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PROJECT TITLE:

SIMULATION, OPTIMAL OPERATION AND SELF-OPTIMIZING CONTROL OF METHANOL PROCESS

by

THEOPHILUS ARTHUR

Acknowledgement

Abstract

This project presents simulation, optimal operation and self-optimizing control of methanol. The plant capacity was estimated to be 5000tons/day. The first task was to simulate the production of syngas by using preformer and an ATR reactor. The next simulation was done for the methanol by using a Lurgi type reactor. The reactor is filled with catalyst in tubes and the heat of reaction is removed by using boiling water. The temperature along the reactor needs to be controlled since it can deactivate the catalyst.

Here, steady state optimization is performed with seven degrees of freedom with the technical objective of maximizing the yield of methanol. The degrees of freedom are flowrate of water and oxygen, pressure of the syngas, pressure of the methanol synthesis, inlet temperature of the ATR reactor, flow ratio of purge and flow ratio of purge from the methanol loop. The optimal nominal values of these were determined after the optimization.

The disturbances considered in the process were the changes in flowrate of natural gas (±20%) and the changes in the composition of the natural gas. After evaluating the loss associated with each of the degrees of freedom, it was discovered that six of these manipulated variables were good candidate control variables and flowrate of oxygen was found out to be a degree of freedom. Out of these candidate control variables, three of them was found out to be self-optimizing variables (both pressures and temperature).

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1 CHAPTER

INTRODUCTION

Methanol is one of the most important bulk chemicals and products of natural gas. Most often than not it is synthesized in large scale plants from syngas. The process consists of three main parts including production of syngas, conversion of syngas to methanol and purification of the crude methanol to obtain the desired specifications. The reactor used for the methanol synthesis is the Lurgi-type which resembles a shell-and-tube heat exchanger than stands vertically and operates at a low pressure. The reactions that occur in the reactor are hydrogenation of carbon monoxide (CO), hydrogenation of carbon dioxide (CO_2) and the reverse water gas shift. More light will thrown on these reactions in the next chapter. The reactor only converts small amount of the syngas into methanol, the unreacted syngas is either recycled or purged. Although the process the process might look very simple, energy demands are large, both in mechanical energy fo the syngas compression and heating and cooling at various stages in the process.

The goal of this project is to simulate the process in UniSim to produce 5000tons/day of pure methanol. Optimization of the process will be carried out, since it is essential to obtain an economically feasible and competetive process. The modeling of the process includes thermodynamics of the chemical components, models of the individual unit operations. The flowsheet was modeled at steady state since it is a very large plant has continuous operation.

Self optimizing control is also one of the areas that will be covered in this project. This topic is not widely acknowledged, overcoming uncertainties in operation is the main reason why we have to select the right variables to control. Control system has been arranged in a hierarchical structure, with each layer operating on a different time scale. Generally, scheduling (weeks), site-wide optimization (days), local optimization (hours), supervisory control (minutes) and regulatory control (seconds). The control variable c interconnects with these layers.

The other objective of this project was to find candidate control variables that possesses good self-optimizing properties for the methanol process, that is for which a constant policy results in a small (economic) loss where there is uncertainty (including disturbances, implementation errors and model errors), [18]. This selection will be done by using trial and error with different

process variable combination. Direct loss evaluation will also be used. Control variables should normally include the active constraints [18], which depend strongly on the actual operation, including cost data.

2 CHAPTER

LITERATURE REVIEW

2.1 Methanol

Methanol also known as methyl alcohol or wood alcohol is a colourless, water-soluble liquid with mild alcoholic odour. It freezes at -97.6°C, boils at 64.6°C and a density of 791kg/m^3 at 20°C. It is polar, acid-base neutral, and generally considered non-corrosive. It is miscible with most organic solvents and is capable of dissolving many inorganic salts.

Methanol can be produced from a variety of sources including natural gas, coal, biomass and petroleum. Some properties of methanol are shown in table 2.1.

Synonyms	Methyl alcohol, wood alcohol
Chemical formular	CH_3OH
Molecular weight	32.04
Chemical composition (%)	
Carbon	37.5
Hydrogen	12.5
Oxygen	50
Melting point	-97.6°C
Boiling point	64.6°C
Density at 20°C	791kg/m^3
Energy content	5420 kcal/kg
	173.2 kcal/mol
Energy of vapourization	9.2 kcal/mol
Flash point	11°C
Explosive limits in air	7 – 36%
Auto ignition temperature	455°C

Table 2.1: Properties of methanol [15]

Table 2.2 summarizes the processes, feedstocks and catalysts for the production of methanol and its precursor syngas. Synthesis of methanol takes place industrially via syngas.

Feedstocks	Process and main reactions	Catalysts
Formation of syngas		
Natural gas	Steam reforming: $CH_4+H_2O \leftrightarrow CO+3H_2$	Ni on Al_2O_3
Natural gas	Autothermal reforming: $CH_4+2O_2 \leftrightarrow CO_2+2H_2O$ Then $CH_4+H_2O \leftrightarrow CO+3H_2$ $CO_2+H_2 \leftrightarrow CO+H_2O$	- Ni on refractory supports
Natural gas	Partial oxidation: $CH_4+1/2O_2 \rightarrow CO+2H_2$	Non-catalytic or lanthanide/Ru Supported by Ru, Ni, Pd
Coal	Gasification (in the presence of H_2O/O_2)	-
Biomass	Gasification	-
Others(e.g.liquefied petroleum gas, naptha, heavy fuel oil)	Steam reforming (light hydrocarbons)	Alkalized Ni on Al_2O_3 or on Ca/ Al_2O_3
Formation of methanol		
Syngas	Methanol synthesis $CO+2H_2 \leftrightarrow CH_3OH$ $CO_2+3H_2 \leftrightarrow CH_3OH+H_2O$	Cu/ZnO/ Al_2O_3 Cu/ZnO/Cr_2O_3/ZnCr
Syngas	Two-step methanol synthesis: $CH_3OH+CO \leftrightarrow HCOOCH_3$, then $HCOOCH_3+2H_2 \leftrightarrow 2CH_3OH$	Potassium methoxide Cu chromite
Methane	Direct oxidation: $CH_4+1/2O_2(N_2O) \leftrightarrow CH_3OH$	Metal oxides (eg MoO_3 based)
Methane	Bioprocessing	Enzymes (eg cytochrome P_{4so}), methanotrophs.

Table 2.2: Feedstocks, processes and catalysts for the production of syngas and methanol [15]

Methanol can be used as a fuel or fuel additive (e.g. neat methanol fuel, methanol blended with gasoline, MTBE, TAME and methanol to gasoline). It can also be used for the production of chemicals like formaldehyde, acetic acid, chloromethanes, methyl methacrylate, dimethyl terephthalate, methyl amines, and glycol methyl ethers. It is also used as a solvent for windshield, antifreeze, inhibitor to hydrate formation in natural gas processing and as a substrate for crop growth.

2.2 Reactions and thermodynamics of synthesis gas production

Natural gas is predominantly made up of methane and for simplicity it will be used in describing the various reactions occurring in steam reforming. The table below shows the various reactions;

Reaction	$\Delta H_{298}^{0} \left(\dfrac{kJ}{mol} \right)$
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	206
$CO + H_2O \leftrightarrow CO_2 + H_2O$	-41
$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	247
$CH_4 \leftrightarrow C + 2H_2$	75
$2CO \leftrightarrow C + CO_2$	-173
$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$	-36
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-803
$CO + 1/2O_2 \rightarrow CO_2$	-284
$H_2 + 1/2O_2 \rightarrow H_2O$	-242

Table 2.3: Reactions during methane conversion with steam and/or oxygen [12]

2.3 Synthesis gas production technologies

Synthesis gas (syngas) is a general term used in describing a mixture hydrogen and carbon monoxide (CO) in different ratios and can be generated from any hydrocarbon feedstock. Synthesis gas can be produced from a large variety of materials which includes natural gas, naptha, residual oil, petroleum coke, biomass and coal. The most material applicable in the production of methanol is natural gas. The production of syngas occupies the major investment cost of GTL plants.

The principal technologies used for the production of syngas are summarized in the table below;

Technology	Advantages	Disadvantages
SMR	· Most extensive industrial experience · Oxygen not required · Lowest process temperature requirement · Best H_2/CO ratio for hydrogen production applications	· H_2/CO ratio often higher than required when CO also is to be produced · Highest air emissions
Heat exchange reforming	· Compact overall size and "footprint" · Application flexibility offers additional options for providing incremental capacity	· Limited commercial experience · In some configurations, must be used in tandem with another syngas generation technology
Two-step reforming[a]	· Size of SMR is reduced · Low methane slip favors high purity syngas applications · Syngas methane content can be tailored by adjusting secondary reformer outlet temperature	· Increased process complexity · Higher process temperature than SMR · Usually requires oxygen
ATR	· Natural H_2/CO ratio often is favorable · Lower process temperature requirement than POX · Low methane slip · Syngas methane content can be tailored by adjusting reformer outlet temperature	· Limited commercial experience · Usually requires oxygen
POX	· Feedstock desulfurization not required. · Absence of catalyst permits carbon formation and, therefore, operation without steam, significantly lowering syngas CO_2 content · Low methane slip · Low natural H_2/CO ratio is an advantage for applications requiring ratio < 2.0	· Low natural H_2/CO ratio is a disadvantage for applications requiring ratio > 2.0. · Very high process operating temperatures · Usually requires oxygen · High temperature heat recovery and soot formation/handling adds process complexity · Syngas methane content is inherently low and not easily modified to meet downstream processing requirements

Table 2.4: Comparison of syngas generation technologies (natural gas feed) [16]

i) SMR

This technology has been the most predominantly used commercially in which steam and methane are converted catalytically and endothermically to hydrogen and carbon monoxide. After the desulphurization of the natural gas feed, the product is mixed with steam (optionally CO_2) and then preheated to about 780K before it enters the reformer tubes. The heat for the endothermic reforming reaction is supplied by the combustion of fuel in the reformer furnace (allothermic operation), [12]. The hot effluent gas exiting the reformer is used for the production of steam. A separator is used in separating water from the syngas by gravitation and the raw syngas is treated further depending on its use.

ii) Heat-Exchange reforming

Large amount of heat is required in the steam reformer and the autothermic reformer (ATR) also produces heat, an advanced technology suggests that the heat from the ATR is used to supply the heat input needed by the steam reformer and this process is known as the heat-exchange reforming or gas-heated reforming. The major advantage of this is the reduction in investment

cost by eliminating the expensive fired reformer. The consequence of this process is that only medium pressure steam can be generated and large electrical power will be needed for the driving of the syngas compressor.

iii) Autothermic reforming (ATR)

Addition of oxygen to the steam reforming process is an alternative measure in obtaining lower H_2/CO ratio. Autothermic reforming is the reforming of light hydrocarbons in a mixture of steam and oxygen in the presence of a catalyst [12]. The reactor is designed with a refractory lined vessel, therefore higher temperature and pressure can be applied than in steam reforming. ATR cannot be used alone; therefore a pre-reformer is installed downstream to it. The ATR converts the remaining methane from the pre-reformer. Air is used to supply the required oxygen.

