

**TECHNO-ECONOMICAL ANALYSIS OF A MODULAR CHEMICAL
LOOPING PLANT FOR THE DEHYDROAROMATIZATION OF
METHANE IN STRANDED NATURAL GAS**

by

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LIST OF SYMBOLS AND ABBREVIATIONS

$\alpha_{i,j}^v$	Relative volatility (-)	C_{TCI}	TCI costs (\$)
$\alpha_{i,j}^m$	Membrane separation factor (-)	$CEPCI_h$	Historical CEPCI (-)
$\bar{P}_{M,i}$	Component membrane permeance (barrer)	$CEPCI_c$	Current CEPCI (-)
a	Scaling law constant (\$)	$COMP$	Complexity (-)
b	Scaling law constant (-)	F	Lang factor or installation factor (-)
C	Equipment cost (\$)	f	Improvement slope (%)
C_0	Equipment cost of reference (\$)	i	Discount rate (%)
C_{COM}	Cost of manufacturing ($\frac{\$}{kg}$)	IMP	Impurities (-)
C_{co}	Equipment cost after time and material correction (\$)	INC	Inclusiveness (-)
$C_{fix,0}$	Fixed cost of pioneer unit (\$)	K_i	Adsorption equilibrium constant (-)
C_{fix}	Fixed cost of production (\$)	K_{DHA}	Dehydroaromatization equilibrium constant (-)
C_{ISBL}	Inside battery limits costs (\$)	n	Scaling factor (-)
C_{opex}	Operating cost ($\frac{\$}{yr}$)	N_i	Component flux ($\frac{mol}{m^2s}$)
$C_{TCI,f}$	Amortized total capital investment ($\frac{\$}{yr}$)	n_l	Plant lifetime in years (-)
		n_y	Number of discounted years (-)

n_g	Cost growth factor (-)	S	Equipment scaling parameter
N_{prod}	Cumulative amount of produced units (-)	S_0	Equipment scaling parameter of reference
P_i^{vap}	Component vapor pressures (Pa)	V_a	Amortized value ($\frac{\$}{yr}$)
P_i	Component partial pressure (Pa)	V_f	Future value of a cash flow (\$)
$P_{i,p}$	Component partial pressure at membrane permeate side (Pa)	V_{NPV}	NPV of an investment (\$)
$P_{i,r}$	Component partial pressure at membrane retentate side (Pa)	V_p	Present value of a cash flow (\$)
		x_i	Component mole fraction in the liquid phase (-)
		y_i	Component mole fraction in the vapor phase (-)
PCT_{new}	Percent of new equipment (%)	APEA	Aspen Process Economic Analyzer
PD	Project definition (-)	Capex	Capacity expenditure
q_i	Component adsorption ($\frac{mol}{m^2}$)	CEPCI	Chemical engineering plant cost index
$q_{i,m}$	Maximum amount of adsorption for species i ($\frac{mol}{m^2}$)	CL	Chemical looping
Q_p	Yearly main product production quantity ($\frac{kg}{yr}$)	COM	Cost of manufacturing
r	Exponent of the experience learning curve (-)	DHA	Dehydroaromatization
		FCI	Fixed capital investment
R_{by}	Byproduct revenue ($\frac{\$}{yr}$)	IRS	Internal revenue service

ISBL	Inside battery limits
MACRS	Modified accelerated cost recovery system
MMSCFD	Millions of standard cubic feet per day
MSCFD	Thousands of standard cubic feet per day
NPV	Net present value
Opex	Operational expenditure
PSA	Pressure swing adsorption
TCI	Total capital investment
TDC	Total direct costs
TSA	Temperature swing adsorption

ABSTRACT

A modular chemical looping plant is proposed for the dehydroaromatization of methane in stranded natural gas to liquid hydrocarbons, which are more easily transportable. The purpose of this thesis is to assess the economic viability of this process compared to flaring of stranded natural gas.

Four plants have been designed in this thesis: two with and two without hydrogen production. The plants with hydrogen production do not have to out compete flaring, instead their goal is to reach a production cost target of \$2 per kg of hydrogen produced. Both the plants with and without hydrogen production have designs aimed at separating the produced benzene/naphthalene mixture into its constituents, to sell the higher priced benzene independently of the naphthalene, and designs that do not separate this mixture, instead selling it as virgin naphtha. All plants have been designed for 50 MSCFD and 175 MSCFD methane feed rates.

The pioneer plants without hydrogen production are not economically viable, as their net present values are always smaller than those of flaring installations. The hydrogen producing pioneer plants also prove incapable of producing hydrogen at sufficiently low costs, mainly due to their high capital costs and low capacities. Using experience learning curves to simulate the cost reducing effects of mass production, the cost of the final, mass-produced plants is estimated. Under the current market conditions, these final plants still prove incapable of replacing flaring, but the final plants with a methane capacity of 175 MSCFD can produce hydrogen below the $2 \frac{\$}{kg}$ cost target. In 2008 and 2013, benzene and naphtha prices were sufficiently high to ensure the economic viability of the final plants with a methane capacity of 175 MSCFD. Under these conditions, their net present value is greater than that of flaring installations and the cost of hydrogen production dips below $0 \frac{\$}{kg}$, due to increased benzene and naphtha revenues.

Chapter 1

INTRODUCTION

The total amount of oil and gas producing wells in the United States has steadily increased over the past decades to a high of around 1 million wells in 2014. Together, all these wells extracted over 96 billion SCFD of natural gas from the USA's natural resources in 2018.¹ About 34% of this natural gas is transported to power plants, where it can be used as a fuel to generate electricity. Natural gas is especially useful as a peak load power station fuel, since gas power stations are extremely flexible and can easily adapt their power output to rapidly changing electricity demands. An estimated 50% is used for commercial and residential heating purposes.² Recently there has also been a renewed interest in converting methane present in natural gas into higher value liquid hydrocarbon products.³ Clearly, natural gas is a valuable natural resource, but even so, not all of the extracted gas ends up being used.

