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University year: 2020-2021



Dedicate

I dedicate this work to...

My dear parents;

Thank you for your support during all these years and God knows they have been long!

Despite the distance that separates us, I have always felt you by my side. For your support and patience, for all of the things that made me here. I hope I can make you proud of my career; for all your sacrifices and for the education you gave me. I love you more than anything and cannot thank you enough for everything you did for me. Thank you so much, I love you.

My big brothers;

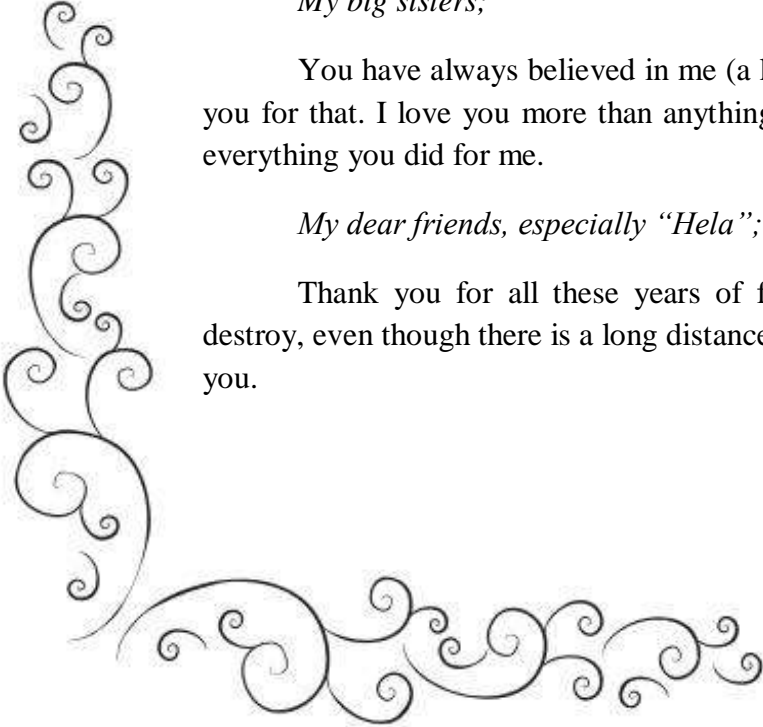
We may not see each other enough but the feelings are sincere. I wish you all the happiness in the world. I love you more than anything and can never thank you enough for everything you did for me.

My big sisters;

You have always believed in me (a little too much by the way) and I thank you for that. I love you more than anything and can never thank you enough for everything you did for me.

My dear friends, especially "Hela";

Thank you for all these years of friendship that the distance could not destroy, even though there is a long distance but I know that I can always count on you.





Thanks

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I thank my supervisor *Dr H.Izza* for her supervision, availability, competence, dedication, commitment and advice that led me to do this thesis.

M' .A.L.Rahmani

I have the honor that you accept to be the President of my thesis jury.

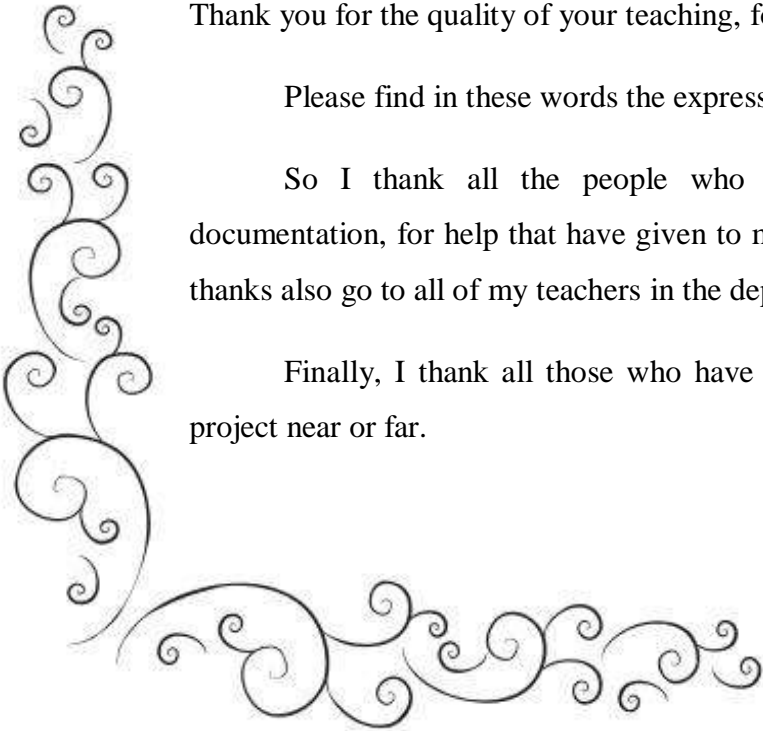
Dr N.Chaouch

I have the honor that you accept to be part of the jury for this thesis. Thank you for the quality of your teaching, for the attention and dedication.

Please find in these words the expression of my deep gratitude.

So I thank all the people who have helped in the search for documentation, for help that have given to me for their efforts and advice. My thanks also go to all of my teachers in the department of processes engineering.

Finally, I thank all those who have contributed to the success of this project near or far.



Abstract:

The industrial methanol production and its description, in this work which has been focused on the research widely, specifically the production from synthetic gas we see the production of synthetic gas in the first place.

We see the production of methanol, reaching to the material balance to calculate the flow of each constituent at different positions, and the heat balance as well of the production we calculate the heat quantities and its amount in each reaction and at different positions also to finally calculate the reactor sizing that respect standards and specifications required : reactor diameter: **1.34m**, reactor height: **3.6m**.

Key words: synthetic gas, material balance, heat balance, reactor sizing, reactor diameter, reactor height.

Résumé :

La production industrielle de méthanol et sa description, dans ce travail qui s'est largement concentré sur la recherche, en particulier la production à partir de gaz de synthèse, nous voyons la production de gaz de synthèse en premier lieu

Nous voyons la production de méthanol, atteindre le bilan matière pour calculer le flux de chaque constituant à différentes positions, et le bilan thermique ainsi de la production nous calculons les quantités de chaleur et sa quantité dans chaque réaction et à différentes positions aussi pour enfin calculer le dimensionnement du réacteur qui respecte les normes et spécifications requises : diamètre de réacteur : **1.34m**, hauteur de réacteur: **3.6m**.

Mots clés: gaz de synthèse, bilan matière, bilan thermique, dimensions de réacteur, diamètre de réacteur, hauteur de réacteur.

ملخص:

إنتاج الميثانول الصناعي ووصفه ، في هذا العمل الذي ركز على البحث على نطاق واسع ، وتحديدًا الإنتاج من الغاز الاصطناعي نرى إنتاج الغاز الصناعي في المقام الأول.

نرى إنتاج الميثانول ، والوصول إلى توازن المواد لحساب تدفق كل مكون في مواضع مختلفة ، وتوازن الحرارة وكذلك الإنتاج نحسب كميات الحرارة وكميتها في كل تفاعل وفي مواضع مختلفة أيضًا إلى النهاية حساب أبعاد المفاعل الذي يحترم المعايير والمواصفات المطلوبة: قطر المفاعل : **1.34 م**، ارتفاع المفاعل : **3.6 م**.

الكلمات المفتاحية : غاز اصطناعي ، ميزان مواد ، ميزان حرارة ، أبعاد المفاعل ، قطر المفاعل ، ارتفاع المفاعل .

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Symbol and its meaning	Unit
P: Pressure	atm
T: Temperature	°C
n: Number of days	d/year
η : Yield of methanol	%
τ : Conversion rate	%
ΔH_i : Enthalpy of constituent	Kcal/mol
G_i : Mass flow of constituent	Kg/h
M_i : Molar mass of each constiteunt	mol
M_m : The average mass molecular	Kg/mol
X_i : Mass concentration of each constituent	Kg
X'_i : Molar concentration of each constituent	%
G_i : Molar flow of each constituent	Kmol/h
Q_i : The amount of heat	Kcal/h
C_p : Specific heat	Kcal/kg°C
X_n : The amount of water formed	kmol of H ₂ O /h
ΔH_R : Thermal effect of the reaction	Kcal/mol
Y_n : The percentage of each fresh gas flow	%
ρ : Density	g/cm ³
ρ_{ch} : The charge density	Kg/m ³
W: The linear speed	m/s
s_c : The cross section	m ²
D_R : Diameter of the reactor	m
V: Special speed	h ⁻¹
V_R : Volume of the reactor	m ³
H_R : Heigt of the reactor	m
ρ_{cat} : Volume mass of the catalyst	Kg/m ³
G_{cat} : Weight of the catalyst	Kg

Γ : Contact time	s
${}^nD^{20}$: Refractive index	-
d_4^{20} : Density	-
N.G: Natural gas	-
S_n : Separator	-
F_n : furnace	-
E_n : Exchanger	-
Q_n : Recirculator	-
K_n : Compressor	-
H: Separator	-
R: Reactor	-

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General Introduction

General introduction

General introduction:

The petrochemical industry, which produces chemicals using oil and natural gas as major raw materials, occupies an important position manufacturing and consuming sectors. Oil and natural gas are composed primarily of hydrocarbons. Most petrochemicals contain hydrogen or carbon or both. Petrochemicals can be converted into thousands of industrial and consumer products, which use actually only 20% to 5% of crude oil and natural gas including plastics, paints, rubber, fertilizers, detergents, dyes, textile and solvents. The industry consists of 2 major divisions. The primary petrochemical industry produces basic chemicals, such as meth, from oil or gas. The secondary industries convert the basic petrochemicals into materials that may be directly used by other industries.

