

CHAPTER VI

CASE STUDY 3: TRI-REFORMING OF CO₂ INTO METHANOL

6.1 Base Case Design

6.1.1 Process Simulation

6.1.1.1 *Initializations and Feeds*

In this case, the process requires three raw materials including flue gas, natural gas and steam. The process allows to convert CO₂ directly without CO₂ separation, leading to a significant reduce in an amount of energy needed from the power plant.

Steam, one of the 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.

In fact, natural gas consists of remarkable amounts of CO₂ 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 CO₂ 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 employed 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 as pointed out in Chapter 5 (20000 kg/hr), the value of flowrate of methane is selected around 9132 kg/hr.

There are two main types of flue gas resulting from natural gas-fired power plants and coal-fired boilers. Typical components for the first may contain 8-10 percent CO₂, 18-20 percent H₂O, 2-3 percent O₂ and 67-72 percent N₂ while those from the latter may include 12-14 percent CO₂, 8-10 percent H₂O, 3-5 percent O₂ and 72-77 percent N₂. SO_x, NO_x and particulate matters could be removed effectively by pollution control technologies but an amount of main constituents remain largely unchanged. As pointed out from Chapter 5, flue gas from a coal-fired

power plant is used as the feed in this work. To adapt for methanol productivity (20000 kg/hr), the value of flowrate of the flue gas is selected around 29856 kg/hr.

6.1.1.2 Tri-reforming Process

The process is reproduced from the work of Minutillo *et al.* (2010); Zhang *et al.* (2013) as a CO₂ conversion process. A typical methanol production as shown in Figure 6.1 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 was used.
- The methanol reactions and kinetic model were employed from the study of Bussche *et al.* (1996).

6.1.1.2.1 Process Flowsheet Description

The feed flue gas is mixed with methane and steam before preheated by the hot flue gas from burning of methane. The preheated feed is then sent to the tri-reforming reactor at 850°C and 1 bar. The effluent from the reactor is cooled to 55°C before compressed to 65.3 bar by a series of compressors and flash drums which allows water to be condensed and removed from syngas. Syngas then is mixed with the recycle stream. After preheated by the effluent from the methanol reactor, the syngas is fed to the isothermal reactor at 220°C to produce methanol. The outflow is expanded and cooled to 35°C and 62.3 bar before injected into the flash drum to remove unreacted gases.

The liquid flow is expanded to 1.2 bar through valves before injected into the flash drum to remove most residual gases. The remaining stream is heated up to 80°C and fed to the distillation column. While the bottom of the column is water, pure methanol comes out of the top in gaseous phase.

Unreacted gases from flash drums are mixed with a mixture of methane and air and then burned to support enough heat for the tri-reforming reactor.

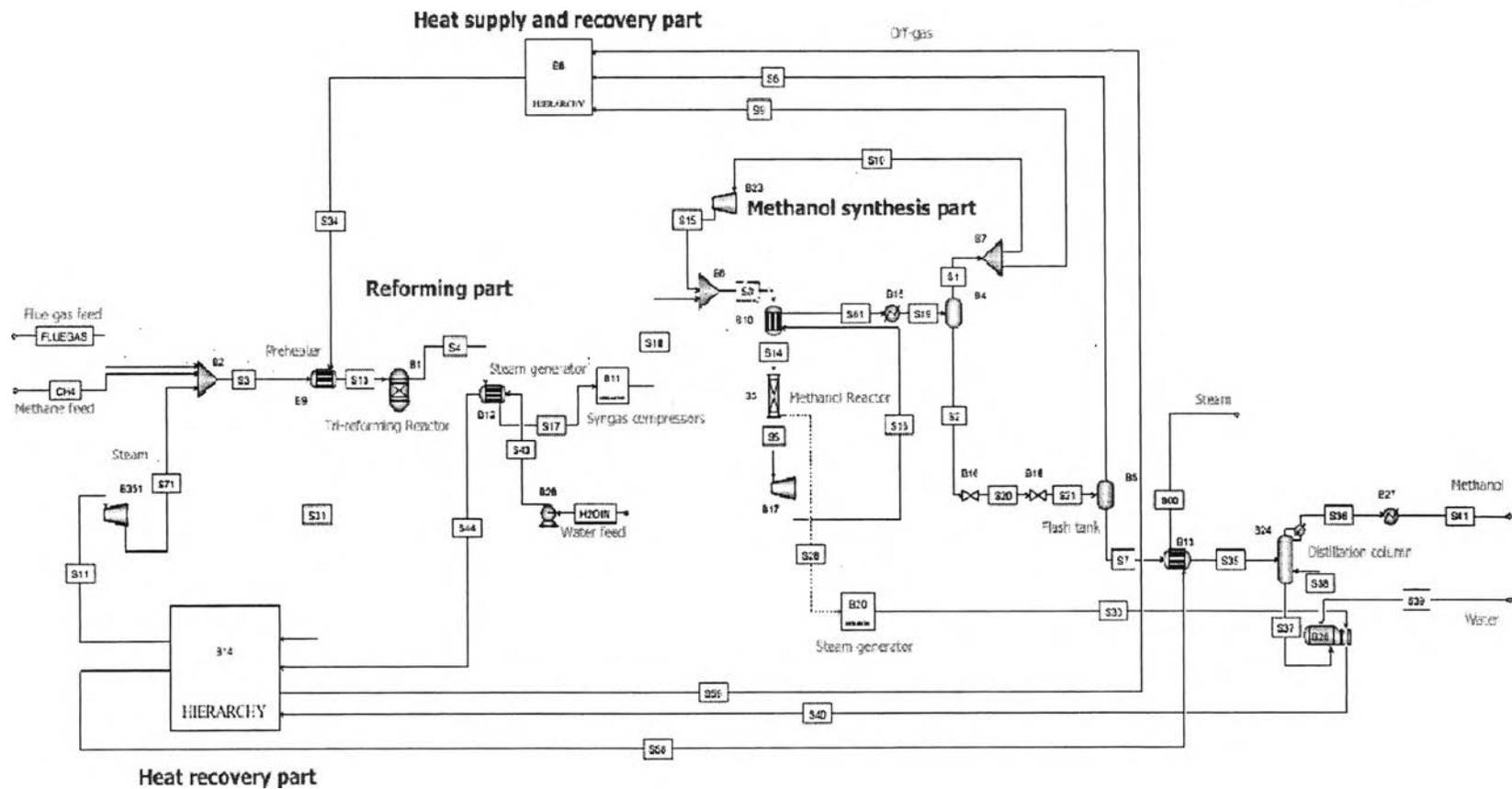


Figure 6.1 Flowsheet of the tri-reforming of CO₂ into methanol for the base case design.

