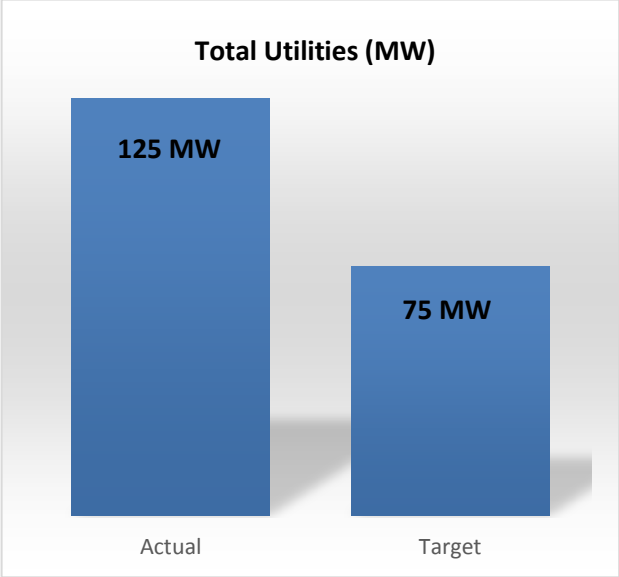


Figure 7 – Total energy required before and after integration.

As shown in Table 4 – some indicators which illustrate some of indicators which may affect directly the process related to product rates and amount of energy consumed in the process.

Table 4 – Key performance indicators related to the process of DME production plant.

Indicator	Value
DME Production rate	44.2 t DME/h
MEOH production rate	63.5 t MEOH/h
Overall CO2 conversion to DME	81.9 %
Overall MEOH conversion to DME	99.9%
Conversion factor	2 t CO_2 /t DME
CO2 use per unit of methanol product	1.39 Kg CO_2/ Kg MEOH
CO2 use per unit of DME product	2 Kg CO_2/ Kg DME
Electricity Usage for DME plant.	0.118 MW /t CO2 0.170 MW /t DME
Specific energy generation from utilities area	0.156 MWh/ t DME
Overall energy consumption	1.69 MWh/ t DME`

3.2. Cost Analysis for Raw Materials and Energy Usage.

One of the most important factor put into consideration for any plant is to gain economical product, Table 5 – show the cost of 1 ton of raw material and total cost per year and also for energy used and electricity.

Table 5 – Costs of raw materials and energy

Material	Cost

H_2 Cost	1.5 $/ Kg [42]
CO_2 Cost	0.183 $ / KG [43,44]
Total CO_2 & H_2 Cost (Raw Material Cost)	300,214,000 $/year
Electricity Cost	36.7 $/ t DME
Cooling water cost	2.313 $/ t DME
Steam Cost	33.1 $/ t DME

After customizing the work with all data and illustrating process, inputs and outputs. Also for work have been done on energy to integrate the maximum amount of energy which maximize the amount of produced DME comparing with energy used in the process. Also generating electricity is an important factor to take in consideration. Key performance indicators describes how the process have been developed, Grand composite curves describes amount of heat integrated within the process as describes previous in Figure 7, Table 6 summarize in brief inputs and outputs of the process.

Table 6 – Simulation inputs and results

CO2 input	88 t/ h
H2 input	12.1 t/ h
MeOH production	541.634 Kt methanol/ year
DME output	378.345 Kt DME/ year
Heating duties	25.6 MW
Cooling duties	49.3 MW
Electricity generation	156 KW

4. Conclusion and Recommendation

This research evaluated economic study of the Power to DME concept by hydrogenation of CO_2. A common modeling platform has been successfully established in the Aspen Plus using consistent data to establish the mass and energy balance for further economic evaluation. CO_2 balance showed that 1 ton of DME need 2 ton of CO_2 as The percent of CO_2 conversion to DME 81.9 with total production rate of DME 44.2 t DME/h and about 378.345 Kt DME/ year, with overall energy integration 40% of total amount of required energy as energy reduced from 125 MW to 75 MW. The process used electricity as source of power and finally cost analysis done over the process plant including raw materials and energy consumption which reached 35.413 $ / t DME for utilities and 36.7 $ / t DME for electricity.