2.4 Thermodynamics and kinetics of methanol synthesis

The three main reactions for the formation of methanol from synthesis gas is made up of hydrogenation of CO, hydrogenation of CO_2 and the reverse water-gas shift reaction. The reaction proceeds as follows;

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H^{\circ}_{298} = -90.8 \text{ kJ/mol} \qquad\qquad (2.1)$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H^{\circ}_{298} = -49.6 \text{ kJ/mol} \qquad\qquad (2.2)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H^{\circ}_{298} = -41 \text{ kJ/mol} \qquad\qquad (2.3)$$
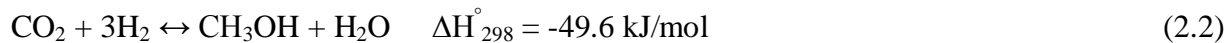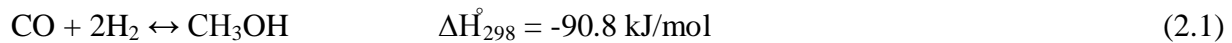
The table below shows the equilibrium data for the methanol forming reactions:

Temp. (K)	CO conversion			CO_2 conversion		
	Pressure (bar)			Pressure (bar)		
	50	100	300	10	100	300
525	0.524	0.769	0.951	0.035	0.052	0.189
575	0.174	0.440	0.825	0.064	0.081	0.187
625	0.027	0.145	0.600	0.100	0.127	0.223
675	0.015	0.017	0.310	0.168	0.186	0.260

Table 2.3: CO and CO_2 equilibrium conversion data [12]

All the three reactions are dependent on each other that is one is linear combination of the others. The rate expressions have been selected from Graaf et al. and the rate equations combining with

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the equilibrium rate constants provide enough information about kinetics of methanol synthesis. The corresponding rate expressions due to the hydrogenation of CO, CO2 and reversed water-gas shift reactions over commercial CuO/ZnO/Al₂O₃ catalysts are:

$$r_1 = \frac{k_1 K_{CO}\left[f_{CO}f_{H_2}^{\frac{3}{2}} - f_{CH_3OH}f_{H_2}^{\frac{1}{2}}K_{p1}\right]}{(1 + K_{CO}f_{CO} + K_{CO_2}f_{CO_2})\left[f_{H_2}^{\frac{1}{2}} + \left(K_{H_2O}\middle/K_{H_2}^{\frac{1}{2}}\right)f_{H_2O}\right]}$$

(2.4)

$$r_2 = \frac{k_2 K_{CO_2}\left[f_{CO_2}f_{H_2}^{\frac{3}{2}} - f_{CH_3OH}f_{H_2O}f_{H_2}^{\frac{3}{2}}K_{p2}\right]}{(1 + K_{CO}f_{CO} + K_{CO_2}f_{CO_2})\left[f_{H_2}^{\frac{1}{2}} + \left(K_{H_2O}\middle/K_{H_2}^{\frac{1}{2}}\right)f_{H_2O}\right]}$$

(2.5)

$$r_3 = \frac{k_3 K_{CO_2}\left[f_{CO_2}f_{H_2} - \dfrac{f_{H_2O}f_{CO}}{K_{p3}}\right]}{\left(1 + K_{CO}f_{CO} + K_{CO_2}f_{CO_2}\right)\left[f_{H_2}^{\frac{1}{2}} + \left(K_{H_2O}\middle/K_{H_2}^{\frac{1}{2}}\right)f_{H_2O}\right]}$$

(2.6)

2.5 Production of methanol

2.5.1 Lurgi low-pressure methanol synthesis process

The process developed by Lurgi Corporation for the synthesis of methanol is made up of a reactor operating at a temperature of 250 - 260°C and a pressure of 50 – 60bar. The reactor is a shell and tube type with the catalysts filled in the tubes. The heat of reaction is removed by circulating cold water on the shell side and this generates high pressure steam for other usage. Feedstock for the production of syngas includes gaseous hydrocarbons such as methane as well as liquid hydrocarbons like naptha. The syngas can be produced via two routes namely steam reforming and partial oxidation. Steam reforming is carried out at temperatures of 850 - 860°C. Desulphurized naptha is contacted with steam at this temperature to produce hydrogen and

carbon oxides. The syngas produced is compressed to 50 – 80bar before it is fed into the methanol reactor. For the second route, heavy residues are fed into a furnace along with oxygen and steam at 1400 - 1450°C and the operating pressure is at 55 – 60bar and this does not require any further compression. Below is the flow scheme for the process;
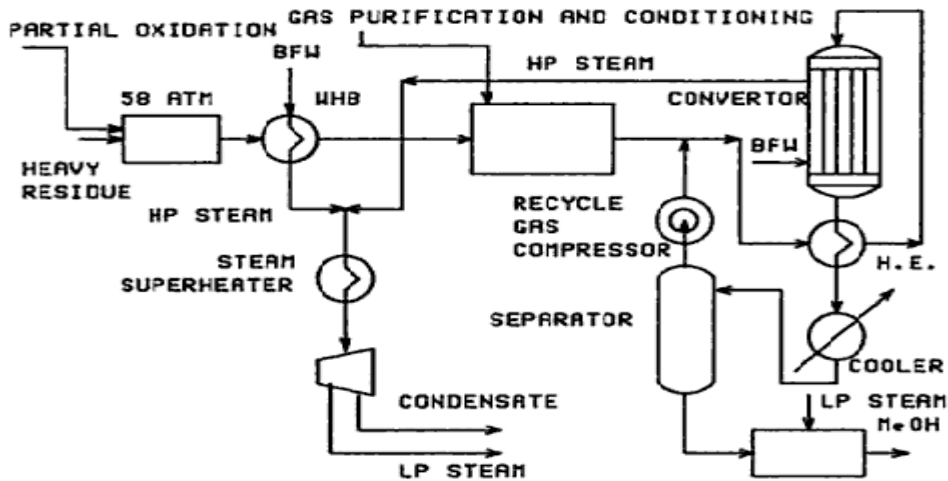
Figure 2.1: Flow sheet of Lurgi low-pressure methanol process, [14]

2.5.2 ICI low-pressure methanol process

This process utilizes the use of an adiabatic reactor and a single catalyst bed. The heat of reaction is removed or quenched by introducing cold reactants at different heights of the catalyst bed. First of all fresh synthesis gas which is compressed and mixed with recycled gas is heated by heat exchange with the reactor effluent. Then about 40% of the stream is sent to the reactor after undergoing supplementary preheating also by the reactor effluent [12]. Then the rest is used as a quench gas for removing the heat of reaction. The products emanating from the reactor is cooled by heat exchanged with the feed and water for the generation of high pressure steam. It is further cooled with an air-cool heat exchanger in which methanol and water are condensed. The separation of gas/liquid takes place in a flash drum under pressure. The gas is recycled after purging small part to keep the inerts level in the loop within limits [12]. Purification of the methanol is done in two different columns. The first column removes gases and other light impurities whiles the second separates methanol from other heavy alcohols. Below is the process flow diagram;
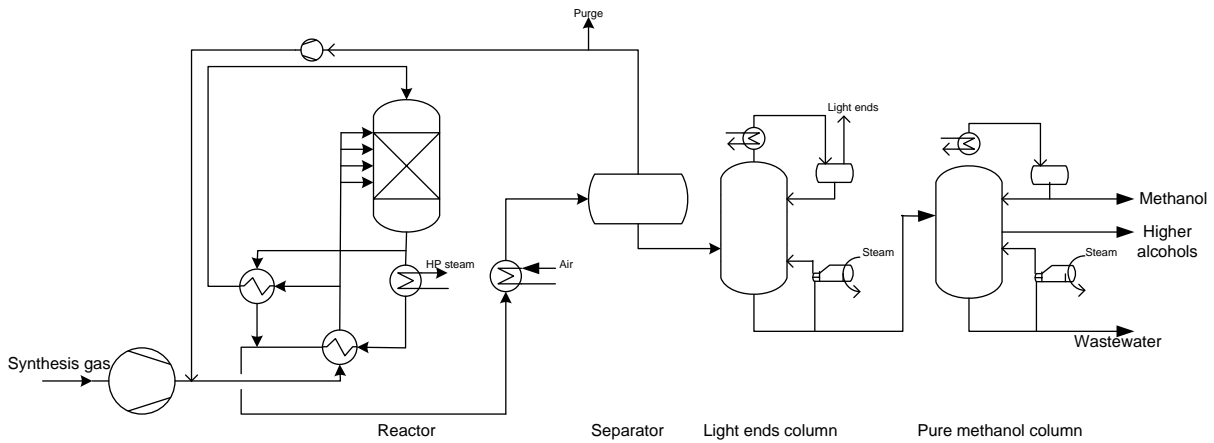
Figure 2.2: Flow scheme of the low-pressure methanol process, [12]

2.5.3 Haldor Topsøe methanol process

This process uses several adiabatic reactors arranged in series and the heat of reaction is removed by intermediate coolers. The synthesis gas flows radially through the catalyst bed and this reduces pressure drop as compared to axial flow []. The purification is the same as the other processes. The flow scheme is shown below;
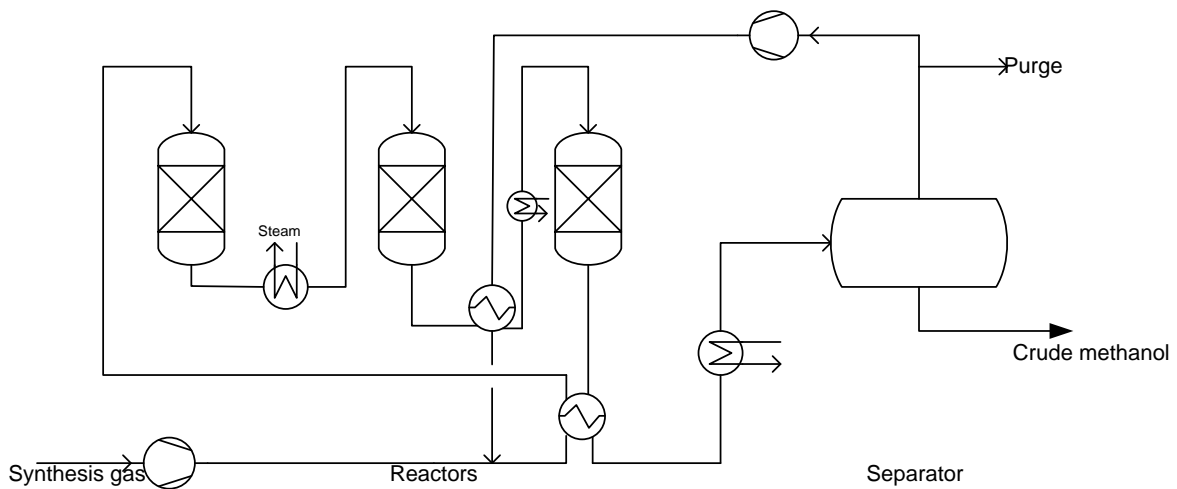
Figure 2.3: Flow scheme of the reaction section of the Haldor Topsøe methanol process, [12]

2.5.4 The MGC low-pressure process

The flow scheme below shows the process developed by Mitsubishi Gas Chemical Company. It uses copper-based methanol synthesis catalyst. It operates at temperatures ranging from 200 - 280ºC over a pressure range of 50 – 150 atm. The temperature of the catalyst bed is kept under control by using quench type converter design, and also some of the heat of reaction is recovered in an intermediate stage boiler. This process utilizes hydrocarbon as feedstock. The raw material is desulphurised and then fed into a steam reformer at 500ºC. The exit stream from the reformer contains hydrogen, carbon monoxide and carbon dioxide at 800 - 850ºC. The gases are compressed in a centrifugal compressor and mixed with the recycle stream before being fed into the converter.
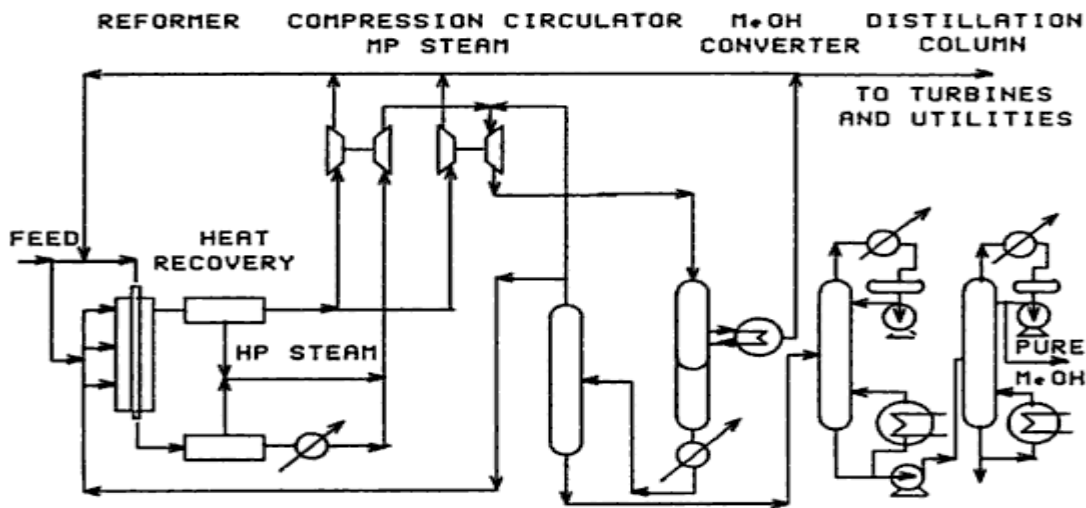
Figure 2.4: Mitsubishi Gas Chemical low-pressure methanol synthesis process, [14]

2.6 Optimization and Self-optimizing control

The overall control objective is to maintain acceptable operation (in terms of environmental impact, load on operators, and so on) while keeping the operating conditions close to economically optimal [18]. Increasing the economics of a process is the sole goal of optimization in process industries. The economic objective is transformed into technical objectives such as increasing the production rate and quality of the product in consideration, also decreasing the consumption of energy as well as maintaining safe operation.

