CHAPTER V

CASE STUDY 2: BI-REFORMING OF CO_2 INTO METHANOL

5.1 Base Case Design

5.1.1 Process Simulation

5.1.1.1 Initializations and Feeds

In this case, the process requires three raw materials including CO_2, natural gas and steam.

Steam, one of feeds to a bi-reforming reactor, is generated as a product of the process. Generally, steam results from the heat recovery of the effluents from reactors. The details of the heat recovery will be displayed in next sections.

Similar to the case study 1, CO_2 fed to this case is captured from flue gas of the coal-fired power plant which was discussed in the CO_2 hydrogenation process. The details of CO_2 capture process was presented in Section 5.1.1.1.1. To adapt for methanol productivity as pointed out in Chapter 5 (20000 kg/hr), the value of flowrate of CO_2 product is chosen at 6721 kg/hr.

In fact, natural gas consists of remarkable amounts of CO_2 and hydrogen sulfide. Therefore, before using for other purposes, natural gas needs to be treated by the acid gas removal process which almost completely removes CO_2 and hydrogen sulfide. This will allows natural gas to meet the pipeline standards and to secure reactor tubes from corrosion. In addition, a distillation column is ordered to separate heavier hydrocarbons from methane. The details of natural gas purification are not within the scope of this thesis, natural gas is assumed as pure methane. To adapt for methanol productivity (20000 kg/hr), the value of flowrate of methane is selected around 9460 kg/hr.

5.1.1.2 Bi-reforming Process

The process is reproduced from the work of Holm-Larsen (2001) as a CO_2 conversion process. A typical methanol production as shown in Figure 5.1 is selected as the base case design.

The major assumptions for simulation are as follows:

- The methanol productivity was fixed at around 20000 kg/hr with its purity higher than 99.5 percent.
- 100 percent purity of methane and CO_2 were used.
- The methanol reactions and kinetic model were employed from the study of Bussche *et al.* (1996).

5.1.1.2.1 Process Flowsheet Description

CO_2 at 1 bar is compressed to 25 bar through a string of compressors before mixing with methane and steam. Preheated by the hot flue gas from burning methane in the bi-reforming reactor, the new stream is fed to the reformer. The effluent from the reactor is cooled to 55°C by a series of heat exchangers, which allows water to be condensed and removed from syngas in the first flash drum.

Syngas from the top of the first flash drum is compressed to 63.3 bar and mixed with the recycle stream. Preheated by the effluent from the methanol reactor, the stream is fed to the isothermal reactor at 220°C. The outflow is expanded and cooled to 35°C and 60.3 bar before injected into the second flash drum to remove most residual gases. The remaining stream is expanded to 17.5 bar and fed to the topping column. At this column, unreacted gases and crude methanol are separated into the overhead and bottom. The final methanol product is purified to 99.7 wt% at the top of the distillation column.

Unreacted gases from the second flash drum and the topping column are mixed with a mixture of methane and air and then burned to support enough heat for the bi-reforming reactor.

The heat recovery system is established to increase the overall energy efficiency and reduce fuel usage. There are three different strategies applied in this case as below.

Heat Recovery from the Hot Syngas Stream

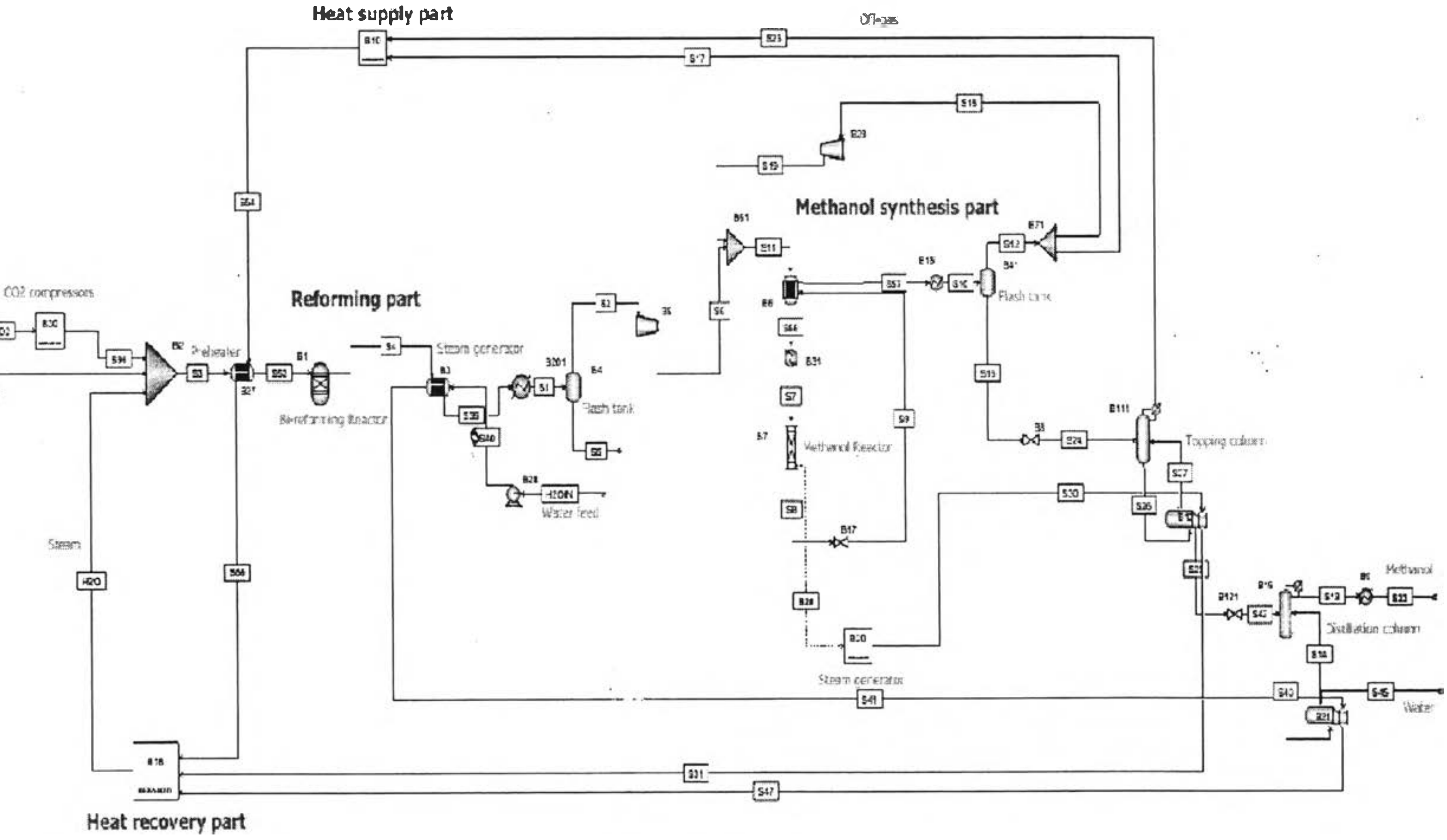
High pressure steam (42 bar, 287°C) was generated by the heat exchange with the hot syngas (920°C) coming out from the reformer. The generated steam is divided into 3 sub-streams; one is recycled to the feed, another is used as a supplementary heat source for the reboiler in the distillation column, and the other is used to generate electricity for supporting the power demand within the process via a 3-stage steam turbine system. The inlet pressures of the steam turbine are as follows: HP steam turbine - 42 bar, MP steam turbine - 16.5 bar, LP steam turbine - 6.5 bar.