Stream Name	Units	S16	S18	S19	S20	S21	S22	S23	S25	S26	S27	S28	S30	S31	S32	S33
Temperature	C	62.0044	209.063	35	35	35	94.5042	141.621	35	206.413	30.8706	338.804	98.1534	251.725	130.898	98.1534
Pressure	bar	72.9912	50	50	50	50	1	50	50	78	1.014	73	1	4.4	50	1
Mole Flows	kmol/hr	2000	5689.82	11380.1	7376.91	4003.6	5897.36	11380.1	7281.02	7281.02	3893.7	2000	5897.36	1943.76	7281.02	2522.31
CO2	kmol/hr	0	215.846	431.698	388.83	42.8767	3.35E-75	431.698	383.775	383.775	6.87381	0	3.35E-75	6.87311	383.775	0
CO	kmol/hr	0	5.76E-06	1.15E-05	1.14E-05	1.26E-07	8.99E-113	1.15E-05	1.12E-05	1.12E-05	1.95E-09	0	8.99E-113	1.95E-09	1.12E-05	0
H2	kmol/hr	0	3504.9	7010.22	6952.75	57.8972	1.04E-106	7010.22	6862.37	6862.37	0.639551	0	1.04E-106	0.639569	6862.37	0
H2O	kmol/hr	2000	978.832	1957.67	6.10432	1951.56	5733.61	1957.67	6.02496	6.02496	1948.73	2000	5733.61	968.264	6.02496	2381.54
METHANOL	kmol/hr	0	990.243	1980.49	29.2264	1951.26	163.755	1980.49	28.8465	28.8465	1937.46	0	163.755	7.69729	28.8465	140.772
DIMET-02	kmol/hr	0	0	0	0	0	0	0	0	0	0	0	0	960.286	0	0
Mass Flows	kg/hr	36030.6	65928.2	131858	32174.7	99684.3	108540	131858	31756.4	31756.4	97491.1	36030.6	108540	62233.4	31756.4	47414.7
CO2	kg/hr	0	9499.33	18999	17112.3	1887	1.47E-73	18999	16889.9	16889.9	302.515	0	1.47E-73	302.484	16889.9	0
CO	kg/hr	0	0.000161224	0.000322441	0.000318904	3.53E-06	2.52E-111	0.000322441	0.000314758	0.000314758	5.45E-08	0	2.52E-111	5.45E-08	0.000314758	0
H2	kg/hr	0	7065.45	14131.8	14015.9	116.714	2.09E-106	14131.8	13833.7	13833.7	1.28926	0	2.09E-106	1.2893	13833.7	0
H2O	kg/hr	36030.6	17633.9	35267.9	109.971	35157.9	103293	35267.9	108.541	108.541	35106.8	36030.6	103293	17443.5	108.541	42904.1
METHANOL	kg/hr	0	31729.5	63459.1	936.477	62522.7	5247.06	63459.1	924.303	924.303	62080.4	0	5247.06	246.638	924.303	4510.63
DIMET-02	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	44239.5	0	0
Volume Flow	l/min	818.561	74075.4	66952.9	64369.8	2585.68	2573.1	107072	63534.2	63987	2515.81	19649	1.29E+06	317006	83304.9	1.29E+06
Mass Fractions																
CO2		0	0.144086	0.144087	0.531857	0.0189297	1.36E-78	0.144087	0.531857	0.531857	0.003103	0	1.36E-78	0.00486048	0.531857	0
CO		0	2.45E-09	2.45E-09	9.91E-09	3.54E-11	2.32E-116	2.45E-09	9.91E-09	9.91E-09	5.59E-13	0	2.32E-116	8.76E-13	9.91E-09	0
H2		0	0.107169	0.107174	0.435619	0.00117083	1.93E-111	0.107174	0.435619	0.435619	1.32E-05	0	1.93E-111	2.07E-05	0.435619	0
H2O		1	0.267472	0.267469	0.00341793	0.352693	0.951658	0.267469	0.00341793	0.00341793	0.360103	1	0.951658	0.280292	0.00341793	0.904869
METHANOL		0	0.481274	0.48127	0.029106	0.627207	0.0483424	0.48127	0.029106	0.029106	0.636781	0	0.0483424	0.00396311	0.029106	0.0951313
DIMET-02		0	0	0	0	0	0	0	0	0	0	0	0	0.710863	0	0
Mole Fractions																
CO2		0	0.0379354	0.0379346	0.0527091	0.0107095	5.68E-79	0.0379346	0.0527091	0.0527091	0.00176537	0	5.68E-79	0.00353599	0.0527091	0
CO		0	1.01E-09	1.01E-09	1.54E-09	3.15E-11	1.52E-116	1.01E-09	1.54E-09	1.54E-09	5.00E-13	0	1.52E-116	1.00E-12	1.54E-09	0
H2		0	0.615995	0.616008	0.942502	0.0144613	1.76E-110	0.616008	0.942502	0.942502	0.000164253	0	1.76E-110	0.000329037	0.942502	0
H2O		1	0.172032	0.172026	0.00082749	0.487452	0.972233	0.172026	0.00082749	0.00082749	0.500482	1	0.972233	0.49814	0.00082749	0.944189
METHANOL		0	0.174038	0.174031	0.00396187	0.487377	0.0277675	0.174031	0.00396187	0.00396187	0.497589	0	0.0277675	0.00396	0.00396187	0.0558105
DIMET-02		0	0	0	0	0	0	0	0	0	0	0	0	0.494035	0	0