1.1 Stranded Natural Gas

Roughly 3% of all the gas extracted in the United States is not transported away from wells for consumption.⁴ Usually, this is due to the location of the wells. If wells are very remote or isolated, transporting the gas away through pipelines can be prohibitively expensive since gasses have low density. To efficiently transport the gas, either large equipment is needed or the gas has to be pressurized to increase its density. The extracted oil, however, is still transported off-site, since it is a liquid and therefore easier to move. This type of unused natural gas is known as *stranded natural gas*. Since this gas remains unused at the well site, it would buildup unless removed in some way. It is therefore usually flared, emitting carbon dioxide in the process. This

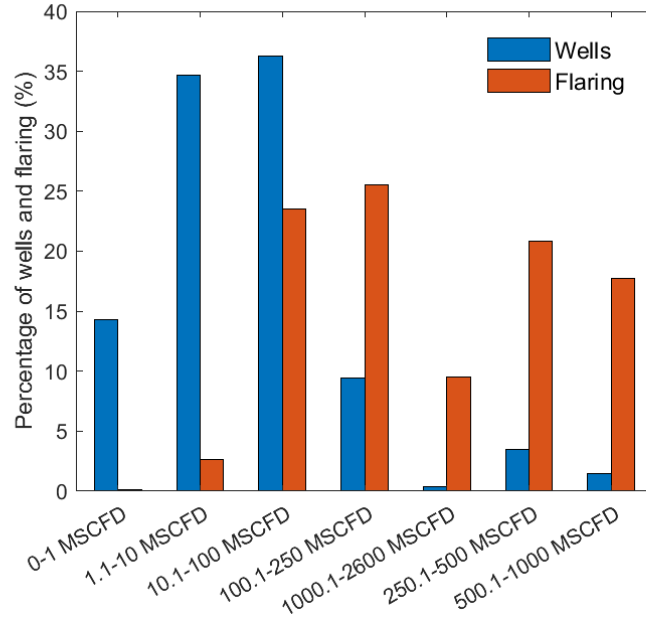


Figure 1.1: Relative number of wells and their contribution to flaring by size in the United States⁴

is still preferable over releasing methane directly in to the atmosphere, since methane is a potent greenhouse gas.⁴

As figure 1.1 shows, smaller wells in the in the size range of 10 to 250 MSCFD are responsible for almost 50% of all flaring activity in the US. Even though these wells are rather small and so the output of a single well is relatively low, the large amount of wells in this size range explains why they account for such a large fraction of the overall flaring activity. In order to reduce the amount of flaring in this well size range, the stranded natural gas has to be moved off-site. One way to do this, would be to use an efficient, modular and small scale gas to liquids conversion process. In this way the gaseous methane present in the natural gas, could be converted into higher value liquid hydrocarbons simplifying transportation. Such a process could remove the necessity of flaring completely and be an on-site, decentralized revenue source.

1.2 Methane Dehydroaromatization using Chemical Looping

Nonoxidative dehydroaromatization (DHA) of methane is a promising approach to converting methane present in stranded natural gas into liquid hydrocarbons. It uses a Mo/H-ZSM-5 catalyst to convert methane into benzene and hydrogen gas. This reaction is, however, thermodynamically limited by the presence of H_2 , as the reaction equilibrium constant shown in equation 1.1 depends on the hydrogen partial pressure to a power of nine.⁵

$$K_{DHA} = \frac{P_{C_6H_6} P_{H_2}^9}{P_{CH_4}^6} \quad (1.1)$$

In order to break this equilibrium limitation, removal of the formed hydrogen gas is of paramount importance. The proposed method can be seen in figure 1.2. Here H_2 is selectively oxidized by passing it through a metal oxide, such as Fe_3O_4 , to produce H_2O . The reduced oxide can then be re-oxidized using steam to produce H_2 or using O_2 , if a pure H_2 product stream is not required. This processing step is known as chemical looping (CL). The produced water can subsequently be removed using a zeolite 3Å TSA unit.⁵

The hydrocarbon stream, now free of H_2 can then be sent through the cycle again to increase the methane to benzene conversion. However, when the concentration of benzene increases, the DHA reaction starts favoring larger aromatics, e.g., toluene and naphthalene. On top of this, high aromatics concentrations in the DHA feed favor coke formation, resulting in lower aromatics yields.⁵ This can be countered by not only removing H_2 in every cycle, but by also removing the hydrocarbons after each dehydroaromatization step.

1.3 Research Objectives

The objective of this thesis is to determine under which market conditions a small scale, modular, transportable, on-site DHA-CL process is an economically viable option to reduce the amount of flaring due to stranded natural gas. This thesis will

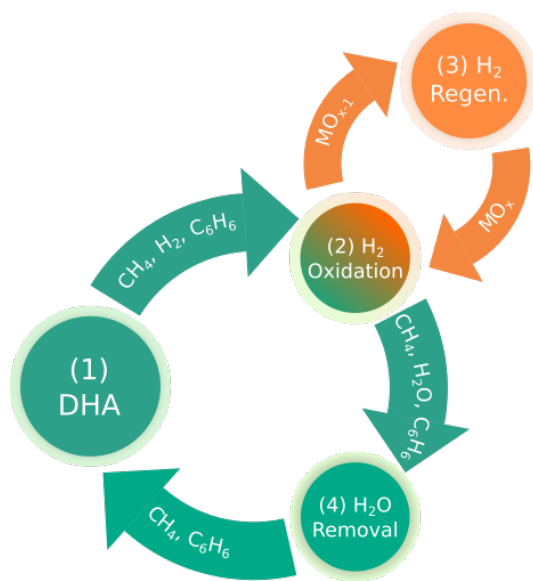


Figure 1.2: Combined dehydroaromatization (DHA) and chemical looping (CL) cycle for methane to liquid hydrocarbon conversion ^a

therefore attempt to create small scale plant designs, that could theoretically be loaded onto 18-wheelers and transported around the country. As can be seen in figure 1.1, wells in the natural gas production range of 10-100 MSCFD and 100-250 MSCFD are responsible for respectively 24% and 26% of all natural gas flaring in the US. On top of this, 47% of all wells lie in those production ranges. Based on these market potentials, the most economically attractive plant capacities were determined to be 50 MSCFD and 175 MSCFD, the approximate centers of of the respective ranges.

The produced liquid hydrocarbon stream is a valuable stream that could lower the net natural gas processing cost to below that of flaring. A carbon tax, which increases the price of carbon emissions associated with flaring natural gas, could also help shift the economic balance in favor of the DHA-CL process and will therefore also be taken into account. Since this technology is capable of producing a pure H_2 stream and the US Department of Energy has expressed interest in technologies that could produce pure hydrogen gas for under $2 \frac{\$}{kg}$, the cost of hydrogen production for these small scale, modular plants will also be determined.

^a Reprinted with permission from Brady, B.; Murphy, B.; Xu, B. *ACS Catal.* **2017**, *7*, 3924-3928. Copyright 2017 American Chemical Society.

Chapter 2

METHODOLOGY OF A TECHNO-ECONOMIC ANALYSIS

Every techno-economical analysis has the same starting point: plant design. Naturally, the design of the plant has a large influence on the final capital and operating costs. Designing a plant is therefore always an iterative process. A design is made based on sound engineering judgement, a cost estimation is performed and the plant is redesigned in the hopes of reducing costs.⁶ An essential part of this process lies in accurately estimating those costs and analyzing what these costs mean for the bottom line. This thesis chapter will therefore focus on providing a brief explanation of chemical process cost estimation and analysis techniques.

