SUDAN UNIVERSITY OF SCIENCE AND TECHNOLOGY

COLLEGE OF PETROLEUM ENGINEEERING AND TECHNOLOGY

DEPARTMENT OF REFINING AND TRANSPORTATION ENGINEERING

Production of Dimethylether (DME) from Methanol Dehydration to be used as alternative Fuel

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Submitted in partial fulfillment of the requirements for the B.sc degree in transportation and refining engineering

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الاستهلال

قَالَ تَعَالَىٰ:

﴿ وَيَسۡـَٔلُونَكَ عَنِ ٱلرُّوحِۖ قُلِ ٱلرُّوحُ مِنۡ أَمۡرِ رَبِّي وَمَآ أُوتِيتُم مِّنَ ٱلۡعِلۡمِ إِلَّا
قَلِيلٗا ٨٥ ﴾

صدق الله العظيم

سورة الاسراء .(85)

Dedication

To our beloved families who supported us strongly and for their patient and confidence they gave to us; we hope that we had made you proud.

To our friend and colleges, who support and encourage us.

Acknowledgment

Thank fulness and appreciation for Allah as always before and after. Without the encouragement and support of some people this thesis would have not been feasible.

We would like to express our gratitude to our supervisor Mrs. Nihad Omer Hassan for her patient and ideal supervision her sage advice in significant advices and patient encouragement aided the writing of this in numerable way.

Abstract

Nowadays, and globally our people severe from environmental pollution, and care about energy supply stability. As we all know that petroleum base fuels have harmful nonfriend emissions like No_x, and So_x so we look after and think about clean and efficient another alternative fuel from other base than crude oil.

DME, is one of the alternatives found which the world think about seriously. In this thesis we will show how to produce DME via dehydration of methanol and a simple simulation of that process trying to be applicable in Sudan.

The process is simulated using ASPEN plus simulation environment version 8.8 with data taken from scientific paper talks about design and simulation of DME production unit with hypothesized feed quantityto study the criteria of the process and how it will be like. Many production scenarios are tested and studied to reach the optimum operating conditions with responding to the produced quantities of DME.

المستخلص

يعاني العالم في هذه الايام من مشكلات البيئة والانبعاثات الضارة هذا الى جانب تفكيره وانشغاله الدائم بكيفية ضمان استقرارية الامداد بالطاقة وكما نعلم ان الوقود من اصل احفوري(البترول) تنتج عنه انبعاثات ضارة بالبيئة ، لذا جاء التفكير في كيفية انتاج وقود نظيف وذو كفاءة عالية ليحل بديلا للمواد البترولية.

ثنائي ميثيل ايثر هو احد هذه البدائل التي وجدت ودرست امكانية انتاجه وعمل نموذج لتلك العملية لمحاولة جعلها قابلة للتطبيق في السودان باستخدام بيانات مأخوذة عن ورقة علمية تتحدث عن تصميم ومحاكاة لوحدة انتاج ثنائي ميثيل ايثر بافتراض كمية التغذية للوحدة لدراسة سلوك هذه العملية وماهية العوامل المؤثرة على كمية ثنائي ميثيل ايثر المنتجة باستخدام برنامج المحاكاة حيث تمت عملية مقارنة بين عدة ظروف تشغيل للوصول للظرف الامثل للتشغيل من حيث كمية ثنائي ميثيل ايثر المتحصل عليها.

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Chapter 1

Introduction

1.1 Introduction

Dimethyleether (DME), also known as methoxymethane, is an organic compound with the formula CH_3OCH_3, simplified to C_2H_6O. The simplest ether, it is a colorless gas that is a useful precursor to other organic compounds and an aerosol propellant that is currently being demonstrated for use in a variety of fuel applications. It is an isomer of ethanol.

DME is used primarily as a propellant and a motor fuel alternative, DME is miscible with most organic solvents and has a high solubility in water. Recently, the use of DME as a fuel additive for diesel engines has been investigated due to its high volatility (desired for cold starting) and high cetane number [1].

In recent years, DME has received attention as an alternative, clean diesel fuel because of its thermal efficiencies equivalent to traditional diesel fuel, lower NO_x emission near-zero smoke and less engine noise. DME is also used as araw material for making chemicals and aerosol propellant such as hair spray, shaving cream to replace ozone-destroying chlorofluorocarbons (CFC) .Recently the process of direct synthesis of DME from syngas as received much attention during twenty years and researchers have developed a hybrid catalyst by the addition of specially treated H-ZSM-5 to the traditional $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst. In contrast to the process of DME production from syngas, since CO2 hydrogenation to DME produces a large amount of water in both methanol synthesis and CO synthesis, the water can deactivate the catalyst [2].

1.2 Problem statement

As well as we know that fuel is very important in life this is used in cooking, heating, and transportation and its shortage make our life hard.DME production in this project will increase fuel quantities used.

1.3 Objectives

After the completion of this project we aim to achieve the following objectives:

1. To produce DME from methanol to use it as an alternative fuel in automobiles.
2. Simulate the process of DME production using ASPEN plus software.
3. Design of distillation column.

Chapter 2

Literature review

2.1 Literature review:

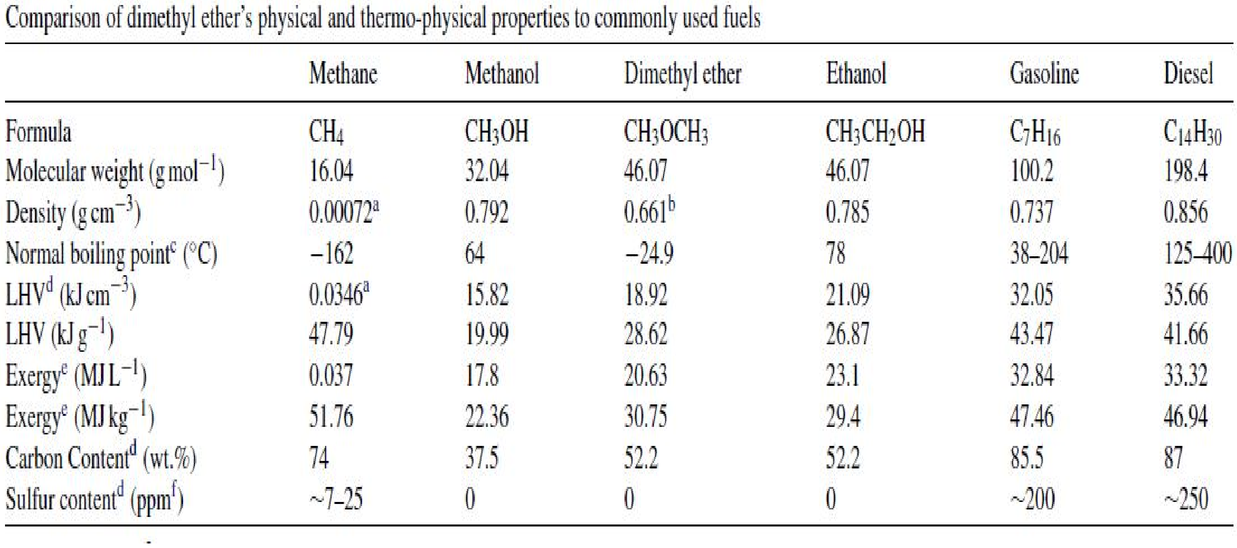
Dimethyl ether (DME) has attracted a worldwide attention because of its potential as an alternative for substituting petroleum. Its use in diesel motors causes low emissions of soot particles and of NO_x. Hence, it can be considered an environmentally compatible fuel. DME production has been investigated by several researchers in many parts of the planet.

At environmental conditions of 1 atmosphere pressure and temperature of 25°C, DME is present in gaseous state. When it is submitted to higher pressures or to lower temperatures it liquefies easily in the same way as LPG.[3]

With ever growing concerns on environmental pollution, energy security, and future oil supplies, the global community is seeking nonpetroleumbased alternative fuels, along with more advanced energy technologies (e.g., fuel cells) to increase the efficiency of energy use.
The most promising alternative fuel will be the fuel that has the greatest impact on society. The major impact areas include well-to-wheelgreenhouse gas emissions, non-petroleum feed stocks, well-to-wheel efficiencies, fuel versatility, infrastructure, availability, economics, and
safety. Compared to some of the other leading alternative fuel candidates (i.e., methane, methanol, ethanol, and Fischer–Tropsch fuels),dimethyl ether appears to have the largest potential impact on society, and should be considered as the fuel of choice for eliminating the dependency on petroleum.DME can be used as a clean high-efficiency compression ignition fuel with reduced NO_x, SO_x, and particulate matter, it can be efficientlyreformed to hydrogen at low temperatures, and does not have large issues with toxicity, production, infrastructure, and transportation as dovarious other fuels. The literature relevant to DME use is reviewed and summarized to demonstrate the viability of DME as an alternativefuel[4].

2.1.1Chemical and Physical properties of DME

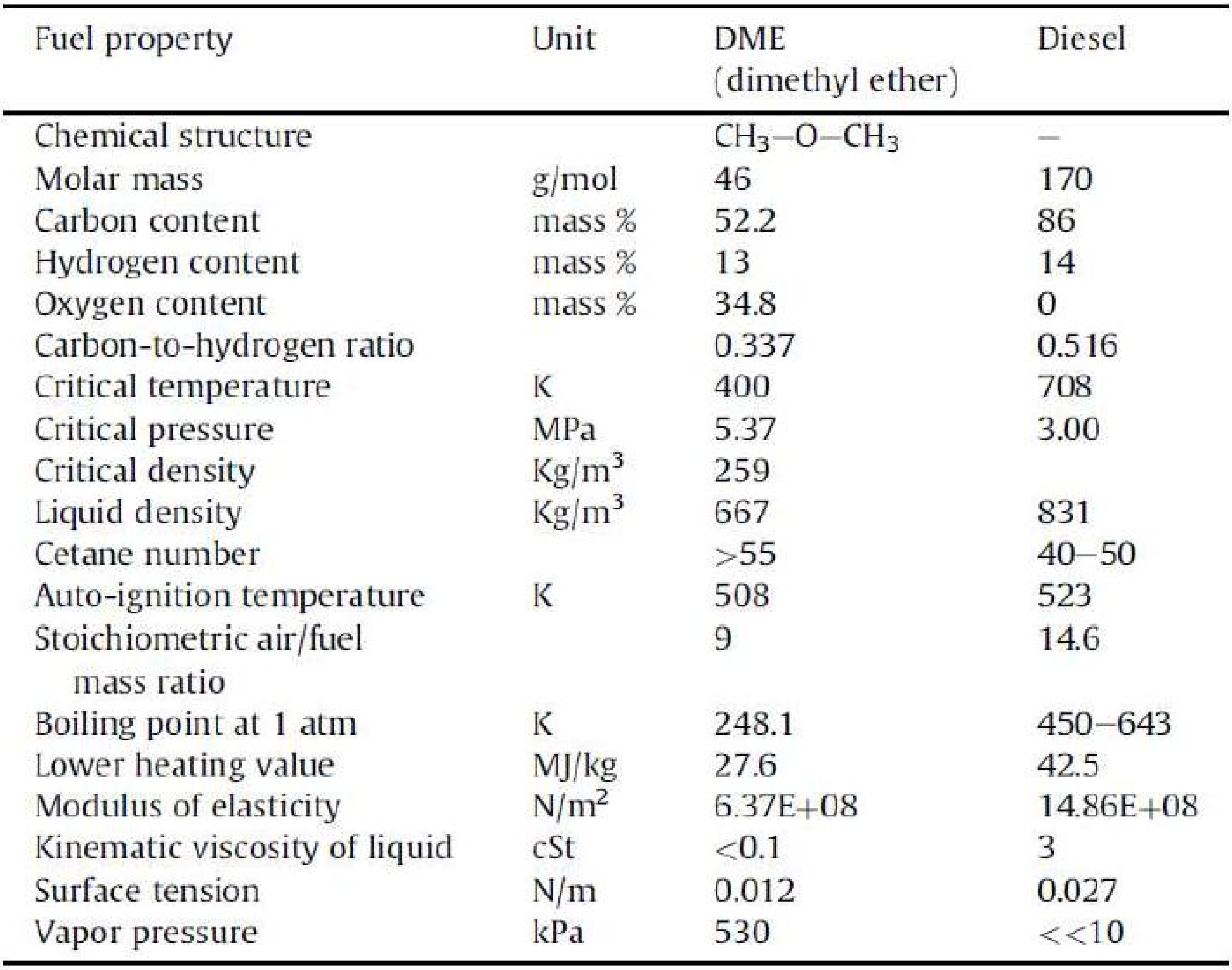
Table 2-1:Comparison of DME physical and thermo physical properties to commonly used fuels