Industrial gases find use in almost every modern manufacturing process. Prominent among gas-using sectors is the chemical industry, where the field of petro chemistry, or petroleum products chemistry, is most important in terms of not only quantities used but also generation of industrial gases. The term “petro chemistry” refers to the field of chemistry concerned with processes for making basic chemicals from petroleum refinery products, natural gas and synthesis gas. In this field, industrial gases are mainly needed as reactants to afford safety to protect the environment for industrial services.

For example, synthesis gas is the main feedstock for the production of methanol, which in turn is or can be the starting material for the manufacture of the following products: Formic acid Acetic acid Formaldehyde etc.... Hydrocarbons such as olefins Hydrocarbon mixtures for fuels (such as because of the wide range of possible applications for methanol, its potential in terms of a methanol-based economy beyond oil and gas are now under discussion. Specifically; the production of alcohols is one of the most important branches of the petrochemical industry; they are widely used for the manufacture of aldehydes and organic acids etc..., currently alcohols are made by different routes:

- Catalytic hydration of olefins.
- Oxidation of liquid and solid paraffins.
- From wood and organic products.
- Synthesis from CO and H₂.

In this project we study industrial methanol production in Algeria.

Chapter I

Synthetic gas "syngas"

I.Synthetic gas “syngas”:

I.1.Syngas:

Syngas is an abbreviation for synthesis gas, which is a mixture comprising of carbon monoxide, carbon dioxide, and hydrogen. The syngas is produced by gasification of a carbon containing fuel to a gaseous product that has some heating value. Some of the examples of syngas production include gasification of coal emissions, waste emissions to energy gasification, and steam reforming of coke.

In figure 1 show the molecule model of mixture $\text{CO} + \text{H}_2$

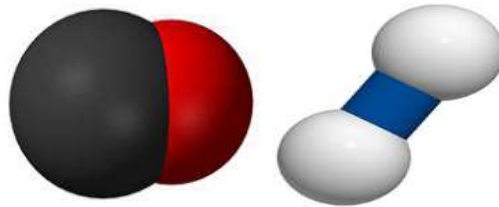


Figure 1.Molecule model of $\text{CO} + \text{H}_2$.

I.2.Source of syngas “raw material”:

Syngas can be produced from many sources, including natural gas(CH_4) or refinery gases, coal, biomass, or virtually any hydrocarbon feedstock, by reaction with steam (steam reforming), carbon dioxide (dry reforming) or oxygen (partial oxidation). Syngas is a mixture consisting primarily of hydrogen (H_2), carbon monoxide (CO) and very often some carbon dioxide (CO_2). Syngas is a building block in chemical industry, which corresponds to 2% of the total primary energy consumption.

Composition of syngas is affected by the feedstock and also the amount of water/oxygen used during gasification process. Typical composition of syngas is shown in Table I. Syngas produced from biomass, such as wood, usually contains lower percentage of CO but higher percentage of hydrocarbons. Depending on the sulfur content in the coal, syngas produced from coal may contain considerable amount of H_2S . Similar to biogas, utilization of syngas also requires removal of impurities, especially NH_3 and H_2S to avoid corrosion. [1]

Table I. Typical composition of syngas.

Character	Unit	Wood	Coal
H ₂	%	30–45	25–30
CO	%	20–30	30–60
CO ₂	%	15–25	5–15
CH ₄	%	8–12	0–5
C ₂ + hydrocarbons	%	1–3	N.A
N ₂	%	1–3	0.5–4
NH ₃	ppm	500–1000	0–3000
H ₂ S	ppm	50–1	2000–10000

I.3. Main properties of syngas:

Different characteristics of syngas can affect the process of combustion in internal combustion (IC) motors. The flammability limit of the syngas is one of the most important properties in IC engine safety and fuel. Also, the laminar flame velocity [2] (burning velocity) is an essential parameter to investigate the operation of the combustion chamber and its emission performance.

I.4. Syngas flammability limits:

The limit of flammability is usually used as an index for the flammability of the gas. This describes the range of the fuel concentrations in the fuel/air mixture at certain temperature and pressure, which allow the ignition of the flame to propagate and sustain the flammability limits [3] are known in line with generally accepted usages as those fuel-air areas where flame propagation can take place and where fire cannot propagate. The fuel, the spread direction, the size and the form of the combustion chamber, the temperature, and the pressure are primarily affected [3]. And for the fuel-air blend, there are two distinct flammability limits, namely the

smallest fuel boundary the flames can propagate is called the lower flammability boundary (LFL), while the richest one is called the upper flammability boundary (UFL). The fact that H₂ and CO are the principal flame-retardant components of syngas inherits the characteristics of these gasses. The presence of inert gasses such as nitrogen and carbon dioxide in the gas mixtures reduces the flammability limit.

I.5.Laminar flame velocity:

The laminar flash speed is the speed at which the flame propagates in the direction of expansion wave surfaces under a laminar flow condition via quiet unbranched fuel-oxidant mixes [4]. Because LFV is highly sensitive to combustion chamber operations and emission performance, it is very important for the investigation of combustion chamber operations. The composition of the fuel, mixture equivalence ratio, temperature, and pressure affects it.

I.6.Syngas composition and its calorific value:

The composition of the manufacturer’s gas depends on feedstock, particulate size, gas flow rate and feedstock flow, chemical reactor configurations, operating conditions or process of gasification, gasificator and catalyst, and gas residence time. But the temperature of the reactor, which in turn is affected by the ER value, mainly influences it. Furthermore, CO, H₂, and CH₄ concentrations in producer gas are also controlled by chemical reactions in the process of gasification.

There is, therefore, a considerable influence on the calorific value of the producer gas on the type of oxidizing agent used for gasification. As ER increases and then the concentrations of these useful components decreases because of the intensification of combustion at higher ER values, the concentrations of CO and H₂ reach the maximum value. As ER increases, the concentrations of CO₂ and N₂ in the producer gas are also increased [5]. Air as an oxidant produces syngas with relatively high levels of nitrogen and thus a lower heat value, which does not normally exceed 6 MJ/Nm³.

The producer’s gas is classified as fuel gas of low quality. The typical biomass gasification composition of an air-borne downdraft reactor with the oxidizer is as follows: 15–20% of H₂, 15–20% of CO, 0.5–2% of CH₄, 10–15% of CO₂, and the rest of the component of N₂, O₂, and CXHY. If the concentration of fuel components is considerably increased and the gas is called a medium heat value, up to 16 MJ/Nm³ [5], where oxygen or water steam or the mixture of both are used.

I.7. Use of syngas:

The name syngas is derived from the use as an intermediate in generating synthetic natural gas and to create ammonia or methanol. It is a gas that can be used to synthesize other chemicals, hence the name synthesis gas, which was shortened to syngas. Syngas is also an intermediate in creating synthetic petroleum to use as a lubricant or fuel.

Syngas has 50% of the energy density of natural gas. It can't be burnt directly, but is used as a fuel source. The other use is as an intermediate to produce other chemicals. The production of syngas for use as a raw material in fuel production is accomplished by the gasification of coal or municipal waste. In these reactions, carbon combines with water or oxygen to give rise to carbon dioxide, carbon monoxide, and hydrogen. Syngas is used as an intermediate in the industrial synthesis of ammonia and fertilizer. During this process, methane (from natural gas) combines with water to generate carbon monoxide and hydrogen.

The gasification process is used to convert any material that has carbon to longer hydrocarbon chains. One of the uses of this syngas is as a fuel to manufacture steam or electricity. Another use is as a basic chemical building block for many petrochemical and refining processes [6].