2.1 Cost Estimation

To determine whether a proposed plant is economically viable, the costs associated with the plant have to be estimated. For the purpose of a techno-economical analysis, a preliminary design estimate is sufficient. This method provides cost estimates with an expected accuracy of 30%.⁷ A higher level of accuracy would require much more detailed engineering and is therefore outside the scope of this thesis.

Costs can be broken down into two main categories: capital costs and operating costs. Capital costs are the up front costs, needed to build the chemical plant. Operating costs are all the costs associated with operating the plant, whether it is on or off-line. Both of these costs scale with plant capacity, which ultimately makes the size of a classical chemical plant the deciding cost factor.⁸ However, since this thesis does not focus on classical, large scale plants, but on small scale, mass produced, modular plants, another effect has to be taken into account: *economies of mass production*.⁹ This effect is quantified through experience learning curves. The following sections

provide a brief explanation of capital costs, operating costs and experience learning effects.

2.1.1 Capital Costs

The capital costs or Capex are the costs needed to build the chemical plant, before operation of the plant starts. Someone new to capital cost estimating might assume these costs are nothing more than the sum of the purchased equipment costs. This, however, is wrong. Although the equipment cost is an important parameter to estimate the total capital cost, it is usually not the biggest contributor. Additional costs have to be made to install the equipment, to prepare the chemical plant site, to acquire the necessary permits, etc.⁸ It is worth noting that software exists which is capable of performing capital cost estimates, e.g., Aspen Process Economic Analyzer.¹⁰ Whenever this software is available, it is highly recommended to use it, since its accuracy is usually higher than that of any other (manual) method.⁷

2.1.1.1 Equipment Costs

The purchased equipment cost is the basis for every capital cost estimation, especially for a preliminary design estimate. Most other costs scale with the purchased equipment cost and it is therefore important to have a good estimate. Equipment cost equations usually take the form of equation 2.1.⁸ Sometimes, they also take the form of equation 2.2.⁷ What the actual scaling parameter S represents, depends on the individual equipment, e.g., the surface area (m^2) for a heat exchanger and the vessel mass (kg) for a pressure vessel.

$$C = C_0 \left(\frac{S}{S_0} \right)^n \quad (2.1)$$

$$C = a + bS^n \quad (2.2)$$

Equations 2.1 and 2.2 are called scaling laws and they show a fundamental principle in chemical process engineering. For almost all processes and equipment the scaling factor n is smaller than one, i.e. doubling the size of the process or equipment will result in the capital cost increasing by less than a factor two. That is the main reason chemical plants are large plants, designed to handle enormous flows and generate enormous outputs. The larger the plant, the lower the capital cost per kg of produced product. This simple, yet important, fact also constitutes the biggest hurdle in designing modular small scale plants, because when increasing capacity improves cost efficiency, decreasing capacity decreases cost efficiency. In fact, for exceedingly small scale plants, the cost no longer decreases when the scale decreases. Effectively, the scaling factor n becomes almost zero.^{7,8}

The difficulty in performing cost estimates using these equations lies not in the equations themselves, but in finding reliable data for their parameters. For simple, well known processes, reliable economic data is usually readily available, but this is not the case for new, unproven technologies. Extensive research might be necessary. On top of this, additional corrections to these equations have to be made to account for changing equipment prices in time. This is done through the use of time dependent capital cost indexes, such as the CEPCI, as seen in equation 2.3.⁷ The CEPCIs are used when the cost equations were created in the past, e.g., if the cost equation was made in 2002, the cost prediction would not necessarily be correct for 2018, which is why a correction factor has to be applied.

$$C_{co} = C \frac{CEPCI_c}{CEPCI_h} \quad (2.3)$$

2.1.1.2 Installed Costs

Purchasing equipment is not enough to make an operational plant. The equipment has to be installed first. This brings additional costs with it. The installation costs take into account additional piping, instrumentation, structural work and the man hours for installation. These cost are quantified through the use of Lang factors

(or installation factors) F . These factors depend on the equipment type and the material of construction, but usually have values between 2 and 5.⁷ The total installed equipment cost is subsequently calculated using equation 2.4.⁷ These costs are also known as the ISBL or inside battery limits costs .

$$C_{ISBL} = \Sigma F_i C_i \quad (2.4)$$

2.1.1.3 Total Capital Investment

The ISBL costs can then be used to determine the total capital investment or TCI . The TCI covers all the costs made and is therefore a complete view of the capital investment a company has to make to acquire a certain plant. It is made up of the ISBL costs, additional direct costs, indirect costs and working capital.⁶ The sum of the ISBL costs and the additional direct costs is the total direct cost (TDC) . Adding the indirect costs to the TDC gives the FCI or fixed capital investment. The working capital is generally around 5% of the FCI. Table 2.1 shows how to calculate the FCI based on ISBL costs.

2.1.1.4 Pioneer Plant Costs

When building a pioneer plant, capital costs tend to be higher than when building a so called n^{th} plant. This tends to be due to i.a. a lack of proper process understanding and underestimation of plant built times.¹² In order to get a proper understanding of the costs associated with building a first, unique pioneer plant it is necessary to understand where these additional costs come from and to be able to quantify them. Equations 2.5 and 2.6 show how to go from n^{th} plant to pioneer plant

Table 2.1: Non ISBL costs of the fixed capital investment¹¹

Item	Description	Amount
Additional direct costs		
Warehouse	On-site storage of equipment and supplies.	4% of ISBL
Site development	Includes fencing, curbing, roads, well drainage, and general paving.	9% of ISBL
Additional piping	To connect ISBL equipment to storage and utilities outside battery limits.	4.5% of ISBL
Indirect costs		
Prorateable costs	This includes fringe benefits, burdens, and insurance of the construction contractor.	10% of TDC
Field expenses	Consumables, small tools and equipment rentals, field services and construction supervision.	10% of TDC
Home office and construction	Engineering plus incidentals, purchasing, and construction.	20% of TDC
Project contingency	Extra cash on hand for unforeseen issues during construction.	10% of TDC
Other costs	Start-up and commissioning costs. Land, rights-of-way, permits, surveys, and fees, etc.	10% of TDC

Table 2.2: Description and value ranges of the parameters used in equation 2.5^{12,13}