Heat Recovery of the Hot Flue Gas Stream

Heat exchanger units with the hot flue gas (~1000°C) are applied to preheat the feed stream and vaporize the partially liquefied steam leaving each turbine.

Reaction Heat Recovery of the Methanol Reactor

Methanol synthesis reaction is extremely exothermic reaction; therefore, a cooling system should be applied to remove the heat and keep the reactor temperature at constant. Normally, the steam is produced by using the heat generated from the reactor. Here, a high pressure steam (42 bar and 253°C) is produced from the methanol reactor cooling system and they are used as a heating utility for the reboiler in the topping column, feed to the reformer and as a source to generate electricity.



5.1 Flowsheet of the bi-reforming of CO_2 into methanol for the base case design.

5.1.1.2.2 Process Input

From the published information, simulation is used to construct the base case. It is important to note that the publication by Holm-Larsen (2001) did not provide all necessary data, and, therefore, some values were made from other papers (Olah *et al.*, 2013; Van-Dal *et al.*, 2013). All input data are presented in Table 5.1.

Table 5.1 Input data of the methanol production

Feed Characteristics	
Variable	**Value**
Flow rate of CO_2 (kg/hr)	6721
Flow rate of CH_4 (kg/hr)	9460
Flow rate of H_2O (kg/hr)	26556
Bi-reforming Reactor Conditions	
Inlet temperature (°C)	920
Inlet pressure (bar)	25
Reactor model in Aspen Plus	Gibbs reactor
Methanol Reactor Conditions	
Inlet temperature (°C)	220
Inlet pressure (bar)	63
Reaction type	Exothermic
Reactor model in Aspen Plus	Plug flow reactor, kinetic model applied (Bussche *et al.*, 1996), isothermal reactor
Methanol Reactor Design	
Number of reactor tubes	2000
Tube diameter (m)	0.045
Tube length (m)	8
Bed voidage	0.4
Catalyst particle diameter (m)	0.0055
Catalyst density (kgcat/m^3cat)	1775
Separation Unit Designs	
The First Flash Tank	
Temperature (°C)	55
Pressure (bar)	25

The Second Flash Tank	
Temperature (°C)	35
Pressure (bar)	60.3
Topping Column	
Number of stages	4
1st stage pressure (bar)	17
Pressure drop (bar)	0.5
Reflux ratio	0.8
Distillation Column	
Number of stages	36
1st stage pressure (bar)	1
Pressure drop (bar)	0.1
Reflux ratio	0.75

5.1.1.3 Simulation Results

The inlets of the process are CO_2, methane, water and air feed. The outlet flows are flue gas, methanol as the top product and water as the bottom product from the distillation column, waste water and the steam. Mass balance and methanol product characterictis results are presented in Table 5.2 and 5.3, respectively.

Table 5.2 Mass balance

Inputs		**Outputs**	
	kg/hr		kg/hr
CO_2 Feed	6721	Flue gas	109395
H_2O Feed	53686	Water	20005
CH_4 Feed	13124	Methanol	20316
Air Feed	102561	Steam	26375
Sum	176091	**Sum**	176091

5.1.2 Sustainability Analysis

As this process is aimed to reduce CO_2 amount in atmosphere, the net CO_2 emission must be evaluated. To attain net CO_2 reduction, the process has to use more CO_2 than it discharges (such as from purge gas) or produces (primarily through energy requirements). The net CO_2 emission is described by the following equation.

$$n_{CO_2,net} = n_{CO_2,purge} + n_{CO_2,utilities} - n_{CO_2,feed} \quad (5.1)$$

This value is negative when the output amount of CO_2 from the process is lower than the input.

Table 5.3 Product characteristics

Variables	Value
Flow rate of methanol product (kg/hr)	20316
Purity (wt%)	99.7
Mass Fraction	
CO_2	85 PPM
H_2	8 PPB
Water	0.003
CO	10 PPB
CH_4	294 PPB
Methanol	0.997

Because the process uses pure CO_2 from the capture unit, CO_2 emission from this unit needs to be calculated for overall evaluation.

Table 5.4 Net CO_2 emission for methanol production

	Value	Unit
Direct (Purge)		
Flue gas	14808.4	kgCO$_2$/hr
Total Direct	14808.4	kgCO_2/hr
Indirect (Utilities)		
Electricity	-330.2	kgCO_2/hr
Total Indirect	-330.2	kgCO_2/hr
Feed	6770.8	kgCO_2/hr
CO_2 Capture	1073.5	kgCO_2/hr
Net CO_2 Emission	8780.9	kgCO_2/hr
	432.2	kgCO_2/tMeOH

Obviously, even though the process is used to reduce CO_2 emissions, operation of the conversion process leads to a non-negligible emission of CO_2 as illustrated in Table 5.4. Different from the CO_2 hydrogenation route, direct emission from burning methane to provide very high temperature for the reformer accounts for the main source of CO_2 emission in methanol production by bi-reforming process. It is around two times larger than the amount of CO_2 utilized in the feed stream. As a result, alternatives for heat support instead of burning of methane have to be assessed.

5.1.3 Economic Evaluation

Since the implementation of the final design is likely based on economic factors, an economic analysis is necessary to evaluate whether the process is feasible in terms of economy or not. This section of the report supports information of economic issue for the base case design which was calculated by using ECON software. The details to calculate the capital and production cost are presented in Appendix B.2.1.

This process design was modeled and simulated by the Aspen Plus 8.6 as mentioned earlier. The capacity of this plant is nearly 20000 kg/hr or around 162 kt/year. The plant operates 333 days/year or approximately 8000 hours/year.

5.1.3.1 Capital Cost of Base Case Design

The outcome of the Total Capital Investment (TCI) calculations for the base case design is 64.12 MM\$. The greatest share of 61 percent is from direct cost section, followed by indirect cost and working capital section comprising 24 and 15 percent, respectively as seen in Figure 5.2.