In figure 2 represent application of syngas:

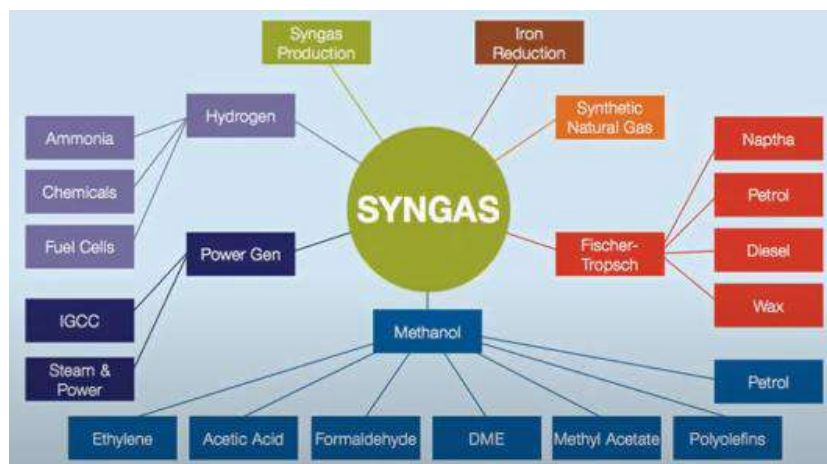


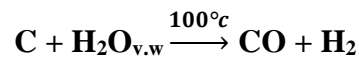
Figure 2. Application of syngas.

I.8. Production of syngas:

The starting gas necessary for the synthesis of methanol has theoretically the following composition:

- **Synthesis gas from coke:**

The oldest method which was mainly used before the Second World War was for the preparation of mixture (CO + H₂) a stream of water vapor is blown through a layer of coke [7].

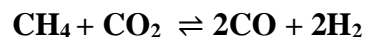
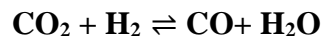
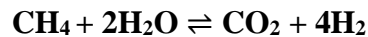


- **Synthesis gas from hydrocarbons:**

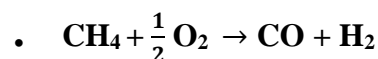
The production of synthesis gas has developed further in the direction of the processes in which natural gas or petroleum products are used as raw materials is made according to two processes either in endothermic reaction by conversion to water vapor, or by partial oxidation with oxygen [8].

- **By conversion to water vapor:**

This method is based in principle on the following reaction:



- **By partial oxidation:**



Using in suitable proportion, Oxygen and methane.

A gas for which the H₂/CO ratio is very close to 2, this during to take into account the losses due to the formation of methane. Or course of methanol synthesis [9].

A gas whose H₂/CO ratio is close to 2.25 is generally used for this synthesis to obtain this value the quantity of CO must be adjusted by diverting part of the gas stream to a CO converter via the steam which eliminates the excess CO by supplying a quantity of hydrogen

and by one of the classical absorption methods the CO₂ is eliminated up to the level of concentration acceptable by the methanol synthesis catalyst. In the second case, we obtain a gas whose H₂/ CO ratio is significantly different from that of methanol synthesis gas a CO defect appears which can be compensated either by eliminating the excess hydrogen on a dry hydrogen purge either by adding CO at the inlet or at the outlet of the primary reforming.

Of the output restores the carbon - hydrogen - oxygen proportions which make it possible to obtain the suitable ratio (≈ 2.25) as some methanol synthesis catalysts are active in the presence of CO₂, absorption in the primary gas can be avoided [9].

Chapter II

Methanol production process

II. Methanol production process:

II.1.Methanol:

Methanol has many names carbonyl methyl or methyl hydrate methyl hydroxide it's also known with wood alcohol with formula CH_3OH , is basically pretty similar to methane the only difference is that we have oxygen and actually the OH group is called hydroxy group and it's the most important because it define the negative pole and the CH_3 is the positive pole and we will have polarity. The representation of methanol is in figure 5 down here:

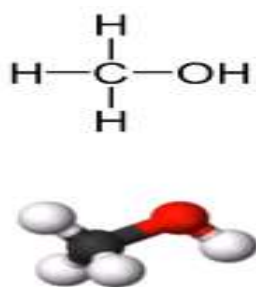


Figure 3.representation of methanol.

Methanol is a mobile, colorless, light volatile liquid with a rather pleasant odor when pure and it' a flammable liquid with a very low boiling point. The data relating to the odor detection threshold are discordant; it is miscible with water, the mixture being with release of heat and contraction, and with most organic solvents (alcohols, ethers...). It dissolves fats and a large number of plastics and mineral salts; it is, in this respect, a better solvent than ethanol.

Methanol occurs naturally in esters tangerine peels for example, it can also produced by some bacteria. The chemical industry uses methanol as the base to make other chemicals.

A vast array of synthetic plastic materials can be produced using methanol derivatives through processes like polymerization and poly condensation.

Almost everything we know today is defined by plastics which are all based on methanol, the word plastic refers to a materials distinctive ability to be shaped and molded

under pressure and at high temperature and then retain its new solid shape after being cooled down. In just few decades, plastic and their almost limitless potential to be chapped at will revolutionize the world's industry and economy, that's why the mid 20th century saw a massive plastic that changed civilization and touched virtually every aspect of human life.

Plastics are quite literally everywhere, food packaging wrapping and storage materials containers of every type and size hundreds of everyday tools and appliances in man-made fabrics, the list is really almost endless.

Methanol is widely used in paint colorings and vanishes; it used to make the long-lasting pigments and lacquers popular among modern artists, it used also in global industry agriculture because it's unique ability to form a variety of useful chemicals, it can be both an insecticide and fertilizer for plants. And here is one extra curios methanol fact; it's also produced in very small quantities by the human body so in a sense everyone has their own personal 24 hour methanol production facility. We can produce from methanol fuel, thermal insulation, wood products and glassing.

II.2.Methanol production in Algeria:

The latter, which is the hydrogenation of carbon monoxide, has become the means of choice for the production of methanol



This method was carried out for the first time in 1923 it is the method used in Algeria

the realization of this process is favored by a high temperature except high pressure as well as the chosen catalyst and the nature of the raw material used it should be noted that the methanol resulting from the distillation of wood represents only a few percent of the total production in the petrochemical industry. Methanol still keeps a big place of choice. it is widely used in the manufacture of formalin and organic solvents.

II.3. Raw material:

The raw material distilled for the synthesis of methanol is the mixture $\text{Co} + \text{H}_2$ this mixture can be obtained by a raw material more available it is a process of conversion of methane by steam or by oxygen.

II.4. Obtaining methods:

- **By the direct oxidation of methane:** $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$

This method is still at the pilot stage. Not used industrially.

- **By direct synthesis:** $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$

Methanol is obtained from synthesis gas under high temperature and high pressure in the presence of a catalyst. This is the process currently used.

II.5. Physicochemical properties of methanol:

Methanol is a colorless liquid at room temperature.

Table II show the different properties of methanol [12]:

Table II. Physicochemical properties.

Properties	Values
Molecular mass	$M = 32$
Density at 20°C	$\rho = 0.7867 \text{ g/cm}^3$
Boiling temperature	$T_b = 64.5^\circ\text{C}$
Melting temperature	$T_M = 97.88^\circ\text{C}$
Critical temperature	$T_C = 240^\circ\text{C}$
Ignition temperature	$T_I = 470^\circ\text{C}$
Vapor density	$= 1.1$
Vapor pressure at 25°C	$P = 0.1632 \text{ bar}$
Molar heat capacity at 25°C	$= 45.2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
Viscosity at 25°C	$= 0.51 \text{ cp (or mpa.s)}$
Specific heat at 25°C	$= 0.599 \text{ kcal / kg}\cdot\text{K}^\circ$
Heat of combustion at 25°C	$= 5419.9 \text{ kcal / kg}$
Heat of vaporization at 25°C	$= 9.19 \text{ kcal / mol}$
Flash point	$= + 6.5^\circ\text{C}$

Refractive index	$n_D^{20} = 1.3285$
Density	$d_4^{20} = 0.792$
Explosion limits in air	6 — 36.5% (wt)

II.6. Use of methanol:

II.6.1. Main uses:

Methanol is an intermediate in the synthesis of the following products:

- Formaldehyde DMT (dimethyl tere phthalate), methyl amines chloro methanes. MAM (methyl methacrylate), Solvents.
- Acetic acid.
- Proteins.
- MTBE (methyl tertio-butyl ether) $\text{CH}_3\text{-C}(\text{CH}_3)_2\text{-O-C-CH}_3$ (CH_3) for essences.
- Fuel (gasoline + methanol + cosolvent or methanol + TBA (tertio-butanol)).

In the organic industry, methanol always keeps a place of choice for a very large part it is used to manufacture formal etc... [13].

- **Manufacture of formal:**

The manufacture of formal by the oxidation of methanol in principle the oxidation of methanol consists of passing an air-vapor mixture of methanol in a catalytic bed near atmospheric pressure and absorbing the product in water.

- **Manufacture of methylamine:**

The interaction of methanol with ammonia carried out at 450 °C. under a pressure of 50100 atm in the presence of alumina catalyst leads to methylamine.

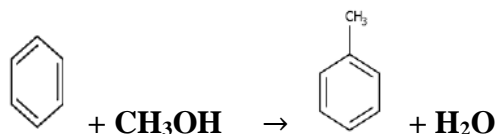
- **Manufacture of Methyl acetate:**

Methanol reacts with acetic acid endowing methyl acetate.