Comparison of dimethyl ether's physical and thermo-physical properties to commonly used fuels

	Methane	Methanol	Dimethyl ether	Ethanol	Gasoline	Diesel
Formula	CH_4	CH_3OH	CH_3OCH_3	CH_3CH_2OH	C_7H_{16}	$C_{14}H_{30}$
Molecular weight ($g\,mol^{-1}$)	16.04	32.04	46.07	46.07	100.2	198.4
Density ($g\,cm^{-3}$)	0.00072[a]	0.792	0.661[b]	0.785	0.737	0.856
Normal boiling point[c] (°C)	−162	64	−24.9	78	38–204	125–400
LHV[d] ($kJ\,cm^{-3}$)	0.0346[a]	15.82	18.92	21.09	32.05	35.66
LHV ($kJ\,g^{-1}$)	47.79	19.99	28.62	26.87	43.47	41.66
Exergy[e] ($MJ\,L^{-1}$)	0.037	17.8	20.63	23.1	32.84	33.32
Exergy[e] ($MJ\,kg^{-1}$)	51.76	22.36	30.75	29.4	47.46	46.94
Carbon Content[d] (wt.%)	74	37.5	52.2	52.2	85.5	87
Sulfur content[d] (ppm[f])	~7–25	0	0	0	~200	~250

Table 2-2:Properties of DME compared with diesel properties



Fuel property	Unit	DME (dimethyl ether)	Diesel
Chemical structure		$CH_3{-}O{-}CH_3$	–
Molar mass	g/mol	46	170
Carbon content	mass %	52.2	86
Hydrogen content	mass %	13	14
Oxygen content	mass %	34.8	0
Carbon-to-hydrogen ratio		0.337	0.516
Critical temperature	K	400	708
Critical pressure	MPa	5.37	3.00
Critical density	Kg/m^3	259	
Liquid density	Kg/m^3	667	831
Cetane number		>55	40–50
Auto-ignition temperature	K	508	523
Stoichiometric air/fuel mass ratio		9	14.6
Boiling point at 1 atm	K	248.1	450–643
Lower heating value	MJ/kg	27.6	42.5
Modulus of elasticity	N/m^2	6.37E+08	14.86E+08
Kinematic viscosity of liquid	cSt	<0.1	3
Surface tension	N/m	0.012	0.027
Vapor pressure	kPa	530	<<10

Table 2-3:Combined properties of various fuels

	Fuel				
Factor	Diesel	LPG	LNG	CNG	DME
UN #	1202	1075	1972	1971	1033
Hazard Class	3	2	2.1	2.1	2.1
Cetane #	40 to 50	NA	<10	<10	55 to 60
RON	15-25	109	127	127	~35
Mass Heating Value	42.5 MJ/kg	46.6 MJ/kg	48.62 MJ/kg	45.71 MJ/kg	27.6 MJ/kg
Volumetric Heating Value	36.04 MJ/l	23.67 MJ/l	21.88 MJ/l	7.93 MJ/l	18.38 MJ/l
Flammability Range	0.6 to 7.5	2.1 to 10.1	4.4 to 17	4.4 to 17	3.4 to 18
Liquid Density	848 g/l	508 g/l	450 g/l	174 g/l	666 g/l
DGE	1.00	1.55	1.56	3.98	1.88
CO_2* non-DGE tailpipe	2.64 kg/l	1.52 kg/l	1.26 kg/l	0.48 kg/l	1.28 kg/l
CO_2* DGE tailpipe	2.64 kg/l	2.36 kg/l	1.96 kg/l	1.91 kg/l	2.41 kg/l
Expansion from liquid to vapour	NA	270 times volume	600 times volume	600 times volume	375 times volume

DME is a liquefied organic compound gas that can be stored in a manner similar to pressurizedHome barbeque propane and other LPG products. DME exists as invisible gaseous etherCompound under atmospheric conditions (0.1 MPa and 298 K) but must be condensed to theLiquid phase by pressurization above its vapor pressure at about 0.5 MPa (5.1 bar/73 psi) at 25°C to be used as a diesel fuel alternative. Like propane, DME is heavier than air Although the principal focus of this study relates to heavy haul diesel engines, DME has been used for decades in a variety of products and applications such as propellants in aerosol cans, solvents and medical treatments due to its lack of toxicity and its ability to be absorbed into the troposphere and, in Asia, as a cooking fuel. DME is considered a refrigerant with a share refrigerant designation R-E170 and is also used in refrigerant blends with butane and propene. DME, when stored at 5.1 bar, is not a cryogenic product therefore storage and handling are much simpler than other products that require special vessels and safety equipment. The fuel's basic chemical properties, independent of the trucking industry and many of these properties.

2.1.2 Physical properties

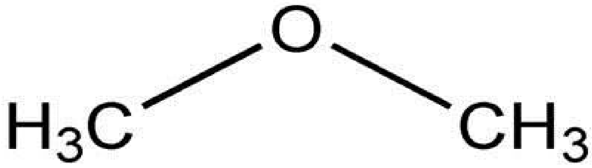
DME is a colorless, almost colorless gas at room temperature and atmospheric pressure. Basic physical properties are shown below

Table 2-4:DME physical properties

Property	Value	Unit
Molecular weight	46.07	-
Boiling point	248.3	K
Freezing point	131.7	K
Vapor density	1.59	-
Critical pressure	52.5	Atm
Critical temperature	402.0	K
Heat of melting	25.6	Cal/g
Heat of vaporization	111.6	Cal/g
Specific heat @ 246˚K(-33˚C)	0.535	Cal/g
Liquid specific gravity	0.66	-

2.2 History of DME

Dimethyl ether (DME) is also referred to as dimethyl oxide, methyl ether, oxybismethane, methoxymethane, methyl oxide, wood ether, N,N-dimethyl ether. The chemical formula is CH3OCH3 with a molecular weight of 46.07. Its structural formula is provided below.



Literature shows that the earliest research regarding DME goes back to the medical fields. According to Donald G. Barceloux in his book “Medical Toxicology of Drug Abuse: Synthesized Chemicals and Psychoactive Plants” (2012), the anesthetic characteristics of DME were studied in some rabbits and pigeons in 1867. Although later it was successfully examined as an “anesthetic agent” in humans, DME was never considered as a trustworthy anesthesia related drug.

Traditionally, DME has been used as a propellant in a wide range of consumer products (Personal care) including shaving creams, hairspray, foams, and antiperspirants (Nexant Inc.,2008). DME is used for these applications because of its higher water solubility relative to other propellants (DuPont, 2000). The first use of DME as an aerosol propellant goes back to the KazoosNobel Corporation in 1963. Akzo Nobel produces chiefly specialty chemicals coatings and paints.In a 1997 review for the United States Department of Energy, Sinor (1997) reports that afterReviewing documents from 1906 onward, there is no database showing the use of DME as anengine fuel before the modern era. In the 1970s and 1980s, oil prices were increased, and someembargos were imposed on oil. As a result, global research and development (R&D) efforts weredirected at finding novel methods of monetizing oil resources by converting them into easilytransportable liquid fuels[6]. Further, there has been a significant impact on the production and use of diesel fuel as a result of new environmental regulations, specifically in the United States. Significant investments have been made to produce “cleaner diesel fuels” andother alternative fuels [5]. From the late 1970s, Amoco (a global oil companylater merged into BP) has participated in R&D work on the production of liquid fuels fromnatural gas[6]. Beside those global efforts, a German patent introduces a“methanol based fuel consisting of non-distilled technical methanol, water, DME and futureadditives” in 1984 [7] and a U.S. patent describes a “method ofoperating a diesel engine with a fuel consisting of 95 to 99.9 percent DME” in 1986 [8]. DME, used as an alternative diesel fuel, performed well in tests and revealed compliancewith “the California ULEV emissions regulations for medium-duty vehicles”[9].To use DME as a diesel-engine fuel, it is necessary to make some changes into the fueldistribution substructures and consider some modifications on the engine itself; this broughtsome challenges into DME’s development as a fuel. Since DME had some similar propertieswith LPG, the main market for DME has been its blending with LPG. It was discovered thatusing blends of maximum 20 % DME in the whole volume of LPG performed well in regularheating and cooking applications. Also, the same blends worked well in automotive uses andAmoco patented those[6].Worldwide efforts were initiated to commercialize the DME business. In the mid-to-late 1990s,Amoco in cooperation with the General Electric Co. (GE) and the Electric Power Developmen Corporation of Japan (EPDC) tried DME as a “gas turbine fuel”. DME performed efficiently inthis test and showed low emissions. That was the start of offering guarantees for DME by GE inthe majority of their advanced turbines[6]. The result of this research was thatDME, as a multipurpose fuel, can be used for “LPG blending”, “power generation”, and “thediesel market”; besides, its usage as a “chemical intermediate for novel pathways to hydrogen,olefins, acetic acid and gasoline” was understood.In 1998, Amoco engaged in a joint project with the “India Oil Company (IOC)” and the “GasAuthority of India (GAIL)”. During the next few years The “International DME Association(IDA)”, the “Japan DME Forum (JDF)”, the “Korea DME Forum (KDF)”, and the “China DMEAssociation

(CDA)" were established around the world. Although China joined the communityof DME-users relatively late, it is now known as the leader in DME production and use.Research advancements are also being made for practical use of DME for power generation.DME is an organic component with the chemical formula CH_3OCH_3 for decades it has been used in variety of products and applications, such as propellants aerosol cans, solvents, and medical treatment due to its lack of odor and toxicity and its ability to be absorbed into the troposphere. DME is also used as cocking fuel in part of Asia. However it also be made into viable alternative for diesel fuel m most notably for use in heavy haul transport vehicles. Unlike conventional diesel which is produced from non-renewable crude oil, DME can be produced anywhere using renewable products like some of the items in the bulleted list above.This provides a great deal of flexibility for production since facilities do not need to be locatednear sources of crude oil but can be setup any place where bio based feedstock or natural gascan be found, or produced. DME has been used in a variety of industrial processes and propellants for years and interest in DME as a fuel for vehicles is also increasing, at least in some countries, "since it can provide energy for large amounts of work both per unit land used to cultivate feedstock, and per unit energy used to produce it". Salsing et al went on to state that "very few (if any) other alternative fuels can propel vehicles so far, using as little land as DME, mainly because the production process is highly efficient".The literature review revealed more methods for DME fuel production than should be describedin this document. In general though, DME is produced via the dehydrogenation reaction ofmethanol, which is made from synthesis gas with carbon monoxide and hydrogen as the maincomponents . Based on current projections, it is likely that the abundance of NorthAmerican natural gas and a high level of animal waste will provide ample sources for futureDME production without reliance on offshore resources. It takes approximately 1.4 tons ofMethanol to produce approximately 1.0 ton of DME. One novel method which started in 2008, involved a 40 million dollar two year research study thatdemonstrated how DME can be produced from the gasification of a feedstock called black liquor (BL). The Bio DME project objective was described as a "Demonstration of an environmentally optimized future biofuel for road transport covering the full chain from production of fuel from biomass to the utilization in vehicles."