Clearly, Figure 5.2 shows the direct costs are what takes the largest piece in the capital investment, thus it is interesting to see what constitutes the direct costs.

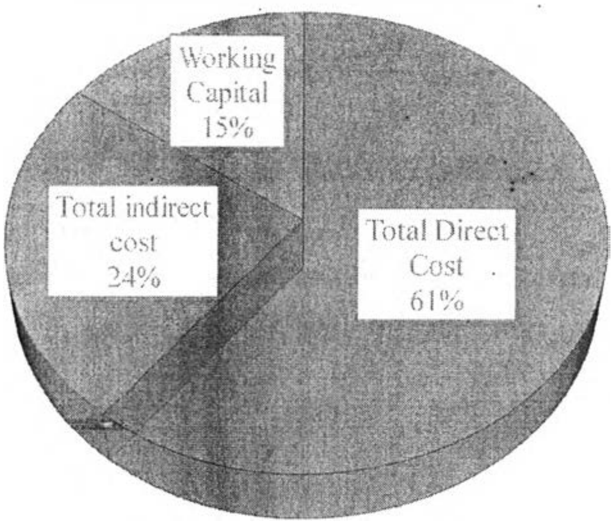


Figure 5.2 Breakdown of the total capital investment.

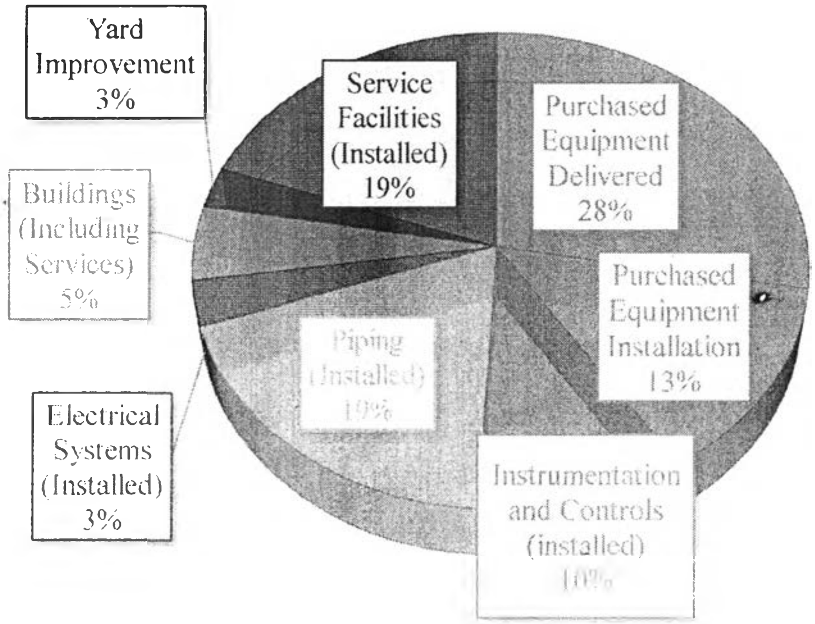


Figure 5.3 Breakdown of the direct cost.

As seen from Figure 5.3, the equipment costs (purchased equipment delivered) contribute the largest weight on the direct costs, hence, it is the most influence on the TCI. Table B.2.8 summarizes sizing and purchase cost of each equipment. The breakdown of equipment costs is illustrated in Figure 5.4 to gain further insight.

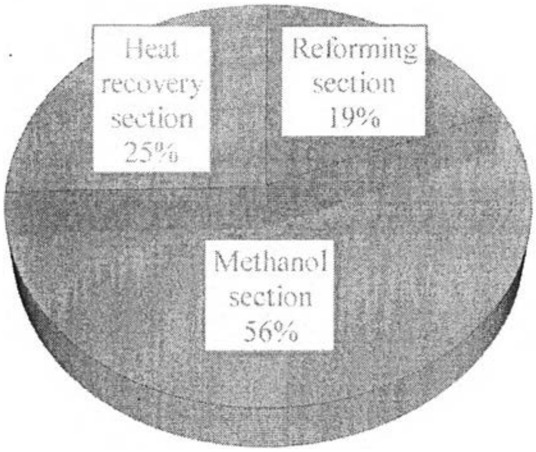


Figure 5.4 Contribution to equipment costs of each area of the process.

As shown in Figure 5.4, the methanol section has the highest portion in all equipment units which makes up 56 percent, followed by the heat recovery and reforming section with 25 and 19 percent, respectively.

5.1.3.2 Production Cost of Base Case Design

The result of the total production cost (without depreciation) calculations for the base case design is 67.89 MM$/year. The greatest share of around 67 percent comes from the variable cost section, followed by the plant overhead, general expenses and fixed charges section constituting 17, 14 and 2 percent, respectively. The breakdown of the total product cost can be seen in Figure 5.5.

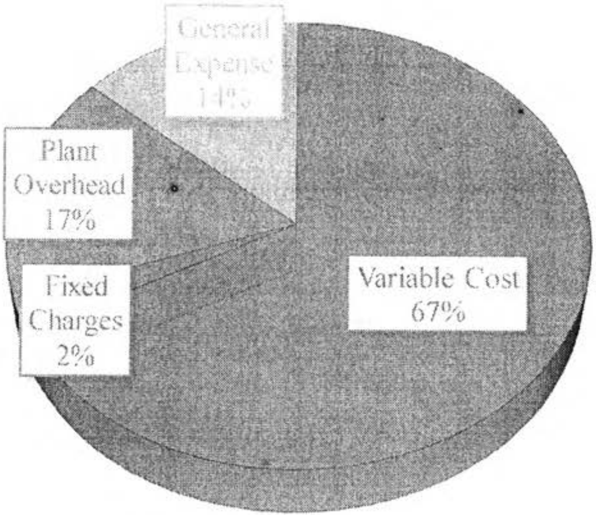


Figure 5.5 Breakdown of the total production cost.

Obviously, the variable cost is the highest portion for the total production cost which mainly results from raw materials as presented in Figure 5.6.