More often than not the there are constraints related to the quality and safe operation of the product and plant respectively. The optimization problem is a mathematical representation of the technical objectives for measuring the performance of the process. The objective function is denoted by *J* in this project and it is defined as;

$$min\ J_u(u,d)$$

subjected to the inequality constraints

$$g(u,d) \leq 0$$

where *u* are the independent variables we can affect (degrees of freedom for optimization) and *d* are independent variables we cannot affect (disturbances).

The objective function *J* can either be maximized or minimized depending on the given problem subjected to constraints by using available inputs and parameters *u* (decision variables). There a whole lot methods used in solving the optimization problem, such methods are beyond the scope of this project.

Self-optimizing control

Self-optimizing control is when acceptable operation (acceptable loss in the objective function) can be achieved by using pre-calculated setpoints,*c*, for the controlled variables (*y*) (without the use of re-optimization when disturbances occur) [18].

Finding such variables begins with the determination of the optimal operation (results of the nominal optimization) and the available degrees of freedom (inputs u). Active constraints or optimal values of variables at constraints should be controlled ("active constraint control"[18]) for optimal operation, and easy relative implementation. Control of unconstrained variables can also be achieved by using some of the available degrees of freedom for such actions.

[19] suggests requirements for unconstrained variable control;

1. It should be easy to measure and control accurately. Small implementation error.

2. Optimal value should be insensitive to disturbances. Small optimal variations

3. It should be sensitive to changes in the manipulated variables (u). Input-output gain should be large.

Direct Loss Evaluation

Brute force method (Direct loss evaluation) [18] is a simple way of finding the candidate control variables (y) and the possible disturbances (d) when they are small in numbers.

The loss (L) can be defined as the difference in the objective function for $J_{opt}(d)$ and $J(u,d)$.

$$L=J_{opt}(d) - J(u,d)$$

Where $J_{opt} = J(u_{opt}(d),d)$ is the result of re-optimizing the problem with the known disturbance present in the optimization problem and $J(u,d)$ is the result when tracking a nominal optimal value when disturbances occur without re-optimizing the problem.

 The loss for the various candidate control variables are then evaluated for the possible disturbance. The candidate control variable (CV) with the smallest worse case or average loss over all the disturbances is then selected as the best candidate [18].

Figure 2.5 shows the objective function value for an increasing disturbance, the re-optimize case ($J_{opt}(d)$) and two candidate control variables y_1 and y_2.
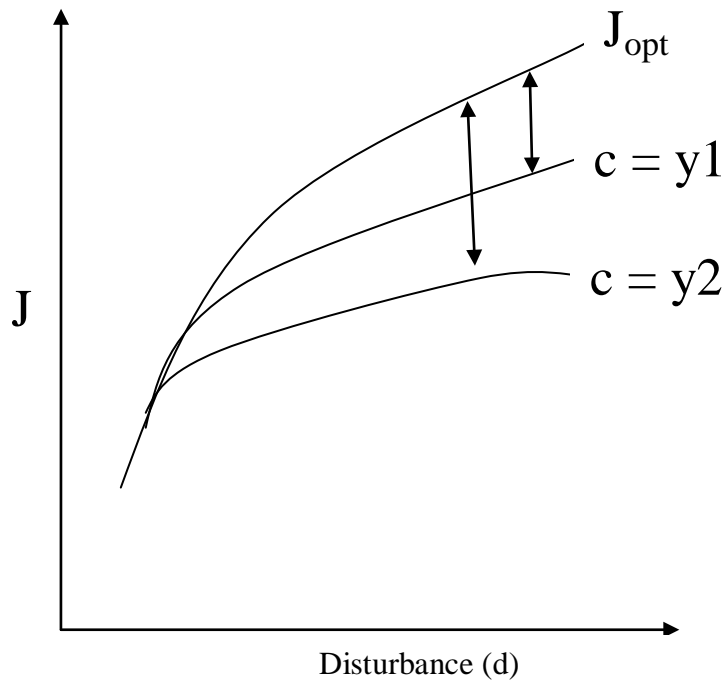
Figure 2.5: Loss in performance when tracking variables(*y*) to references(*c*) instead of re-optimizing (*Jopt(d)*) when disturbances (*d*) are present. Here y1 is a better variable to control than y2. The figure illustrates the case where the objective is to maximize the objective function (*J*).

3 CHAPTER

PROCESS DESCRIPTION
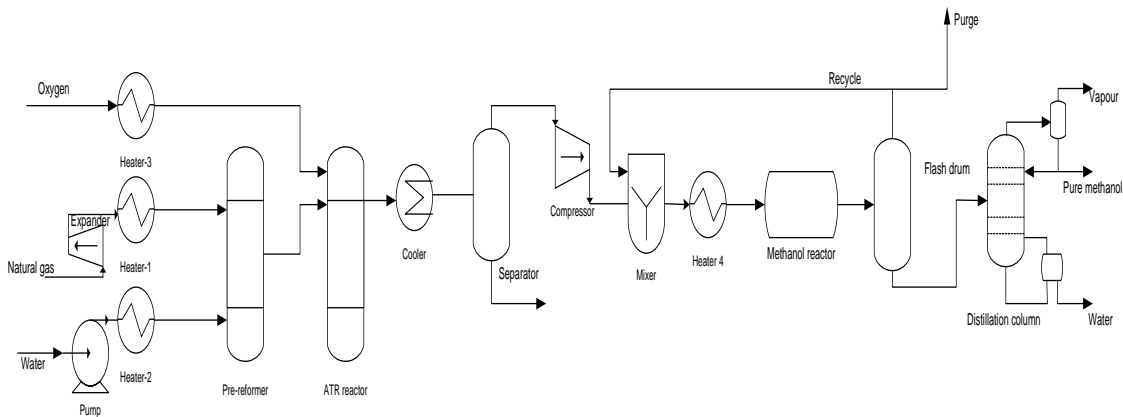
Figure 3.1: Process flowsheet for methanol production

The detailed description of methanol synthesis is described in this chapter. The synthesis gas used for the production of methanol can be made from natural gas. Natural gas at [50ºC, 70bar] is first of all expanded to reduce the pressure to [30bar]. Water is also needed for the reforming of the natural gas. Water at [30ºC, 1bar] is pumped to increase the pressure to 30bar. The resulting solutions are then preheated to reach vapour phase prior to entering the pre-reformer.

3.1 Pre-reforming

Pre-reforming is the term that has been applied to the low temperature steam-reforming of hydrocarbons in a simple adiabatic reactor. The pre-reformer utilizes the heat content of the feed stream to drive the steam reforming reaction at low temperatures. This reactor also uses nickel catalyst to promote the rate of the reaction. This pre-reformer is able to convert the higher hydrocarbons into methane and carbon dioxide. It operates at a temperature of about 497ºC, [12]. The pre-reforming reactions result in an equilibrium gas mixture containing hydrogen, carbon monoxide, carbon dioxide, methane and steam as per the reactions given below:

	Reaction	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/Kmol)	T_{carnot} (K)
1	$C_2H_6 + 2H_2O \rightarrow 2CO + 5H_2$	347.24	215.70	441.41	786.66
2	$C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2$	521.46	282.52	801.81	650.35
3	$n\text{-}C_4H_{10} + 4H_2O \rightarrow 4CO + 9H_2$	676.77	365.62	1044.14	648.16
4	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	205.88	141.97	214.47	959.95
5	$CO + H_2O \leftrightarrow H_2 + CO_2$	-41.14	-28.61	-42.05	978.36

Table 3.1: Pre-reforming reactions

In the pre-reformer, the endothermic reaction is followed by the exothermic methanation and shift reactions, adjusting the chemical equilibrium between the carbon oxides, methane, hydrogen and water according to above reactions.

3.2 Autothermic reaction

ATR operates at low steam to carbon ratios [1] and the development of new burner designs ensuring safe operation and high on-stream factors. The alternative measurement to achieve lower H_2/CO ratios is the addition of oxygen. Autothermic reforming is the reforming of light hydrocarbons in a mixture of steam and oxygen in the presence of a catalyst, [11]. The oxidation reaction is used to adjust a synthetic ratio [7]. In this project, the autothermal reforming processes was used to produce synthesis gas with a synthetic ratio of approximately 2. The reactions occurring in the ATR reactor is shown below:

	Reaction	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/Kmol)	T_{carnot} (K)
1	$CH_4 + 1.5O_2 \leftrightarrow CO + 2H_2O$	-519.60	-543.80	81.23	-6396.65
2	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	205.88	141.97	214.47	959.95
3	$CO + H_2O \leftrightarrow H_2 + CO_2$	-41.14	-28.61	-42.05	978.36

Table 3.2: Reactions occurring in the ATR reactor

3.3 Separation process

Since all the reactions occurring in the ATR are exothermic reactions, the temperature of the product is very high. The products need to be cooled to a lower temperature before the separation can take place. After cooling the products, it is then separated into the synthesis gas part leaving at the top of the separator whiles the water in the mixture leaves at the bottom.

3.4 Compression

The pressure of the synthesis gas emanating from the separator is increase from 30bar to 80bar and this is done by using a compressor. The compressed mixture is then mixed with a recycle stream from the flash drum as shown in the flow sheet. The temperature of the resulting mixture is then raised to 270ºC before it enters the methanol reactor.