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, 337°C) was generated by the heat exchange with the hot syngas (850°C) coming out from the tri-reforming reactor. The generated steam is divided into 2 sub-streams; one is recycled to the feed and another is used to generate electricity for supporting the power demand via 3-stage steam and gas turbine systems. The inlet pressures of the steam turbine are as follows: HP steam turbine - 42 bar, MP steam turbine - 16.5 bar and LP steam turbine - 6.5 bar. The inlet pressures of the gas turbine are as follows: HP gas turbine - 62.3 bar, MP gas turbine - 20 bar and LP gas turbine - 8 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 and gas streams leaving each turbine.

Reaction Heat Recovery of the Methanol Reactor

Since methanol synthesis reaction is extremely exothermic reaction, a cooling system must 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, high pressure steam (42 bar and 253°C) is produced from the methanol reactor cooling system and it is used as a heating utility for the reboiler in the distillation column, feed to the reformer and as a source to generate the electricity.

6.1.1.2.2 Process Input

From the published information, simulation is used to construct the base case. It is important to note that the publication does not provide all the necessary data, and therefore some values were made from other papers (Minutillo *et al.*, 2010; Van-Dal *et al.*, 2013). All input data are presented in Table 6.1.

Table 6.1 Input data of the methanol production

| Feed Characteristics | |
|---|---|
| Variable | Value |
| Flow rate of flue gas (kg/hr) | 29856 |
| Flow rate of CH ₄ (kg/hr) | 9132 |
| Flow rate of H ₂ O (kg/hr) | 7085 |
| Tri-reforming Reactor Conditions | |
| Inlet temperature (°C) | 850 |
| Inlet pressure (bar) | 1 |
| Reactor model in Aspen Plus | Gibbs reactor |
| Methanol Reactor Conditions | |
| Inlet temperature (°C) | 220 |
| Inlet pressure (bar) | 65 |
| Reaction type | Exothermic |
| Reactor model in Aspen Plus | Plug flow reactor, kinetic model applied (Bussche <i>et al.</i> , 1996), isothermal reactor |
| Methanol Reactor Design | |
| Number of reactor tubes | 13000 |
| Tube diameter (m) | 0.045 |
| Tube length (m) | 11 |
| Bed voidage | 0.4 |
| Catalyst particle diameter (m) | 0.0055 |
| Catalyst density (kgcat/m ³ cat) | 1775 |
| Separation Unit Designs | |
| The First Flash Tank | |
| Temperature (°C) | 35 |
| Pressure (bar) | 62.3 |
| The Second Flash Tank | |
| Temperature (°C) | 31 |
| Pressure (bar) | 1.2 |
| Distillation Column | |
| Number of stages | 28 |
| 1 st stage pressure (bar) | 1 |
| Pressure drop (bar) | 0.1 |
| Reflux ratio | 0.6 |

6.1.1.3 Simulation Results

The inlets of the process are the flue gas, methane, water and air feed. The outlet flows are the flue gas, methanol as the top product and water as the bottom product of the distillation column, waste water and the steam. Mass balance and methanol product characteristics results are presented in Table 6.2 and 6.3, respectively.

Table 6.2 Mass balance

| Inputs | | Outputs | |
|-----------------------|---------------|------------|---------------|
| | kg/hr | | kg/hr |
| Flue gas Feed | 29856 | Flue gas | 126782 |
| H ₂ O Feed | 41508 | Water | 677 |
| CH ₄ Feed | 13112 | Methanol | 20055 |
| Air Feed | 98539 | Steam | 34187 |
| Sum | 183014 | Sum | 183013 |

Table 6.3 Product characteristics

| Variable | Value |
|---------------------------------------|---------|
| Flow rate of methanol product (kg/hr) | 20055 |
| Purity (wt%) | 99.6 |
| Mass Fraction | |
| CO ₂ | 0.001 |
| CH ₄ | 5 PPM |
| CO | 12 PPM |
| H ₂ | 2 PPM |
| Water | 0.003 |
| Methanol | 0.996 |
| N ₂ | 131 PPM |

6.1.2 Sustainability Analysis

As this process is aimed to reduce CO₂ amount in atmosphere, the net CO₂ emission must be evaluated. To attain net CO₂ reduction, the process has to use more CO₂ than it discharges (such as from purge gas) or produces (primarily through energy requirements). The net CO₂ emission is described by the following equation.

$$n_{CO_2,net} = n_{CO_2,purge} + n_{CO_2,utilities} - n_{CO_2,feed} \quad (6.1)$$

This value is negative when the output amount of CO₂ from the process is lower than the input.

Obviously, even though the process is used to reduce CO₂ emissions, operation of the conversion process leads to a non-negligible emission of CO₂ as illustrated in Table 6.4. Different from the CO₂ hydrogenation route, direct emission from burning methane to provide very high temperature for the reformer accounts for the main source of CO₂ emission in the tri reforming process. Table 6.4 shows that the amount of CO₂ emission from direct burning of methane is around three times larger than the amount of CO₂ created by using electricity as well as two times higher than the CO₂ feed to the process. As a result, alternatives for heat support instead of burning of methane have to be assessed.

Table 6.4 Net CO₂ emission for methanol production

| | Value | Unit |
|------------------------------------|---------|--------------------------|
| Direct (Purge) | | |
| Flue gas from burning of methane | 14596.2 | kgCO ₂ /hr |
| Total Direct | 14596.2 | kgCO ₂ /hr |
| Indirect (Utilities) | | |
| Electricity | 4158.0 | kgCO ₂ /hr |
| Total Indirect | 4158.0 | kgCO ₂ /hr |
| Feed | | |
| | 6232.1 | kgCO ₂ /hr |
| Net CO₂ Emission | 12522.1 | kgCO ₂ /hr |
| | 624.4 | kgCO ₂ /tMeOH |

6.1.3 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.3.1.

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.

6.1.3.1 Capital Cost of Base Case Design

The outcome of the Total Capital Investment (TCI) calculations for the base case design is 196.71 MM\$. The greatest share of 61 percent is from direct cost section, followed by indirect cost and working capital section comprising of 24 and 15 percent, respectively as seen in Figure 6.2.

Clearly, Figure 6.2 shows that the direct costs are what takes the largest piece in the capital investment, thus it is interesting to see what constitutes the direct costs.