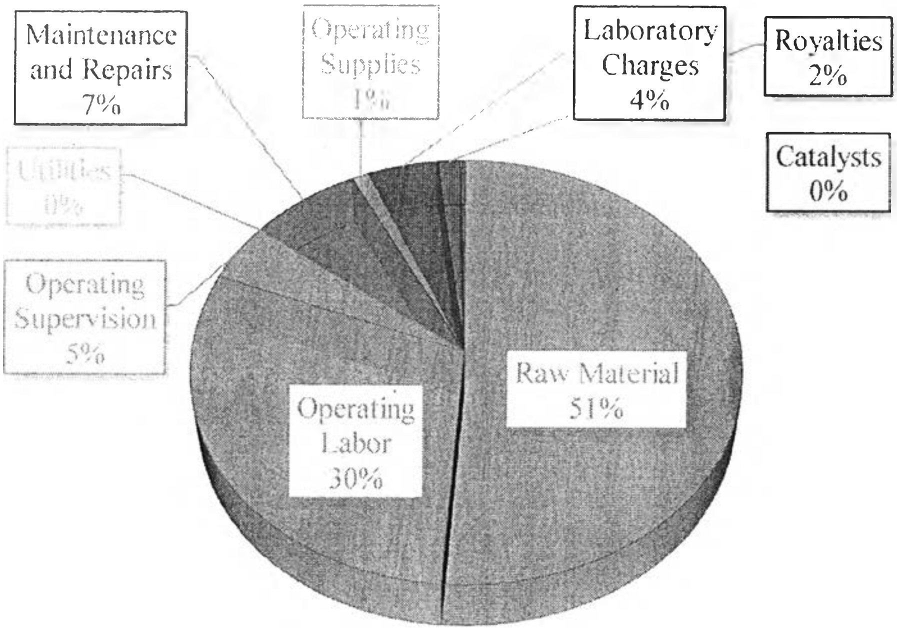


Figure 5.6 Breakdown of the variable cost.

Therefore, next interesting evaluation for the production cost is to show each of raw material to see which components have the most effects. The result is presented in Figure 5.7.

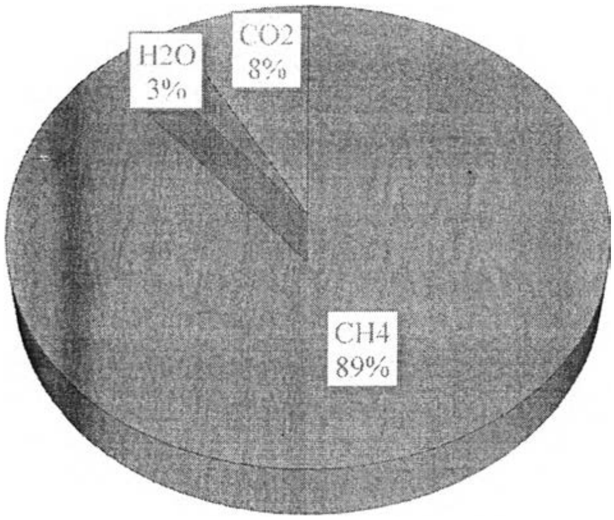


Figure 5.7 Breakdown of raw materials cost.

In a bi-reforming process, a large amount of methane is utilized to supply heat and the reactant in the bi-reforming reactor. Combining with the high price of methane, above 100 and 5 times higher than that of demineralized water and CO_2, respectively, the cost of methane accounts for nearly 90 percent of the cost for raw materials as illustrated in Figure 5.7.

5.1.3.3 Economic Sensitivity Analysis of Base Case Design

The economic sensitivity analysis is made to the raw materials, product price, labor cost, capital cost, equipment cost and utilities cost.

As seen from Figure 5.8, the highest influence on Net Present Value (NPV) is the price of product, which makes the product become the primary factor affecting the profit. Furthermore, the capital cost has the high impact on the NPV.

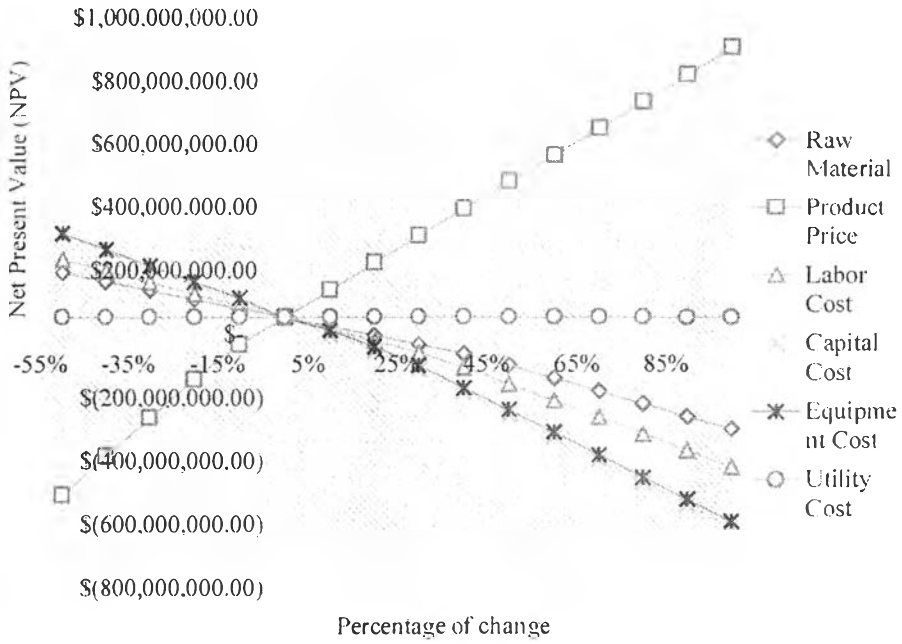


Figure 5.8 Sensitivity analysis compare to NPV.

5.1.3.4 Profitability of Base Case Design

Profitability is the measure of the amount of profit that can be obtained from a given situation. It is as common denominator for all business activities. The determination and analysis of profits obtainable from the investment of capital and the choice of the best investment among various alternatives are major goals of the investment analysis.

For this work, the life time of the project is assumed to be 20 years. The plant will be built in US. The MARR (Minimum Acceptable Rate of Return) is fixed to be 15 percent. The depreciation for the plant is estimated to be 20 years by MACRS method. The income tax rate that has to be paid to the government is assumed to be 30 percent. According to the increase of methanol price in the future, the inflation is set. The inflation rate of construction, product and total product cost are assumed to be 2 percent, 10 percent and 10 percent, respectively. The inflation rate of product is set by the real increasing price data in the previous year (Zicha, 2014) and the rests are set by using the product price as reference. The details of all assumption are presented in Table B.2.12. The summary of investment analysis for the base case design is shown in Table 5.5.

Table 5.5 Profitability of the base case

Profitability	
not include time value of money	
Rate of Return	38%
Pay Back Period	2.02
Net Return	$ 14,898,589.61
include time value of money	
Annual End of Year cash flows and discounting	
Net Present Worth	$ 34,805,987.00
DCFR	0.20
Continuous cash flows and discounting	
Net Present Worth	$ 37,338,698.23
DCFR	0.18

According to the result, all of the parameters are in high positive values which mean this project is clearly good for investment. Moreover, the cumulative cash flow and the breakeven points of the project shown in Figure 5.9 revealed that the process is likely to be the potential design to invest in terms of economic. However, the process did not meet the environmental requirement. After the process is improved, the profit and quality of environment should be increased concurrently.