Parameters	Description	Range
PCT_{new}	Estimate of unproven technology incorporated in commercial use	0-100
IMP	Factor for impurities present in the process	0-5
$COMP$	Block count of all process steps in plant	> 0
INC	Percentage of land purchase, initial inventory, preoperating personnel included in analysis	0-100
PD	Levels of site-specific information and engineering included in estimate	2-8

costs.^{12,13} The parameters in equation 2.5 are clarified and explained in table 2.2. The cost growth factor n_g is almost always smaller than one.¹²

$$n_{growth} = 1.1219 - 0.00297PCT_{new} - 0.02125IMP - 0.01137COMP + 0.00111INC - 0.06361PD \quad (2.5)$$

$$C_{TCI}^{pio} = \frac{C_{TCI}^n}{n_g} \quad (2.6)$$

2.1.2 Operating Costs

Operating costs or Opex are the costs needed to operate the chemical plant after it has been built. Some of these costs are only accrued when the plant is up and running, the variable costs, whilst others have to be paid even if the plant is off-line, the so called fixed costs.⁸

2.1.2.1 Variable Costs

The variable costs only have to be paid when the plant is on-line, they are not accrued when the plant is not producing product. The variable costs generally scale linearly with the plant capacity, so there is little to no scaling advantage to be had. The variable cost consist of two subcategories:

Raw Material Costs

These are the costs of the materials consumed in the chemical process. This includes products such as feedstocks and catalyst material. Acquiring accurate pricing data for chemicals feedstocks and catalysts can be difficult, especially considering most data that is available on the internet pertains to feedstocks and catalysts for laboratory use. These materials abide by much higher purity standards and are a lot more expensive than bulk, industrial grade raw materials.⁷

Utility Costs

These are the costs of providing utilities such as heating and cooling. Fuel for heaters, cooling water, steam, electricity etc. all have a certain cost associated with them. Cost estimation software such as Aspen Process Economic Analyzer has built in prices for these utilities and is capable of calculating these costs quite accurately.^{7,10} If this software is not available, the utility requirements need to be calculated directly from heat and mass balances and prices have to be found in literature.⁸ For large scale plants, utility costs are often minimized using heat and power integration.

2.1.2.2 Fixed Costs

The fixed costs are accrued whether or not the plant is up and running. They generally do not scale linearly with plant size, but they do scale with capital costs. They consist of the following subcategories:

Salaries

Every plant needs operators in order to safely operate and maintain the plant. The average operator in the United States makes approximately $50,000 \frac{\$}{yr}$.⁷ The total amount of operators necessary depends greatly on the complexity and risk inherent to the process. Estimating the amount of operators is not an easy task and, although flow sheets that aim to provide guidance in this estimation exist, one of the most useful sources of information is industrial experience.⁷

Overhead Costs

Operators do not work alone, but within the structure of an existing company. As such, they are supervised and have other departments, e.g., human resources, working beside them. They also have health insurance, 401K retirement plans, training courses and other benefits. The costs of all of these are accounted for in the overhead costs.⁷ These costs amount to an additional 90% of the operator salaries.¹¹

Maintenance

Chemical plants require maintenance to operate safely and efficiently. Annual maintenance costs amount to approximately 3% of ISBL costs.¹¹

Insurance

No plant is allowed to run without insurance covering it. The total annual insurance cost is about 0.7% of the FCI.¹¹

2.1.3 Economies of Mass Production

As stated in section 2.1.1.1 companies reduce costs per kg produced by building large scale plants, since capital costs usually increase less than linearly with scale. This has led the chemical industry to build enormously large plants to improve profit margins. Even though this reduces the capital cost per kg produced, the absolute capital cost of these large scale plants tends to be extremely large. Plants costing more than a billion dollars are not uncommon.⁹ This inhibits innovation in the chemical industry, as companies are generally unwilling to take risks when such a large amount of money is at stake. There is, however, another approach to reducing costs. Instead of increasing the size of the plant, it is also possible to increase the amount of plants made, i.e., mass producing smaller scale plants. By forgoing the effects of economies of scale, it is possible to take advantage of economies of mass production. When building a lot of similar units, experience in building and operating these units is gained at a quicker pace than when building just one unit. This experience translates itself in real

Table 2.3: Description and value ranges of the parameters used in equation 2.9¹⁵

Parameters	Description	Range
COMP	Block count of all process steps in plant	> 0
SOLIDS	Factors in the presence of solid processing steps	0 or 1
PRIMARY	Factors in whether in product is a primary product	0 or 1
LIQUID	Factors in whether in product is a liquid	0 or 1

cost reductions: capital and fixed operating costs decrease with every new unit built. This effect is quantified by experience learning curves. These curves usually take the form of equation 2.7.¹⁴ The exponent of the experience learning curve is often related to the improvement slope f , as in equation 2.8.¹⁵

$$C_{fix} = C_{fix,0} N_{prod}^{-r} \quad (2.7)$$

$$f = 2^{-r} \quad (2.8)$$

For most products, the improvement slope f lies somewhere between 70% to 90%, meaning that every doubling of cumulative production (N_{prod}) leads to a decrease in production costs (C_{fix}) of 30% to 10% respectively.¹⁴ The improvement slope of a chemical process can be predicted based on process characteristics as shown in equation 2.9,¹⁵ whose parameters and their values are described in table 2.3.

$$f = 92.3 - 3.2COMP + 6.5SOLID + 5PRIMARY + 5LIQUID \quad (2.9)$$

Although the principle of experience learning is an empirically well observed phenomenon in almost all industries, care should be taken to not blindly follow these equations. Cost reductions do not appear spontaneously: cost reduction is never an automatic process. Reducing costs by mass producing requires a willingness to learn,

not only for management and engineering, but also for the operators running the plant. Corporate management must create a work environment in which cost reduction goals are constantly on everyone's mind and, most importantly, a business must be willing to invest in a product without a certain guarantee of profit. There are numerous success stories of companies basing their policies on the experience learning effect, but there are plenty of failures as well.¹⁶

2.2 Investment Analysis

The capital and operating costs themselves already paint a decent picture of the viability of an investment project, such as a chemical plant. Combined with the projected revenues, which can be acquired by multiplying the product flow rates with the product prices, it becomes possible to roughly assess whether a profit can be made. However, to truly assess whether a project can turn a profit, a more rigorous approach has to be taken. This approach needs to take taxes, depreciation and the time value of money into account. One of the most commonly used investment parameters, which takes all these factors into account, is the net present value (NPV) of an investment. Alternatively, the cost of manufacturing can also be used to assess the economical viability of a production process.⁷

2.2.1 The Time Value of Money

The value of money is time dependent, i.e., money now is worth more than money later. This is due to the fact that money now can be invested in e.g., other projects or investment portfolios. Money now, in other words, makes money later. It therefore becomes necessary to bring all cash flows to a common point in time in order to accurately compare them. The most common way to do this is by actualizing all future cash flows to the present, which is done by using equation 2.10.⁸ The values produced by plugging cash flows into equation 2.10 are known as discounted cash

flows. Another approach is to spread out a present cash flow over all future years, this is known as amortizing a cost and is done according to equation 2.11.⁸

$$V_p = V_f \frac{1}{(1+i)^{n_y}} \quad (2.10)$$

$$V_a = V_p \frac{i(1+i)^{n_i}}{(1+i)^{n_i} - 1} \quad (2.11)$$

Equations 2.10 and 2.11 both share the parameter i . This parameter is known as the discount rate and expresses the yearly compound interest rate a company can expect on a current investment. This parameter depends on the company and is often taken to be equal to the companies' cost of capital. For the chemical industry, the discount rate is often taken equal to 10%.¹¹