2.2.1 DME Environmental standards and regulations:

Residues of dimethyl ether are exempted from the requirement of a tolerance when used as a propellant in accordance with good agricultural practice. This exemption is applied to inert (or occasionally active) ingredients in pesticide formulations applied to growing crops or to raw agricultural commodities after harvest (40 CFR 180.910 and 40 CFR 180.930: Code of Federal Regulations, 2007a).The Code of Federal Regulations, 2007b, (40 CFR 60.489) promulgates standards ofperformance for equipment leaks of Volatile Organic Compounds (VOC) in the SyntheticOrganic Chemical Manufacturing Industry (SOCMI). The intended effect of these standards is torequire all newly constructed, modified, and reconstructed SOCMI process units to use the bestdemonstrated system of continuous emission reduction for equipment leaks of VOC, consideringcosts, non-air quality health and environmental impact and energy requirements. DME producedby process units, either as an intermediate or a final product, is covered under this regulation.The 8-hr time-weighted average Workplace Environmental Exposure Level (WEEL) for DME is1000 parts per million (ppm) [10] .

2.2.2 Different uses of Dimethyl Ether:

DME is listed as a High Production Volume (HPV) chemical[11] . It is an emerging alternative to traditional fuels such as diesel and propane [12].DME production is a mature technology that is utilized in a numberof countries including Canada, Japan, China, Korea, and India. It has a variety of applications:

- Use as a liquefied petroleum gas (LPG) substitute for cooking and heating. DME combustion produces very low NOx and CO emissions and no sulfur or soot emissions.
- Use as a chlorofluorocarbon (CFC) substitute for propellants in cosmetic- or paint aerosol Cans[13].
- Use as a diesel substitute. DME has a high cetane number (55) and can be combusted in diesel-powered vehicles that have been retrofitted to run on DME or in purpose built engines.
- Use as a precursor to dimethyl sulfate and acetic acid production
- Use as a refrigerant.
- Use as a rocket propellant.
- Use as carrier for livestock insect sprays and foggers.
- Use as a solvent for extraction of organic compounds.

Before 1990, DME was only used as an aerosol propellant commercially and known as “nonozone-layer depleting replacement for chlorofluorohydrocarbons”[6]. In recenttimes, DME is more considered as an alternative and/or additive fuel and covers a wide area ofapplications. It is now known for its different applications as a fuel for transportation, cookingand heating, and power generation [14] DME has been used in limited amountto freeze meat and fish by direct immersion [7].

2.2.3 Organizations involved in DME development:

There are many types of organizations involved with DME both past and present. Vehicle manufacturers, who will ultimately build, sell and maintain DME poweredvehicles are also involved in research and development of DME and will be discussed.For the most part, DME vehicles have been limited to those produced specifically for researchstudies, and most of these have taken place in Asia although some work has been done inEurope and North America. Volvo and Mack trucks have eachidentified DME as a promising alternative fuel, however, neither manufacturer has committed ta firm date to begin production for North America. Further field testing (and presumably Infrastructure development) are required in order for the OEMs to be confident that DME fueledvehicles can be successfully marketed and fielded in a market dominated by diesel poweredvehicles.

2.2.3.1 A list of some of the major vehicle and product development projects:

- The Penn State/Volvo Oak Ridge 2014 *Emissions and Performance Benchmarking of a Prototype Dimethyl Ether-Fueled Heavy-Duty Truck* mentioned already.
- In Europe, several countries, such as Sweden, Netherland, and Austria, have headed the development of DME-fueled vehicles including trucks, buses, and passenger cars.
- In South Korea, trucks, buses, and passenger cars using DME fuel have been developed by research institutes and universities.
- Pyo et al. developed a DME fuel supply system and a modified heavy-duty DME-fueled bus using an in-line pump.
- In addition, C.S. Lee of Hanyang University developed a DME passenger car, and KATECH developed a medium-sized vehicle using DME fuel.
- The Volvo/Chemrec black liquor DME project mentioned various times in this report.
- Recently, the International Energy Agency conducted a project for DME fuel titled ‘Fuel and Technology Alternatives for Bus’ (Annex 37, IEA Implementing Agreements on Advanced Motor Fuels). In addition, the International DME Association (IDA) was established in 2001, and many research institutes, universities and companies researching DME fuel participate in the IDA.
- AVL (Austria) has promoted research and development of DME-fueled engines since 1995.

- Development of a DME-fueled city bus with an oxidation catalytic converter in 2000, based on a VOLVO DH10A engine.

Figure (2-1):Example of DME fuel tank[15]

CHAPTER 3

Methodology

3.1 Process Description and Simulation

In this project we try to recover dimethylether form methanol by chemical process runs at specific rectors and distillation that we have to design using simulation program (ASPEN plus) with hypothetical data.

Methanol inter conversion reactor to give dimethylether and water by the chemical reaction:

$2CHOH_3 \rightarrow C_2H_6O_2+H_2o$

Then produced dim ethylether is fed to distillation to give purer product. We were made many experiences to get the perfect design of distillation. We need to know the required specification of dimethylether that make it available to be marketing and useful.

Data related to the process:

- -the operating conditions
- -type of the contacting device
- -stage and reflux
- -number of equilibrium stage
- -the column diameter and number of real stage
- -the column internals design data and the mechanical design data.

The data was gathered and the process was simulated by (Aspen Hysys) three times with different distillation size and different operation conditions then the results compared on base of that the most purer result the optimum

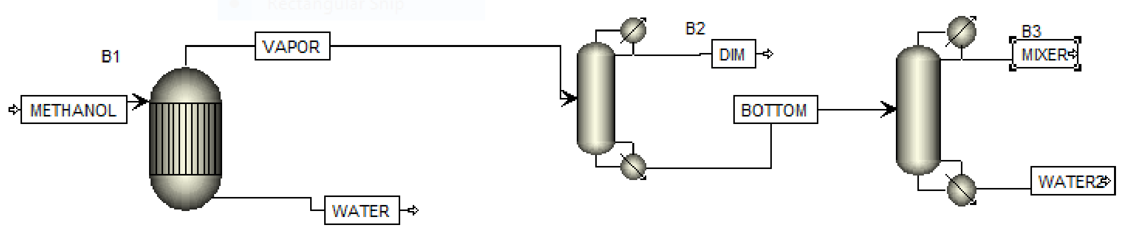


Figure (3-1):Simulation of methanol to DME process

3.2 Material and Energy balance

A good understanding of material balance calculations is essential in process design

The general conservation equation for any process system can be written as:

Material out =Material in + Generation _ Consumption _ Accumulation (3.1)

For steady state process the accumulation term will be zero

Material balance around reactor

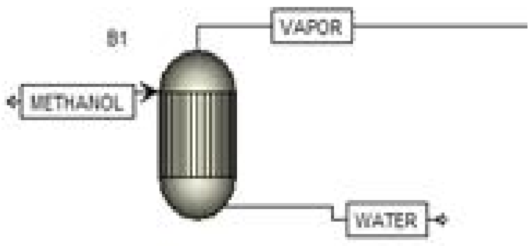


Figure (3-2):DME reactor

1. The base of calculation is set to the fresh feed
2. Composition of the reactor feed was assumed
3. Only one reaction, methanol to DME

Conversion of reaction = $\frac{product\ amount}{feed\ amount}$ (3.2)

The amount of summation produced amount of DME and water to the total amount of methanol.

Conversion = $\frac{276.267}{282.1} = 0.97$

Conversion = $\frac{N_{A0}-N_A}{N_{A0}}$ (.3.3)

Where

N_{A0} = the amount of methanol entering the reactor

N_A = the amount unreacted of methanol

From eq3.1 we found that N_{Ao} =8.4

The amount of methanol reacted = 282.1 – 8.4 =273.63

Mass balance around the reactor using the extent of the reaction (ξ):

$$NA = NA0 - 2\xi \quad (3.4)$$

$$N_B = N_{B0} - \xi \quad (3.5)$$

$$N_C = N_{C0} - \xi \quad (3.6)$$

Degree of freedom analysis (fd)

Number of unknown = 4

Number of independent equation = 3

Specification = 1

Degree of freedom = 0

From equation 3.2 ξ = 136.84

Energy balance:

In – consumption = out

In = -21.255 kj/mol

Out = -8.838 + -6.497

Consumption = in – out

= -5.92 kj/mol

Table (3-1):Flow rate and composition of stream entering and leaving the reactor

		Feed			Out	
component	composition	Molar flow	Mass flow	composition	Molar flow	Mass flow
methanol	1	282.1	9039.093	0.21	5.719	183.008
DME	0	0	0	0.51	138.022	6349.012
Water	0	0	0	0.46	126.570	2278.26
Total	1	282.1	9039.093	1	270.311	8810.28

Note: the calculated output is for vapor phase.