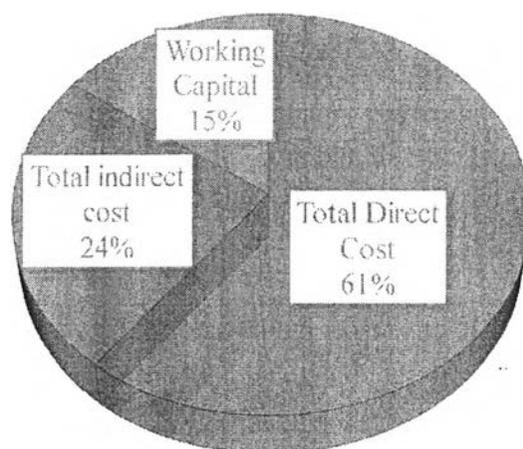


Figure 6.2 Breakdown of the total capital investment.

As seen from Figure 6.3, 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.3.8 summarizes sizing and purchased cost of each equipment. The breakdown of equipment costs is illustrated in Figure 6.4 to gain further insight.

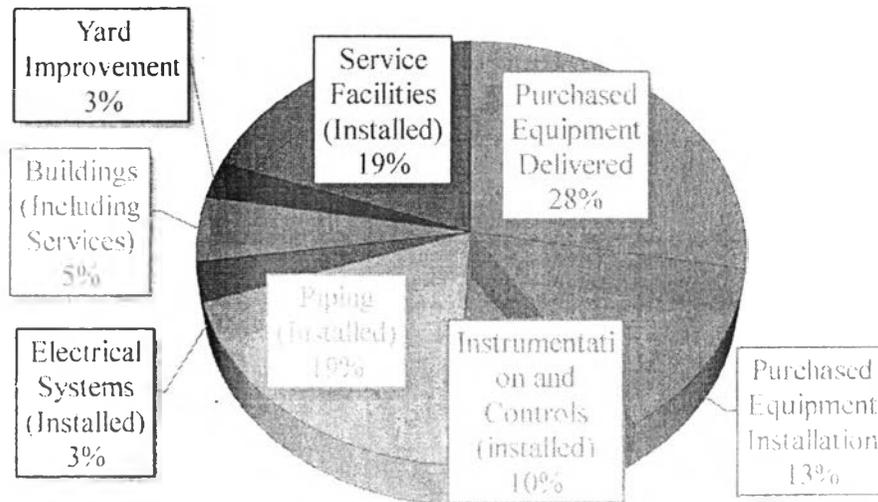


Figure 6.3 Breakdown of the direct cost.

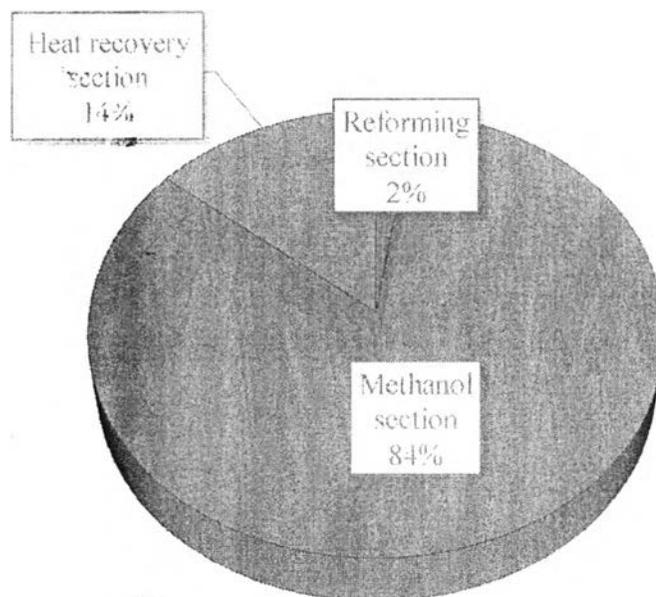


Figure 6.4 Contribution to equipment costs of each area of the process.

As shown in Figure 6.4, 84 percent of the equipment cost comes from the methanol plant, which contributes the highest portion in all equipment

units, followed by the heat recovery and the reforming part with 14 and 2 percent, respectively.

6.1.3.2 Production Cost of Base Case Design

The total production cost (without depreciation) for the base case design is 96.10 MM\$/year. The greatest share of around 63 percent comes from the variable cost section, followed by the plant overhead, general expense and fixed charges section, constituting 18, 14 and 5 percent, respectively. The breakdown of the total product cost can be seen in Figure 6.5.

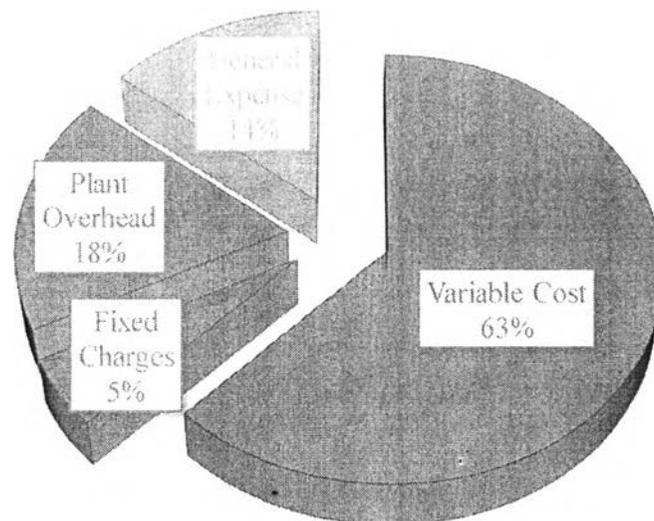


Figure 6.5 Breakdown of the total production cost.

Obviously, the variable cost is the highest portion for the total production cost which mainly results from raw materials and operating labor section as presented in Figure 6.6.

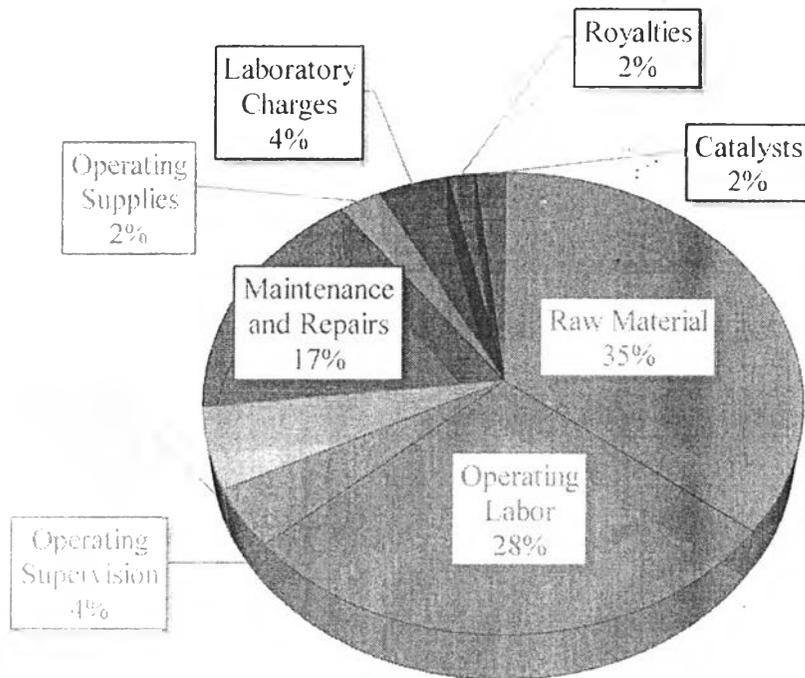


Figure 6.6 Breakdown of the variable cost.