2.2.2 Net Present Value

The net present value of an investment is the overall profit (or loss) an investment is estimated to make after all the cash flows have been actualized to the present. The NPV can be calculated using equation 2.12.

$$V_{NPV} = \sum_{i=1}^{n_l} V_{p,i} \quad (2.12)$$

A viable investment must, at the very least, have a positive NPV. If the NPV is not positive, the investment amounts to a net loss and would therefore be a terribly unattractive investment. To determine the NPV, all the cash flows, present and future, as well as the plant lifetime n_l must be determined. The lifetime of a plant is usually measured in decades and lifespans as high as 30 or 50 years are not uncommon.⁸

2.2.2.1 Initial Investment

The initial investment is equal to the TCI. A more rigorous NPV calculation might spread the TCI out over the construction period of the plant. The construction

Table 2.4: Distribution of TCI costs over plant construction period¹¹

Project completion	Activity Description	Project Cost
0%-33%	Project plan and schedule established; conceptual and basic design engineering, permitting completed. P&IDs complete. Major equipment bid packages issued, engineering started on selected sub-packages.	8%
33%-66%	All detailed engineering including foundations, structure, piping, electrical, site, etc. complete; all equipment and instrument components purchased and delivered; Major equipment built and installed.	60%
66%-100%	Complete process equipment setting, piping, and instrumentation installation complete; pre-commissioning complete; and commissioning, start-up, and initial performance test complete.	32%

time can be estimated from the TCI of a plant and usually lies between 18 to 42 months, depending on the size of the plant.¹⁷ Costs tend to be accrued more towards the end of a project than towards the beginning. A typical distribution of the initial capital investment is shown in table 2.4.

2.2.2.2 Ongoing Cash Flows

After the plant has been built, products can be sold and revenues, and hopefully profits, can be made. This profit is taxed by the state and federal government at an average combined rate of approximately 25.7%.¹⁸ This reduces the net profit a company makes. To reduce the amount of taxes a company pays, it is allowed to charge a fraction of the capital depreciation each year as an expense for tax purposes. Equations 2.13 to 2.16 allow for the calculation of the yearly cash flows, based on previously determined operating costs, revenues and depreciation.⁸

$$Expenses = Opex + Depreciation \quad (2.13)$$

$$\text{Income Tax} = (\text{Revenue} - \text{Expenses})(\text{Tax Rate}) \quad (2.14)$$

$$\text{Net Profit} = \text{Revenue} - \text{Expenses} - \text{Income Tax} \quad (2.15)$$

$$\text{Cash Flow} = \text{Net Profit} + \text{Depreciation} \quad (2.16)$$

Depreciation takes into account the fact that chemical equipment loses value as it ages. When a plant is decommissioned, some equipment may be salvaged and sold at a price lower than the original equipment price, but most often the salvage value is close to zero. This represents a real expense for a company making an investment, which is why the government allows its inclusion as an expense for tax purposes. The current method used by the IRS to determine the maximum amount a company can claim as depreciation per year is the MACRS method. This accelerated method of depreciation uses a double declining balance method and switches to a straight line depreciation method when this yields a greater depreciation allowance. The idea behind an accelerated depreciation method such as MACRS, is that it is better to pay less taxes now and more in the future, since money now is worth more than money later. The amount of years a company is allowed to depreciate depends on the equipment and plant type and the total depreciation may never exceed the FCI.^{7,8}

2.2.3 Cost of Manufacturing

An alternative to performing a full NPV calculation is determining the cost of manufacturing of the most important product. This is easier than calculating the NPV and gives a quick idea of whether or not a process is viable: if the cost of manufacturing lies below the current market price of that product, a profit can be made. It is calculated by amortizing the TCI over the entire plant life (equation 2.11), adding this 'yearly cost' to the operating costs and subsequently dividing this sum by the yearly amount of product. If byproducts are generated, their values can be

subtracted from the costs, i.e., they represent a revenue. Equation 2.17⁷ shows the COM calculation.

$$C_{COM} = \frac{C_{opex} + C_{TCI,f} - R_{by}}{Q_p} \quad (2.17)$$

The COM is a less rigorous investment parameter than the NPV, since it does not take taxation or depreciation schemes into account, but it is more transparent. The COM allows a potential investor to look at the cost sources independently: the contribution of capital and operating costs to the overall production cost can easily be assessed, as well as the monetary effect of byproduct generation.⁸

Chapter 3

ALTERNATIVE HYDROGEN REMOVAL TECHNIQUES

Since the equilibrium conversion of the DHA reactor is severely limited by the presence of H_2 , as mentioned in section 1.2, it is important to efficiently remove as much hydrogen from the recycle stream as possible. Apart from using chemical looping to convert the H_2 into H_2O and then removing the H_2O using temperatures swing adsorption, as is the goal of this thesis, there are a variety of other ways to directly remove the H_2 from the hydrocarbon stream. All of them have their distinct (dis)advantages. Before going into the details of designing a DHA-CL plant, it is therefore useful to take a look at these competing technologies, to get a sense of where chemical looping is situated with respect to other hydrogen removal techniques.

The following literature study focuses on the three major methane-hydrogen separation techniques used in industry: cryogenic separation, membrane separation and pressure swing adsorption (PSA). The reactor product stream contains at most 30% hydrogen gas and, since the goal is to create a modular plant, has a flow rate below 0.7MMSCFD.

3.1 Cryogenic Separation

Cryogenic separation is one of the most common gas separation techniques in industry. Like other distillation techniques it uses the difference in volatility between components to separate them. The major difference between classical distillation and cryogenic distillation lies in the fact that, even though the components in the mixture can have a high relative volatility, their absolute volatility is low. Therefore the incoming feed requires extensive cooling, called refrigeration, which is generally highly expensive.

3.1.1 Separability

The main working principle of cryogenic separation lies in applying sufficient cooling so that part of the feed is condensed, resulting in a vapor-liquid equilibrium. The less volatile component will preferentially condense, whilst the more volatile component will remain in the vapor phase, resulting in an enrichment of the more volatile component in the vapor phase.