It is used for the production of pharmaceutical coloring products.

- **Manufacture of toluene:**

Benzene reacts at 370 °C. And under pressure 50atm, in the presence of zinc phosphate

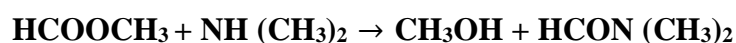


- **Production of methylated amines:**

Sodium methanol adds to carbon dioxide.



Occurs is used to prepare dimethylformamide.



The essential interest of methanol in the various techniques is that it can be used as a solvent to extract mercaptans from gasoline, can be used as a fuel or as a component of motor fuels [14].

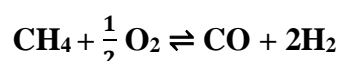
II.7.Process theory:

The manufacture of methanol is mainly based on carrying out the following reaction.



The gas mixture necessary for the transformation must have a hydrogen/carbon ratio equal to 2.25; the mixture is compressed to 200/300atm, hydrogen and monoxide gases can be obtained by:

- Partial oxidation of methane (natural gas):



- By steam cracking with water vapor:



The yield of methyl alcohol is low at equilibrium the initial gas mixture must be recycled several times the conversion of the initial charge of $\text{CO} + 2\text{H}_2$ into methanol is favored by a high pressure and a low temperature it is carried out on an appropriate catalyst.

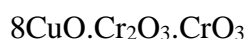
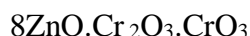
This synthetic methanol is practically possible at a temperature between 300/400°C and does not occur in the absence of the catalyst.

In general, the rise in temperature is a favorable factor not only to the conversion but to the disappearance of all the side reactions giving rise to various products such as methane, formal, dimethyl ether in practice the conversion of the methanol gas load is between 5 and 20%.

II.8.Choosing an appropriate catalyst:

The properties which are required of a good catalyst which can be used in manufacture are above all the following good catalytic action that is to say with good selectivity. The maximum possible acceleration towards obtaining synthesis equilibrium resistance to poisoning long life and mechanical stability at a bearable price the catalyst currently used is the catalyst based on zinc oxide.

The catalysts chosen are:

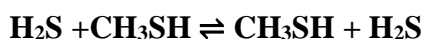
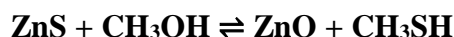


The catalyst for methanol must be selective in order to direct the hydrogenation of carbon monoxide or carbon dioxide to produce as pure a methanol as possible.

Scientific research in past years has been particularly concerned with the study of mixed catalysts based on zinc oxide. All catalysts which absolutely do not dissociate methanol can be used for its synthesis.

The resistance of the catalyst to poisoning is a particularly important point in all the catalytic processes it is necessary to distinguish between the poisons which decrease the activity of the catalyst and those which direct the reaction in another direction than that envisaged.

The catalysts which cause poisons of the first category are the organic combinations of sulfur acting according to the following equations:



Catalysts containing copper can therefore only be used with perfectly purified gases. The purity of the methanol obtained also depends very much on the purity of the catalysts used.

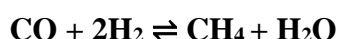
II.9. Catalysis mechanism:

The mixture ($\text{Co} + 2\text{H}_2$) is adsorbed on the catalyst the phenomenon which follows the adsorption that is to say in the synthesis of methanol and which the meeting of chemisorbed molecules of Co and H_2 on the surface of the catalyst. The last step in the process is desorption of the catalysis product.

II.10. Secondary reactions:

During the transformation of synthesis gas on contact, in particular with relatively long residence times, it produces secondary reactions which are:

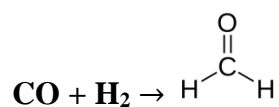
- methanation:



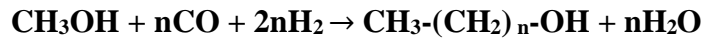
- the formation of methyl ether:



- the formation of formalin:



- the formation of higher alcohols:



II.11. Influence of parameters:

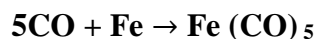
- **The influence of the temperature:**

The reaction is exothermic therefore according to the principle of chatelier it does not bother to decrease the temperature to increase the yield the temperature varies between 240/400°C. The catalysts are zinc oxides ZnO.CrO₃.CuO.

- **The influence of the catalyst:**

The catalyst chosen must be very selective for the main reaction this choice depends on its composition and its preparation the addition of certain constituents to the catalyst modifies the activity of the catalysts based on ZnO is the most selective. It is resistant to high temperatures and poisoning by impurities.

Cu-based catalysts are very active but less selective; they are sensitive to impurities and have little resistance to high temperatures. If the walls of installations where the piping is made of iron, they are attacked by Co to form pentacarbonyl iron Fe (CO)₅.



Pentacarbonyl decomposes giving iron dust promoting the formation of methane; the internal walls must therefore be made of copper alloy or alloy steel.

The influence of both pressure and temperature are represented in the curve bellow:

- **The influence of pressure and temperature:**

The influence is summarized in the following curve:

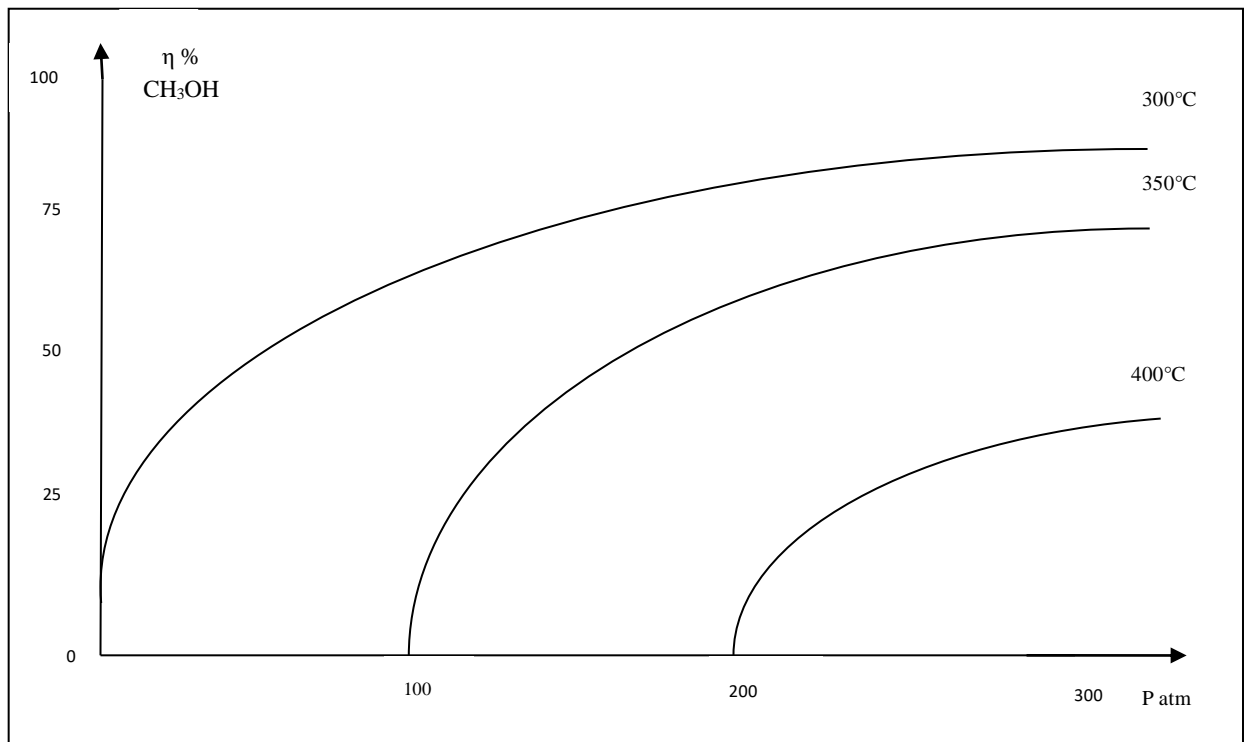


Figure 4. Curve of the influence of pressure and temperature.

the reaction is carried out with decrease in volume therefore it is necessary to increase the pressure to increase the yield the pressure is equal to 300atm if the pressure is increased or by this value the process is not profitable because the increase in yield in methanol is not foreseen by the investments due to the increase in reactor volume.

II.12.Security:

- **Toxicity:**

Methanol is very toxic: 25 to 100 cm^3 of methanol ingested by humans can cause death.

Methanol vapors are also toxic: the maximum permissible levels in the air are

- 200 p.p.m for exposed persons 8h.
- 1000 p.p.m for exposed people 1h.
- 1 p.p.m (part per million) = 10 by mass.

- **Risk of fire and explosion:**

Flash point in closed cup 12°C

Auto-ignition temperature: 470°C

In the event of a fire, the recommended extinguishing means are water spray and special foams to store flammable

- **Storage and handling:**

Methanol can be stored in ordinary steel tanks an atmosphere under inert gas (nitrogen) recommended handling of methanol requires the usual precautions for a flammable product aspiration of vapors above workstations is recommended [15].