Table 8 – Material streams

Table 9 – Material streams

Appendix A. Material streams for process

Tables 7-9 illustrates all material streams for the whole process. Input, output and subprocess streams.

Table 7 – Material streams

Stream Name	Units	CO2	H2	PUR	PURGE	S1	S2	S3	S4	S8	S9	S10	S11	S12	S13	S14	S15
Temperature	C	25	25	30.8706	35	67.5952	34.8983	153.487	60	156.084	150.986	175.694	212.447	295	217.448	295	295
Pressure	bar	1	30	1.014	50	1.014	1.014	78	1	78	78	78	78	77.9933	77.9933	77.9933	77.9933
Mole Flows	kmol/hr	1999.55	6002.34	109.9	95.8999	3893.7	4003.6	1999.55	2000	6002.34	8001.9	15282.9	15282.9	11379.6	5689.82	5689.82	5689.82
CO2	kmol/hr	1999.55	0	36.0029	5.05479	6.87381	42.8767	1999.55	0	0	1999.55	2383.33	2383.33	431.691	215.846	215.846	215.846
CO	kmol/hr	0	0	1.24E-07	1.48E-07	1.95E-09	1.26E-07	0	0	0	0	1.12E-05	1.12E-05	1.15E-05	5.76E-06	5.76E-06	5.76E-06
H2	kmol/hr	0	6002.34	57.2576	90.3858	0.639551	57.8972	0	0	6002.34	6002.34	12864.7	12864.7	7009.79	3504.9	3504.9	3504.9
H2O	kmol/hr	0	0	2.83572	0.0793562	1948.73	1951.56	0	2000	0	0	6.02496	6.02496	1957.66	978.832	978.832	978.832
METHANOL	kmol/hr	0	0	13.8035	0.379943	1937.46	1951.26	0	0	0	0	28.8465	28.8465	1980.49	990.243	990.243	990.243
DIMET-02	kmol/hr	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mass Flows	kg/hr	88000	12100	2193.29	418.271	97491.1	99684.3	88000	36030.6	12100	100100	131856	131856	131856	65928.2	65928.2	65928.2
CO2	kg/hr	88000	0	1584.48	222.46	302.515	1887	88000	0	0	88000	104890	104890	18998.7	9499.33	9499.33	9499.33
CO	kg/hr	0	0	3.48E-06	4.15E-06	5.45E-08	3.53E-06	0	0	0	0	0.000314758	0.000314758	0.000322448	0.000161224	0.000161224	0.000161224
H2	kg/hr	0	12100	115.424	182.207	1.28926	116.714	0	0	12100	12100	25933.7	25933.7	14130.9	7065.45	7065.45	7065.45
H2O	kg/hr	0	0	51.0863	1.42962	35106.8	35157.9	0	36030.6	0	0	108.541	108.541	35267.9	17633.9	17633.9	17633.9
METHANOL	kg/hr	0	0	442.293	12.1742	62080.4	62522.7	0	0	0	0	924.303	924.303	63459	31729.5	31729.5	31729.5
DIMET-02	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Volume Flow	l/min	822028	84219.2	45537.2	836.824	16371.9	2590.66	13951.7	818.548	47503.5	61280	124996	135304	113736	47893.7	56867.9	56867.9
Mass Fractions																	
CO2		1	0	0.722424	0.531857	0.003103	0.0189297	1	0	0	0.879121	0.795485	0.795485	0.144086	0.144086	0.144086	0.144086
CO		0	0	1.59E-09	9.91E-09	5.59E-13	3.54E-11	0	0	0	0	2.39E-09	2.39E-09	2.45E-09	2.45E-09	2.45E-09	2.45E-09
H2		0	1	0.0526263	0.435619	1.32E-05	0.00117083	0	0	1	0.120879	0.196681	0.196681	0.107169	0.107169	0.107169	0.107169
H2O		0	0	0.0232921	0.00341793	0.360103	0.352693	0	1	0	0	0.000823179	0.000823179	0.267472	0.267472	0.267472	0.267472
METHANOL		0	0	0.201658	0.029106	0.636781	0.627207	0	0	0	0	0.00700992	0.00700992	0.481274	0.481274	0.481274	0.481274
DIMET-02		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mole Fractions																	
CO2		1	0	0.327598	0.0527091	0.00176537	0.0107095	1	0	0	0.249885	0.155947	0.155947	0.0379354	0.0379354	0.0379354	0.0379354
CO		0	0	1.13E-09	1.54E-09	5.00E-13	3.15E-11	0	0	0	0	7.35E-10	7.35E-10	1.01E-09	1.01E-09	1.01E-09	1.01E-09
H2		0	1	0.520999	0.942502	0.000164253	0.0144613	0	0	1	0.750115	0.841771	0.841771	0.615995	0.615995	0.615995	0.615995
H2O		0	0	0.0258028	0.00082749	0.500482	0.487452	0	1	0	0	0.000394229	0.000394229	0.172032	0.172032	0.172032	0.172032
METHANOL		0	0	0.125601	0.00396187	0.497589	0.487377	0	0	0	0	0.0018875	0.0018875	0.174038	0.174038	0.174038	0.174038