The feasibility of this separation technique depends heavily on the relative volatility of the key constituents of the mixture. The relative volatility α^v can be expressed in terms of the equilibrium vapor and liquid mole fractions as shown in equation 3.1¹⁹ Assuming that the liquid is an ideal mixture and that the vapor phase follows the ideal gas law, equation 3.1 simplifies to 3.2.

$$\alpha_{1,2}^v = \frac{y_1/x_1}{y_2/x_2} \quad (3.1)$$

$$\alpha_{i,j}^v = \frac{P_i^{vap}}{P_j^{vap}} \quad (3.2)$$

The relative volatility α^v of a methane hydrogen mixture in the applicable temperature range (approximately $-180^\circ C$) is of the order 10^5 , indicating that the separation is easily doable and a simple flash drum would suffice.¹⁰ This is in agreement with literature, which suggest that cryogenic separation can achieve hydrogen purities above 95% at recoveries ranging between 92% and 98% using partial condensation in flash drums.²⁰

3.1.2 Operation & Associated Costs

Since the absolute volatility of methane and hydrogen is high, high pressures and low temperatures are required to facilitate partial condensation. Typical operating pressures range from 20 to 80 bar, with temperatures around $-180^\circ C$. These conditions lend themselves to the use of aluminum multi-pass heat exchangers and expensive

cold-resistant flash drums. In order to reduce the cooling requirement the vapor and liquid exit stream exiting the flash drum are often used to partially cool the inlet stream. Turbo expansion of the hydrogen product can also be used to reduce the cooling requirement. Due to the extreme operating conditions, both Capex and Opex of cryogenic units are high.¹⁹

A change in the incoming feed composition can easily be offset by changing the operating temperature and the amount of cooling too guarantee an almost constant output composition, with minimal loss of recovery. An exception to this flexibility lies in its sensitivity to the presence of heavier hydrocarbons, such as benzene and naphthalene. These components are likely to freeze during cooling and might plug the heat exchangers.²⁰ It is thus of immense importance to ensure that no heavy hydrocarbons are present in the feed and that the upstream separation units function properly. The heavier hydrocarbons would therefore have to be removed before the hydrogen can be removed.

Cryogenic separation achieves the best results for feeds consisting of 30% to 70% hydrogen, where the goal is to reach purities of above 95%. Due to the high Capex of cryogenic units, this technology does not lend itself to small flow rates. Though it has excellent economies of scale, this can not be taken advantage of in small scale modular units.²⁰

3.2 Membrane Separation

Membrane separations use a physical barrier to separate the different components of a feed stream. One of the components in the feed stream will usually preferentially transport through the membrane, which allows for the extraction of the more mobile component and thus for the purification of the less mobile compound. Membrane gas separation is an often used technique for methane-hydrogen separation.

3.2.1 Separability

The mechanism by which hydrogen is extracted from a mixed feed through a membrane is called solution-diffusion. The more mobile hydrogen will first dissolve in the membrane, after which the molecule will diffuse through the membrane and desolve again on the permeate side.¹⁹ This mechanism is the mechanism by which hydrogen transport occurs in dense, polymeric membranes, which are currently the only membranes that have reached commercialization.²⁰ The flux of a species through the membrane is given by equation 3.3.¹⁹

$$N_i = \bar{P}_{M,i}(P_{i,f} - P_{i,p}) \quad (3.3)$$

Equation 3.3 clearly shows that this is a pressure driven process. As such, a higher pressure drop over the membrane will result in a higher flux and thus less required surface area, which is the primary cost driver in membrane separation units. Membrane gas separation therefore occurs at elevated pressures.

Apart from the component flux, the separation factor $\alpha_{i,j}^m$ is the most important system parameter, since it defines the membrane's ability to separate the compounds. The more $\alpha_{i,j}^m$ deviates from 1, the easier the separation will be. It is defined as the ratio of the permeances.¹⁹

$$\alpha_{i,j}^m = \frac{\bar{P}_{M,i}}{\bar{P}_{M,j}}. \quad (3.4)$$

In general the permeances and therefore the selectivity of a membrane depend heavily on feed composition and operating temperature and pressure. Rising temperatures generally increase flux, since both solubility and diffusivity increase with increasing temperature, but this often goes hand in hand with a reduction in membrane selectivity. The permeances, corresponding fluxes and the separation factor should always be experimentally determined over a broad range of compositions, temperatures and pressures. Swelling of the membrane can also significantly change its characteristics. Separation factors in rubber polymers can reach as high as 2, with glassy polymers

reaching even higher selectivities at 11.3. However, purities higher than 90% hydrogen are rarely achieved using membrane separation.¹⁹

3.2.2 Operation & Associated Costs

Since membrane gas separation is a pressure driven process, it is usually operated at high pressures on the feed side ranging from 20 bar to 35 bar, with pressures sometimes going as high as 110 bar. The permeate side is often kept at atmospheric conditions. Operating temperatures depend heavily on the thermal stability of the membrane. For dense polymeric membranes, temperatures rarely exceed 70°C.²⁰ At these temperatures, the heavier hydrocarbons would start to condense, which would lead to extensive fouling of the membrane. Therefore the heavier hydrocarbons have to be removed before the hydrogen can be removed with membrane separation. Alternatively, ceramic membranes, which remain thermally stable at much higher temperatures could be used. These, however, have not found widespread industrial use yet.²⁰

If the former option is chosen, special care should still be taken to avoid concentration polarisation and other external mass transfer resistances. It is possible that the less permeable components build up at the surface of the membrane, thereby restricting mass transport through the membrane. However, in gas separations these effects are usually negligible and it is possible to design the membrane modules in such a way to further reduce these effects.¹⁹

The modules themselves are mostly designed as hollow-fiber modules, since they offer a higher packing density, mechanical strength and a better gas flow distribution. This is only possible due to the minimal fouling risk inherent in methane-hydrogen gas feeds.¹⁹ Since membranes are designed in a modular way, changing the capacity of a membrane system is easy: just add or remove modules.²⁰

Membrane units are often the most economic choice for capacities below 25 MMSCFD. When the scale allows for the use of membranes, it is a reliable choice. Things seldom go wrong in membrane separations and it is easy to reduce the capacity of a unit just by decreasing the feed pressure. The capital investment is low, installation

and operation are relatively cheap, there are little rotating parts and it generally has a low environmental impact.²¹ Though membrane units are quite insensitive to changes in feed compositions, it is still relatively difficult to ensure a truly constant purity.

As a side note, it is worth mentioning that membrane modules are notoriously difficult to cost. This is one of the reasons software packages such as Aspen Process Economic Analyzer do not have costing for membranes built in and it is highly recommended to get direct quotes from membrane manufacturers.²² The total cost of a membrane unit is determined primarily by the membrane surface area and therefore the cost of the membrane per square meter itself. This depends heavily on the cost of membrane production and on the required lifetime of the membranes. The latter is primarily determined by the operating conditions itself. A membrane lifetime of 3 to 5 years is typical. A membrane unit will therefore require significant additional capital investments every couple of years to replace the membranes.²³⁻²⁶

3.3 Pressure Swing Adsorption

Adsorption makes use of adsorption beds to which components preferentially adsorb. The components which are more likely to adsorb are therefore extracted from the feed stream, purifying and enriching it in the components less likely to adsorb. In general hydrogen gas is less likely to adsorb than other gasses or light hydrocarbons. The reactant stream could therefore be purified of methane to achieve a pure hydrogen gas.