Because the operating labor section depends on the capital cost; therefore, next interesting evaluation for the production cost is to show each of raw material to see which components have the most effects. These results are presented in Figure 6.7.

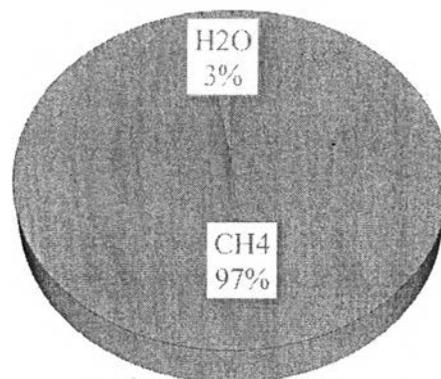


Figure 6.7 Breakdown of raw materials cost.

In a tri-reforming process, a large amount of methane is utilized to supply heat and the reactant in the tri-reforming reactor. Combining with the high price of methane, above 100 times higher than that of demineralized water, the cost of methane accounts for 97 percent of the cost for raw materials as illustrated in Figure 6.7.

6.1.3.3 Economic Sensitivity Analysis of Base Case Design

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

As seen from Figure 6.8, the highest influence to the Net Present Value (NPV) is the capital cost and this makes the capital cost become the primary factor affecting the profit. Furthermore, the price of methanol has the high impact on the NPV.

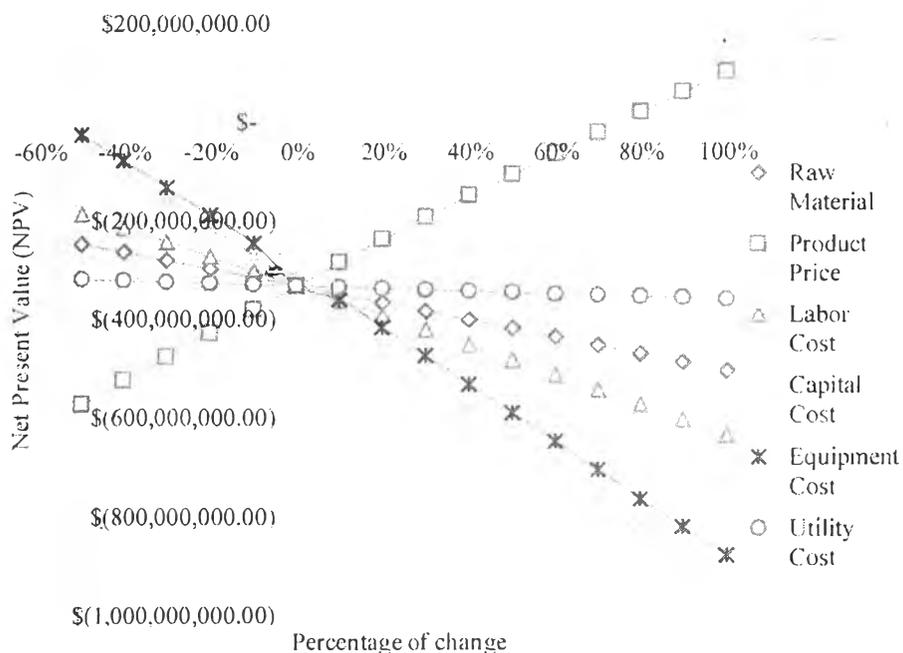


Figure 6.8 Sensitivity analysis compare to NPV.

6.1.3.4 Profitability of Base Case Design

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

In 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.3.12. The summary of investment analysis for the base case design is shown in Table 6.5.

Table 6.5 Profitability of the base case

| Profitability | |
|--|---------------------|
| not include time value of money | |
| Rate of Return | -41% |
| Pay Back Period | -2.30 |
| Net Return | \$ (111,881,138.05) |
| include time value of money | |
| Annual End of Year cash flows and discounting | |
| Net Present Worth | \$ (547,975,244.00) |
| DCFR | 0.15 |
| Continuous cash flows and discounting | |
| Net Present Worth | \$ (588,082,341.26) |
| DCFR | 0.14 |

According to the result, all parameters are of negative values, which means this project is clearly not worth for investment. Moreover, cumulative cash flow shows that the plant will have no profit after constructed as seen in Figure 6.9. Therefore, the process must be improved to achieve both environmental and economic targets.

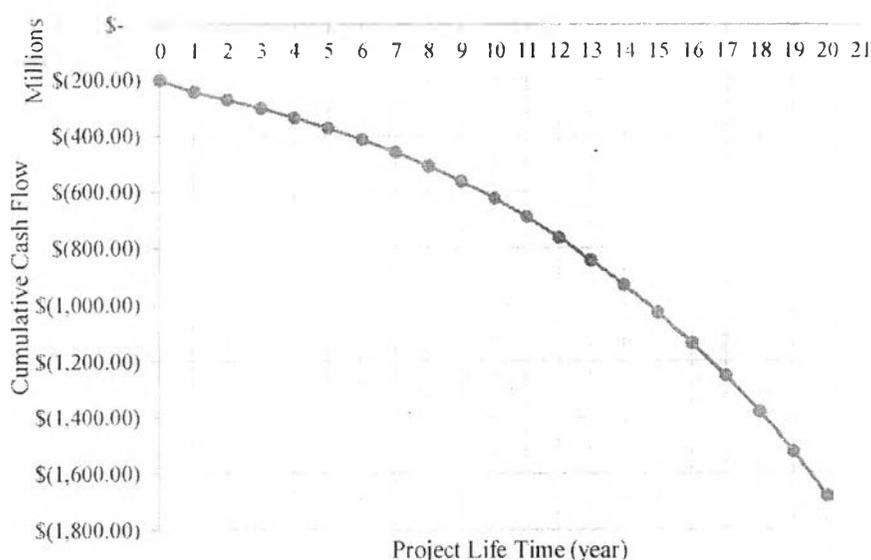


Figure 6.9 Cumulative cash flow for 20 year project of the base case.