3.5 Methanol synthesis

The make-up synthesis gas and the recycle at [270ºC, 80bar] contains mostly hydrogen, carbon monoxide and carbon dioxide. The main reactions for the methanol formation are hydrogenation of CO, hydrogenation of CO_2 and then coupled with the reverse water gas shift reaction. Methanol is thermodynamically less stable [12] and therefore the catalyst used should be very selective. The three reactions are as follows:

	Reaction	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS(J/Kmol)	T_{carnot} (K)
1	$CO + 2H_2 \leftrightarrow CH_3OH$	-90.45	-25.15	-219.13	412.77
2	$CO_2 + 3 H_2 \leftrightarrow CH_3OH + H_2O$	-49.43	3.46	-177.09	279.12
3	$CO_2 + H_2 \leftrightarrow H_2O + CO$	+41.14	28.61	42.05	978.36

Reactions (1) – (3) are not independent [11] so that one is a linear combination of the other ones. The rate expressions for methanol synthesis from Graaf et al. [10]. The rate of reaction constants combined with the equilibrium rate constants provides enough information about kinetics of methanol synthesis.

$$r_1 = \frac{k_1 K_{CO}\left[f_{CO}f_{H_2}^{\frac{3}{2}} - f_{CH_3OH}f_{H_2}^{\frac{1}{2}}K_{p1}\right]}{(1 + K_{CO}f_{CO} + K_{CO_2}f_{CO_2})\left[f_{H_2}^{\frac{1}{2}} + \left(K_{H_2O} \middle/ K_{H_2}^{\frac{1}{2}}\right)f_{H_2O}\right]}$$

(3.1)

$$r_2 = \frac{k_2 K_{CO_2} \left[f_{CO_2} f_{H_2}^{\frac{3}{2}} - f_{CH_3OH} f_{H_2O} f_{H_2}^{\frac{3}{2}} K_{p2} \right]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) \left[f_{H_2}^{\frac{1}{2}} + \left(K_{H_2O} \Big/ K_{H_2}^{\frac{1}{2}} \right) f_{H_2O} \right]}$$

(3.2)

$$r_a = \frac{k_3 K_{CO_2}\left[f_{CO_2}f_{H_2} - \dfrac{f_{H_2O}f_{CO}}{K_{p3}}\right]}{\left(1 + K_{CO}f_{CO} + K_{CO_2}f_{CO_2}\right)\left[f_{H_2}^{\frac{1}{2}} + \left(K_{H_2O} \middle/ K_{H_2}^{\frac{1}{2}}\right)f_{H_2O}\right]}$$

(3.3)

The reaction rate constants, adsorption equilibrium constants and reaction equilibrium constants which appear in kinetics expressions are tabulated in tables 3.1 – 3.3, respectively.

k = Aexp(B/RT)	A	B
k_1	$(4.89 \pm 0.29) \times 10^7$	$-63{,}000 \pm 300$
k_2	$(1.09 \pm 0.07) \times 10^5$	$-87{,}500 \pm 300$
k_3	$(9.64 \pm 7.30) \times 10^6$	$-152{,}900 \pm 6800$

Table 3.1: Rate constants of methanol synthesis reactions

K = Aexp(B/RT)	A	B
K_{CO}	$(2.16 \pm 0.44) \times 10^{-5}$	$46{,}800 \pm 800$
K_{CO2}	$(7.05 \pm 1.39) \times 10^{-7}$	$61{,}700 \pm 800$
$\left(K_{H_2O} \middle/ K_{H_2}^{\frac{1}{2}}\right)$	$(6.37 \pm 2.88) \times 10^{-9}$	$84{,}000 \pm 1400$

Table 3.2: Adsorption equilibrium constants of methanol synthesis reactions

$K_p = 10^{(A/T - B)}$	A	B
K_{p1}	5139	12.621
K_{p2}	3066	10.592
K_{p3}	-2073	-2.029

Table 3.3: Equilibrium constants of methanol synthesis reactions

The product is cooled to 30ºC from Greef et al. [14] with the aid of cooling water. Gas/liquid separation is carried out in a vessel under pressure. The gas is recycled after purging a small part to keep the level of inerts within the loop within limits. The crude methanol is then sent to the purification section. The design specifications and catalyst information for industrial methanol reactor is given in the table below;

Parameter	Value
Number of tubes	2962
Density (kgm^{-3})	1770
Particle diameter (m)	5.47×10^{-3}
Heat capacity ($kJ\ kg^{-1}\ K^{-1}$)	5
Length of reactor (m)	7.022
Bed void fraction	0.39
Density of catalyst bed (kgm^{-3})	1140
Tube inner diameter (m)	0.038
Tube outer diameter (m)	0.042

3.6 Purification

The water-methanol mixture is distilled in order to meet the final specifications. It is essential for methanol to be stabilized (either by distillation or by deep flashing) in order to remove volatile components such as CO_2 and permit shipment and transport in atmospheric vessels. There are three grades of methanol namely: *chemical grade AAA (99.85wt% MeOH, 0.1wt% water, and concentrations of higher alcohols at parts-per-million levels), Fuel grade (97wt% MeOH, 1 wt% water, 1.5wt% alcohols and 0.5wt% of process oil) and MTBE grade (97wt% MeOH, 1wt% water, 2wt% alcohols, 150ppm methyl acetate, 0.3wt% inert liquid medium).*

4 CHAPTER

UNISIM REVIEW

Methanol production from synthesis gas is simulated using Honeywell UniSim Design R380 with Peng Robinson fluid package. The pressure drop across all the unit operations is set to 0 kPa. The simulation overview will be divided into several sections namely feed conditioning, pre-reforming, autothermic reforming (ATR), methanol production and purification.

4.1 Feed Conditioning
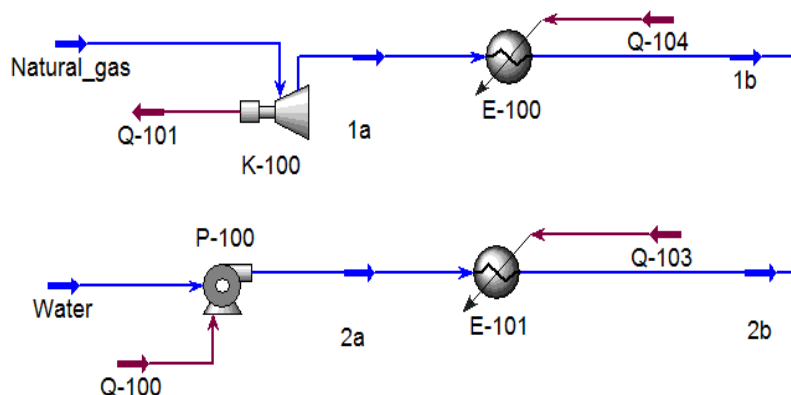
Figure 4.1: Feed conditioning

As shown in the figure above, natural gas with the composition shown below;

Component	Mole fraction
Nitrogen	0.006
Methane	0.955
Ethane	0.03
Propane	0.005
n-Butane	0.004

Table 4.1: Natural composition

The natural gas is introduced at [50ºC, 70bar], it is then expanded by K-101 to [30bar] before it is preheated by E-100 to (500 ºC). Water at [30ºC, 1bar] is also pumped to (30bar) and then preheated to (500 ºC) by E-101 as depicted in figure 4.1. The preheated natural gas and water then enters the pre-reformers.

4.2 Pre-reforming
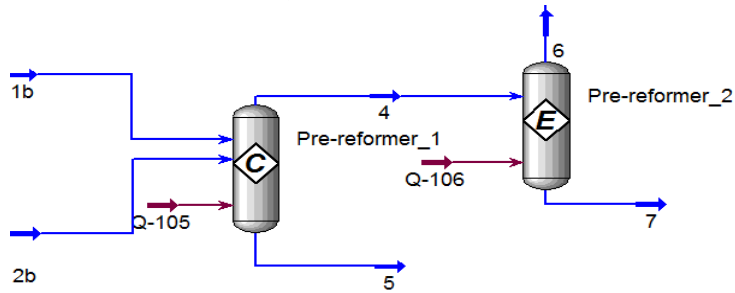
Figure 4.2: Pre-reformers

The figure above shows the pre-reformers for the synthesis gas production part. It is made up of two reactors; the first one is modeled as a conversion reactor in which the higher hydrocarbons namely ethane, propane and n-butane are converted into hydrogen and carbon monoxide through conversion reactions. It is an adiabatic reactor and all the reactions have 100% conversion. All the reactions are endothermic.

The main components that should be present for the reaction to proceed are the preheated natural gas (stream 1b) and steam (stream 2b). The unconverted natural gas (mainly methane) and the products as a result of the three reactions (stream 4 at 313.6ºC) are then fed into the next pre-reformer which is an equilibrium reactor and also modeled as an adiabatic reactor. The reactions that goes on in this equilibrium reactor is the steam reforming of methane and the water gas shift reaction. Both reactions are exothermic. The products (stream 6) from the second pre-reformer are mainly methane, water, hydrogen, carbon monoxide and carbon dioxide. The carbon monoxide content in (stream 6) reduces due to the water gas shift reaction.

4.3 Autothermic reforming (ATR)

The ATR is an adiabatic reactor and it is model as an equilibrium reactor in UniSim and all the reactions are defined as equilibrium reactions.
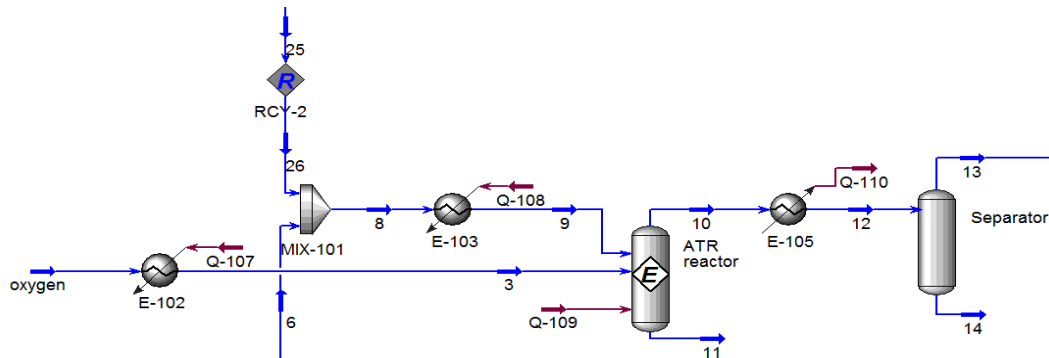
Figure 4.3: Autothermic reforming and separation

From the figure above it shows that the products from the pre-reformers is mixed with a recycle from the methanol reactor and then the mixture is preheated to [675ºC] and a pressure of [30bar]. Another stream entering the ATR reactor is pure oxygen originally at [5ºC, 30bar] is preheated to [200ºC, 30bar]. The reactions taking place in the ATR are oxidation of methane, steam reforming of methane and water gas shift reaction. All the reactions taking place in this reactor are exothermic by nature. The components emanating from this reactor as products are hydrogen, carbon monoxide, water and carbon dioxide. The resulting product is then cooled down and then separated into the syngas part (stream 13) and water (stream 14) as shown in the diagram above.

4.4 Methanol production
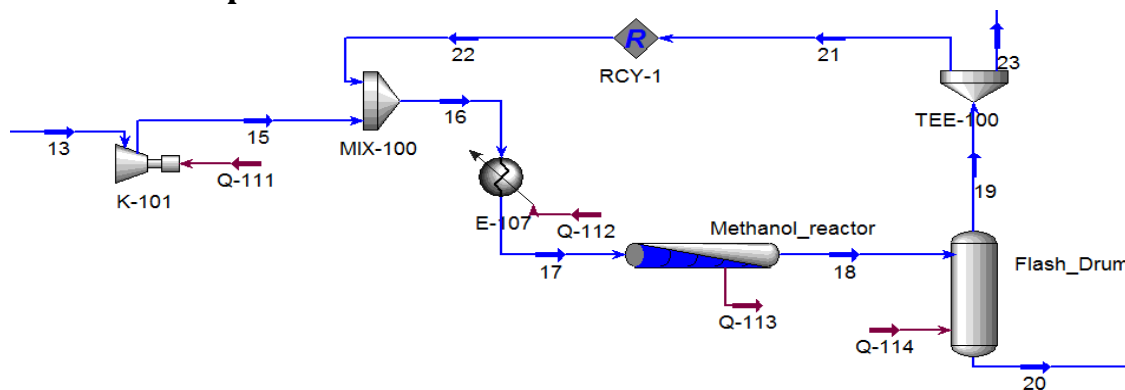
Figure 4.4: Methanol production

22

The synthesis gas leaving the separator is compressed to [80bar] and then mixed with the recycle stream from the flash drum. The temperature of the mixture is then increased from [209ºC] to [270ºC]. The methanol reactor is a plug flow reactor (PFR) with 2962 tubes inside. All the reactions (CO hydrogenation, CO_2 hydrogenation and the reverse water gas shift) are modeled as a heterogeneous catalytic reaction and the reactions are exothermic. The exiting temperature is specified as 250ºC. The crude methanol leaving the reactor (stream 18) at [250ºC, 80bar] is flashed in a flash drum and the streams exiting this equipment are at a temperature of [30ºC, 80bar]. Stream [19] is recycled after purging small part to keep the level of inert in the loop within limits. Stream [20] consisting mainly of methanol and water is then sent to the distillation column.