3.3.1 Separability

Adsorption can either be a process controlled by thermodynamics or by kinetics. If the latter controls, the purification is controlled by the speed and ease by which the molecules are able to diffuse through the adsorbent beds. The separation can for example be determined by the size-exclusion principle.¹⁹ If thermodynamics is the

controlling factor, the adsorption amount is determined by the adsorption isotherm, such as the Langmuir isotherm from equation 3.5.²⁷

$$q_i = \frac{q_{i,m}K_iP_i}{1 + \sum_j K_jP_j} \quad (3.5)$$

Equation 3.5 clearly shows that adsorption is a pressure driven process. A higher species partial pressure will result in more adsorption. Adsorption is therefore usually carried out at elevated pressures, between 15 bar and 30 bar.²⁰ The selectivity of the adsorption process is determined by the separation factor $\alpha_{i,j}$ (equation 3.6). A separation factor differing from one implies easier separation.

$$\alpha_{i,j} = \frac{q_{i,m}K_i}{q_{j,m}K_j} \quad (3.6)$$

Since the equilibrium constants depend heavily on the mixture composition and temperature, so does the separation factor. For methane-hydrogen mixtures the separation factor is generally high and high hydrogen purities (above 99%) are easily attainable.²⁰

3.3.2 Operation & Associated Costs

Since adsorption is a primarily pressure driven process, high operating pressures between 15 bar and 30 bar are common. Temperatures are usually kept ambient, unless working with a temperature swing adsorption setup instead of pressure swing adsorption. Common adsorbents are molecular sieves, activated carbon, activated alumina or silica gels. Modern beds often consist of multiple layered beds with different adsorbents.²⁰

Adsorption is an intrinsically non-steady state process. After a while the beds reach saturation (breakthrough) and they have to be regenerated. When using pressure swing adsorption, this is done by decreasing the operating pressure and purging the bed with a purge gas. Often, part of the purified H_2 gas is used as the purge gas resulting in reduced H_2 recovery. Typical recoveries range from 65% to 90%. After

purging the unit is repressurized and purification can start again. Typically these cycles take approximately 16 to 20 minutes. To ensure a continuous operation, 4 to 16 units are operated in a staggered manner. An alternative to pressure swing adsorption is temperature swing adsorption. Instead of changing the operating pressures, the temperature dependence of the equilibrium constant K_i is used to regenerate the beds. However, cooling down and warming up the adsorption beds is a slower process than changing the pressure, resulting in cycle times measured in hours or days instead of minutes, especially in the case of large, industrial scale units.^{19,20}

Pressure swing adsorption has a number of advantages compared to competing technologies. As stated before, extremely high H_2 purities can be reached relatively easily. Due to the fact that the total amount of impurities adsorbed depends on the partial pressure of the impurities in the gas mixture, the process is self-correcting to variations in feed composition. Higher impurity concentrations imply higher partial pressures and therefore more adsorption, partially offsetting the variation in feed composition. Should the variation in composition be too large to self-correct, a simple cycle time adjustment is often sufficient to offset this. It is also a highly reliable technology, with an availability that often exceeds 99.8%. On top of this it can easily deal with capacity variations as low as -70% and as high as $+30\%$ of design capacity.²⁰

However, when applying PSA to the feed stream of interest, problems arise. PSA is primarily useful for the purification of high H_2 content gas streams. Purifying gas streams below 50% hydrogen is not economical. This is due to the fact that PSA is used to purify H_2 streams, not to remove H_2 from a stream. If PSA was used directly on the hydrogen/hydrocarbon stream, without first converting the hydrogen into H_2O as is done in the proposed chemical looping process, it would in fact remove all the hydrocarbons, which are the majority components. When using physical separation techniques, it is advised to remove minority streams from the feed, not majority streams. It is, however, a relatively good choice for small scale plants, since it scales down reasonably well. The optimal operating feed flow rate ranges between 1 MMSCFD and 90 MMSCFD, so only relatively small scale plants can reasonably be made to run economically.^{19,20}

Chapter 4

PLANT DESIGN

As stated in section 2, the single most important cost determining aspect of a techno-economical analysis is plant design. The process of designing a plant is therefore an iterative process. After every design stage, a cost assessment is made, which allows for the identification of the most expensive process steps. This subsequently allows for a redesign, in the hopes of reducing the cost of these steps and of the overall plant. The results of this process will be presented in this thesis chapter. Four different plant designs have been made: two without H_2 production and two with. All plants have been designed for methane feed rates of 50 MSCFD and 175 MSCFD, as these were determined to be the most economically attractive plant sizes in section 1.

Before diving deeper into the plant design, a couple of assumptions have to be made: the plant feed is always assumed to be 100% methane. The DHA reaction is assumed to go to equilibrium, to have a 20% single pass benzene to naphthalene conversion and to have no coke formation. H_2 is fully converted to H_2O in the CL step and this reaction is assumed to be 100% selective to H_2 .

All plants were modeled in Aspen Plus, using the above mentioned assumptions. Feed and product flow rates for all designs can be found in appendix A.

4.1 Plants without Hydrogen Production

These plants have been designed to not produce H_2 as a byproduct. As the goal of this thesis was to design and cost economically attractive gas to liquid conversion plants, the decision was made to produce no other gaseous side products, since this seemed to be counter to the primary design goal. An additional benefit of this design is the fact that oxygen, instead of steam, can be used to regenerate the CL bed, the