5.2 Sensitivity Analysis

Özkara-Aydmoğlu (2010) indicated that the inlet reactor temperature, pressure and feed compositions to the reformer are key factors in the improvement of the syngas synthesis, resulting in higher methanol productivity. In addition, methanol yield depends on the inlet temperature and pressure of the methanol reactor as pointed out in Chapter 5. All factors, therefore, are varied respectively and observed how the net CO_2 emission and production cost are changing. The production cost in this section is calculated by the following equation.

$$\begin{aligned} &Production\ cost \\ &\qquad = Natural\ gas\ purchase\ cost \\ &\qquad + CO_2\ captured\ cost + Demineralized\ water\ cost \\ &\qquad + Utilities\ cost \end{aligned} \tag{5.2}$$

Although this is the simple form of the real production cost, it is still valuable to evaluate the process in this step. The reason is the production cost mainly depends on the cost of raw materials as discussed above. In addition, basically if the process structure does not change significantly between different scenarios, the variation of production cost leading to the change of capital cost will result in the same trend. Therefore, the above equation will be used as a tool to quickly evaluate the economic aspect in next sections.

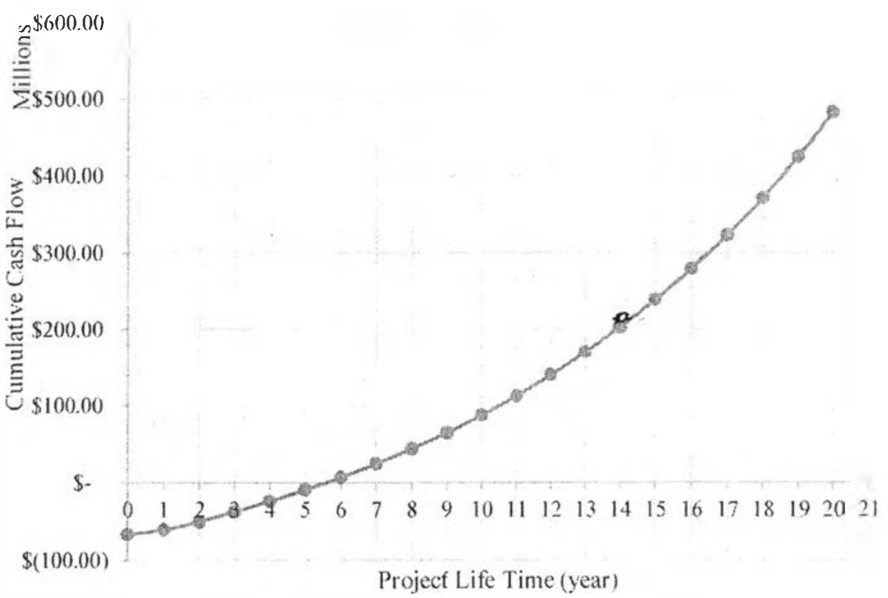


Figure 5.9 Cumulative cash flow for 20 year project of the base case.

To compare among difference scenarios, the methanol productivity is fixed at around 20000 kg/hr with its purity higher than 99.5 percent.

5.2.1 Bi-reforming-related Variables

5.2.1.1 Inlet Bi-reforming Reactor Temperature

Table 5.6 Relationship between the inlet bi-reforming reactor temperature and net CO_2 emission

Temperature (°C)	Direct CO_2 Emission (kg CO_2/tMeOH)	Indirect CO_2 Emission (kgCO_2/tMeOH)	Net CO_2 Emission (kg CO_2/tMeOH)	Methanol Productivity (kg/hr)	Methanol Purity
905	386.9	43.6	430.5	19987	0.9868
910	389.5	41.1	430.6	20116	0.9914
915	392.2	38.7	430.9	20239	0.9958
920	395.6	36.6	432.2	20316	0.9974

Table 5.7 Relationship between the inlet bi-reforming reactor temperature and production cost

Temperature (°C)	Energy Consumption (electricity) ($/tMeOH)	Water Consumption ($/tMeOH)	Methane Cost ($/tMeOH)	CO_2 Capture Cost ($/tMeOH)	Production Cost ($/tMeOH)
905	-0.9	5.9	125.8	11.9	142.6
910	-1.1	5.9	126.4	11.8	142.9
915	-1.3	5.8	127.0	11.7	143.3
920	-1.5	5.8	127.9	11.7	143.9

Tables 5.6 and 5.7 show the effect of the inlet bi-reforming reactor temperature on the net CO_2 emission and production cost. This plot shows that the lower the temperature of the reformer, the less net CO_2 emission and production cost per ton of methanol is observed. When the temperature increases, more power generation from the reformer outlet stream contributes to the reduction of net power demand as well as indirect CO_2 emission. However, this trend could not compensate for the increase of direct CO_2 emission due to the increase in natural gas burning at elevated temperatures. Similarly, the decrease of electricity cost could not offset the rise of natural gas cost when higher temperature is employed. The temperature at 915°C is chosen as the new temperature of the process because it satisfies the constraints mentioned above. Noting that in this study the process generated more

electricity power than that it required, the energy consumption therefore has the negative value.

5.2.1.2 Inlet Bi-reforming Reactor Pressure

Table 5.8 Relationship between the inlet bi-reforming reactor pressure and net CO_2 emission

Pressure (bar)	Direct CO_2 Emission ($kgCO_2$/tMeOH)	Indirect CO_2 Emission ($kgCO_2$/tMeOH)	Net CO_2 Emission ($kgCO_2$/tMeOH)	Methanol Productivity (kg/hr)	Methanol Purity
25	392.2	38.7	430.9	20239	0.9958
27	394.2	36.3	430.5	20024	0.9886
29	396.2	34.5	430.7	19817	0.9815
31	398.2	33.3	431.6	19613	0.9744

Table 5.9 Relationship between the inlet bi-reforming reactor pressure and production cost

Pressure (bar)	Energy Consumption (electricity) ($/tMeOH)	Water Consumption ($/tMeOH)	Methane Cost ($/tMeOH)	CO_2 Capture Cost ($/tMeOH)	Production Cost ($/tMeOH)
25	-1.3	5.8	127.0	11.7	143.3
27	-1.6	5.8	126.5	11.8	142.6
29	-1.8	5.9	125.9	12.0	141.9
31	-2.0	5.9	125.4	12.1	141.4

Interestingly, when the reformer pressure changes, there is a trade-off in terms of net CO_2 emission. The pressure at 27 bar shows the lowest net CO_2 emission as illustrated in Table 5.8. At higher pressure, the direct CO_2 emission increases because of the less methanol productivity which results from the lower CO/CO_2. At the same time, less electric power at the syngas compressor and more power generation cause less indirect CO_2 emission. These two trends are toward the opposite direction and nothing seems to be more significant than another. It is noticed and the best performance is obtained at 27 bar. Meanwhile, a decrease of production cost is witnessed when higher pressure is used as a consequence of higher electric power generation and lower natural gas burning as shown in Table 5.9. However, the base case is still kept as the operating pressure of 25 bar since the process can produce pure methanol with 99.5 percent and 20000 kg/hr. Noting that in this study the process generated more electricity power than that it required, the energy consumption therefore has the negative value.