Material balance around distillation 1

The first distillation column in the flow process diagram of DME production is designed in order to separate DME from other components coming out of the reactor

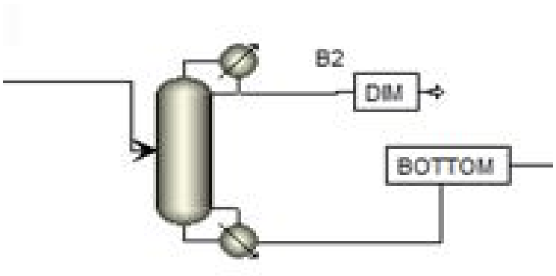


Figure (3-3):Distillation column 1

Assumptions:

1. All DME goes in the distillate
2. Only trace amount of methanol goes in the distillate.
3. All water goes in the bottom

Input = output

$F = D + B$ (3.7)

Component balance:

1. DME balance

$X_D F = X_D D + X_D B$ (3.8)

$(0.51)(270.03) = X_D(135.159) + (0.021)(153.15)$

From equation (3.8)

$X_D = 0.90$

2. Water balance:

$X_W F = X_W D + X_W B$

(0.46)(270.032) = (0)(135.159) + (0.93)(135.15)

126.576 = 126.576 (water was totally distillated)

3. Methanol balance:

$X_M F = X_M D + X_M B$

(0.021)(270.032) = (0)(135.159) + (0.042)(135.159)

5.719 = 5.719 (methanol was totally distillated)

Energy balance:

In + generation –out = consumption

Generated = 0

-8.838 + (0) - (-4.141 + -5.468) = consumption

Consumption = 0.771 kj/mol

Table (3-2):Flow rate and composition of stream entering and leaving the distillation

		feed			distellate			Bottom	
component	Composition	Molar flow	Mass flow	composition	Molar flow	Mass flow	Composition	Molar flow	Mass flow
methanol	0.021	5.719	183.00	0.004	trace	0	0.042	5.719	138.008
DME	0.51	138.022	6349.012	0.99	135.159	6217.314	0.021	2.863	131.698
Water	0.46	126.570	2278.26	0.006	trace		0.936	126.576	2278.368
Total	1	270.03	8810.272	1	135.159	6217.314	1	135.158	2592.958

Material balance around distillation 2:

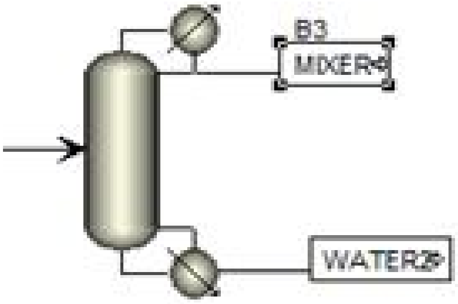


Figure (3-4):Distillation column 2

1. DME material balance

   $X_D\ F = X_D\ D + X_D\ B$

   (0.021)(135.15) = (0.026)(108.12) + (0)(27.032)

   (2.863 =2.863)

2. Water balance:

   $X_W\ F = X_W\ D + X_W\ B$

$(0.93)(135.15) = (0.92)(108.12) + (X_W)(27.032)$

$X_W = 1$

3. Methanol balance:

$X_M\ F = X_M\ D + X_M B$

(0.042)(135.15) = (0.052)(108.12) + (0)(27.032)

5.719 = 5.719

Energy balance

In + generation – out = consumption

Generated = 0

-5.468 + (0) – (-3.62 + (-1.247)) = consumption

Consumption = -0.608 kj/mol

Table (3-3):Flow rate and composition of stream entering and leaving the distillation

		feed			distillate			Botoom	
Component	Composition	Molar flow	Mass flow	composition	Molar flow	Mass flow	composition	Molar flow	Mass flow
Methanol	0.04	5.719	138.008	0.052	5.719	138.008	0	0	0
DME	0.021	2.863	131.698	0.026	2.863	131.698	1	27.032	486.576
Water	0.93	126.576	2278.368	0.92	99.544	1791.792	0	0	
Total	1	135.15	2529.9	1	108.12	2061.498	1	0	486.576

Design of distillation:

3.3 Introduction:

Distillation column is the most popular and important separation method in the petroleum industries for purification of final products. Distillation columns are made up of several components, each of which is used either to transfer heat energy or to enhance mass transfer. A typical distillation column contains a vertical column where trays or plates are used to enhance the component separations, a reboiler to provide heat for the necessary vaporization from the bottom of the column, a condenser to cool and condense the vapor from the top of the column, and a reflux drum to hold the condensed vapor so that liquid reflux can be recycled back from the top of the column.

3.4 Distillation Column design:

The design of a distillation column can be divided into the following steps:

1. Specify the degree of separation required: set product specifications.
2. Select the operating conditions: batch or continuous; operating pressure.
3. Select the type of contacting device: plates or packing.

4. Determine the stage and reflux requirements: the number of equilibrium stages.
5. Size the column: diameter, number of real stages.

3.4.1 Selection of operating conditions:

The separation of liquid mixtures by distillation depends on differences in volatility between the components. The greater the relative volatilities, the easier the separation. This operation is classified into two types; batch and continuous operation. Batch operation should be considered when the quantity to be distilled is small; when it is produced at irregular intervals; when a range of products has to be produced; or when the feed composition is likely to vary considerably.

The distillation is considered as multi-component system, which limits the choice to the continuous distillation.

In the section below the feed, the more volatile components are stripped from the liquid and this is known as the stripping section. Above the feed, the concentration of the more volatile components is increased and this is called the enrichment, or more commonly, the rectifying section.

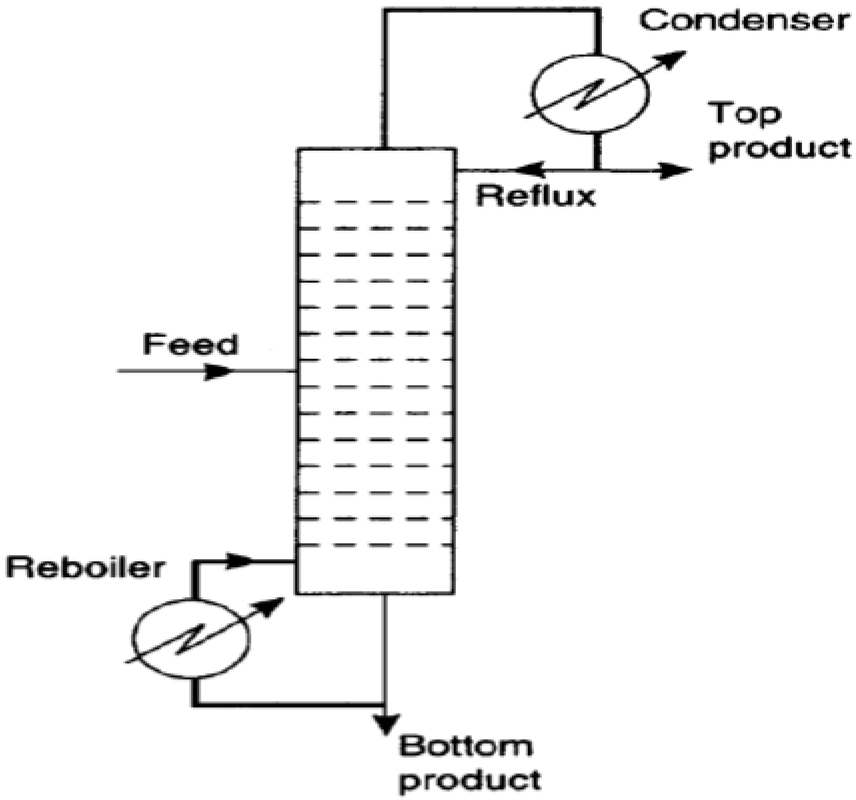


Figure (3-5):Schematic of distillation

3.4.2 Reflux considerations:

The reflux ratio, $R,$ is normally defined as:
The number of stages required for a given separation will be dependent on the reflux ratio used.
(R= $flowreturnedasreflux/flowoftopproducttakenoff$)
In an operating column the effective reflux ratio will be increased by vapour condensed within the column due to heat leakage through the walls. With a well-lagged column the heat loss will be small and no allowance is normally made for this increased flow in design calculations. If a column is poorly insulated, changes in the internal reflux due to sudden changes in the external conditions, such as a sudden rain storm, can have a noticeable effect on the column operation and control.

$$N_{min} = \frac{\left[\log\left[\frac{\mathrm{xlk}}{\mathrm{xhk}}\right]_{\mathrm{d}}\left[\frac{\mathrm{xhk}}{\mathrm{xlk}}\right]_{\mathrm{b}}\right]}{\log\ \alpha_{\mathrm{lk}}} \qquad (3.9)$$

Where

α_{lk} = average relative volatility of the light key with respect to the heavy key.

X_{lk} = light key concentration.

X_{hk} = heavy key concentration.

The relative volatility is taken as the geometric mean of the values at the column top and bottom temperature. To calculate these temperature initial estimates of the compositions must be made. So the calculation of minimum number of stage by the Fensek equation is trial and error procedure.

3.4.3 Minimum reflux ratio:

As the reflux ratio is reduced a *pinch point* will occur at which the separation can only be achieved with an infinite number of stages. This sets the minimum possible reflux ratio for the specified separation.

3.4.4 Feed point location:

The precise location of the feed point will affect the number of stages required for a specified separation and the subsequent operation of the column. As a general rule, the feed should enter the column at the point that gives the best match between the feed composition (vapour and liquid if two phases) and the vapour and liquid streams in the column. In practice, it is wise to provide two or three feed-point nozzles located round the predicted feed point to allow for uncertainties in the designcalculations and data, and possible changes in the feed composition after start-up.

Equations used:

$$\sum \frac{\propto_i * x_{fi}}{\propto_i - \lambda} = q - 1 \qquad (3\text{-}10)$$

$$N_{min} = \sum \frac{\propto_i * D_{xi} * D}{\propto_i - \lambda} \qquad (3\text{-}11)$$

$$R_{min} = \frac{V_{min}}{D} \qquad (3\text{-}12)$$

$$\frac{N - N_{min}}{N+1} = 1 - \exp\left[\left(\frac{\frac{1+54.4(R-R_{min})}{R+1}}{\frac{11+117.2(R-R_{min})}{R+1}}\right) * \left(\frac{\frac{R-R_{min}}{R+1} - 1}{\left[\frac{R-R_{min}}{R+1}\right]^{0.5}}\right)\right] \qquad (3\text{-}13)$$

$$\frac{N_R}{N_S} = [\left(\frac{x_{HK,F}}{x_{LK,F}}\right) * \left(\frac{x_{LK,B}}{x_{HK,D}}\right)^2 \left(\frac{B}{D}\right)]^{0.206} \qquad (3\text{-}14)$$

$$V_{min} = \sum \frac{\propto_i * D_{xi} * D}{\propto_i - \lambda} \qquad (3\text{-}15)$$

Where:

$\propto_i$≡average relative volatility of component I with respect to the reference component

x_{fi} ≡ the ratio of the concentration of component to the total concentration of the feed

q ≡ Feed status

N_{min} ≡ Minimum number of stages at total reflux include in the reboiler

N≡ number of stages

D_{xi} ≡ The percentage of extracted of the component i

R_{min} ≡ Minimum reflux ratio

V_{min} ≡ vapor flow rate

D≡ distillate

R≡ total reflux

$x_{HK,F}$ ≡ Fraction of the heavy key component in the feed

$x_{LK,F}$ ≡ Fraction of the light key component in the feed

$x_{HK,B}$ ≡ Fraction of the heavy key component in the bottom

$x_{LK,D}$ ≡ Fraction of the light key component in the distillate

B≡ bottom

$N_R \equiv numberofstagesintherectifyingsection$.

$N_S \equiv numberofstagesinthestrippingsection$.

3.5 Cost Estimation

The goal of any manufacturing company is to make money. This is realized by producingproducts with a high market value from raw materials with a low market value

Total cost = fixed cost + operating cost (3.16)

1. Fixed cost = Capital cost + transporting + constriction (3.17)
2. Operating cost = Depreciation + material +electricity +operator + maintenance
   -Annual material cost = Annual cost = 12*30*24*(flow rate)*(price) (3.18)

   -Depreciation = capital cost *(x)% anticipated life (3.19)

   -Electricity = cost * x kw (3.20)

-Operator cost:

A single operator works for 49 weeks a year (3 weeks' time off for vacation and sick leave), five 8-hour shifts a week.

- Chemical plant normally operates 24 hours/day.