II.13. Technological diagram description:

The gas coming from the pressure reduction and filtration station at a pressure of 34 bars and extended a second time up to 32 bars by an expansion valve then enters the separator (S₁) to remove the heavy hydrocarbons (C₅ +) at ball bottom (S₁).

The natural gas (NG) leaving the head of the separator (S₁) and preheated to 400°C in the conversion zone of (F) is desulphurized in the reactor (D) the sulphide gas mixed with the vapor of water enters the radiation zone of the furnace (F₁) at a temperature of 800°C and a pressure equal to 27 bars in the presence of (Ni/Al₂O₃).

The synthesis gas leaving the furnace at a temperature equal to 850°C cools in the exchanger (E) until a T = 375 ° c joins the subsequent cooling (E) then passes through (S₂) to recover the condensed water.

The gas recovered at the head of the separator (S₃) where the condensed water is eliminated at the bottom of the (S₃).

the dry synthesis gas leaves the head of the flask (S₃) with a pressure equal to 17.5 bars and a T = 40°C passes through the compressor (K₁) where it will be compressed to 52 bars at T=122°C this compressor is equipped with a separator (H) which prevents oil droplets from being entrained. The compressed gas flows to the synthesis loop before being mixed

with the unconverted gas. The mixture will be compressed in the recirculator in (K₂) and then repressed to the reactor (R) with a temperature $T = 70 \text{ }^\circ\text{C}$ and a pressure $p = 52 \text{ bar}$.

Part of this synthesis gas will serve as quench gas in the reactor and the other part of the same gas passes through the exchanger (E₄) where it will be heated up to 250°C the hot reaction gas coming out of the reactor it is towards to the top of the reactor.

The quench gas injected into the bed serves to maintain the temperature between 250/275°C.

The reactive reactions of the reactor at 275°C join the exchanger (E₄) where they will be cooled to 150°C and then cooled in (E₅) to $T = 40^\circ\text{C}$ by the water.

The liquid methanol gas are separated in (S₄) the unconverted gas is recycled to the second separator (S₅) after being relaxed in (V₂) or the separated in (S₅) of the purge gas.

The crude methanol coming out of the bottom of (S₅) is sent to the rectification session where dimethyl ether alcohols and water are eliminated.

And the methanol is obtained for distillation with a concentration that equals 99.95% [15].

The technological diagram that has been described is right in the next pages:

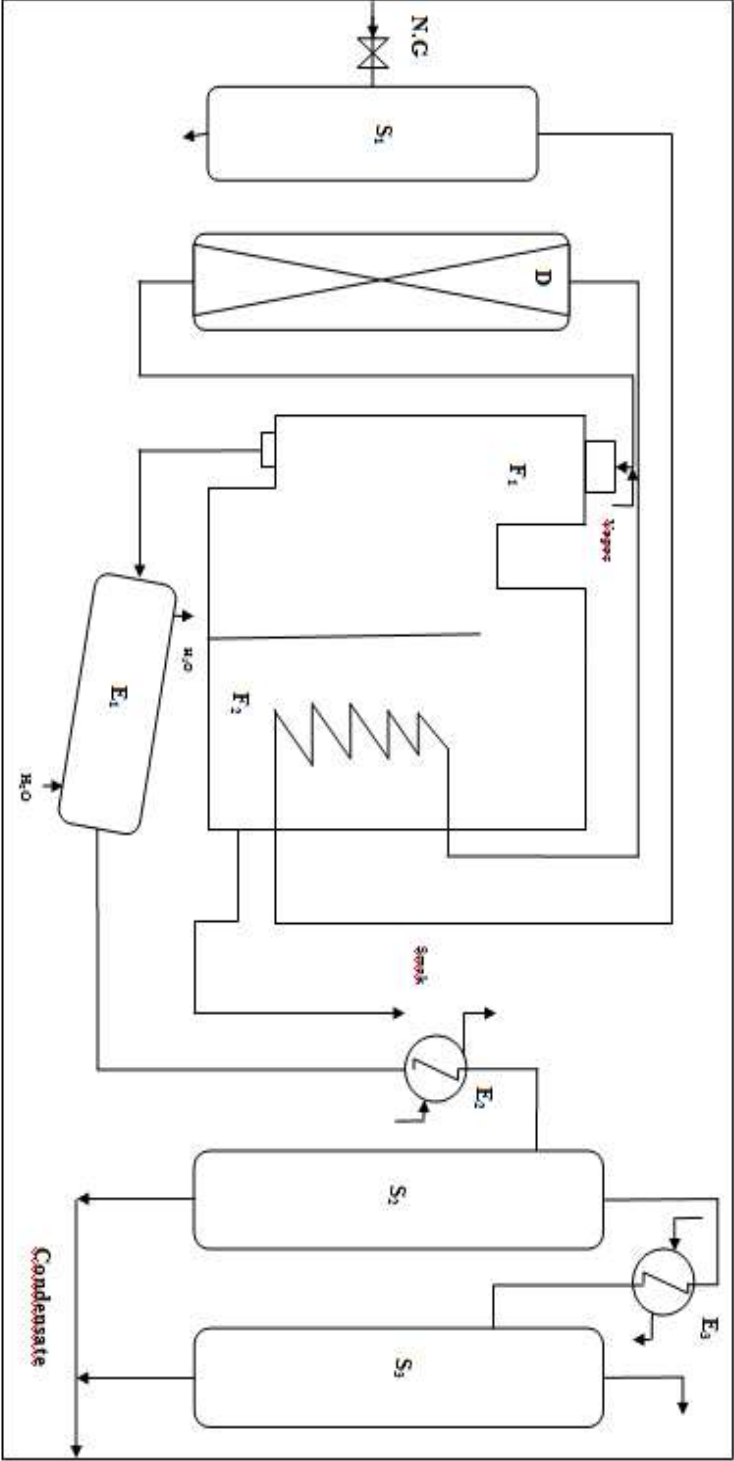


Figure 5. Syngas separation and desulfurization section.

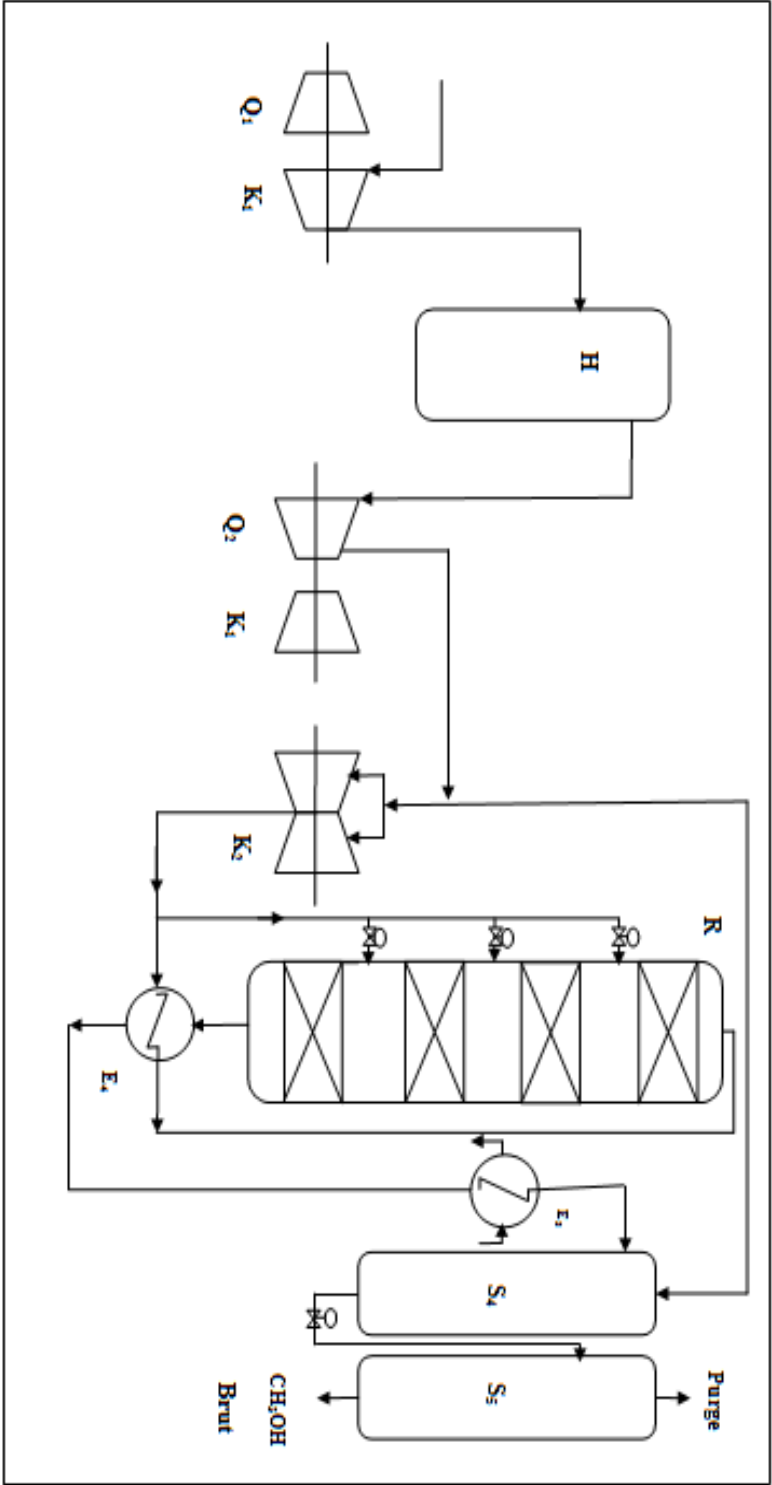


Figure 6. Separation and recirculation section and synthesis loop.