Stream Name	Units	S34	S35	S36	S37	S38	S39	S40	S41	S42	S43	S44	S47	S48	WATER
Temperature	C	64.2646	25	98.1534	103.149	72.5977	202.355	204.48	246.723	290	131.897	250.765	57.4049	133.156	98.5839
Pressure	bar	1	1	1	77.9933	77.9933	5	5	4.9	4.9	50	1	1	1	1
Mole Flows	kmol/hr	1943.82	1020.22	3375.05	5689.82	5689.82	1943.82	1943.82	1943.82	1943.76	11380.1	1944.601689	972.087969	972.51372	1949.88
CO2	kmol/hr	6.87362	6.87311	0	215.846	215.846	6.87362	6.87362	6.87362	6.87311	431.698	6.87311	1.64736	5.23E+00	1.52E-78
CO	kmol/hr	1.95E-09	1.95E-09	0	5.76E-06	5.76E-06	1.95E-09	1.95E-09	1.95E-09	1.95E-09	1.15E-05	1.95E-09	1.95E-09	8.81E-30	5.25E-117
H2	kmol/hr	0.63956	0.639569	0	3504.9	3504.9	0.63956	0.63956	0.63956	0.639569	7010.22	0.639569	0.639569	5.74E-63	6.05E-111
H2O	kmol/hr	7.97345	46.0989	3352.07	978.832	978.832	7.97345	7.97345	7.97345	968.264	1957.67	968.264	7.2492	961.83888	1940.75
METHANOL	kmol/hr	1928.34	7.45353	22.9833	990.243	990.243	1928.34	1928.34	1928.34	7.69729	1980.49	7.69729	3.40084	4.31	9.1262
DIMET-02	kmol/hr	0	959.151	0	0	0	0	0	0	960.286	0	960.286	959.151	1.13484	0
Mass Flows	kg/hr	62235.5	45560.3	61124.9	65928.2	65928.2	62235.5	62235.5	62235.5	62233.4	131858	62233.47692	44500.2853	1.77E+04	35255.6
CO2	kg/hr	302.507	302.484	0	9499.33	9499.33	302.507	302.507	302.507	302.484	18999	302.484	72.484	2.30E+02	6.71E-77
CO	kg/hr	5.45E-08	5.45E-08	0	0.000161224	0.000161224	5.45E-08	5.45E-08	5.45E-08	5.45E-08	0.000322441	5.45E-08	5.45E-08	2.47E-28	1.47E-115
H2	kg/hr	1.28928	1.2893	0	7065.45	7065.45	1.28928	1.28928	1.28928	1.2893	14131.8	1.2893	1.2893	1.16E-62	1.22E-110
H2O	kg/hr	143.644	830.485	60388.4	17633.9	17633.9	143.644	143.644	143.644	17443.5	35267.9	17443.5	130.485	17313.1	34963.2
METHANOL	kg/hr	61788	238.827	736.434	31729.5	31729.5	61788	61788	61788	246.638	63459.1	246.638	108.827	137.81042	292.423