The number of operator needed in the plant in any time is given by

$$\frac{annual\ plant\ shift}{annual\ labor\ shift} \qquad (3.21)$$

Total = fixed +operation (3.22)

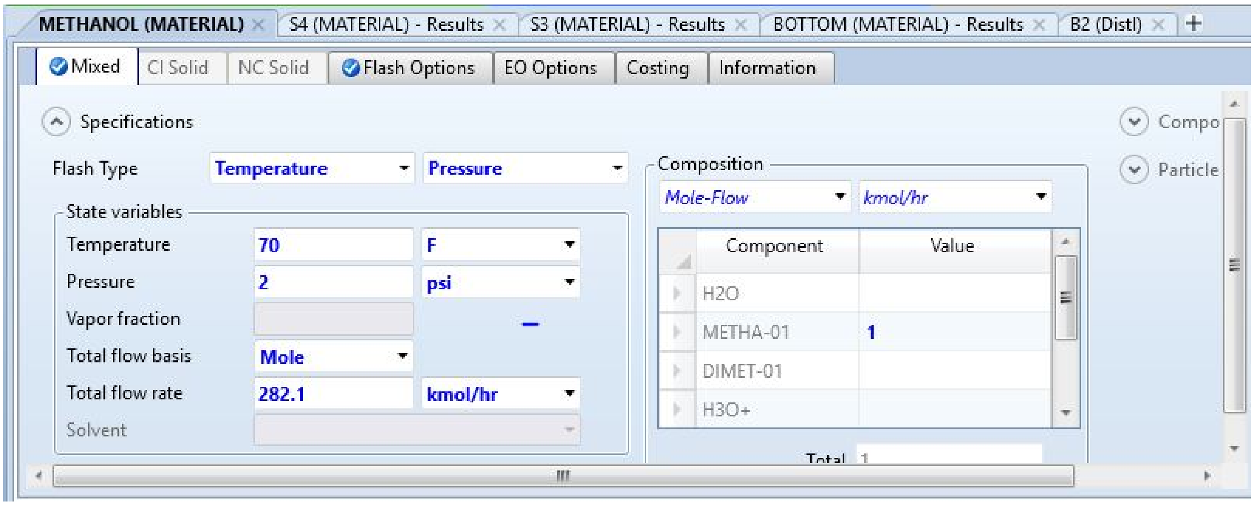
CHAPTER 4

Result and discussion

4.1 Result:

A hypothesis data was used to simulate the process of producing DME in ASPEN plus simulation with respect to chosen scientific paper.

Feed temperature is considered as constant, the reactor temperature changed three times to test the results, which is found that the produced DME quantity increased as well as temperature increases. The optimum operating condition with respect to DME in the top of the distillation column produced is when temperature equals to 100˚C.



Flash Type: Temperature | Pressure

State variables

Temperature	70	F
Pressure	2	psi
Vapor fraction		
Total flow basis	Mole	
Total flow rate	282.1	kmol/hr
Solvent		

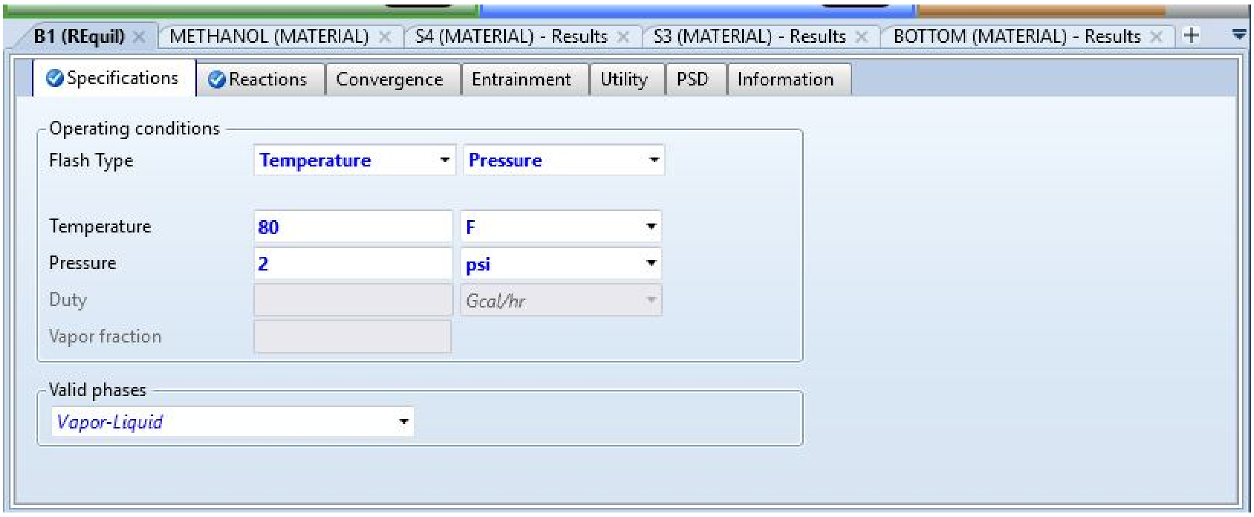
Composition: Mole-Flow | kmol/hr

Component	Value
H2O	
METHA-01	1
DIMET-01	
H3O+	

Total 1

Figure (4-1): feed specifications

`



Operating conditions

Flash Type: Temperature, Pressure

Temperature: 80 F

Pressure: 2 psi

Duty: Gcal/hr

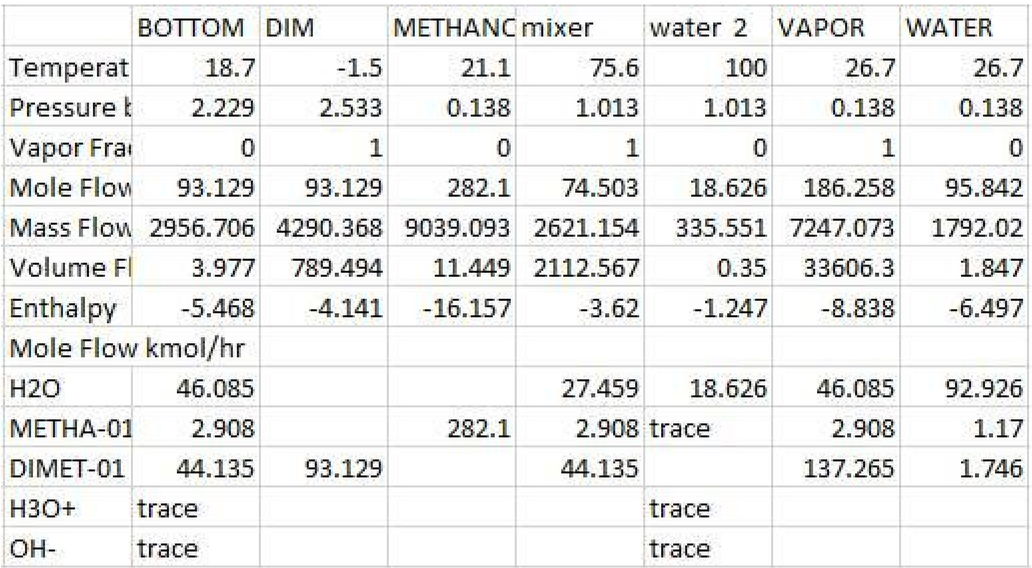
Vapor fraction:

Valid phases: Vapor-Liquid

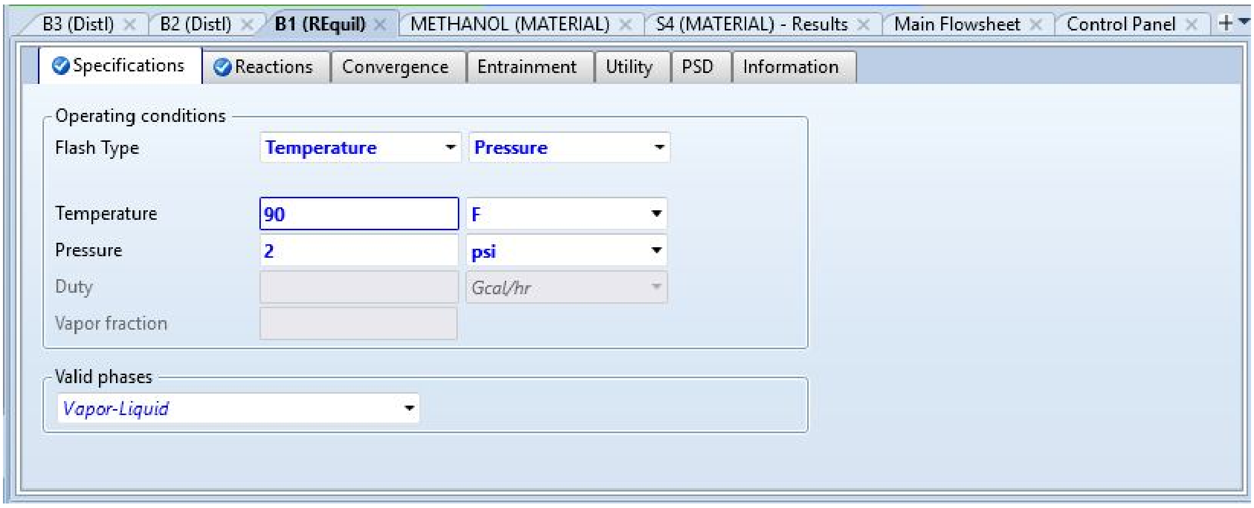
Figure (4-2): reactor operating conditions1

At 80˚C → 93.129 kmol/hr

Table 4-1:DME produced at 80˚C



	BOTTOM	DIM	METHANC	mixer	water 2	VAPOR	WATER
Temperat	18.7	-1.5	21.1	75.6	100	26.7	26.7
Pressure b	2.229	2.533	0.138	1.013	1.013	0.138	0.138
Vapor Fra	0	1	0	1	0	1	0
Mole Flow	93.129	93.129	282.1	74.503	18.626	186.258	95.842
Mass Flow	2956.706	4290.368	9039.093	2621.154	335.551	7247.073	1792.02
Volume Fl	3.977	789.494	11.449	2112.567	0.35	33606.3	1.847
Enthalpy	-5.468	-4.141	-16.157	-3.62	-1.247	-8.838	-6.497
Mole Flow kmol/hr							
H2O	46.085			27.459	18.626	46.085	92.926
METHA-01	2.908		282.1	2.908	trace	2.908	1.17
DIMET-01	44.135	93.129		44.135		137.265	1.746
H3O+	trace				trace		
OH-	trace				trace		



Operating conditions

Flash Type: Temperature, Pressure

Temperature: 90 F

Pressure: 2 psi

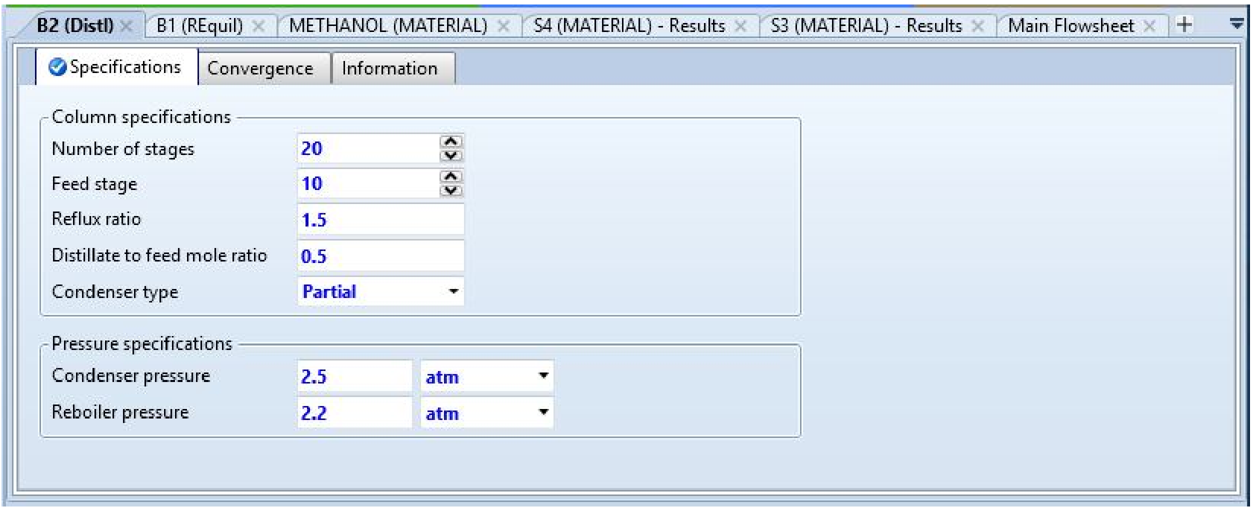
Duty: Gcal/hr

Vapor fraction:

Valid phases

Vapor-Liquid

Figure (4-3):reactor operation condition2



Column specifications

Number of stages: 20

Feed stage: 10

Reflux ratio: 1.5

Distillate to feed mole ratio: 0.5

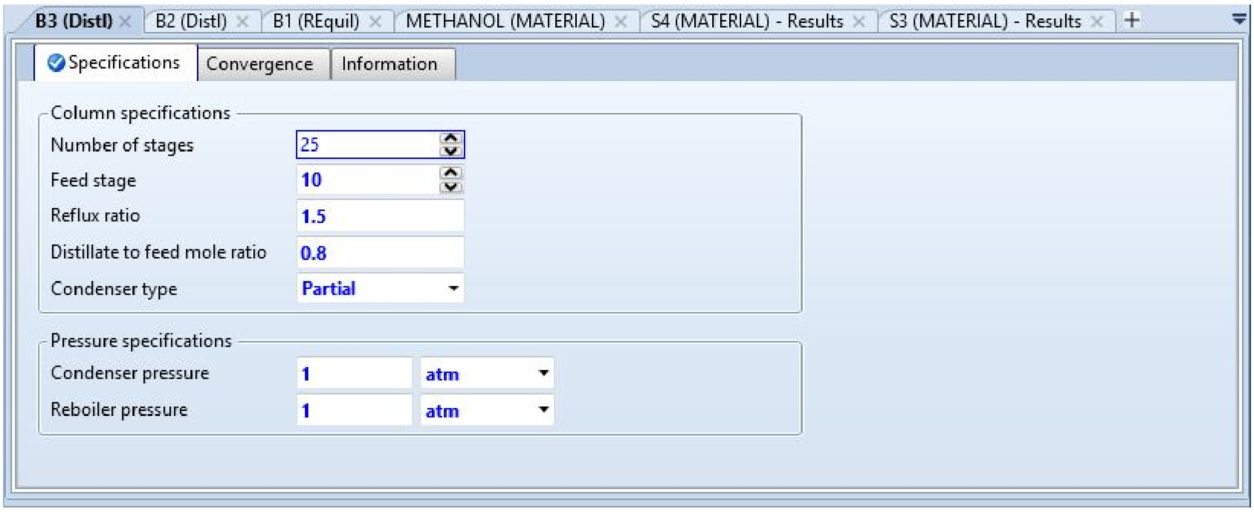
Condenser type: Partial

Pressure specifications

Condenser pressure: 2.5 atm

Reboiler pressure: 2.2 atm

Figure (4-4): column specification1



Column specifications

Number of stages: 25

Feed stage: 10

Reflux ratio: 1.5

Distillate to feed mole ratio: 0.8

Condenser type: Partial

Pressure specifications

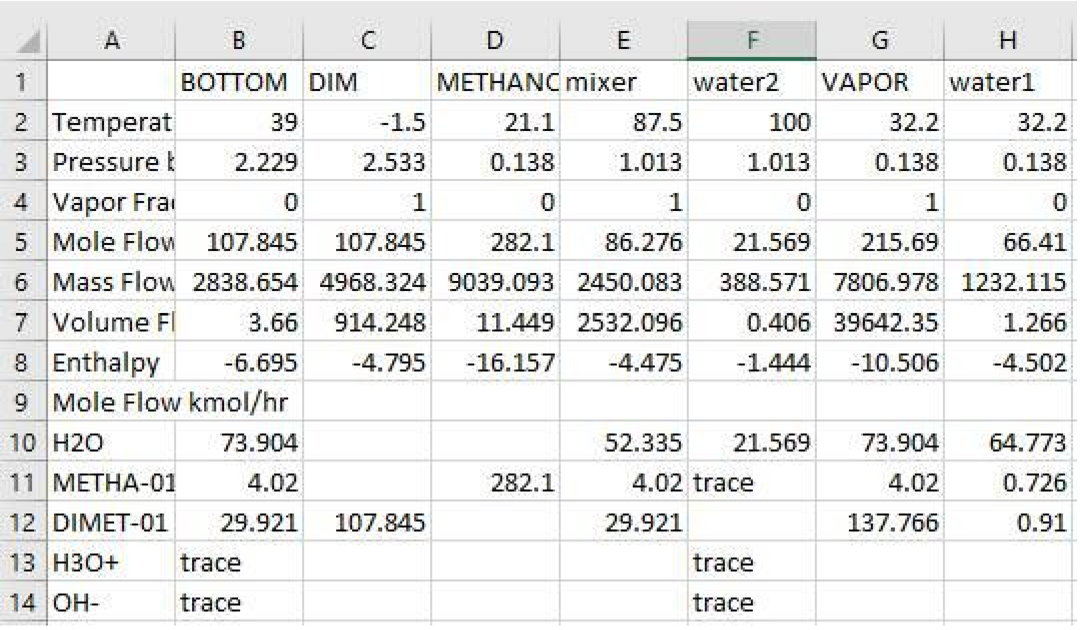
Condenser pressure: 1 atm

Reboiler pressure: 1 atm

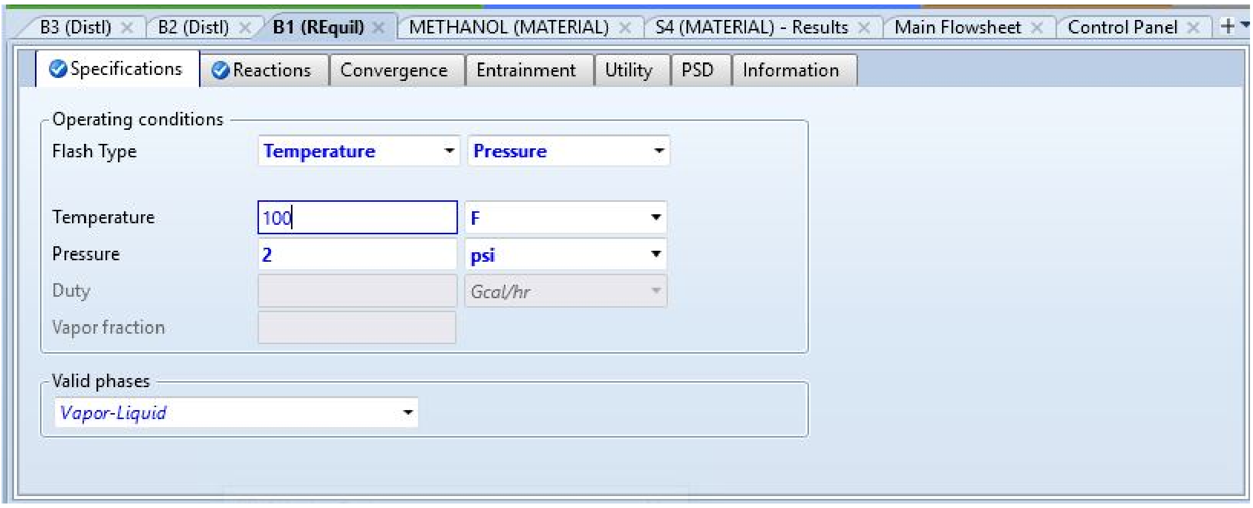
Figure (4-5): Column specifications2

At 90˚ C →107.845 kmol/hr

Table4-2:DME produced at 90˚C



	A	B	C	D	E	F	G	H
1		BOTTOM	DIM	METHANC	mixer	water2	VAPOR	water1
2	Temperat	39	-1.5	21.1	87.5	100	32.2	32.2
3	Pressure b	2.229	2.533	0.138	1.013	1.013	0.138	0.138
4	Vapor Frac	0	1	0	1	0	1	0
5	Mole Flow	107.845	107.845	282.1	86.276	21.569	215.69	66.41
6	Mass Flow	2838.654	4968.324	9039.093	2450.083	388.571	7806.978	1232.115
7	Volume Fl	3.66	914.248	11.449	2532.096	0.406	39642.35	1.266
8	Enthalpy	-6.695	-4.795	-16.157	-4.475	-1.444	-10.506	-4.502
9	Mole Flow kmol/hr							
10	H2O	73.904			52.335	21.569	73.904	64.773
11	METHA-01	4.02		282.1	4.02	trace	4.02	0.726
12	DIMET-01	29.921	107.845		29.921		137.766	0.91
13	H3O+	trace				trace		
14	OH-	trace				trace		



Operating conditions

Flash Type: Temperature, Pressure

Temperature: 100 F

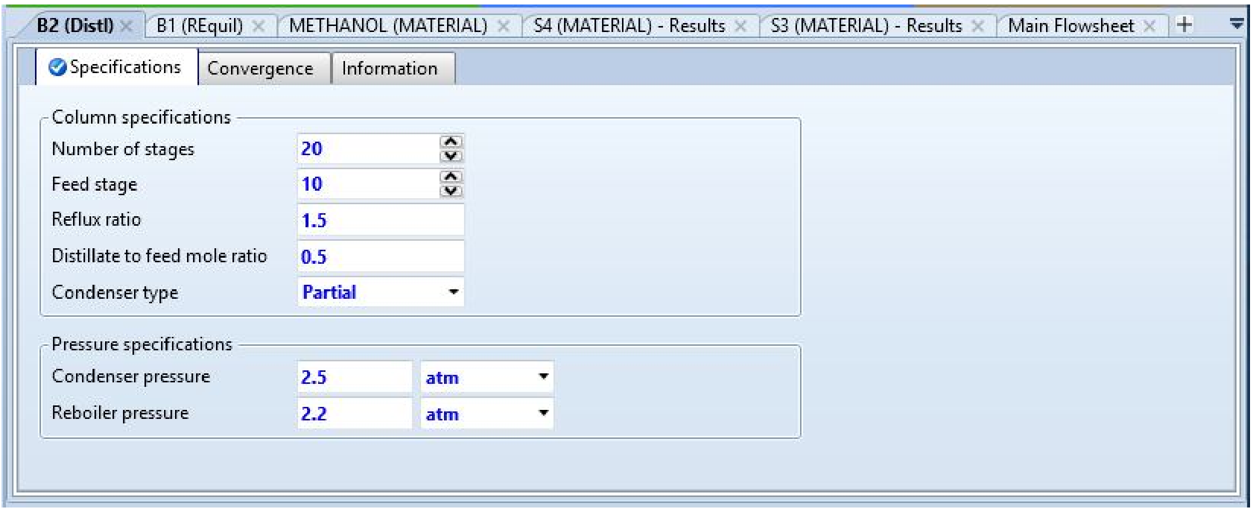
Pressure: 2 psi

Duty: Gcal/hr

Vapor fraction:

Valid phases: Vapor-Liquid

Figure (4-6): rector operation condition 3



Column specifications

Number of stages: 20

Feed stage: 10

Reflux ratio: 1.5

Distillate to feed mole ratio: 0.5

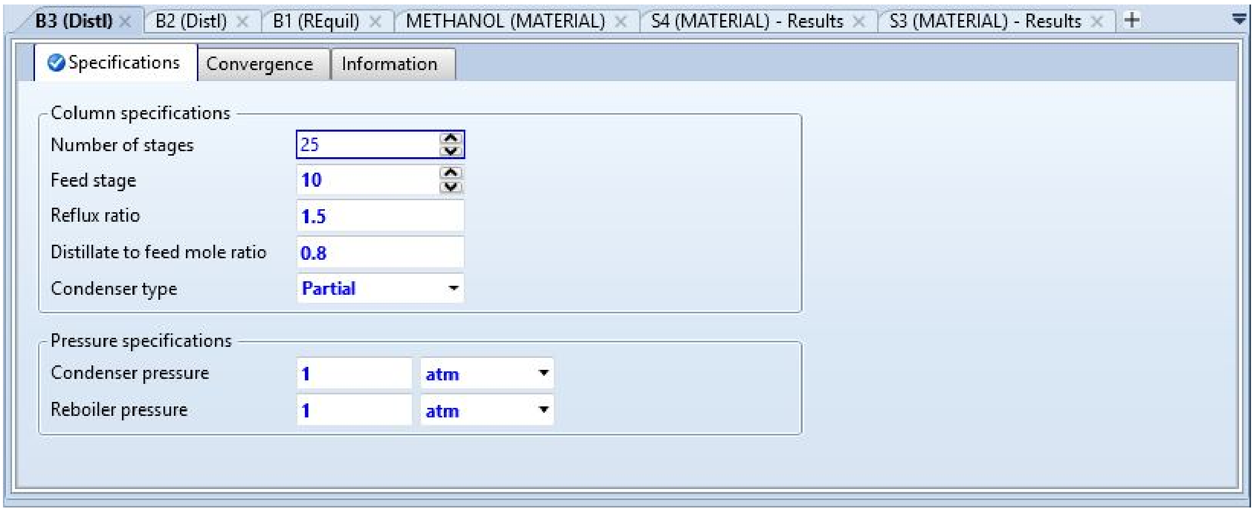
Condenser type: Partial

Pressure specifications

Condenser pressure: 2.5 atm

Reboiler pressure: 2.2 atm

Figure (4-7): column specifications



Column specifications

Number of stages: 25

Feed stage: 10

Reflux ratio: 1.5

Distillate to feed mole ratio: 0.8

Condenser type: Partial

Pressure specifications

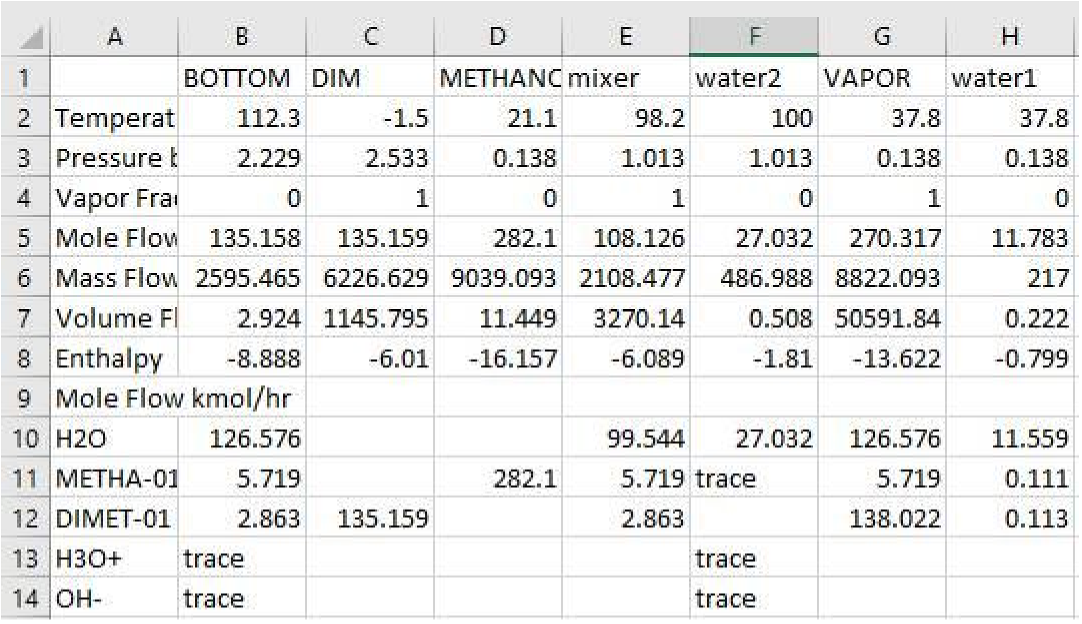
Condenser pressure: 1 atm

Reboiler pressure: 1 atm

Figure (4-8): Column specifications

At 100˚ C → 143.242 kmol/hr

Table 4-3:DME produced at 100˚C



	A	B	C	D	E	F	G	H
1		BOTTOM	DIM	METHANC	mixer	water2	VAPOR	water1
2	Temperat	112.3	-1.5	21.1	98.2	100	37.8	37.8
3	Pressure	2.229	2.533	0.138	1.013	1.013	0.138	0.138
4	Vapor Fra	0	1	0	1	0	1	0
5	Mole Flow	135.158	135.159	282.1	108.126	27.032	270.317	11.783
6	Mass Flow	2595.465	6226.629	9039.093	2108.477	486.988	8822.093	217
7	Volume Fl	2.924	1145.795	11.449	3270.14	0.508	50591.84	0.222
8	Enthalpy	-8.888	-6.01	-16.157	-6.089	-1.81	-13.622	-0.799
9	Mole Flow kmol/hr							
10	H2O	126.576			99.544	27.032	126.576	11.559
11	METHA-01	5.719		282.1	5.719	trace	5.719	0.111
12	DIMET-01	2.863	135.159		2.863		138.022	0.113
13	H3O+	trace				trace		
14	OH-	trace				trace		

DATA ANALYSIS AND RUSLT:

Table 4-4:DME produced versus reactor temperature

Temperature ˚C	DME produced Kmol/hr
80	93.129
90	107.845
100	135.159

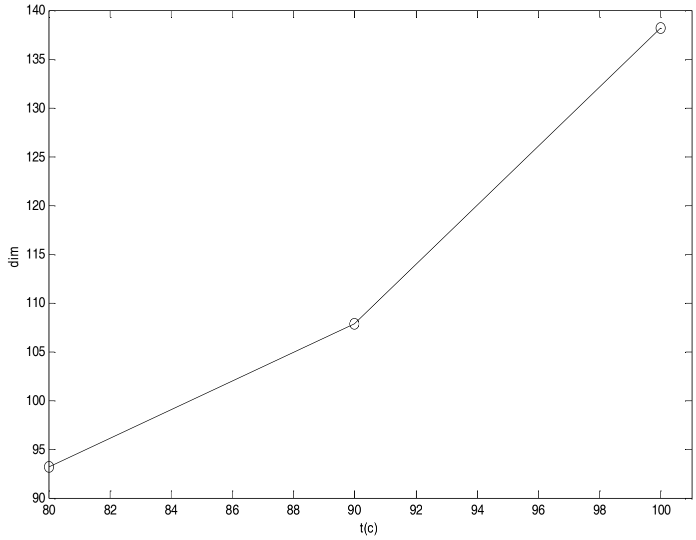


Figure (4-9): Relation between produced DME and reactor temperature

4.2 Design calculation

The actual results (manual calculated values):

Table 4-5:Molar flows of components

	Feed		Distillate		Bottom	
	Molar flow kmol/hr	Ratio	Molar flow kmol/hr	Ratio	Molar flow kmol/hr	Ratio
DME	137.265	0.736	93.129	0.999	44.135	0.473
H_2O	46.085	0.247	0.005	0.0000005	46.085	0.494
Methanol	2.908	0.015	0.005	0.0000005	2.908	0.031
Total	186.258	1	93.129	1	93.128	1

DME→haevy key (H.K)

H2O→light key (L.K)

Antoine equation :

$$\ln p^{\circ} = A - \frac{B}{T + C}$$

Table 4-6:Components Antoine constants

Component	A	B	C
Methanol	8.0724	1574.99	238.87
DME	4.11475	894.669	-30.604
Water	5.20389	1733.926	-39.485

The manual calculation:

The vapor pressure of water

$= 0.232$ bar

The vapor pressure of methanol

$= 172$bar

The vapor pressure of DME

$= 2.2$bar

We have to calculate the relative volatility for the three components:

$\propto_{water} = \frac{P^{\circ}}{Pt} = \frac{0.238}{0.138} = 1.72$

$\propto_{methanol} = \frac{p^{\circ}}{pt} = \frac{172}{0.138} = 1246$

$\propto_{DME} = \frac{p^{\circ}}{pt} = \frac{2.2}{0.138} = 15.94$

After that $\propto_{average}$had been calculated

$\propto_{average} = \frac{1}{\propto_{heavy\ key}} = \frac{1}{1.72} = 0.581$

From eq(4-2) $N_{min} = 10\ trays$

From eq(4-1) $\boldsymbol{\lambda}$= 2.2

From eq(4-6) $V_{min} = 106$

From eq(4-3) $R_{min} = 1.13$

Assume : R=1.5R_{min}

R=1.695

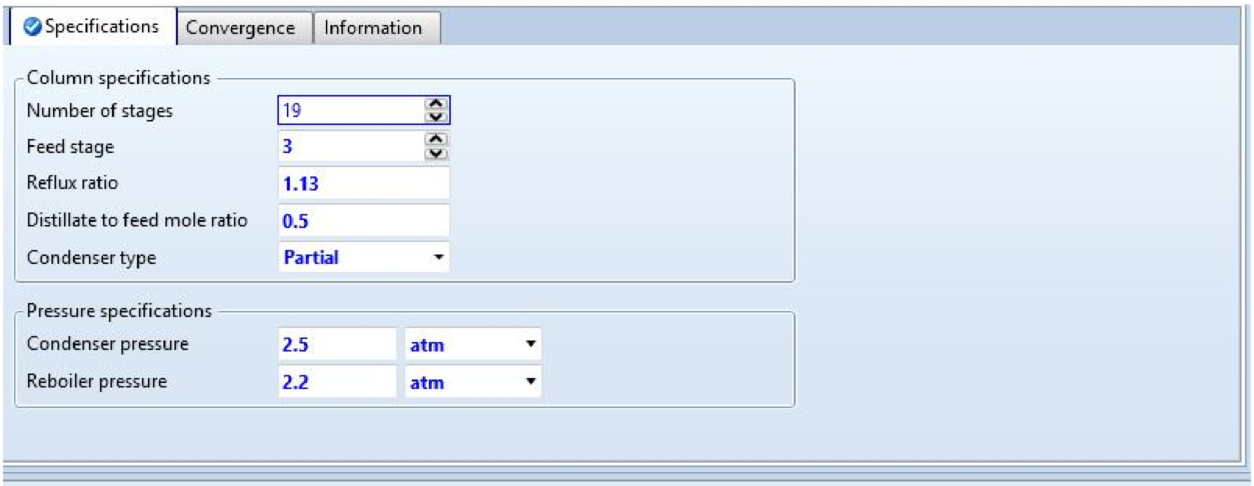
From eq(4-4) N=19 trays

From eq(4-5) $\frac{N_R}{N_S} = 5$

$$N_R = 5N_S$$

$$N_R + N_S = 19$$

$5N_S + N_S = 19 \quad \gg \quad N_S = 3$



Column specifications

Number of stages: 19

Feed stage: 3

Reflux ratio: 1.13

Distillate to feed mole ratio: 0.5

Condenser type: Partial

Pressure specifications

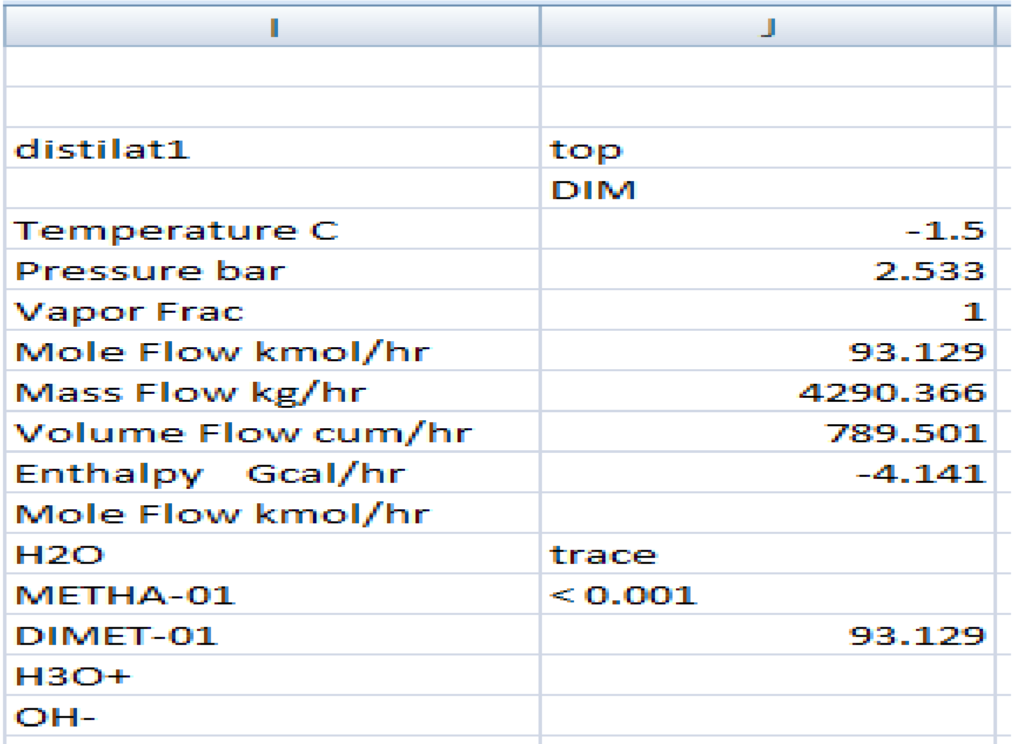
Condenser pressure: 2.5 atm

Reboiler pressure: 2.2 atm

Figure (4-10):Column specifications

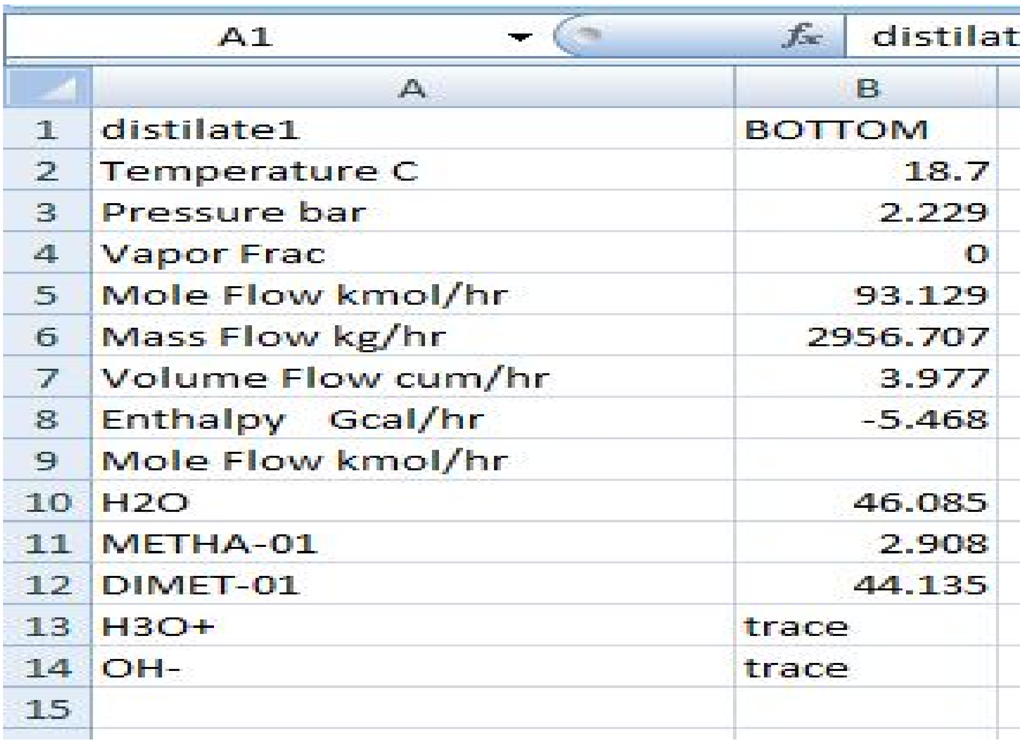
After applying the above actual results of the number of stages and feed stage and reflux ratio the following values are resulted

Table 4-7:Component (DME) in the top stream



I	J
distilat1	top
	DIM
Temperature C	-1.5
Pressure bar	2.533
Vapor Frac	1
Mole Flow kmol/hr	93.129
Mass Flow kg/hr	4290.366
Volume Flow cum/hr	789.501
Enthalpy Gcal/hr	-4.141
Mole Flow kmol/hr	
H2O	trace
METHA-01	< 0.001
DIMET-01	93.129
H3O+	
OH-	

Table 4-8:Component (DME) in the bottom stream



	A	B
1	distilate1	BOTTOM
2	Temperature C	18.7
3	Pressure bar	2.229
4	Vapor Frac	0
5	Mole Flow kmol/hr	93.129
6	Mass Flow kg/hr	2956.707
7	Volume Flow cum/hr	3.977
8	Enthalpy Gcal/hr	-5.468
9	Mole Flow kmol/hr	
10	H2O	46.085
11	METHA-01	2.908
12	DIMET-01	44.135
13	H3O+	trace
14	OH-	trace
15		

4.3 cost estimation calculation

1. fixed cost

Distillation fixed cost =

115613 + (115613*0.05) + (115613*0.4) = $ 167638.85

Reactor fixed cost =

26400 + (26400*0.05) + (26400*0.04) = $ 38280

Where

Transportation = 0.05 * capital cost

Constriction = 0.4 * capital cost

Total fixed cost = (2*167638.85) + 38280

= $ 373557.7

4. operating cost:

Material +operator + maintenance

Material cost:

Material name	Classification	Price ($/Kg)	Flow rate (Kg/h)	Annual cost ($)
Methanol	Raw material	0.300	9039.93	23431498.5
Die methyl-eyther	Product	4.06	6226.629	218742971.2

Material cost = $ 23431498.5 /yr

Annual labor shift = 49*5 = 245 shifts per operator per year

Annual plant shift = 365*3 = 1095 operating shift per year

The number of operator needed in the plant = 4.5 ≈ 5

For three plant the number of operator needed = 15 per shift

Where each labor will receive an average salary of $ 14400 /yr the operator cost will be

15 * 14400 = $ 216000 /yr

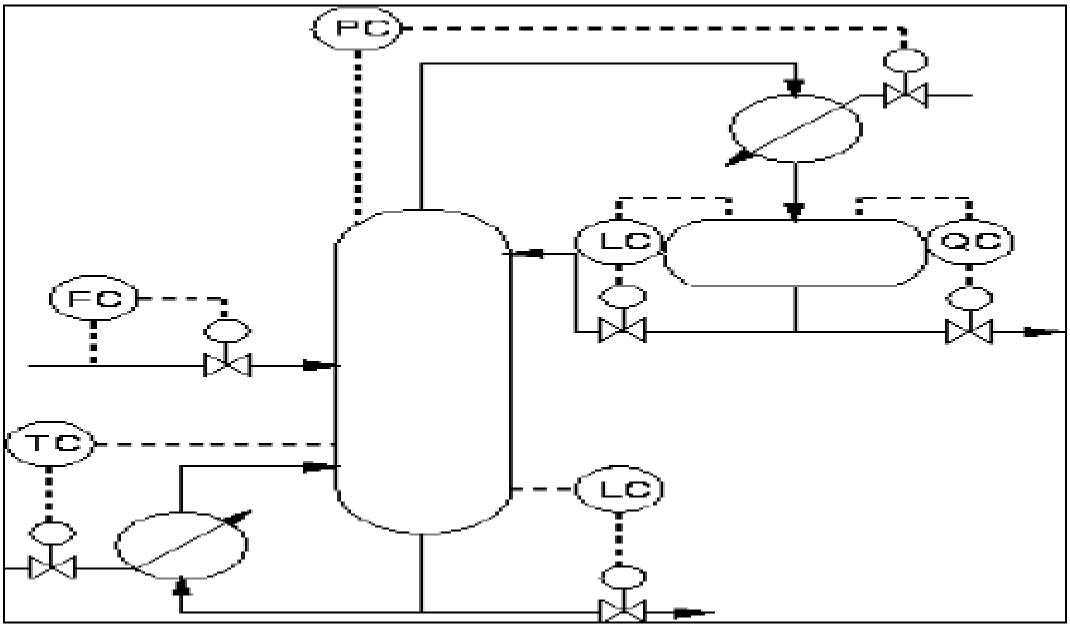
Maintenance = $ 216000 /yr

Total operating cost = 216000 + 216000 +23431498.5 = $ 23863498.5

Total cost = 373557.7 + 23863498.5 = $ 24237056.2.

4.4 Control loop of Distillation Column:

The control loop of distillation column is important to maintain the quality of a product orthe flow rates at required conditions. For example, if the product quality is not at specified conditions, the control valve will automatically decrease the valve opening. As a result ofthat, the reflux ratio will increase until the product quality achieves the required. Also, it necessary sometimes to regulate the pressure .



Figure(4-11): distillation control loop

Chapter 5

Conclusion and recommendations

Conclusion and recommendations

5.1 Conclusion:

After studying the process of DME production and optimizing it by simulation it found that DME can be produced via methanol dehydration and can be sold as an alternative fuel replacing petroleum based vehicle fuels. This process had been simulated and optimized to reach the optimum operation condition with respect to DME productivity which reached its highest value when reactor temperature reached 100°C.

5.2 Recommendation:

- perform more studies on this concern
- contact with global energy companies who developed this technology to exchange knowledge and experiences between those companies and our national energy companies to investigate the ability of using of DME as an alternative fuel, because of its proven advantages in serving energy supply and environment friend fuels fields.
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- In the other hand we recommend to look after new versions of simulation software to help researchers solving their problems and designing their samples easily.

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