Chapter III

Calculation part

III. Calculation part:

III.1. Problem representation:

These studies based on the description of methanol production process from syngas mainly devoted to the size of the reactor.

So, the main goal is to find the dimensions of the reactor.

III.2. Starting data:

- 1- Methanol's ability = 450 t/day
- 2- The number of days $n=330$ d/year
- 3- The yield of methanol $\eta = 10\%$
- 4- The conversion rate $\tau = 13\%$
- 5- The temperature at the entry $T_{en} = 250^{\circ}\text{C}$
- 6- The temperature at the exit $T_{ex} = 275^{\circ}\text{C}$
- 7- Pressure $P=52\text{atm}$
- 8- Composition of the charge: in table 1III.

Table III. The composition of the synthesis gas: mass percentage.

Constituents	CO	CO ₂	H ₂	CH ₄	N ₂ +He	H ₂ O	(CH ₃) ₂ O	CH ₃ OH	C ₄ H ₉ OH	Σ
Entrance	24.3	30.2	17	16.4	10.1	0.2	0.1	1.7	-	100%
Exit	18.1	25.4	15.3	16.6	9.87	2.32	0.11	12.1	0.2	100%

III.3. Material balance of methanol production:

III.3.1. Calculation procedure:

At the exit and the entry of the reactor we calculate:

- The mass flow of methanol from methanol's ability.
- The mass flow of syngas from the yield and after calculating the mass flow of syngas each constituent from the mass flow of syngas and mass percentage (%mass) we calculate the mass flow of each constituent.

- The average mass molecular from the mass concentration and the mass molar of each constituent.
- The molar concentration of each constituent.
- The molar flow of each constituent.
- Heat balance in the reactor and at the level of each catalytic.
- Calculate the quantity of the feed (gas at each tray).
- Calculate the percentage (% flow) of gas at each tray.
- Calculate of diameter and high of the reactor.

III.3.2. Calculate the mass flow of methanol in kg/h:

$$G_{\text{Methanol}} = \frac{450}{24} \times 10^3$$

$$G_m = 18750 \text{ kg / h}$$

III.3.3. Calculate the mass flow of syngas:

We have the yield $\eta = 10\%$

$$10\% \text{ of methanol} \longrightarrow 18750 \text{ kg / h}$$

$$100\% \longrightarrow G_{s,g}$$

$$G_{s,g} = \frac{18750 \times 100}{10}$$

$$G_{s,g} = 18750 \text{ kg / h}$$

III.3.4. Calculate the mass flow of each constituent at the entry of the reactor:

Calculate the mass flow of (CO):

$$G_{\text{co}} = G_{s,g} \frac{\% \text{CO}}{100}$$

$$G_{\text{co}} = 5118.75 \text{ kg / h}$$

We calculate the other flows the same way.

III.3.5. Calculate molar concentration of each constituent:**III.3.5.1. Calculate the average mass molecular:**

$$M_m = \frac{1}{\sum \frac{X_i}{M_i}}$$

X_i : The mass concentration of each constituent.

M_i : The mass molar of each constituent.

$$M_m = 8.7 \text{ kg / kmol}$$

III.3.5.2. Calculate the molar concentration of (CO) (molar percentage):

$$X'_{co} = X_{co} \frac{M_m}{M_{co}}$$

$$X'_{co} = 24.3 \times \frac{8.7}{28}$$

$$X'_{co} = 7.55 \%$$

We calculate the other % molar the same way.

III.3.6. Calculates molar flow of each constituent at the entry of the reactor:

Molar flow of (CO):

$$G'_{co} = \frac{G_{co}}{M_{co}}$$

$$G'_{co} = 182.8 \text{ kmol / h}$$

We calculate the other flows the same way.

All calculates are summarized in the next table:

Table IV. Balance material, at the entry of the Reactor.

Constituents	%mass	%molar	Mi Kg / kmol	%mass flow Kg / h	%molar flow Kmol / h
CO	24.3	7.55	28	5118.75	182.8
CO ₂	30.2	5.97	44	5662.5	128.7
H ₂	17	73.86	2	1875	937.5
CH ₄	16.4	8.91	16	3075	192.19
N ₂ + He	10.1	3.13	28	1893.75	67.63
H ₂ O	0.2	0.09	18	37.5	2.08
(CH ₃) ₂ O	0.1	0.01	46	18.75	0.41
CH ₃ OH	1.7	0.46	32	318.75	9.96
C ₄ H ₉ OH	–	–	74	–	–
Σ	100	99.98	Mm = 8.7	18000	1521.27

III.4. Calculation The mass flow of each constituent at the exit of the reactor:

Calculates the mass flow of (CO):

$$G_{co} = G_{s,g} \frac{\%co}{100}$$

$$G_{co} = 350.63 \text{ kg / h}$$

We calculate the other flows the same way.

III.5. Calculates the molar percentage at the exit of the reactor:

III.5.1. calculates the average mass molecular at the exit of the reactor:

$$M_m = \frac{1}{\sum \frac{x_i}{M_i}}$$

$$M_m = 9.28 \text{ kg / kmol}$$

III.5.2. calculates the concentration molecular of (CO) (molar percentage):

$$X'_{co} = X_{co} \frac{Mm}{Mco}$$

$$X'_{co} = 18.1 \times \frac{9.23}{28}$$

$$X'_{co} = 5.99 \%$$

We calculate the other % molecular the same way.

III.6. Calculates molar flow of each constituent at the exit of the reactor:

Molar flow of (CO): $G'_{co} = \frac{G_{co}}{Mco}$

$$G'_{co} = 12.52 \text{ kmol / h}$$

We calculate the other flows the same way.

All calculates are summarized in the following table:

Table V. Balance material, at the exit of the Reactor.

Constituents	%mass	%molar	Mi Kg / kmol	%mass flow Kg / h	%molar flow Kmol / h
CO	18.1	5.99	28	350.63	12.53
CO ₂	25.4	5.35	44	4762.5	108.24
H ₂	15.3	70.99	2	2868.75	1434.38
CH ₄	16.6	9.63	16	3093.75	193.36
N ₂ + He	9.87	3.27	28	1850.63	66.09
H ₂ O	2.32	1.19	18	435	24.17
(CH ₃) ₂ O	0.11	0.02	46	20.63	0.45
CH ₃ OH	12.1	3.51	32	2268.75	70.74

C₄H₉OH	0.2	0.02	74	37.5	0.51
Σ	100	99.97	Mm = 9.28	15688.14	1910.47

III.7.Heat balance:

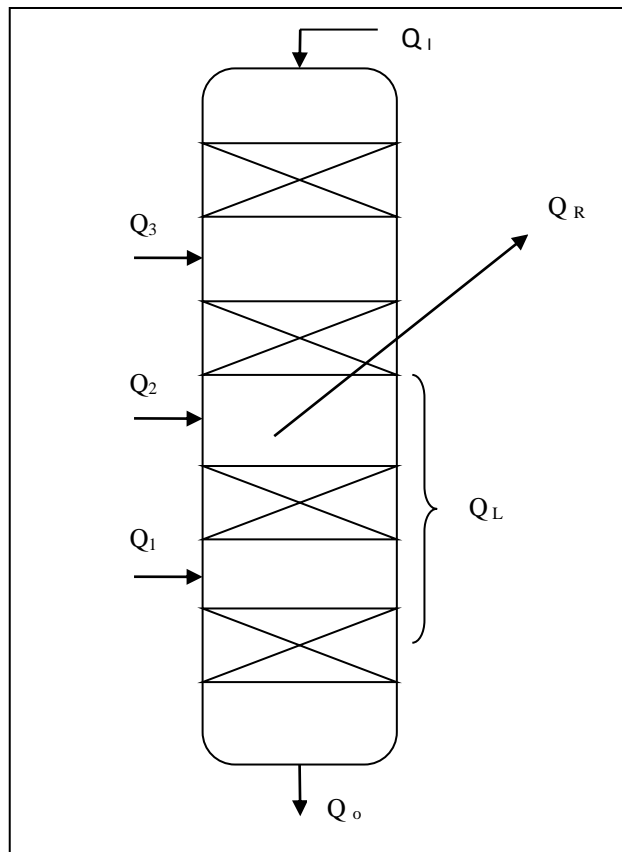


Figure 7.Heat balance diagram.