4.5 Purification
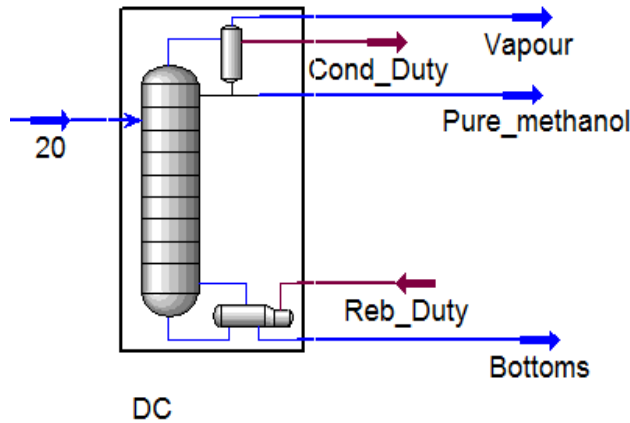
Figure 4.5: Purification of crude methanol

Figure 4.5 shows the purification of the crude methanol into pure methanol (99% purity). The purification is done using a distillation column [DC]. The column is made up of 20 stages and the condenser and the reboiler pressures are 90kPa and 100kPa respectively. The stream [Bottoms] consists of 99% of water. The pure methanol is exiting at [20ºC, 90kPa].

5 CHAPTER

RESULTS AND DISCUSSIONS

5.1 Degrees of Freedom Analysis

There are two main types of degree of freedom namely dynamic degrees of freedom N_m (m denotes manipulated) and steady state degrees of freedom N_{ss}. N_m is usually obtained by process insight as the number of independent variables that can be manipulated by external means. Generally, it is given by the number of adjustable valves plus other adjustable mechanical and electrical devices. N_{ss} on the other hand is the number of variables needed to be specified in order for the simulation to converge. The steady state degrees of freedom is then obtained from the equation below;

$$N_{ss} = N_m - (N_{om} + N_{oy})$$ ....(5.1)

Where N_{om} and N_{oy} denotes number of manipulated variables with no steady state effect and the number of variables that need to be controlled ....respectively.

In this project since we are dealing with steady state process the manipulated variables can be specified from the process insight, which implies $N_{ss} = N_m$. The degrees of freedom (u) = output variables (y), this means we can make our selected manipulated variables to be the candidate control variables.

5.2 Optimization results

In the optimization problem, the methanol production rate is set as the objective function and it is formulated as follows:

Max J = Methanol production rate (F_{CH3OH}).

The main objective was to find the optimal nominal values for the chosen candidate controlled variables that was going to give us 5000ton/day of pure methanol.

Seven decision (manipulated) variables, which includes flowrate of water (F_{H2O}) and oxygen (F_{O2}), synthesis gas pressure (P_1), methanol synthesis pressure (P_2), inlet temperature of ATR (T) and purge from the methanol synthesis loop (R_1) and ratio of purge from the plant (R_2). The main reason to develop an optimal oxygen flowrate is to give lower H_2/CO ratio. Optimal inlet temperature of ATR is chosen in order to in order to increase the amount of H_2 and CO and at the

same time to prevent the deactivation of the catalyst and also it is because of metallurgical constraints of the reactor vessel. Since both steam reforming and partial oxidation is hindered by elevated pressures, the need to find an optimal pressure for the synthesis of natural gas is of importance here. High investment cost for the compression of syngas prior to the methanol synthesis reactor has led us to find the optimal pressure for operating the methanol reactor. The ranges for the manipulated variables are:

$3000 < F_{O2} < 6000$ kgmole/hr

$4000 < F_{H2O} < 10000$ kgmole/hr

$25 < P_1 < 40$ bar

$50 < P_2 < 100$ bar

$0.04 < R_1 < 0.1$

$0.1 < R_2 < 0.9$

$600 < T < 675°C$

5.3 Disturbances

The optimal operation was modeled without consideration of disturbances but this is not true in practice since there might an error with the control system of the plant. Disturbances (errors) will therefore occur since the representation is not the perfect model for the real plant.

The following disturbances (errors) were considered for this process:

- d_1: Feed rate of natural gas reduced by 20% (5920 kgmole/hr)
- d_2: Feed rate of natural gas reduced by 15% (6290 kgmole/hr)
- d_3: Feed rate of natural gas reduced by 10% (6660 kgmole/hr)
- d_4: Feed rate of natural gas reduced by 5% (7030 kgmole/hr)
- d_5: Feed rate of natural gas increased by 5% (7770 kgmole/hr)
- d_6: Feed rate of natural gas increased by 10% (8140 kgmole/hr)
- d_7: Feed rate of natural gas increased by 15% (8510 kgmole/hr)
- d_8: Feed rate of natural gas increased by 20% (8880 kgmole/hr)
- d_9: Feed composition of natural gas reduced by 5%
- d_{10}: Feed composition of natural gas reduced by 10%

The base value for natural gas flowrate was 7400kgmole/hr.

The changes in the composition are shown in the table below;

Component	Base case	-5% change	-10% change
Nitrogen	0.006	0.0557	0.1054
Methane	0.955	0.90725	0.8595
Ethane	0.03	0.0285	0.027
Propane	0.005	0.00475	0.0045
n-butane	0.004	0.0038	0.0036

Table 5.1: Natural gas composition

When disturbances occur the optimal nominal values of the selected controlled variables change and these changes are summarized in table 5.2.

	J	F_{O2}	F_{H2O}	P_1	P_2	R_1	R_2	T
Nominal	5617	4400	5000	29.95	79.88	0.042	0.3	675
d_1	4582	3699	4292	27.76	80.71	0.045	0.15	671.6
d_2	4890	3926	4559	29.79	79.98	0.043	0.17	675
d_3	5147	4110	4900	29.85	79.94	0.047	0.22	675
d_4	5390	4290	5002	29.88	79.91	0.041	0.26	675
d_5	5898	4774	5001	29.95	79.88	0.042	0.3	674.9
d_6	6218	5030	4873	30	79.29	0.04	0.26	675
d_7	6552	5407	5014	29.95	79.88	0.078	0.33	675
d_8	6840	5598	5410	30.06	79.59	0.04	0.13	675
d_9	5238	5175	5310	29.84	79.92	0.041	0.25	672.7
d_{10}	4920	4771	4824	29.87	79.91	0.042	0.26	675

Table 5.2: Optimal values for vaious disturbances

Implementation error which is associated with the candidate controlled variables was not considered in this project. The question to be answered here is which of these candidate controlled variables can we keep constant all the time without reoptimizing the process when disturbances occur. (*self-optimizing variable*). The answer to this question is not straight forward. The best way for selection of the candidate control variables is by computing the loss associated with each of the candidate controlled variables kept constant at its nominal optimal value, which is given by $L = J(u,d) - J_{opt}(d)$ [17]. The results are summarized in table 5.3.

	Loss with $F_{O2}=4400$	Loss with $F_{H2O}=5000$	Loss with $P_1=29.95$	Loss with $P_2=79.88$	Loss with $R_1=0.042$	Loss with $R_2=0.30$	Loss with $T=675$
Nominal	0	0	0	0	0	0	0
d_1	63	39	0	0	432	236	0
d_2	99	25	0	0	462	303	0
d_3	37	34	0	0	27	78	0
d_4	21	158	0	0	17	33	0
d_5	65	45	0	0	90	5	0
d_6	13	13	0	0	45	25	0
d_7	48	64	0	0	10	99	0
d_8	128	32	0	0	82	46	0
d_9	77	210	0	0	54	51	0
d_{10}	5	23	0	0	30	101	0
Average loss	55.6	64.3	0	0	124.9	97.7	0

Table 5.3: Loss for alternative controlled variables

From the table it suggests that some of the candidate controlled variables are active and therefore they have to be controlled in the process.

Keeping all the other variables constant except oxygen showed a small loss compared to the other alternatives in the objective function. This clearly indicates that the flowrate of oxygen depends more on the flowrate of natural gas than that of water. This is true because keeping the ratio of oxygen to methane in the right proportion lowers the ratio of H_2/CO. The methanol synthesis depends more on this ratio which shows that it should be approximately 2. This can be confirmed from the oxidation of methane reaction which produces CO and water. Adjusting the flowrate of water and keeping the other variables constant is really not necessary because water is being produced in most of the reactions. If the flowrate of oxygen is not controlled to give a proper ratio, either more or less CO will be produced and this can reduce or increase the H_2/CO ratio respectively.

The other trials were to keep all the other variables constant except the recycle ratios (R_1 and R_2), and the results was very poor relative to the other trials, showing that the these ratios are independent on the flowrate of natural gas.

The trial for both the pressure of the syngas and the methanol synthesis as well as the temperature gave a zero loss. This is true because the conversion of methane to syngas decreases when the pressure increases, but the temperature on the other hand can increase the conversion but due to the metallurgical constraints of the equipments it is better to keep it at the nominal

optimal value. These three variables are our active constarints in this process, controlling them is very necessary.

The comparison between oxygen and water is shown graphically in figures 5.1 and 5.2 respectively.