6.2 Sensitivity Analysis

Zhang *et al.* (2013) indicated that the inlet reactor temperature, pressure and feed compositions to the reformer are key factors in the improvement of syngas synthesis, which results 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 CO₂ emission and production cost are changing. The production cost in this section is calculated by the following equation.

Production cost

$$= \text{Natural gas purchase cost} \quad (6.2)$$

$$+ \text{Demineralized water cost} + \text{Utilities cost}$$

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.

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

6.2.1 Tri-reforming-related Variables

6.2.1.1 *Inlet Tri-reforming Reactor Temperature*

Table 6.6 Relationship between the inlet tri-reforming reactor temperature and net CO₂ 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 |
|------------------|--|--|---|-------------------------------|-----------------|
| 800 | 391.0 | 230.5 | 621.5 | 19776 | 0.9926 |
| 820 | 400.9 | 220.6 | 621.5 | 19947 | 0.9952 |
| 840 | 411.7 | 211.7 | 623.4 | 20027 | 0.9955 |
| 850 | 417.1 | 207.3 | 624.4 | 20055 | 0.9956 |
| 860 | 422.4 | 202.9 | 625.3 | 20080 | 0.9957 |
| 880 | 433.2 | 194.8 | 628.0 | 20104 | 0.9959 |
| 900 | 443.9 | 187.0 | 630.9 | 20119 | 0.9961 |

The lower the temperature of the reformer is applied, the less net CO₂ emission and production cost per ton of methanol are observed as shown in Tables 6.6 and 6.7. When the temperature increases, more power generation contributes to the reduction of net power demand as well as indirect CO₂ emission. However, this trend could not compensate for the increase of direct CO₂ emission due

to the increase in amount of natural gas that is consumed at elevated temperatures to support the heat in the reformer. Similarly, the decrease of electricity cost could not offset the rise of natural gas cost when higher temperature is employed as observed in Table 6.7. The temperature at 840°C is chosen as the new temperature of the process because it satisfies constraints mentioned above.

Table 6.7 Relationship between the inlet tri-reforming reactor temperature and production cost

| Temperature (°C) | Energy Consumption (electricity) (\$/tMeOH) | Water Consumption (\$/tMeOH) | Methane Cost (\$/tMeOH) | Production Cost (\$/tMeOH) |
|------------------|---|------------------------------|-------------------------|----------------------------|
| 800 | 21.1 | 5.5 | 126.7 | 153.4 |
| 820 | 20.2 | 5.5 | 127.7 | 153.5 |
| 840 | 19.4 | 5.5 | 128.9 | 153.8 |
| 850 | 19.0 | 5.5 | 129.5 | 153.9 |
| 860 | 18.6 | 5.5 | 130.0 | 154.0 |
| 880 | 17.9 | 5.5 | 131.0 | 154.3 |
| 900 | 17.1 | 5.5 | 131.9 | 154.5 |

6.2.1.2 Inlet Tri-reforming Reactor Pressure

Table 6.8 Relationship between the inlet tri-reforming reactor pressure and net CO₂ 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 |
|----------------|--|--|---|-------------------------------|-----------------|
| 1.0 | 411.7 | 211.7 | 623.4 | 20027 | 0.9955 |
| 1.1 | 411.7 | 199.3 | 611.0 | 19994 | 0.9954 |
| 1.2 | 411.7 | 188.5 | 600.2 | 19958 | 0.9954 |
| 1.3 | 411.8 | 178.8 | 590.6 | 19920 | 0.9953 |
| 1.4 | 411.9 | 170.2 | 582.1 | 19878 | 0.9952 |
| 1.5 | 412.2 | 162.6 | 574.7 | 19825 | 0.9946 |
| 1.6 | 412.5 | 155.6 | 568.1 | 19770 | 0.9939 |

From Tables 6.8 and 6.9, it is observed that the higher the pressure of the reformer, the lesser the net CO₂ emission and production cost per ton

of methanol are obtained. At higher reformer pressures, a slight increase of direct CO₂ emission due to less methanol productivity is compensated by less electric power at the syngas compressors, allowing the process to achieve lower net CO₂ emission. Lower burning natural gas and less electricity demand are the main factors to permit lower production cost. However, the base case is still kept at 1 bar since only at 1 bar the process can produce pure methanol with 99.5 percent and 20000 kg/hr.

Table 6.9 Relationship between the inlet tri-reforming reactor pressure and production cost

| Pressure (bar) | Energy Consumption (electricity) (\$/tMeOH) | Water Consumption (\$/tMeOH) | Methane Cost (\$/tMeOH) | Production Cost (\$/tMeOH) |
|----------------|---|------------------------------|-------------------------|----------------------------|
| 1.0 | 19.4 | 5.5 | 128.9 | 153.8 |
| 1.1 | 18.3 | 5.5 | 128.8 | 152.5 |
| 1.2 | 17.3 | 5.5 | 128.7 | 151.4 |
| 1.3 | 16.4 | 5.4 | 128.6 | 150.4 |
| 1.4 | 15.6 | 5.4 | 128.5 | 149.5 |
| 1.5 | 14.9 | 5.4 | 128.4 | 148.8 |
| 1.6 | 14.3 | 5.4 | 128.4 | 148.1 |

6.2.1.3 CH₄ Feed Ratio

Table 6.10 Relationship between the CH₄/Flue gas ratio and net CO₂ emission

| Ratio of CH ₄ /flue gas | 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 |
|------------------------------------|--|--|---|-------------------------------|-----------------|
| 0.548 | 412.7 | 217.8 | 630.4 | 19519 | 0.9905 |
| 0.558 | 411.6 | 214.3 | 625.9 | 19809 | 0.9943 |
| 0.567 | 411.7 | 211.7 | 623.4 | 20027 | 0.9955 |
| 0.578 | 412.4 | 210.9 | 623.3 | 20248 | 0.9958 |
| 0.598 | 413.9 | 213.6 | 627.5 | 20631 | 0.9964 |
| 0.618 | 415.5 | 215.8 | 631.3 | 20983 | 0.9969 |
| 0.638 | 417.2 | 217.5 | 634.7 | 21292 | 0.9973 |

Interestingly, when the CH₄/Flue gas changes, there is a trade-off in terms of net CO₂ emission as illustrated in Table 6.10. The base case (0.567)

shows the second lowest net CO₂ emission with negligible difference compared to the lowest (0.578). When the CH₄/Flue gas ratio increases, both direct and indirect CO₂ emission rise because both the amount of burning gas and the electricity demand increase at the syngas compressors. At lower ratio, the net CO₂ emission increases due to the less methanol productivity which is the most significant factor. Meanwhile, an increase of production cost is witnessed when higher ratio is used as seen in Table 6.11. As the CH₄/Flue gas ratio increases, more natural gas is required, causing a significant elevation of the production cost. The reformer pressure is kept the same as the base case because it still satisfies all constraints above.