Heat balance is determined from the following equation:

$$Q_I = Q_O + Q_L$$

Q_I : The amount of incoming heat.

Q_O : The amount of outgoing heat.

Q_L : Lost heat.

$$Q_L = Q_1 + Q_2 + Q_3 + Q_t + Q_R$$

Where:

Q_R : The heat of reaction (heat released in the reactor).

Q_1, Q_2, Q_3 : Heat at each tray.

Q_i : The amount of heat at the top of the reactor.

III.7.1. The reactions taking place in the reactor:

1. $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} \quad \Delta H = -24\text{kcal/mol}$
2. $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \quad \Delta H = +11\text{kcal/mol}$
3. $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H = -49\text{kcal/mol}$
4. $4\text{CO} + 8\text{H}_2 \rightleftharpoons \text{C}_4\text{H}_9\text{OH} + 3\text{H}_2 \quad \Delta H = -35\text{kcal/mol}$
5. $2\text{CH}_3\text{OH} \rightleftharpoons (\text{CH}_3)_2\text{O} + \text{H}_2\text{O} \quad \Delta H = +10\text{kcal/mol}$

Calculation of the molar flow of the formed products according to table V is shown in table VI below:

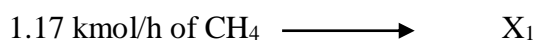
$$G_F = G_O - G_I$$

Table VI. Calculate of the molar flow of the formed products.

Products	G'_I at the enter Kmol/h	G'_O at the exit Kmol/h	$G'_O - G'_I$ Kmol/h
CH_4	192.19	193.36	1.17
H_2O	2.08	24.17	22.09
$(\text{CH}_3)_2\text{O}$	0.41	0.45	0.04
CH_3OH	9.96	70.74	60.78
$\text{C}_4\text{H}_9\text{OH}$	–	0.51	0.51

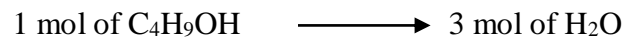
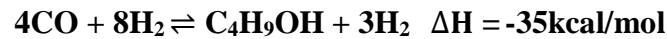
III.7.2. Calculation of the amount of water formed for reactions 2 to 5:

- For reaction N ° 3:



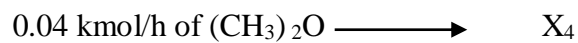
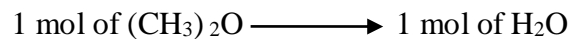
$$X_1 = 1.17 \text{ kmol of H}_2\text{O /h}$$

- For reaction N°4 :



$$X_2 = 1.53 \text{ kmol of H}_2\text{O /h}$$

- For reaction N°5 :



$$X_4 = 0.04 \text{ kmol/h of H}_2\text{O}$$

- For reaction N°2:



$$\Sigma X_i + X \text{ mole of H}_2\text{O} = 22.09 \text{ kmol/h of H}_2\text{O}$$

$$X = 22.09 - 2.74$$

$$X = 19.35 \text{ kmol/h of H}_2\text{O}$$

III.7.3. Calculation of the heat released by each reaction:

- For reaction N° 1:

$$Q_1 = \Delta H_R^1 \times G'_{\text{CH}_3\text{OH}}$$

ΔH_R^1 : Thermal effect of the reaction N°1.

$G'_{\text{CH}_3\text{OH}}$: Molar flow of methanol.

$$Q_1 = -1697.76 \text{ kcal/h}$$

- For reaction N° 2:

$$Q_2 = \Delta H_R^2 \times G'_{\text{H}_2\text{O}}$$

ΔH_R^2 : Thermal effect of reaction N° 2.

$G'_{\text{H}_2\text{O}}$: Molar flow of water.

$$Q_2 = 265.87 \text{ kcal/h}$$

- For reaction N° 3:

$$Q_3 = \Delta H_R^3 \times G'_{\text{CH}_4}$$

ΔH_R^3 : Thermal effect of reaction N°3.

G'_{CH_4} : Molar flow of methane.

$$Q_3 = -9474.64 \text{ kcal/h}$$

- For reaction N° 4:

$$Q_4 = \Delta H_R^4 \times G'_{C_4H_9OH}$$

ΔH_R^4 : Thermal effect of reaction N°4.

$G'_{C_4H_9OH}$: Molar flow of butanol.

$$Q_4 = -17.85 \text{ kcal/h}$$

- For reaction N° 5:

$$Q_5 = \Delta H_R^5 \times G'_{(CH_3)_2O}$$

$$Q_5 = 4.5 \text{ kcal/h}$$

Calculation of the total heat released in the reactor:

$$\sum_{i=1}^n Q_i = Q_1 + Q_2 + Q_3 + Q_4 + Q_5 = Q_R$$

$$Q_R = 10919.88 \text{ kcal/h}$$

III.7.4. Heat balance at each catalytic tray:

We have:

- C_{p_o} : specific heat at $T_o = 275^\circ \text{C}$.
- C_{p_i} : specific heat at $T_i = 250^\circ \text{C}$.
- C_{p_f} : specific heat at $T_f = 70^\circ \text{C}$.

And:

$$C_{p_o}^{275} = 0.869 \text{ kcal/kg}^\circ\text{C}.$$

$$C_{p_i}^{250} = 0.866 \text{ kcal/kg}^\circ\text{C}.$$

$$C_{p_f}^{70} = 0.869 \text{ kcal/kg}^\circ\text{C}.$$

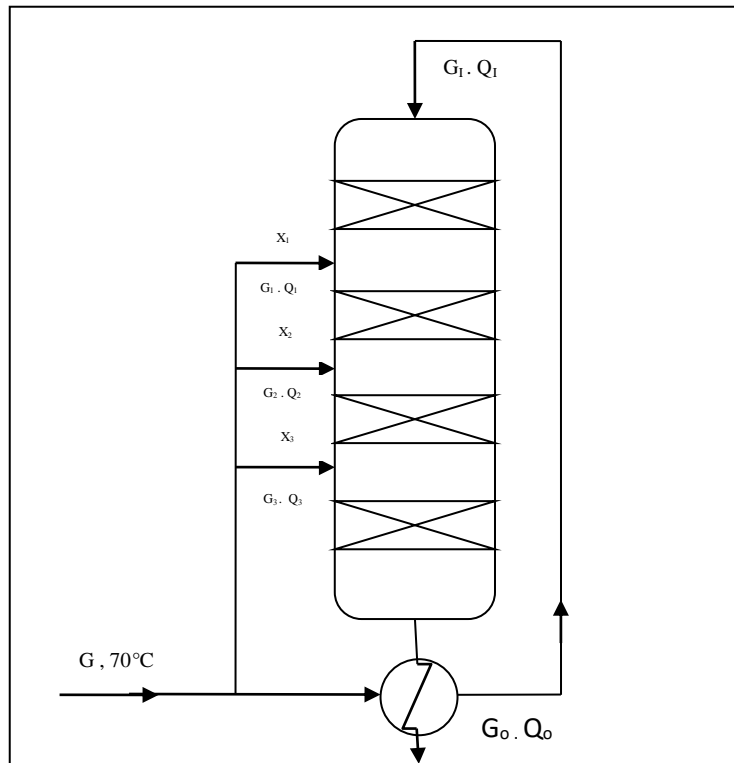


Figure 9. Heat balance at each catalytic tray.

- Heat balance at the 1st tray:

The flow rate of the load is extended to equal 1 kg/h at the level of the 1st tray.