5.2.1.3 CO_2 Feed Ratio

Table 5.10 Relationship between the CO_2/CH_4 ratio and net CO_2 emission

Ratio of CO_2/CH_4	Direct CO_2 Emission ($kgCO_2/tMeOH$)	Indirect CO_2 Emission ($kgCO_2/tMeOH$)	Net CO_2 Emission ($kgCO_2/tMeOH$)	Methanol Productivity (kg/hr)	Methanol Purity
0.212	398.2	37.5	435.7	19703	0.9768
0.229	395.8	37.3	433.1	19902	0.9839
0.246	393.8	37.9	431.6	20092	0.9906
0.259	392.2	38.7	430.9	20239	0.9958
0.261	391.8	38.9	430.7	20268	0.9968

Table 5.11 Relationship between the CO_2/CH_4 ratio and production cost

Ratio of CO_2/CH_4	Energy Consumption (electricity) (\$/tMeOH)	Water Consumption (\$/tMeOH)	Methane Cost (\$/tMeOH)	CO_2 Capture Cost (\$/tMeOH)	Production Cost (\$/tMeOH)
0.212	-0.7	6.0	125.6	9.9	140.8
0.229	-0.9	5.9	126.1	10.5	141.6
0.246	-1.2	5.9	126.6	11.2	142.5
0.259	-1.3	5.8	127.0	11.7	143.3
0.261	-1.3	5.8	127.1	11.8	143.4

Table 5.10 shows the relationship between the CO_2/CH_4 ratio and net CO2 emission. The more the CO_2 feed is introduced, the less net CO_2 emission per ton of methanol is observed. When more CO_2 is injected, the direct CO_2 emission decreases because of higher methanol productivity. Regarding the production cost, the story is completely different. As the CO_2/CH_4 ratio increases, the production cost of the process increases as shown in Table 5.11. Although increasing of CO_2 feed makes the cost of electricity reduce, it cannot offset the increase of cost of buying more natural gas to burn and capturing more CO_2 from flue gases. In this case, the base case (0.259) is still employed to guarantee the methanol yield and purity. Noting that in this

study the process generated more electricity power than that it required, the energy consumption therefore has the negative value.

5.2.1.4 H_2O Feed Ratio

Table 5.12 Relationship between the H_2O/CH_4 ratio and net CO_2 emission

Ratio of H_2O/CH_4	Direct CO_2 Emission ($kgCO_2/tMeOH$)	Indirect CO_2 Emission ($kgCO_2/tMeOH$)	Net CO_2 Emission ($kgCO_2/tMeOH$)	Methanol Productivity (kg/hr)	Methanol Purity
2.442	392.3	36.2	428.5	20140	0.9930
2.459	392.2	37.0	429.2	20168	0.9938
2.476	392.2	37.7	430.0	20197	0.9946
2.493	392.2	38.4	430.6	20227	0.9954
2.500	392.2	38.7	430.9	20239	0.9958
2.510	392.1	39.2	431.3	20257	0.9963

Table 5.13 Relationship between the H_2O/CH_4 ratio and production cost

Ratio of H_2O/CH_4	Energy Consumption (electricity) ($/tMeOH)	Water Consumption ($/tMeOH)	Methane Cost ($/tMeOH)	CO_2 Capture Cost ($/tMeOH)	Production Cost ($/tMeOH)
2.442	-1.6	5.8	126.8	11.8	142.8
2.459	-1.5	5.8	126.8	11.8	143.0
2.476	-1.4	5.8	126.9	11.7	143.1
2.493	-1.3	5.8	127.0	11.7	143.2
2.500	-1.3	5.8	127.0	11.7	143.3
2.510	-1.3	5.8	127.1	11.7	143.3

Tables 5.12 and 5.13 show the relationship between the H_2O/CH_4 ratio and net CO_2 emission as well as production cost. The more the H_2O feed is introduced, the more net CO_2 emission per ton of methanol is observed. When more H_2O is injected, even though less amount of direct CO_2 emission acquires due to the decrease of CO_2 released from the stack, the increase of the indirect CO_2 emission is more significant. Additionally, quite noticeable rise of production cost is observed at higher ratios. Lower power generation and higher natural gas usage are main factors contributing to the increase of production cost. The new operating condition of H_2O/CH_4 ratio of 2.493 is selected after this step. Noting that in this study the process

generated more electricity power than that it required, the energy consumption therefore has the negative value.

5.2.2 Methanol Synthesis-related Variables

5.2.2.1 Inlet Methanol Reactor Temperature

Table 5.14 Relationship between the inlet methanol reactor temperature and net CO_2 emission

Temperature (°C)	Direct CO_2 Emission (kgCO$_2$/tMeOH)	Indirect CO_2 Emission (kgCO$_2$/tMeOH)	Net CO_2 Emission (kgCO$_2$/tMeOH)	Methanol Productivity (kg/hr)	Methanol Purity
215	390.8	37.1	428.0	20280	0.9971
220	392.2	38.4	430.6	20227	0.9954
230	396.2	43.2	439.4	20069	0.9903
240	401.4	50.1	451.5	19856	0.9832
245	404.4	54.2	458.6	19729	0.9789

Table 5.15 Relationship between the inlet methanol reactor temperature and production cost

Temperature (°C)	Energy Consumption (electricity) ($/tMeOH)	Water Consumption ($/tMeOH)	Methane Cost ($/tMeOH)	CO_2 Capture Cost ($/tMeOH)	Production Cost ($/tMeOH)
215	-1.4	5.8	127.1	11.7	143.1
220	-1.3	5.8	127.0	11.7	143.2
230	-0.9	5.9	126.8	11.8	143.5
240	-0.4	6.0	126.5	11.9	144.0
245	0.0	6.0	126.2	12.0	144.3

When changing the inlet reactor temperature, the process shows the lowest net CO_2 emission at the inlet reactor temperature of 215°C as illustrated in Table 5.14. Because the methanol synthesis from CO_2 and hydrogen is exothermal reaction, it is disadvantageous to methanol production when the reaction temperature increases. As a result, the direct CO_2 emission increases because of more unreacted CO_2 in purge gases. In addition, at higher temperatures, higher unreacted gases require more energy at the recycle compressor, which leads to an increase of indirect CO_2 emission. At lower inlet temperatures, the reaction is kinetically limited, which makes simulation not converge. Additionally, quite noticeable rise of the production cost is observed in Table 5.15 due to the higher requirement of electricity demand when elevated temperatures are employed. In this step, 215°C is chosen as the new temperature of the process. Noting that in this study the process generated more electricity power than that it required, the energy consumption therefore has the negative value.