DIMET-02	kg/hr	0	44187.2	0	0	0	0	0	0	44239.5	0	44239.5	44187.2	52.2812	0
Volume Flow	l/min	893008	404954	1440.06	27767	24958.7	249391	250077	280188	305938	100437	466079	150612	315.404	830.098
Mass Fractions															
CO2		0.00486068	0.00663921	0	0.144086	0.144086	0.00486068	0.00486068	0.00486068	0.00486048	0.144087	0.00486048	0.001628843	0.012970028	1.90E-81
CO		8.76E-13	1.20E-12	0	2.45E-09	2.45E-09	8.76E-13	8.76E-13	8.76E-13	8.76E-13	2.45E-09	8.76E-13	1.22E-12	1.39E-32	4.17E-120
H2		2.07E-05	2.83E-05	0	0.107169	0.107169	2.07E-05	2.07E-05	2.07E-05	2.07E-05	0.107174	2.07E-05	2.90E-05	6.52E-67	3.46E-115
H2O		0.00230807	0.0182283	0.987952	0.267472	0.267472	0.00230807	0.00230807	0.00230807	0.280292	0.267469	0.280292	0.002932228	0.976310434	0.991706
METHANOL		0.992811	0.00524201	0.012048	0.481274	0.481274	0.992811	0.992811	0.992811	0.00396311	0.48127	0.00396311	0.002445535	7.77E-03	0.00829436
DIMET-02		0	0.969862	0	0	0	0	0	0	0.710863	0	0.710863	0.99296442	0.002948212	0
Mole Fractions															
CO2		0.00353614	0.00673691	0	0.0379354	0.0379354	0.00353614	0.00353614	0.00353614	0.00353599	0.0379346	0.00353599	0.001694661	0.005377816	7.81E-82
CO		1.00E-12	1.91E-12	0	1.01E-09	1.01E-09	1.00E-12	1.00E-12	1.00E-12	1.00E-12	1.01E-09	1.00E-12	2.00E-12	9.06E-33	2.69E-120
H2		0.000329022	0.000626896	0	0.615995	0.615995	0.000329022	0.000329022	0.000329022	0.000329037	0.616008	0.000329037	0.000657933	5.90186E-66	3.10E-114
H2O		0.00410194	0.0451854	0.99319	0.172032	0.172032	0.00410194	0.00410194	0.00410194	0.49814	0.172026	0.49814	0.00745735	0.989023456	0.99532
METHANOL		0.992033	0.00730583	0.00680976	0.174038	0.174038	0.992033	0.992033	0.992033	0.00396	0.174031	0.00396	0.00349849	0.004431814	0.00468039
DIMET-02		0	0.940145	0	0	0	0	0	0	0.494035	0	0.494035	0.986691566	0.001166914	0
Vapor Phase															

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