a)
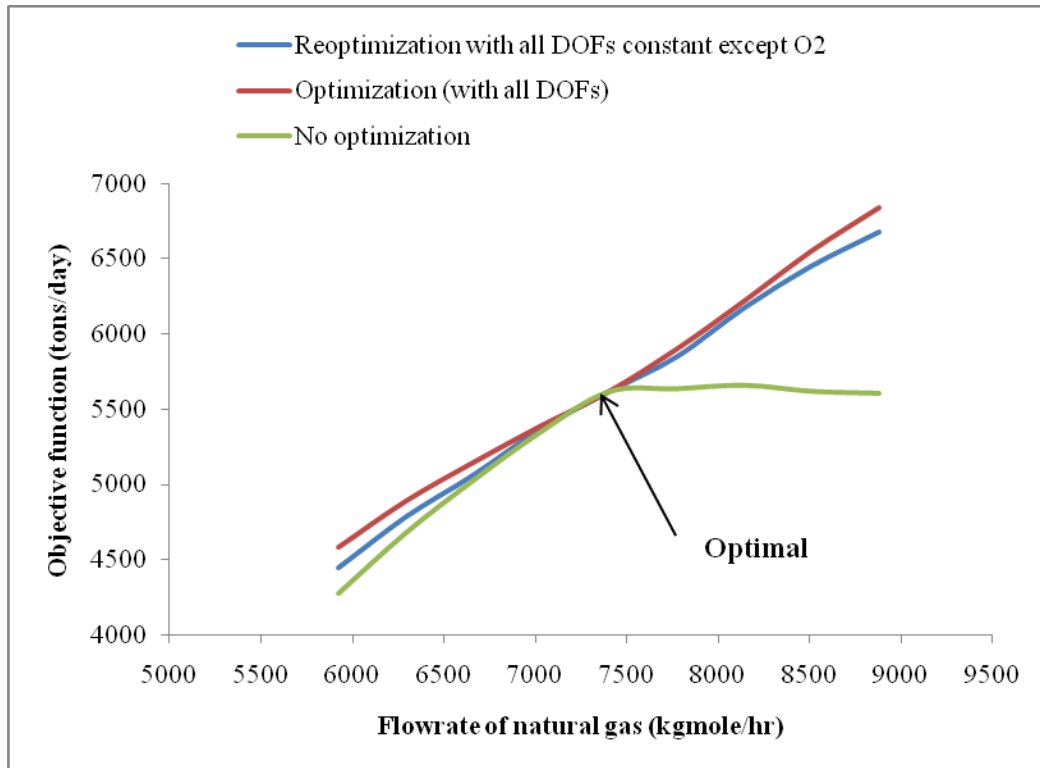
b)
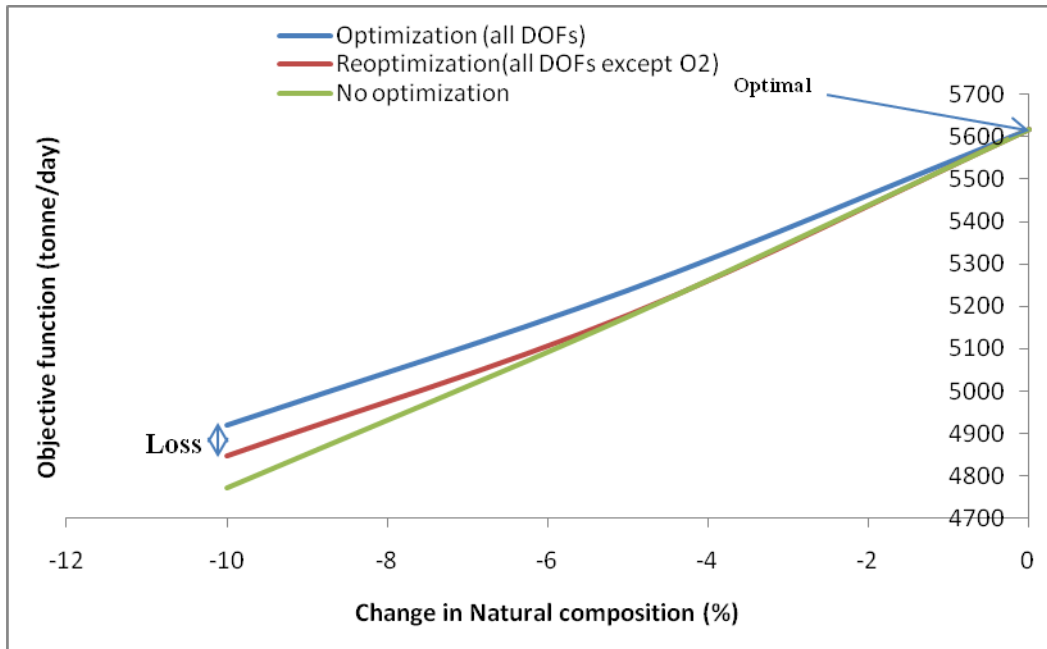
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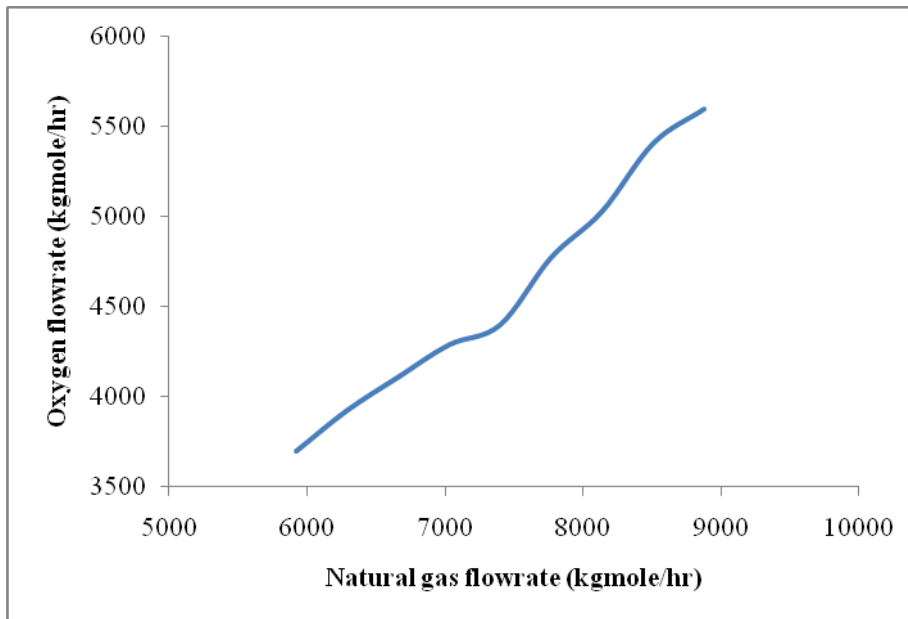
Figure 5.1: Analysis with oxygen as the manipulated variable

a)
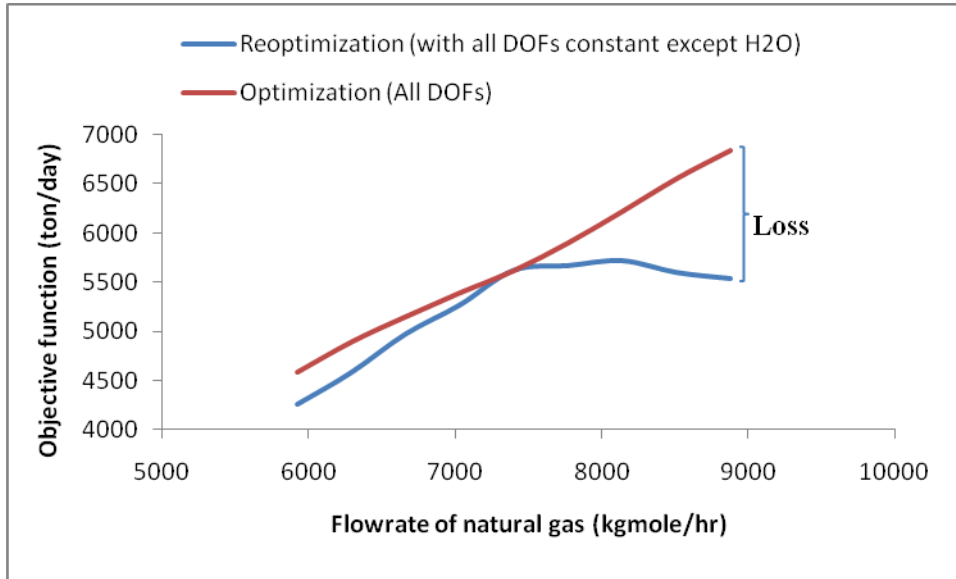
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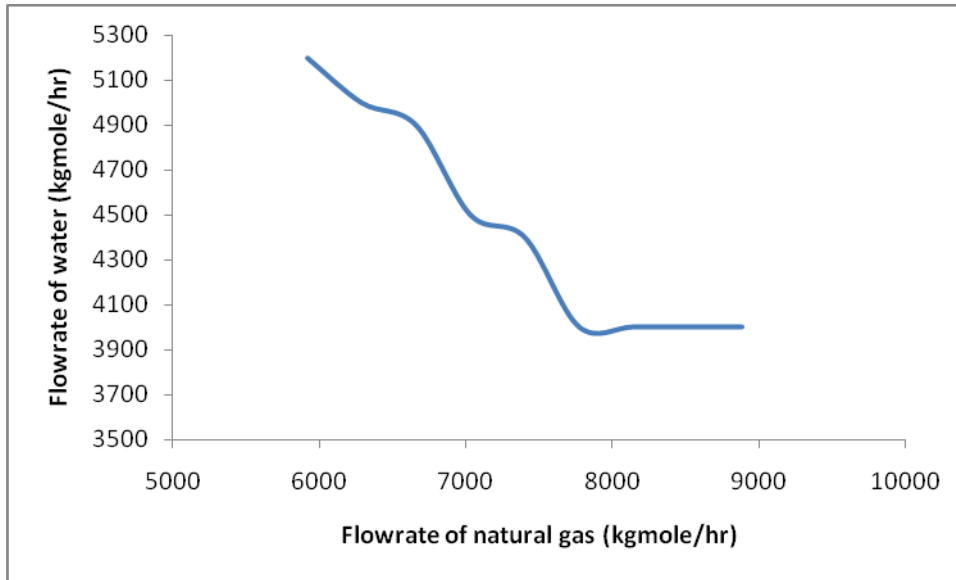
Figure 5.2: Analysis with water as manipulated variable

6 CHAPTER

CONCLUSION

Simulation

In this project a methanol plant with a production rate of 5000tons/day is simulated with UniSim by using information obtained from literature. There were uncertainties in some of the parameters used for the simulation of the methanol reactor. A typical example is the number of tubes in the reactor, there were different values suggested by literature. The heterogenous kinetics used also contained some uncertainties, since no experiment was performed to find out these expressions in the project. Therefore it cannot be confidently concluded that this process mimics a real process plant.

Optimization

With refernce to the developed simulated process it became obvious that the performance of a methanol plant can be improved by changing the operating conditions from what is practised in industries. Seven variables were chosen as the degree of freedom (manipulated) variables and their optimal nominal values were obtained after the optimization.

It was assumed that $y = u$, this then automatically transforms the degree of freedoms to candidate control variables (CVs). Loss evaluation was performed on each of these variables by keeping six of them constant whiles one is allowed to fluctuate. After the computation it was found that the best way of running this plant is by keeping the variables F_{H2O}, P_1, P_2, R_1,R_2 and T at their nominal optimal values while the flowrate of oxygen is manipulated. The candidate control variables are then the six mentioned above.

The *self-optimizing* variables found were P_1, P_2, and T, since keeping them constant gave the same value for the objective function as when the process was reoptimized in the presence of disturbances. The disturbances considered in the project were $\pm 20\%$ change in the flowrate of natural gas flowrate and also -5% and -10% change in the composition of natural gas.

Recommendation

It would have been a good idea for the one simulating the process to have at least some kind of exposure to the process by visiting an operating plant to have a look at how things are done over there.

Also more combinations should have been done with the candidate control variables to see if there might be a more proper self-optimizing variable will be found relative to the ones found in this project. This was not done due to time constraints.

Further work

This projects needs to be continued, so that it can be extended into the dynamic mode to see how the plant behaves in reality. A good control variable should be detected for the manipulated variable flowrate of oxygen. Heat integration sholud also be considered to cut down cost in the process. Equipment sizing, developing some control structures is also another task to be looked at in the future. The other idea is to look at incorporating a CO_2 capturing plant to remove some of the CO_2 from the syngas before it enters the methanol reactor.

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APPENDIX

A: Loss Evaluation
The loss evaluation was computed by using the equation shown below;

$$L = J(u,d) - J_{opt}(d)$$

The results for the $J_{opt}(d)$ for all degrees of freedom are shown in the table A-1

	F_{O2}=4400 kgmole/hr	F_{H2O}=5000 kgmole/hr	P_1=29.95bar	P_2=79.88bar	R_1=0.042	R_2=0.30	T=675°C
Nominal	5617	5617	5617	5617	5617	5617	5617
d_1	4448	4255	4582	4582	3828	4055	4582
d_2	4787	4579	4890	4890	4154	4479	4890
d_3	5065	4969	5147	5147	4507	4611	5147
d_4	5372	5264	5390	5390	4798	4782	5390
d_5	5848	5664	5898	5898	5036	4958	5898
d_6	6173	5715	6218	6218	4949	4940	6218
d_7	6452	5595	6552	6552	4903	4928	6552
d_8	6678	5533	6840	6840	4804	4772	6840
d_9	5180	5153	4920	4920	4703	4711	4920
d_{10}	4848	4713	5238	5238	4254	4324	5238

Table A-1: Optimal values for different DOFs when varying their optimal nominal value

B: Sensitivity analysis

The range of values chosen for the optimization of the DOFs were not just selected but a sensitivity analysis was done by case studying how they vary with the objective function. Figure B1 shows the results of the operation.