5.2.2.2 Inlet Methanol Reactor Pressure

Table 5.16 Relationship between the inlet methanol reactor pressure and net CO_2 emission

Pressure (bar)	Direct CO_2 Emission ($kgCO_2$/tMeOH)	Indirect CO_2 Emission ($kgCO_2$/tMeOH)	Net CO_2 Emission ($kgCO_2$/tMeOH)	Methanol Productivity (kg/hr)	Methanol Purity
55	397.5	31.2	428.7	20051	0.9897
57	395.8	32.5	428.3	20110	0.9916
59	394.1	34.0	428.1	20167	0.9934
61	392.5	35.5	428.0	20222	0.9952
63	390.8	37.1	428.0	20280	0.9971

Table 5.17 Relationship between the inlet methanol reactor pressure and production cost

Pressure (bar)	Energy Consumption (electricity) ($/tMeOH)	Water Consumption ($/tMeOH)	Methane Cost ($/tMeOH)	CO_2 Capture Cost ($/tMeOH)	Production Cost ($/tMeOH)
55	-2.1	5.9	126.8	11.8	142.5
57	-1.9	5.9	126.9	11.8	142.6
59	-1.8	5.8	126.9	11.8	142.8
61	-1.6	5.8	127.0	11.7	143.0
63	-1.4	5.8	127.1	11.7	143.1

Table 5.16 shows that the higher the pressure of the methanol reactor is applied, the less net CO_2 emission per ton of methanol is observed. Obviously, since the methanol production causes a decline in the number of moles, the reaction is appropriate to elevated pressures. Hence, the direct CO_2 emission decreases

due to a lower amount of CO_2 released from the stack. However, the higher the inlet pressure is applied, the more electric power at the inlet and recycle compressors is required, leading to more indirect CO_2 emission. In this case, the increase of indirect CO_2 emission is made up for by the decrease of direct CO_2 emission. Therefore, less net CO_2 emission is seen at higher pressures. Contradictory to the net CO_2 emission, the increase of production cost is observed as the pressure increases due to the lower power generation and higher electricity demand as seen in Table 5.17. In this case, 61 bar is selected as a new operating pressure. Noting that in this study the process generated more electricity power than that it required, the energy consumption therefore has the negative value.

5.2.3 Optimal Design Factors and Performance Results

Table 5.18 Comparison of operating conditions between the optimized and base case

Specification	Base Case	Optimized Case
Reforming Variables		
Inlet reactor temperature (°C)	920	915
Inlet reactor pressure (bar)	25	25
CO_2/CH_4	0.259	0.259
H_2O/CH_4	2.500	2.493
Methanol Synthesis Variables		
Inlet reactor temperature (°C)	220	215
Inlet reactor pressure (bar)	63	61

After the sensitivity analysis, new operating conditions of the process are presented in Table 5.18. Table 5.19 shows and compares the results the optimized case with those from the base case. Obviously, the optimized case shows good competitiveness to the base case in terms of environment as well as economy. Regarding net CO_2 emission, there is a slight reduction of 1 percent from 432.2 to 428.0 $kgCO_2/tMeOH$. The process witnesses a decrease of 0.26 MM$ in an amount of capital cost of the optimized case as compared to the base case while the most dramatic decrease is seen in the production cost of the optimized case with a reduction of 0.47 MM$/year.

Table 5.19 Comparison of environmental and economic aspects between the optimized and base case

Specification	Base Case	Optimized Case
Net CO_2 emission ($kgCO_2/tMeOH$)	432.2	428.0
Capital cost (MM$)	64.12	63.86
Production cost (MM$/year)	67.89	67.42

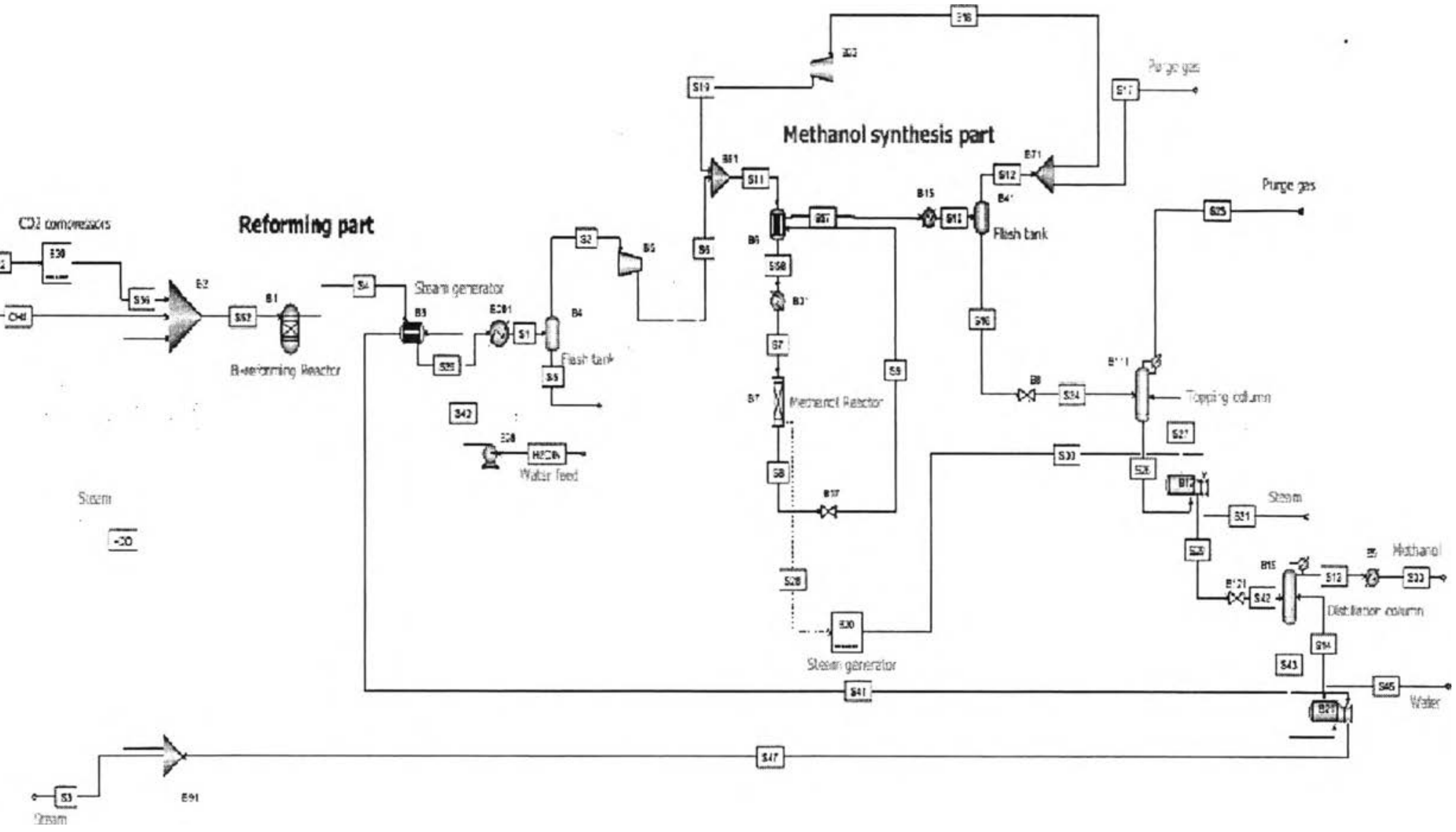
Although the optimized case achieves better results than the base case in both CO_2 emission and economic aspects, the process is still far from our target in terms of negative net CO_2 emission.