Table 6.11 Relationship between the CH₄/Flue gas ratio and production cost

| Ratio of CH ₄ /flue gas | Energy Consumption (electricity) (\$/tMeOH) | Water Consumption (\$/tMeOH) | Methane Cost (\$/tMeOH) | Production Cost (\$/tMeOH) |
|------------------------------------|---|------------------------------|-------------------------|----------------------------|
| 0.548 | 20.0 | 5.6 | 128.1 | 153.6 |
| 0.558 | 19.7 | 5.5 | 128.4 | 153.5 |
| 0.567 | 19.4 | 5.5 | 128.9 | 153.8 |
| 0.578 | 19.3 | 5.4 | 129.7 | 154.5 |
| 0.598 | 19.6 | 5.4 | 131.2 | 156.1 |
| 0.618 | 19.8 | 5.3 | 132.5 | 157.6 |
| 0.638 | 19.9 | 5.2 | 133.7 | 158.9 |

6.2.1.4 H₂O Feed Ratio

Table 6.12 Relationship between the H₂O/Flue gas ratio and net CO₂ emission

| Ratio of H ₂ O/flue gas | 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 |
|------------------------------------|--|--|---|-------------------------------|-----------------|
| 0.339 | 413.765 | 214.128 | 627.893 | 19766 | 0.9970 |
| 0.359 | 413.020 | 213.162 | 626.182 | 19879 | 0.9965 |
| 0.379 | 412.226 | 212.203 | 624.429 | 19973 | 0.9959 |
| 0.392 | 411.712 | 211.684 | 623.396 | 20027 | 0.9955 |
| 0.399 | 411.407 | 211.455 | 622.862 | 20054 | 0.9953 |
| 0.418 | 410.584 | 210.820 | 621.404 | 20126 | 0.9947 |
| 0.438 | 409.920 | 210.327 | 620.248 | 20184 | 0.9937 |

The more the H₂O feed is introduced, the less net CO₂ emission and production cost per ton of methanol are observed as illustrated in Table 6.12 and 6.13, respectively. When more H₂O is injected, both direct and indirect CO₂ emission reduce as a consequence of higher methanol productivity. Additionally, more methanol yield plays a key role in the reduction of the production cost. The new operating condition of H₂O/Flue gas ratio of 0.399 is selected after this step.

Table 6.13 Relationship between the H₂O/Flue gas ratio and production cost

| Ratio of H ₂ O/flue gas | Energy Consumption (electricity) (\$/tMeOH) | Water Consumption (\$/tMeOH) | Methane Cost (\$/tMeOH) | Production Cost (\$/tMeOH) |
|------------------------------------|---|------------------------------|-------------------------|----------------------------|
| 0.339 | 19.6 | 5.5 | 129.6 | 154.7 |
| 0.359 | 19.6 | 5.5 | 129.4 | 154.4 |
| 0.379 | 19.5 | 5.5 | 129.1 | 154.0 |
| 0.392 | 19.4 | 5.5 | 128.9 | 153.8 |
| 0.399 | 19.4 | 5.5 | 128.8 | 153.7 |
| 0.418 | 19.3 | 5.5 | 128.5 | 153.3 |
| 0.438 | 19.3 | 5.5 | 128.2 | 153.0 |

6.2.2 Methanol Synthesis-related Variables

6.2.2.1 Inlet Methanol Reactor Temperature

Table 6.14 Relationship between the inlet methanol reactor temperature and net CO₂ 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 |
|------------------|--|--|---|-------------------------------|-----------------|
| 210 | 408.386 | 206.316 | 614.702 | 20632 | 0.9952 |
| 220 | 411.407 | 211.455 | 622.862 | 20491 | 0.9953 |
| 230 | 416.094 | 223.022 | 639.116 | 20296 | 0.9953 |
| 240 | 422.860 | 238.858 | 661.718 | 20054 | 0.9953 |
| 250 | 431.396 | 259.924 | 691.320 | 19710 | 0.9931 |

When changing the inlet temperature of the methanol reactor, the process shows the lowest net CO₂ emission at the inlet reactor temperature of 210°C as illustrated in Table 6.14. Because the methanol synthesis from CO₂ and

hydrogen is exothermal reaction, it is disadvantageous to the methanol production when the reaction temperature increases. As a result, the direct CO₂ emission increases because of the more unreacted CO₂ in purge gases. In addition, at higher temperatures, higher unreacted gases require more energy at the recycle compressor, leading to an increase of indirect CO₂ 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 due to higher requirement of electricity demand when elevated temperatures are employed as illustrated in Table 6.15. In this step, 210°C is chosen as the new temperature of the process.

Table 6.15 Relationship between the inlet methanol reactor temperature and production cost

| Temperature (°C) | Energy Consumption (electricity) (\$/tMeOH) | Water Consumption (\$/tMeOH) | Methane Cost (\$/tMeOH) | Production Cost (\$/tMeOH) |
|------------------|---|------------------------------|-------------------------|----------------------------|
| 210 | 18.9 | 5.4 | 129.2 | 153.6 |
| 220 | 19.4 | 5.5 | 128.8 | 153.7 |
| 230 | 20.5 | 5.6 | 128.6 | 154.6 |
| 240 | 21.9 | 5.7 | 128.5 | 156.2 |
| 250 | 23.8 | 5.9 | 128.5 | 158.2 |

6.2.2.2 Inlet Methanol Reactor Pressure

Table 6.16 Relationship between the inlet methanol reactor pressure and net CO₂ 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 |
|----------------|--|--|---|-------------------------------|-----------------|
| 59 | 409.7 | 203.1 | 612.8 | 20165 | 0.9953 |
| 61 | 409.2 | 203.6 | 612.8 | 20212 | 0.9953 |
| 63 | 408.8 | 204.8 | 613.6 | 20256 | 0.9953 |
| 65 | 408.4 | 206.3 | 614.7 | 20296 | 0.9953 |
| 67 | 408.0 | 208.0 | 616.0 | 20333 | 0.9953 |
| 69 | 407.7 | 209.9 | 617.6 | 20368 | 0.9953 |

The higher the pressure of the methanol reactor is applied, the more net CO₂ emission per ton of methanol is observed as illustrated in Table 6.16. Obviously, since the methanol production causes a decline in the number of moles, the reaction is appropriate to elevated pressures. Hence, the direct CO₂ emission decreases due to a lower amount of CO₂ released from the stack. However, the higher the inlet pressure is applied, the more electricity at the inlet and recycle compressors is required, leading to more indirect CO₂ emission. In this case, the decrease of direct CO₂ emission is made up for by the increase of indirect CO₂ emission. Therefore, higher net CO₂ emission is seen at higher pressures in Table 6.16. In addition, quite noticeable increase of production cost is observed when increasing pressure (see Table 6.17) due to lower power generation and higher electricity demand. In this case, 59 bar is selected as a new operating pressure.