(a)
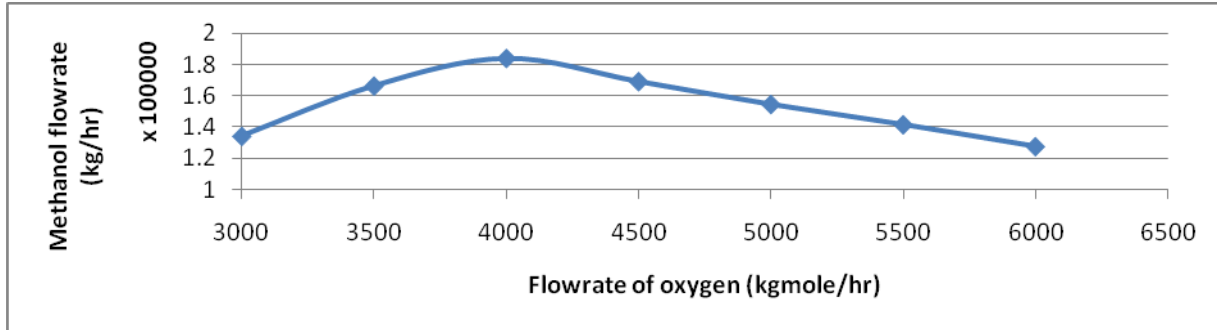
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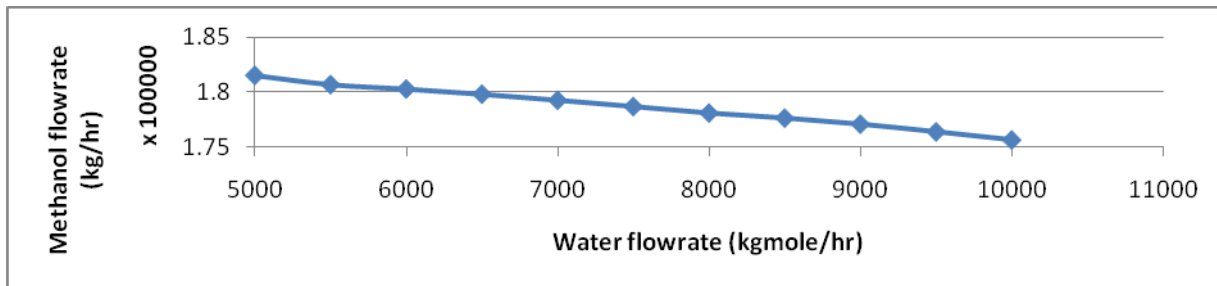
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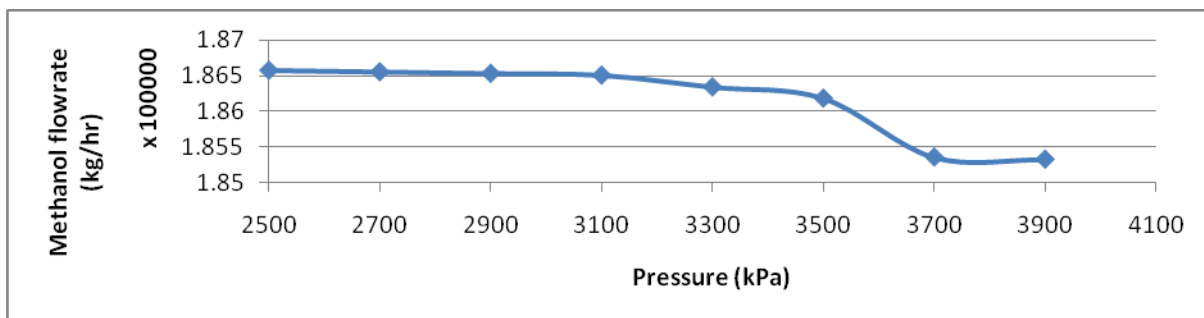
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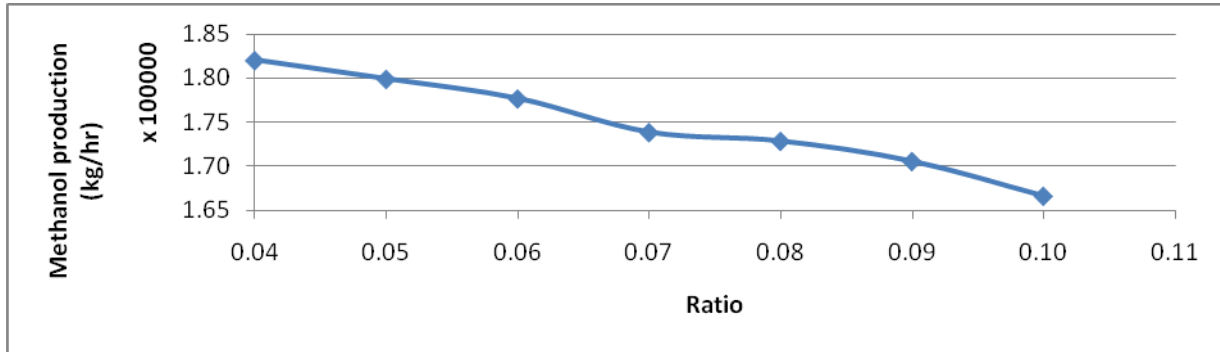
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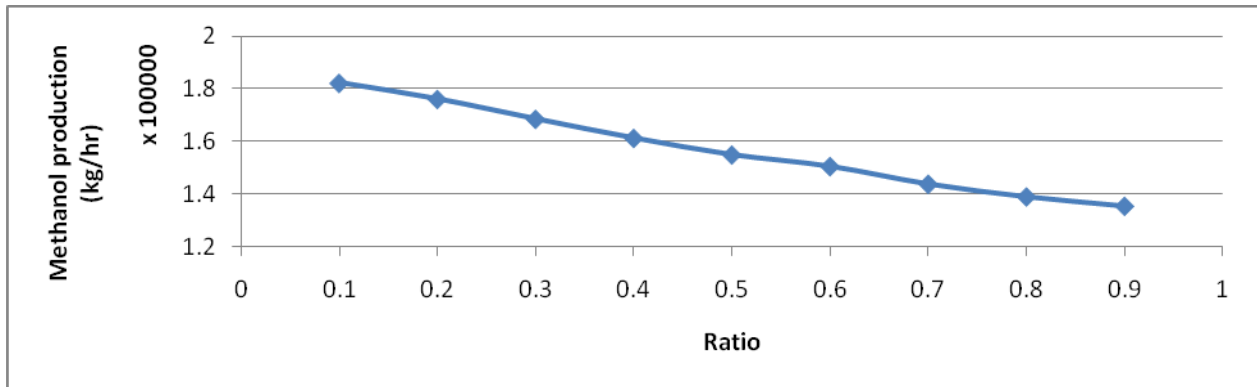
(f)
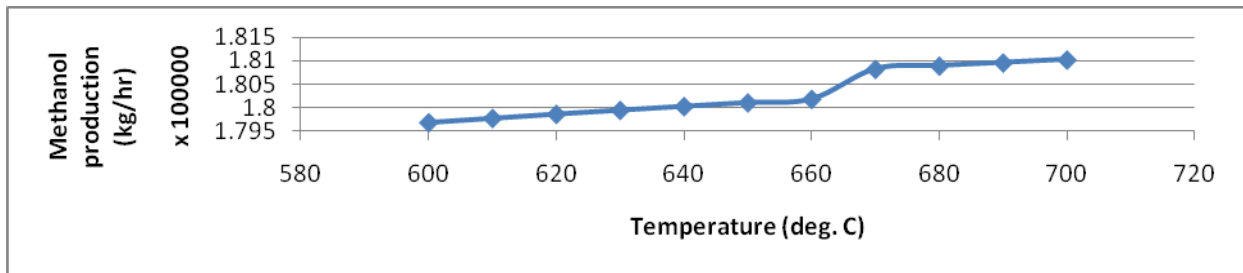
Figure B1: Sensitivity analysis of (a) oxygen flowrate, (b) water flowrate, (c) pressure of syngas, (d) ratio of recycle, (e) ratio of purge and (f) inlet temperature of ATR reactor.

C: Simulation in UniSim

- **Process flowsheet**

The figure C1 shows the overall PFD for the entire process plant. It has been divided into two sections for easier view that is C1 and C2.
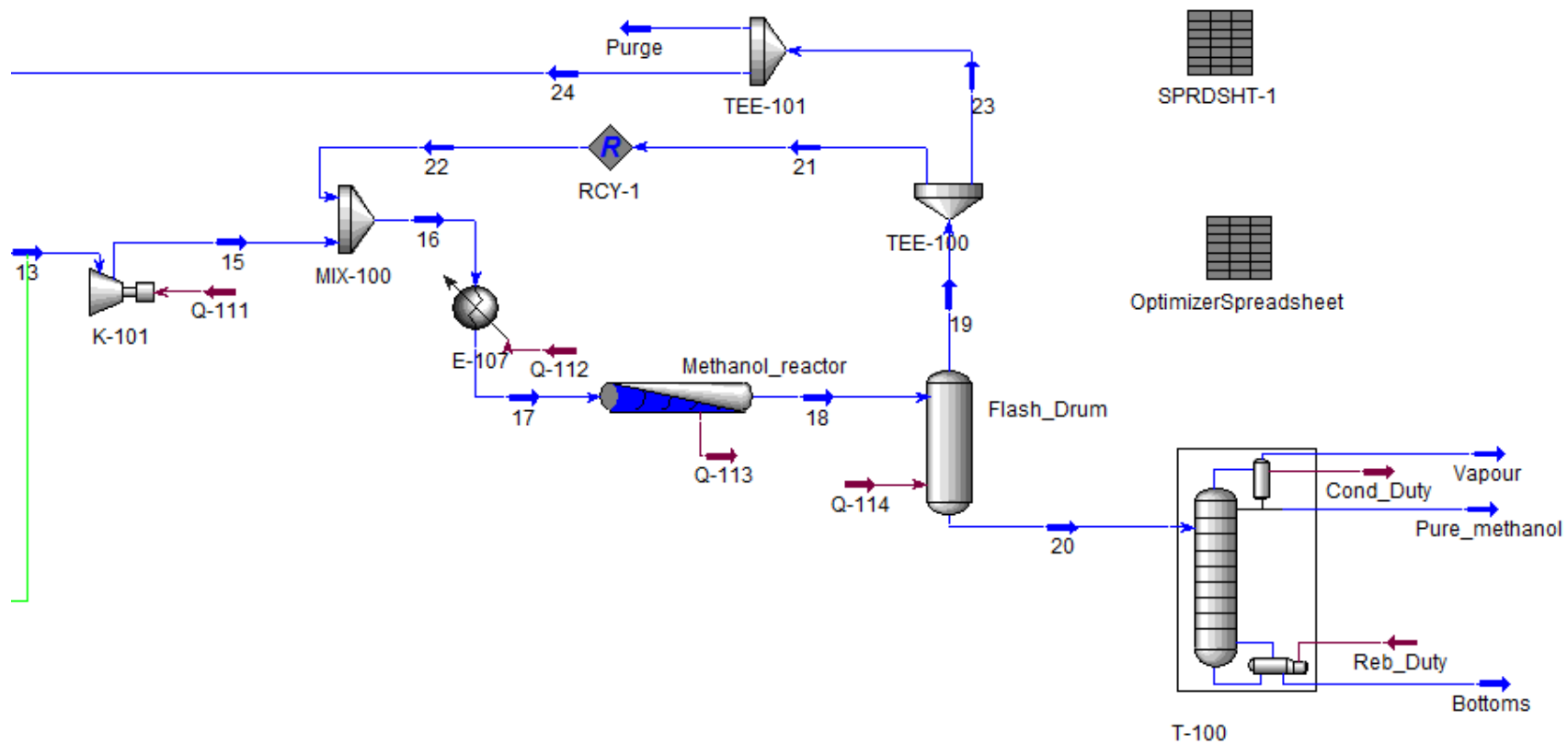
Figure C1