5.3 Alternative Design Ideas

From the results of sustainability analysis and economic evaluation, the alternative idea is to employ some free heat from the power plant. The purpose of this alternative is to avoid burning natural gas to support heat for the reformer. The flowsheet of this process is presented in Figure 5.10.

5.3.1 Performance Results

As seen in Table 5.20, the alternative shows the better results in terms of economy. Because the new process does not consist of power generation systems, it allows to reduce the cost to construct the plant. The capital cost witnesses a significant decrease of around 23 percent from 63.86 to only 49.01 MM$. In addition, there is a remarkable decline in the production cost of approximately 13 MM$ annually from 67.42 to a mere 54.08 MM$ per year. Those savings permit the process to become more feasible in terms of economy as pointed out in Figure 5.11.



5.10 Flowsheet of the bi-reforming of CO_2 into methanol for the alternative case design.

Table 5.20 Comparison of environmental and economic aspects between the optimized and alternative case

Specification	Optimized Case	Alternative Case
Net CO_2 emission ($kgCO_2/tMeOH$)	428.0	1257.1
Capital cost (MM$)	63.86	49.01
Production cost (MM$/year)	67.42	54.08

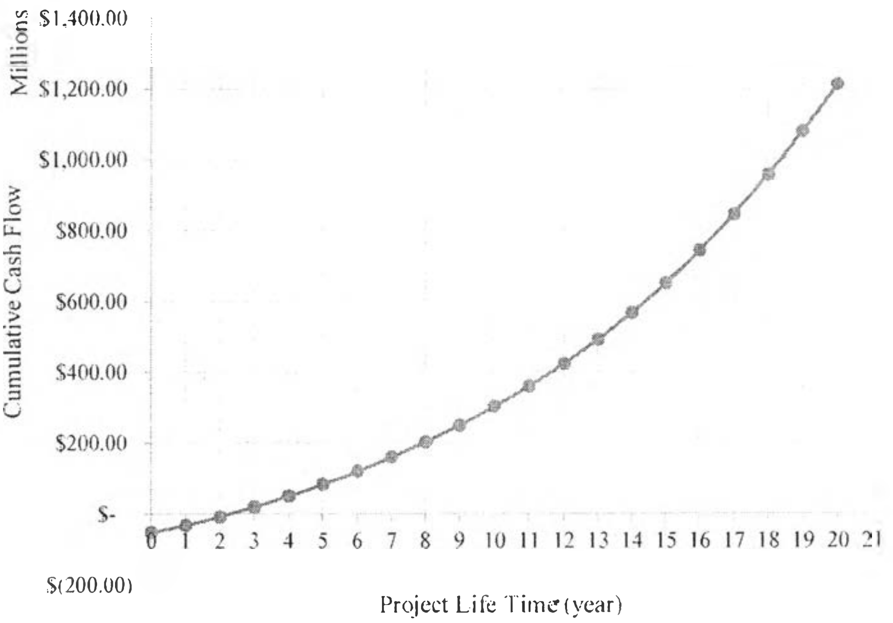


Figure 5.11 Cumulative cash flow for 20 year project of the alternative case.

Interestingly, although the new process does not need the burning of natural gas for heat support, the net CO_2 emission is notably higher than that from the optimized case. Thus, it is necessary to find out reasons to explain this problem. A complete detail in terms of CO_2 emission of the alternative process is presented in Table 5.21.

Table 5.21 Net CO_2 emission for methanol production

	Value	Unit
Direct (Purge)		
Purge gas 1	22693.8	kgCO_2/hr
Purge gas 2	5655.7	kgCO_2/hr
Total Direct	28349.4	kgCO_2/hr
Indirect (Utilities)		
Electricity	2720.7	kgCO_2/hr
Total Indirect	2720.7	kgCO_2/hr
Feed	6721.3	kgCO_2/hr
CO_2 Capture	1073.5	kgCO_2/hr
Net CO_2 Emission	25422.4	kgCO_2/hr
	1257.1	kgCO_2/tMeOH

Obviously, direct CO_2 emission accounts for the main source of CO_2 emission in the alternative case. It is around ten times larger than the amount of CO_2 created by electricity. Direct CO_2 emission results from purge gases released from the stacks, consisting of purge gas 1 and 2 with full details displayed in Table 5.22.

Table 5.22 Purge gas stream characteristics

Variable	**Value**	
	Purge gas 1	**Purge gas 2**
Flow rate (kg/hr)	2191	1143
Mass flow components (kg/hr)		
CO_2	723	773
CH_4	879	195
CO	202	23
H_2	342	27
Water	2	2
Methanol	43	123

As pointed out in Table 5.22, both purge gas streams contain a noticeable amount of unreacted reactants such as methane, carbon oxide and hydrogen beside CO_2. CO_2 is the primary greenhouse gas emitted through human activities but methane is one of the most severe greenhouse gas. This can be explained by the fact that methane traps radiation more efficiently than CO_2 although its lifetime in the air is quite shorter than CO_2. Therefore, if methane exists in the process, it must be reported as carbon equivalents of global warming potential (GWP). The calculation of GWP is described by the following equation

$$GWP = F_{CO_2} + 25F_{CH_4} + 298F_{N_2O} \tag{5.3}$$

Clearly, a significant volume of methane is emitted from the alternative process, which results in a remarkable increase of direct CO_2 emission particularly as well as net CO_2 emission in general. Apparently, unreacted methane plays a key role in controlling CO_2 emission reduction in the alternative case.