Table 6.17 Relationship between the inlet methanol reactor pressure and production cost

| Pressure (bar) | Energy Consumption (electricity) (\$/tMeOH) | Water Consumption (\$/tMeOH) | Methane Cost (\$/tMeOH) | Production Cost (\$/tMeOH) |
|----------------|---|------------------------------|-------------------------|----------------------------|
| 59 | 18.6 | 5.4 | 129.1 | 153.1 |
| 61 | 18.7 | 5.4 | 129.1 | 153.2 |
| 63 | 18.8 | 5.4 | 129.2 | 153.4 |
| 65 | 18.9 | 5.4 | 129.2 | 153.6 |
| 67 | 19.1 | 5.4 | 129.3 | 153.8 |
| 69 | 19.2 | 5.4 | 129.3 | 154.0 |

6.2.3 Optimal Design Factors and Performance Results

After the sensitivity analysis, new operating conditions of the process are presented in Table 6.18. Table 6.19 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 economics. Regarding net CO₂ emission, there is a slight reduction of 2 percent from 624 to 613 kgCO₂/tMeOH. The process witnesses a decrease of 1.86 MM\$ per year in an amount of the production cost of the optimized case as compared to the base case while the

most dramatic decrease is seen in the capital cost of the optimized case with near 2 MMS\$.

Table 6.18 Comparison of operating conditions between the optimized and base case

| Specification | Base Case | Optimized Case |
|-------------------------------------|-----------|----------------|
| Tri-reforming Variables | | |
| Inlet reactor temperature (°C) | 850 | 840 |
| Inlet reactor pressure (bar) | 1 | 1 |
| CH ₄ /Flue gas | 0.567 | 0.567 |
| H ₂ O/Flue gas | 0.392 | 0.399 |
| Methanol Synthesis Variables | | |
| Inlet reactor temperature (°C) | 220 | 210 |
| Inlet reactor pressure (bar) | 65 | 59 |

Table 6.19 Comparison of environmental and economic aspects between the optimized and base case

| Specification | Base Case | Optimized Case |
|---|-----------|----------------|
| Net CO ₂ emission (kgCO ₂ /tMeOH) | 624.4 | 612.8 |
| Capital cost (MMS\$) | 196.71 | 194.72 |
| Production cost (MMS\$/year) | 96.10 | 94.23 |

Although the optimized case achieves better results than the base case in both CO₂ emission and economic aspects, the process is still far from our targets which require negative net CO₂ emission as well as making profits. Figure 6.10 shows that the new case is also impossible to attract the investment from investors.

6.3 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 the burning of natural gas to support heat for the reformer. The flowsheet of this process is presented in Figure 6.11.

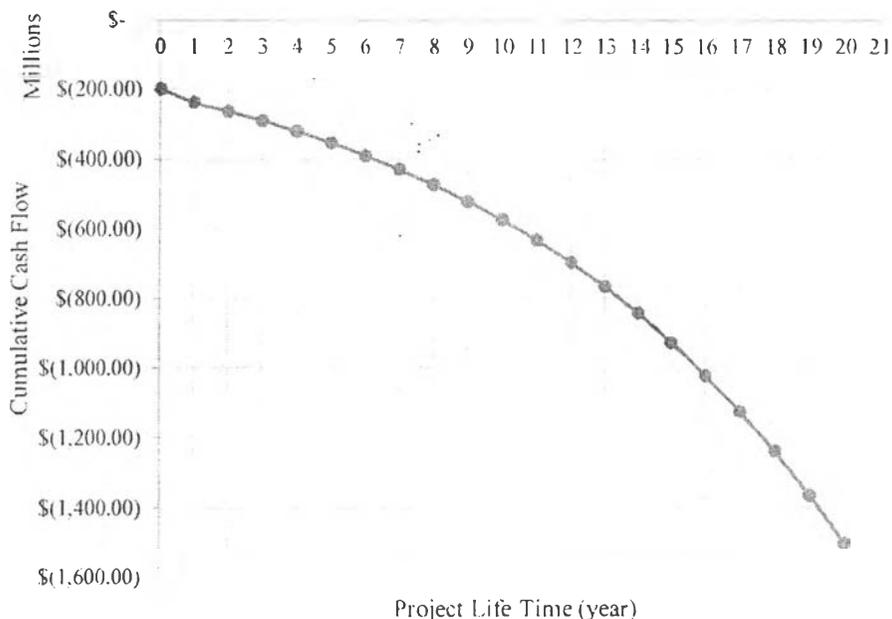


Figure 6.10 Cumulative cash flow for 20 year project of the optimized case.

6.3.1 Performance Results

Obviously, because employing free heat sources from the power plant, the alternative case witnesses a remarkable reduction in net CO₂ emission, with 66 percent lower than the optimized case, 208 kgCO₂/tMeOH compared with 613 kgCO₂/tMeOH in the optimized case. It is worth mentioning that current conventional methanol plants are emitting around 540 kgCO₂ per ton of methanol produced (Institute, 2014). Thus, the amount of CO₂ released from the alternative case is more than two times lesser than that discharged from traditional processes. Although the new process does not achieve our target that is negative net CO₂ emission, it could be considered a promising approach for treatment of CO₂ in terms of environment when the free heat is utilized.

As seen in Table 6.20, the alternative shows better results in terms of economic aspects. Because the new process does not consist of a gas power generation system, it allows a reduction in the cost to construct the plant. The capital cost witnesses a slight decrease of around 3 percent from 194.72 to around 188 MM\$. In

addition, there is a significant decline in the production cost of approximately 6 MM\$ annually from 94.23 to a mere 88 MM\$ per year. However, the improvement is not good enough to make the alternative become more attractive for investment as pointed out in the cumulative cash flow of the project shown in Figure 6.12.

Table 6.20 Comparison of environmental and economic aspects between the optimized and alternative case

| Specification | Optimized Case | Alternative Case |
|---|----------------|------------------|
| Net CO ₂ emission (kgCO ₂ /tMeOH) | 612.8 | 207.6 |
| Capital cost (MM\$) | 194.72 | 188.36 |
| Production cost (MM\$/year) | 94.23 | 88.51 |
| Product sales (MM\$/year) | 77.36 | 77.36 |

Obviously, it is necessary to find out reasons to explain this problem. Simply, the product sales revenue minus the production cost gives the gross profit or gross earnings. In addition, the production cost is considerably influenced from the capital cost. Thus, gross profit is primarily affected by the product sales, the capital and production cost. Generally speaking, the process can become profitable if the earnings from selling products are higher than the cost for making products. Clearly, in this process this condition is not satisfied. This can explain why the process is not appealing to invest.