Figure C2

- **Stream conditions**

Name	Natural_gas	1a	1b	Water	2a	2b	5
Vapour Fraction	1	1	1	0	0	1	0
Temperature [C]	50	0	500	30	30	500	305
Pressure [kPa]	7000	2995	2995	100	2995	2995	2995
Molar Flow [kgmole/h]	7400	7400	7400	5000	5000	5000	0
Mass Flow [kg/h]	124647	124647	124647	90076	90076	90076	0
Liquid Volume Flow [m3/h]	405	405	405	90	90	90	0
Heat Flow [kJ/h]	-557461742	-567629021	-379646604	-1429160784	-1428814328	-1127278456	0
Molar Enthalpy [kJ/kgmole]	-75333	-76707	-51304	-285832	-285763	-225456	-256575
Name	**4**	**6**	**26**	**8**	**9**	**oxygen**	**3**
Vapour Fraction	1	1	1	1	1	1	1
Temperature [C]	305	449	-22	363	675	5	200
Pressure [kPa]	2995	2995	2995	2995	2995	2995	2995
Molar Flow [kgmole/h]	13747	13032	4427	17458	17458	4300	4300
Mass Flow [kg/h]	214723	214722	58635	273357	273357	137600	137600
Liquid Volume Flow [m3/h]	529	520	150	671	671	121	121
Heat Flow [kJ/h]	-1506914881	-1506915278	-320887070	-1827802348	-1566896483	-3850644	22162454
Molar Enthalpy [kJ/kgmole]	-109619	-115636	-72489	-104696	-89751	-895	5154
Name	**11**	**10**	**12**	**14**	**13**	**15**	**22**
Vapour Fraction	0	1	1	0	1	1	1
Temperature [C]	1058	1058	17	17	17	142	30
Pressure [kPa]	2995	2995	2995	2995	2995	7988	7908
Molar Flow [kgmole/h]	0	32082	32082	5269	26814	26814	151828
Mass Flow [kg/h]	0	410956	410956	95275	315681	315681	2011510
Liquid Volume Flow [m3/h]	0	955	955	96	859	859	5161
Heat Flow [kJ/h]	0	-1544732630	-2883571220	-1510633385	-1372937835	-1273882932	-10761339555
Molar Enthalpy [kJ/kgmole]	-48149	-48149	-89881	-286723	-51203	-47509	-70879

Name	16	17	18	19	21	23	24
Vapour Fraction	1	1	1	1	1	1	1
Temperature [C]	46	270	250	30	30	30	30
Pressure [kPa]	7908	7908	7908	7908	7908	7908	7908
Molar Flow [kgmole/h]	178641	178641	165356	158141	151815	6326	4428
Mass Flow [kg/h]	2327191	2327191	2327184	2094288	2010516	83772	58640
Liquid Volume Flow [m3/h]	6020	6020	5669	5375	5160	215	151
Heat Flow [kJ/h]	-12035222487	-10760727787	-11538645197	-11206112062	-10757867579	-448244482	-313771138
Molar Enthalpy [kJ/kgmole]	-67371	-60237	-69781	-70861	-70861	-70861	-70861

Name	Purge	20	Vapour	Pure_methanol	Bottoms
Vapour Fraction	1	0	1	0	0
Temperature [C]	30	30	21	21	100
Pressure [kPa]	7908	7908	90	90	100
Molar Flow [kgmole/h]	1898	7215	529	6588	97
Mass Flow [kg/h]	25131	232897	19620	211520	1756
Liquid Volume Flow [m3/h]	65	293	26	266	2
Heat Flow [kJ/h]	-134473345	-1791221053	-163273947	-1602869091	-27291671
Molar Enthalpy [kJ/kgmole]	-70861	-248279	-308370	-243311	-280323

- **Compositions**

Name	Natural_gas	1a	1b	Water	2a	2b	5
Comp. Mole Frac (Methanol)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Comp. Mole Frac (CO_2)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Comp. Mole Frac (CO)	0.000	0.000	0.000	0.000	0.000	0.000	0.002
Comp. Mole Frac (H_2O)	0.000	0.000	0.000	1.000	1.000	1.000	0.984
Comp. Mole Frac (Hydrogen)	0.000	0.000	0.000	0.000	0.000	0.000	0.005
Comp. Mole Frac (Nitrogen)	0.006	0.006	0.006	0.000	0.000	0.000	0.000
Comp. Mole Frac (Methane)	0.955	0.955	0.955	0.000	0.000	0.000	0.009
Comp. Mole Frac (Ethane)	0.030	0.030	0.030	0.000	0.000	0.000	0.000
Comp. Mole Frac (Propane)	0.005	0.005	0.005	0.000	0.000	0.000	0.000
Comp. Mole Frac (n-butane)	0.004	0.004	0.004	0.000	0.000	0.000	0.000
Comp. Mole Frac (Oxygen)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Name	**4**	**6**	**26**	**8**	**9**	**oxygen**	**3**
Comp. Mole Frac (Methanol)	0.000	0.000	0.004	0.001	0.001	0.000	0.000
Comp. Mole Frac (CO_2)	0.000	0.024	0.113	0.046	0.046	0.000	0.000
Comp. Mole Frac (CO)	0.049	0.001	0.204	0.052	0.052	0.000	0.000
Comp. Mole Frac (H_2O)	0.315	0.336	0.000	0.251	0.251	0.000	0.000
Comp. Mole Frac (Hydrogen)	0.119	0.067	0.621	0.207	0.207	0.000	0.000
Comp. Mole Frac (Nitrogen)	0.003	0.003	0.020	0.008	0.008	0.000	0.000
Comp. Mole Frac (Methane)	0.514	0.570	0.038	0.435	0.435	0.000	0.000
Comp. Mole Frac (Ethane)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Comp. Mole Frac (Propane)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Comp. Mole Frac (n-butane)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Comp. Mole Frac (Oxygen)	0.000	0.000	0.000	0.000	0.000	1.000	1.000

Name	11	10	12	14	13	15	22
Comp. Mole Frac (Methanol)	0.001	0.001	0.001	0.004	0.000	0.000	0.004
Comp. Mole Frac (CO_2)	0.038	0.038	0.038	0.001	0.045	0.045	0.113
Comp. Mole Frac (CO)	0.244	0.244	0.244	0.000	0.292	0.292	0.204
Comp. Mole Frac (H_2O)	0.164	0.164	0.164	0.996	0.001	0.001	0.000
Comp. Mole Frac (Hydrogen)	0.541	0.541	0.541	0.000	0.647	0.647	0.621
Comp. Mole Frac (Nitrogen)	0.004	0.004	0.004	0.000	0.005	0.005	0.020
Comp. Mole Frac (Methane)	0.009	0.009	0.009	0.000	0.010	0.010	0.038
Comp. Mole Frac (Ethane)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Comp. Mole Frac (Propane)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Comp. Mole Frac (n-butane)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Comp. Mole Frac (Oxygen)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Name	16	17	18	19	21	23	24
Comp. Mole Frac (Methanol)	0.004	0.004	0.044	0.004	0.004	0.004	0.004
Comp. Mole Frac (CO_2)	0.103	0.103	0.110	0.113	0.113	0.113	0.113
Comp. Mole Frac (CO)	0.217	0.217	0.195	0.204	0.204	0.204	0.204
Comp. Mole Frac (H_2O)	0.000	0.000	0.001	0.000	0.000	0.000	0.000
Comp. Mole Frac (Hydrogen)	0.624	0.624	0.594	0.621	0.621	0.621	0.621
Comp. Mole Frac (Nitrogen)	0.018	0.018	0.019	0.020	0.020	0.020	0.020
Comp. Mole Frac (Methane)	0.034	0.034	0.037	0.038	0.038	0.038	0.038
Comp. Mole Frac (Ethane)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Comp. Mole Frac (Propane)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Comp. Mole Frac (n-butane)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Comp. Mole Frac (Oxygen)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Name	Purge	20	Vapour	Pure_methanol	Bottoms		
Comp. Mole Frac (Methanol)	0.004	0.910	0.125	0.994	0.002		
Comp. Mole Frac (CO_2)	0.113	0.077	0.699	0.006	0.000		
Comp. Mole Frac (CO)	0.204	0.003	0.042	0.000	0.000		
Comp. Mole Frac (H_2O)	0.000	0.008	0.000	0.000	0.998		

Comp. Mole Frac (Hydrogen)	0.621	0.000	0.082	0.000	0.000
Comp. Mole Frac (Nitrogen)	0.020	0.001	0.010	0.000	0.000
Comp. Mole Frac (Methane)	0.038	0.002	0.043	0.000	0.000
Comp. Mole Frac (Ethane)	0.000	0.000	0.000	0.000	0.000
Comp. Mole Frac (Propane)	0.000	0.000	0.000	0.000	0.000
Comp. Mole Frac (n-butane)	0.000	0.000	0.000	0.000	0.000
Comp. Mole Frac (Oxygen)	0.000	0.000	0.000	0.000	0.000

- **PERFORMANCE LOSS EVALUATION**

	FO2=4400 kgmole/hr			F$_{H2O}$=5000 kgmole/hr		
	J(u,d)	Jopt (d)	Loss	J(u,d)	Jopt (d)	Loss
Nominal	5617	5617	0	5617	5617	0
d_1	4385	4448	63	4216	4255	39
d_2	4688	4787	99	4554	4579	25
d_3	5028	5065	37	4935	4969	34
d_4	5351	5372	21	5106	5264	158
d_5	5783	5848	65	5619	5664	45
d_6	6160	6173	13	5702	5715	13
d_7	6404	6452	48	5531	5595	64
d_8	6550	6678	128	5501	5533	32
d_9	5103	5180	77	4943	5153	210
d_{10}	4843	4848	5	4690	4713	23
Average loss			55.6			64.3

	P_1=29.95bar			P_2=79.88bar		
	J(u,d)	Jopt (d)	Loss	J(u,d)	Jopt (d)	Loss
Nominal	5617	5617	0	5617	5617	0
d_1	4582	4582	0	4582	4582	0
d_2	4890	4890	0	4890	4890	0
d_3	5147	5147	0	5147	5147	0
d_4	5390	5390	0	5390	5390	0
d_5	5898	5898	0	5898	5898	0
d_6	6218	6218	0	6218	6218	0
d_7	6552	6552	0	6552	6552	0
d_8	6840	6840	0	6840	6840	0
d_9	4920	4920	0	4920	4920	0
d_{10}	5238	5238	0	5238	5238	0
Average loss			0			0

	R$_1$=0.042			R$_2$=0.30			T=675°C		
	J(u,d)	Jopt (d)	Loss	J(u,d)	Jopt (d)	Loss	J(u,d)	Jopt (d)	Loss
Nominal	5617	5617	0	5617	5617	0	5617	5617	0
d$_1$	3696	3828	132	3819	4055	236	4582	4582	0
d$_2$	3692	4154	462	4176	4479	303	4890	4890	0
d$_3$	4480	4507	27	4533	4611	78	5147	5147	0
d$_4$	4781	4798	17	4749	4782	33	5390	5390	0
d$_5$	4946	5036	90	4953	4958	5	5898	5898	0
d$_6$	4904	4949	45	4915	4940	25	6218	6218	0
d$_7$	4893	4903	10	4829	4928	99	6552	6552	0
d$_8$	4722	4804	82	4726	4772	46	6840	6840	0
d$_9$	4649	4703	54	4660	4711	51	5238	5238	0
d$_{10}$	4224	4254	30	4223	4324	101	4920	4920	0
Average loss			94.9			97.7			0

NOMENCLATURE

$J_{opt}(d)$ .... J when re-optimizing the disturbance

L .... Loss from optimum

d .... Disturbance

CV .... Control variable

MV .... Manipulated variable

DoF .... Degrees of freedom

u .... Input

y .... Output

ΔH .... Enthalpy of reaction [kJ/mol]

ΔG .... Gibbs Energy [kJ/mol]

ΔS .... Entropy, [J/Kmol]

B .... Activation energy

R .... Universal gas constant

A .... Frequency factor for the reaction

C_p .... Specific heat of the gas constant pressure, [J/mol]

D_i .... Tube inside diameter, [m]

f_i .... Partial fugacity of component i, [bar]

F .... Total molar flowrate, [kgmole/hr]

k_1 .... rate constant for 1st rate equation of methanol synthesis reaction, [mol/kg s bar$^{-1/2}$]

k_2 .... rate constant for 2nd rate equation of methanol synthesis reaction, [mol/kg s bar$^{-1/2}$]

k_3 .... rate constant for 3rd rate equation of methanol synthesis reaction, [mol/kg s bar$^{-1/2}$]

K_i .... Adsorption equilibrium constant for component i, bar^{-1}

T .... *Temperature, K*

ρ_b .... *Density of catalytic bed, $[kg/m^3]$*