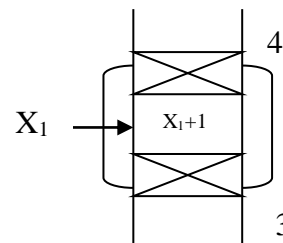
X_1 : mass flow at the level of 1st tray:

$$t_s \times C_{ps} + X_1 \times t_f \times C_{pf} = (1 + X_1) C_{pe} \times t_e$$

$$X_1 = \frac{(T_s \times C_{ps}) - (T_e \times C_{pe})}{(T_e \times C_{pe}) - (T_f \times C_{pf})}$$

$$X_1 = \frac{(275 \times 0.869) - (250 \times 0.866)}{(250 \times 0.866) - (70 \times 0.803)}$$

$$X_1 = 0.140 \text{ kg/h}$$



- At the level of the 2nd tray:

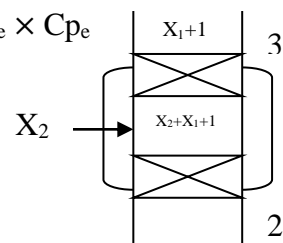
X_2 : mass flow at the level of 2nd tray:

$$X_2 \times T_f \times C_{pf} + (1 + X_1) T_s \times C_{ps} = (1 + X_1 + X_2) T_e \times C_{pe}$$

$$X_2 = \frac{(1 + X_1)(T_s \times C_{ps} - T_e \times C_{pe})}{T_e \times C_{pe} - T_f \times C_{pf}}$$

$$X_2 = \frac{1.140(275 \times 0.869 - 250 \times 0.866)}{(250 \times 0.866) - (70 \times 0.803)}$$

$$X_2 = 0.158 \text{ kg/h}$$



- At the level of the 3rd tray:

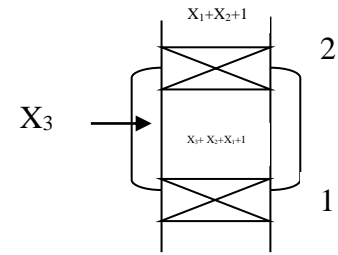
X_3 : mass flow at the level of 3rd tray:

$$X_3 \times T_f \times C_{pf} + (1 + X_1 + X_2) T_s \times C_{ps} = (1 + X_1 + X_2 + X_3) T_e \times C_{pe}$$

$$X_2 = \frac{(1 + X_1 + X_2) (T_s \times C_{ps} - T_e \times C_{pe})}{T_e \times C_{pe} - T_f \times C_{pf}}$$

$$X_2 = \frac{1.298(275 \times 0.866 - 250 \times 0.866)}{(250 \times 0.866) - (70 \times 0.803)}$$

$$X_2 = 0.181 \text{ kg/h}$$



III.7.5. Calculates the quantities of the fresh gas injected:

We have:

$$1 + X_1 + X_2 + X_3 = 1.479 \text{ kg/h}$$

- Into the 1st tray:

$$G_{s,g} \longrightarrow 1.479$$

$$G_1 \longrightarrow 0.140$$

$$G_1 = 1774.85 \text{ kg/h}$$

- Into the 2nd tray:

$$G_{s,g} \longrightarrow 1.479$$

$$G_2 \longrightarrow 0.158$$

$$G_2 = 2003.04 \text{ kg/h}$$

- Into the 3rd tray:

$$G_{s,g} \longrightarrow 1.479$$

$$G_3 \longrightarrow 0.181$$

$$G_3 = 2294.62 \text{ kg/h}$$

- Into the top of the reactor:

$$G_t = G_{s,g} - (G_1 + G_2 + G_3)$$

$$G_t = 18750 - 6072.51$$

$$G_t = 12677.49 \text{ kg/h}$$

III.7.6. Calculating the percentage of each fresh gas flow:

- At the 1st tray:

$$G_{s,g} \longrightarrow 100\%$$

$$G_1 \longrightarrow Y_1$$

$$Y_1 = 9.46 \%$$

- At the 2nd tray:

$$G_{s,g} \longrightarrow 100\%$$

$$G_2 \longrightarrow Y_2$$

$$Y_3 = \frac{2003.04 \times 100}{18750}$$

$$Y_2 = 10.68 \%$$

- At the 3rd tray:

$$G_{s,g} \longrightarrow 100\%$$

$$G_3 \longrightarrow Y_3$$

$$Y_3 = \frac{2294.62 \times 100}{18750}$$

$$Y_3 = 12.24 \%$$

- At the top of the reactor:

$$G_{s,g} \longrightarrow 100\%$$

$$G_t \longrightarrow Y_t$$

$$Y_t = \frac{12677.49 \times 100}{18750}$$

$$Y_t = 67.61 \%$$

III.7.7. Calculates the heat quantities:

- At the top:

$$Q_t = G_t \times c_p^{250} \times 250$$

$$Q_t = 2744676.59 \text{ kcal/h}$$

- At the 1st tray:

$$Q_1 = G_1 \times c_p^{70} \times 70$$

$$Q_1 = 99764.32 \text{ kcal/h}$$

- At the 2nd tray:

$$Q_2 = G_2 \times c_p^{70} \times 70$$

$$Q_2 = 112590.88 \text{ kcal/h}$$

- At the 3rd tray:

$$Q_3 = G_3 \times c_p^{70} \times 70$$

$$Q_3 = 128980.59 \text{ kcal/h}$$

Table VII. Calculate of the heat quantity:

$Q_i = G_i \times C_{Pi} \times T_i$				
G kg/h	% mass	C_{Pi} kcal/kg.°C	Q_i kcal/h	T°C
$G_1=12677.49$	67.61	0.866	2744676.59	250
$G_1=1774.85$	9.46	0.803	99764.32	70
$G_2=2003.04$	10.69	0.803	112590.88	70
$G_3=2294.62$	12.24	0.803	128980.59	70
$\Sigma=18750$	100	-	3086012.38	-

III.7.8. Calculate of the enter heat into the reactor:

$$Q_E = Q_1 + Q_2 + Q_3 + Q_t + Q_R$$

$$Q_E = 3096932.26 \text{ kcal/h}$$

III.7.9. Calculate of the outgoing heat:

$$Q_O = G_{s,g} \times c_p^{275} \times 275$$

$$Q_O = 18750 \times 0.869 \times 275$$

$$Q_O = 4480781.25 \text{ kcal/h}$$

III.7.10. Calculate of the waste heat:

$$Q_W = Q_E - Q_O$$

$$Q_W = -1383848.99 \text{ kcal/h}$$

III.7.11. Calculate of the percentage of losses:

$$\% \text{ losses} = \left| \frac{Q_W}{Q_E} \right|$$

$$\% \text{ losses} = \left| \frac{-1383848.99}{3096932.26} \right|$$

$$\% \text{ losses} = 0.45 \%$$

III.8. Reactor sizing:

- Calculate of the charge volume flow: $V_{ch} = \frac{Gsg}{\rho ch}$

Where: $\rho_{ch} = 14.93 \text{ kg/m}^3$

$$V_{ch} = \frac{18750}{14.93}$$

$$V_{ch} = 1255.86 \text{ m}^3/\text{h}$$

- Calculate of the cross section of the reactor:

$$S_c = \frac{V_{ch}}{3600W}$$

Where: W: is the linear speed of gas in the reactor, $W = 0.25 \text{ m/s}$

$$S_c = \frac{1255.86}{3600 \times 0.25}$$

$$S_c = 1.4 \text{ m}^2$$

- Diameter of the reactor:

$$D_R = 2\sqrt{\frac{S_c}{\pi}}$$

$$D_R = 2\sqrt{\frac{12.68}{3.14}}$$

$$D_R = 1.34 \text{ m}$$

- Volume of the reactor:

$$V_R = \frac{V_{ch}}{V}$$

V: is the special speed.

Where: $V = 250 \text{ h}^{-1}$

$$V_R = \frac{1255.86}{250}$$

$$V_R = 5.02 \text{ m}^3$$

- Height of the reactor:

$$H_R = \frac{V_R}{S_c}$$

$$H_R = \frac{5.02}{1.4}$$

$$H_R = 3.6 \text{ m}$$

- Weight of the reactor:

$$G_{cat} = \rho_{cat} \times V_R$$

ρ_{cat} : volume mass of the catalyst.

Where: $\rho_{cat} = 1400 \text{ kg/m}^3$

$$G_{cat} = 1400 \times 5.02$$

$$G_{cat} = 7028 \text{ kg}$$

- Contact time:

$$\Gamma = \frac{1}{V} \times h$$

$$\Gamma = \frac{1}{250} \times 3600$$

$$\Gamma = 14.4 \text{ S}$$

General Conclusion

General conclusion

General conclusion:

Methanol is one of most important feedstocks for the chemical, petrochemical, and energy industries. Abundant and widely distributed resources, a relative low level of impurities as well as low price make natural gas the predominant feedstock for methanol production. The realization of industrial methanol production is favored by a high temperature under high pressure as well as the chosen catalyst and the nature of the raw material used. The increasing demand for the bulk chemical results in ever rising single plant capacities, whereby indirect synthesis routes via reforming of methane suppress production from bio resources and other renewable alternatives.

The description of methanol industrial production process from synthesis gas is the main goal of this project, the production of syngas consists on coke or from hydrocarbons in the first place or by partial oxidation, by conversion to water vapor as well. This lead us to producing methanol because synthetic gas is the main feedstock to methanol by 2 principal obtaining methods, the fist is direct synthetic or the direct oxidation of methane.

The calculation part is mainly centered on the reactor:

- We established the material balance, the mass flow of syngas and methanol and molar concentration of each constituent and molar flow are determined

The thermal balance has been established to reach our goal and find out the the dimensions of the reactor after calculating the flow percentage and the quantity of the feed for yield $\eta = 10\%$.

The chemical industry uses methanol as the base to make other chemicals. A vast array of synthetic plastic materials can be produced using methanol derivatives through processes.

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