As mentioned above, the capital cost has certain effects on the production cost through fixed-capital investment. In turn, the capital cost significantly depends on equipment costs. Therefore, the equipment costs will have certain impacts on the production cost. In the tri-reforming process, as a result of the high nitrogen content in the flue gas, the mass flow rates and the energy fluxes are very high, resulting in large-sized equipment. Undeniably, how to dispose of high concentration of nitrogen plays a key role in making the tri-reforming process become more feasible in terms of economy.

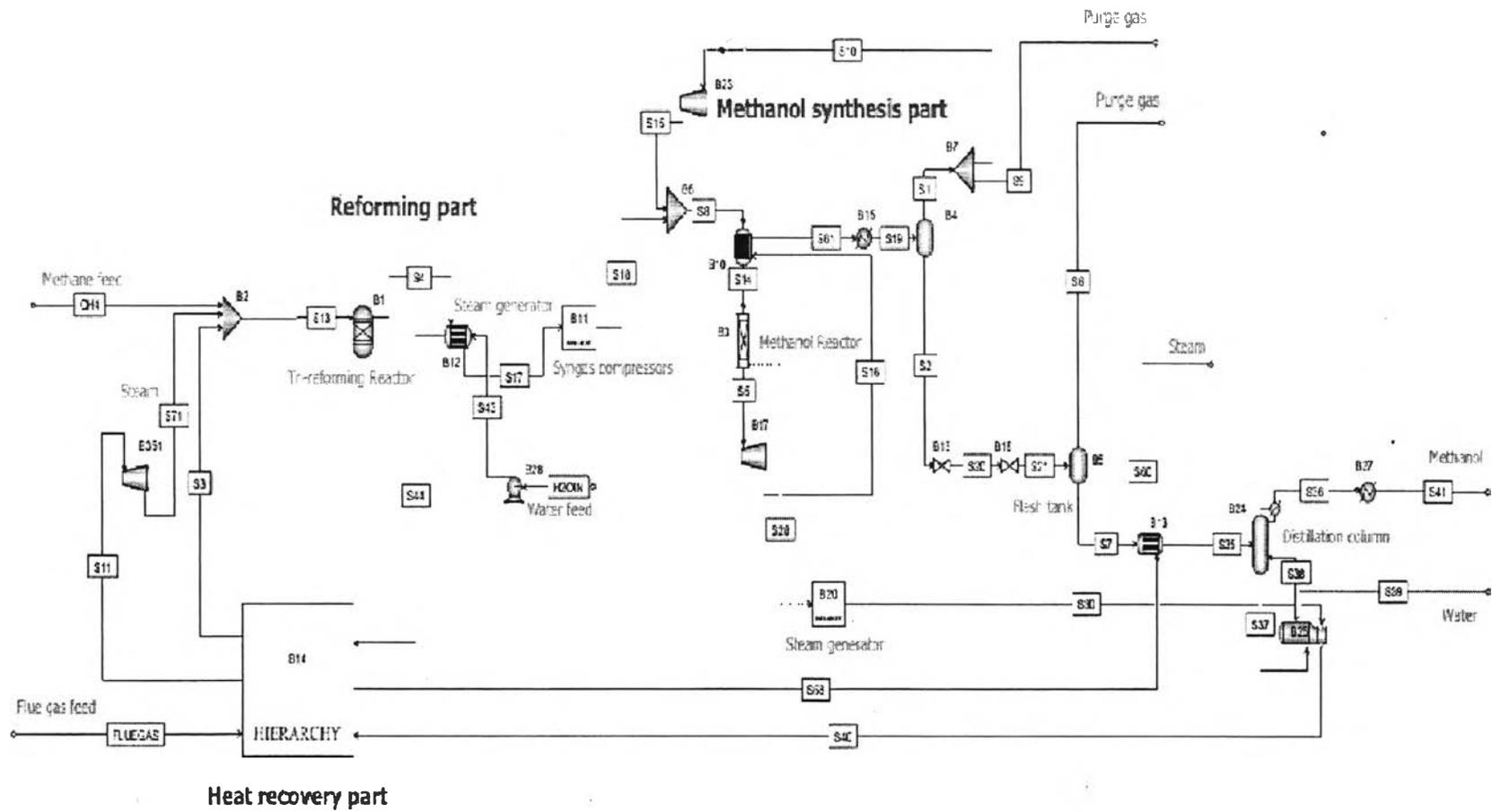


Figure 6.11 Flowsheet of the tri-reforming of CO₂ into methanol for the alternative case design.

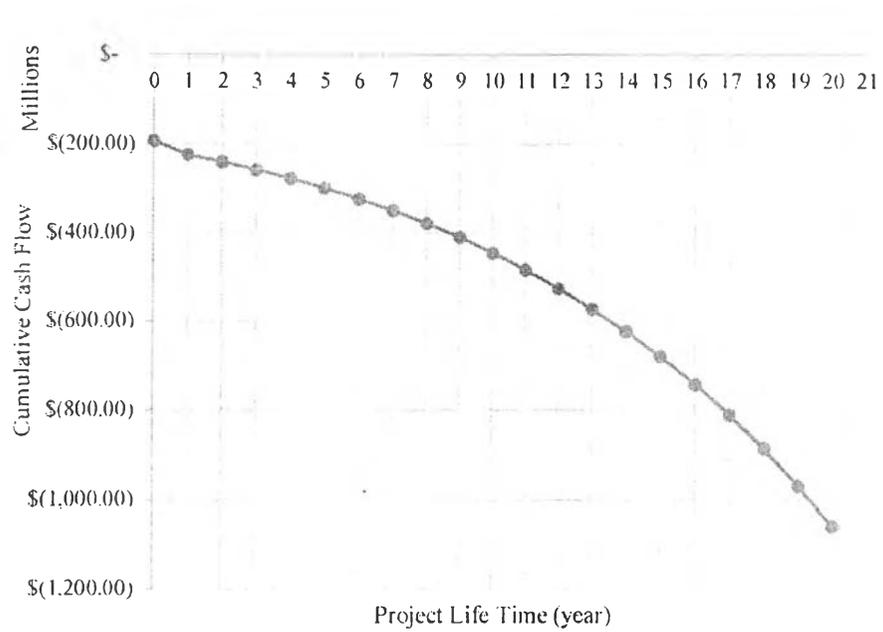


Figure 6.12 Cumulative cash flow for 20 year project of the alternative case.