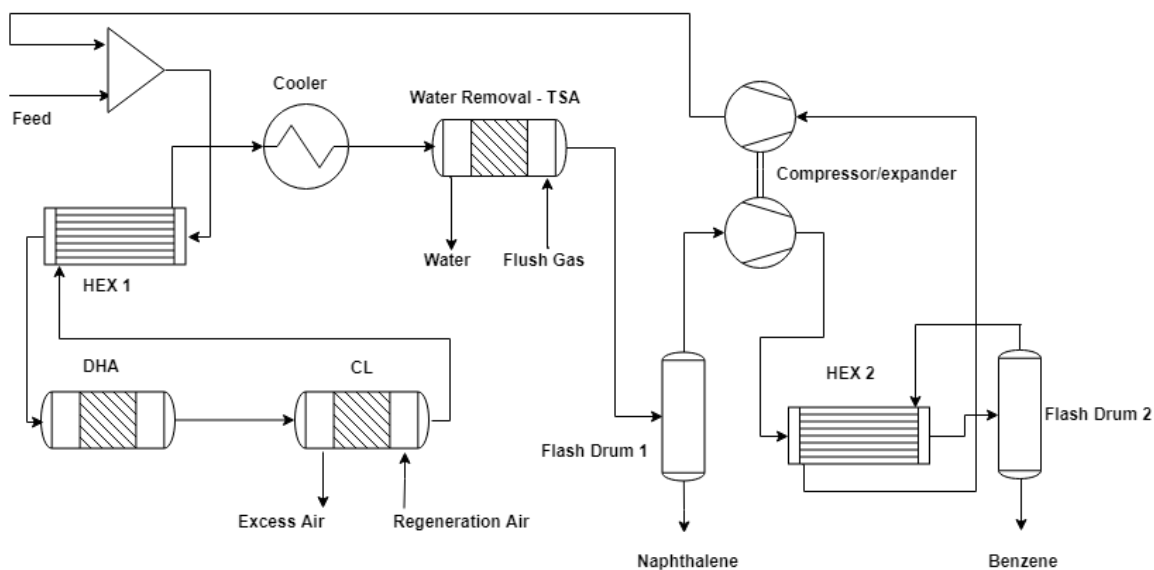


Figure 4.1: Process flow diagram of the plant with full hydrocarbon separation and without hydrogen production (Design 1)

kinetics of which are much faster. A potential downside of these fast kinetics is that over-oxidation poses a real risk.

4.1.1 Full Hydrocarbon Separation

The first plant design (Design 1) aims to convert methane into benzene and naphthalene and to subsequently separate these two components fully. This way, the higher value benzene can be sold separately from the less expensive naphthalene. The hope being that the additional separation cost is offset by the markup in product sales prices. Since benzene and naphthalene have markedly different boiling points (80°C and 218°C respectively¹⁷), flash distillation was chosen as the separation method. The process flow diagram of this plant can be seen in figure 4.1. The operating conditions of the flash drums were chosen to obtain a 96wt% benzene purity and an 83wt% naphthalene purity and can be found in table 4.1 together with the operating conditions of all the other equipment. For brevity's sake, the part of the plant containing the DHA, CL and TSA units will be referred to as the reactor section, whilst the part containing the flash drums will be called the separation section.

Table 4.1: Operating conditions of the plant with full hydrocarbon separation and without hydrogen production

Process equipment	Temperature ($^{\circ}C$)	Pressure (<i>bar</i>)
DHA	800	1
CL Reduction	750	1
Oxidation	850	1
Water removal - TSA Adsorption	250	1
Regeneration	500	1
Flash Drum 1	28	1
Flash Drum 2	10	30

In order to reduce the utility requirements, heat and power integration was performed. The CL exit stream is used to preheat the incoming DHA feed in heat exchanger 1 (HEX 1) and the exit stream of Flash Drum 2 is used to precool the feed entering Flash Drum 2 in heat exchanger 2 (HEX 2). Both heat exchanges have a minimum 20°C temperature difference to maintain a sufficiently large heat transfer driving force. Some of the power needed to compress the gas stream leaving Flash Drum 1 is also recuperated in the expansion of the stream leaving HEX 2. Additionally the heat generated in the exothermic CL looping step is used to provide heat to the endothermic DHA reaction and to preheat the flush gas entering the TSA unit. The leftover heat is dissipated using an additional water cooled heat exchanger. This additional heat exchanger network is not shown in the diagram of figure 4.1, but is conceptually visualized in figure 4.2.

To reduce the cost of the separation section, multiple reactor sections can be put in series before the process stream is sent to the separation section. This increases the overall methane conversion, thereby lowering the gas flow rate going into the separation section. This allows for a smaller separation section and could in principle offset the cost increase of additional reactor sections. Since this causes the composition of the gas entering the separation section to change, the operating conditions of the flash drums

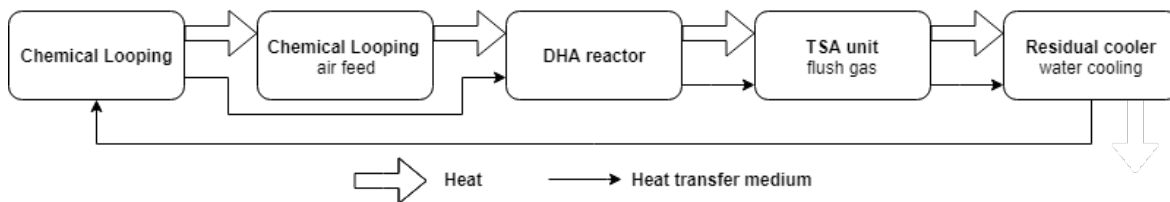


Figure 4.2: Additional heat exchanger network for the distribution of heat generated during CL with oxygen as re-oxidizer

need to change too. Table 4.2 lists the operating conditions of the flash drums for one to four of these stages.

4.1.2 No Hydrocarbon Separation

This plant (Design 2) does not attempt to fully separate the benzene/naphthalene mixture, but aims to sell it as virgin naphtha. The operating temperature of the TSA unit is lowered to approximately 50° C in order to increase the capacity, and decrease the selectivity, of the zeolite bed. This results in the removal of all the H_2O and most of the hydrocarbons (95% benzene and 100% naphthalene removal was assumed), whilst also decreasing the size of the TSA beds, potentially reducing costs. It should be noted, however, that naphthalene is a highly viscous substance at these temperatures, which may result in operational difficulties when introducing it to a zeolite adsorption column. Since water is immiscible with benzene and naphthalene, a decanter can be used to remove the H_2O rich phase from the hydrocarbon rich phase. This allows for the removal of the entire separation section from the previous design, replacing it with a condenser and a decanter, as seen in figure 4.3. Table 4.3 shows the operating conditions for this design. The additional heat exchanger network for the removal of heat from the exothermic CL reaction (figure 4.2) is still present.

4.2 Plants with Hydrogen Production

Since the US Department of Energy has expressed interest in technologies that can produce pure hydrogen gas for under $2 \frac{\$}{kg}$, additional plants have been designed that produce pure hydrogen as a main product. To do this, steam has to be used to

Table 4.2: Flash drum operating conditions of the plant with full hydrocarbon separation and without hydrogen production with one to four reactor stages in series

Process equipment	Temperature ($^{\circ}C$)	Pressure (<i>bar</i>)
1 Stage		
Flash Drum 1	28	1
Flash Drum 2	10	30
2 Stages		
Flash Drum 1	43	1
Flash Drum 2	10	30
3 Stages		
Flash Drum 1	51	1
Flash Drum 2	10	30
4 Stages		
Flash Drum 1	56	1
Flash Drum 2	10	30

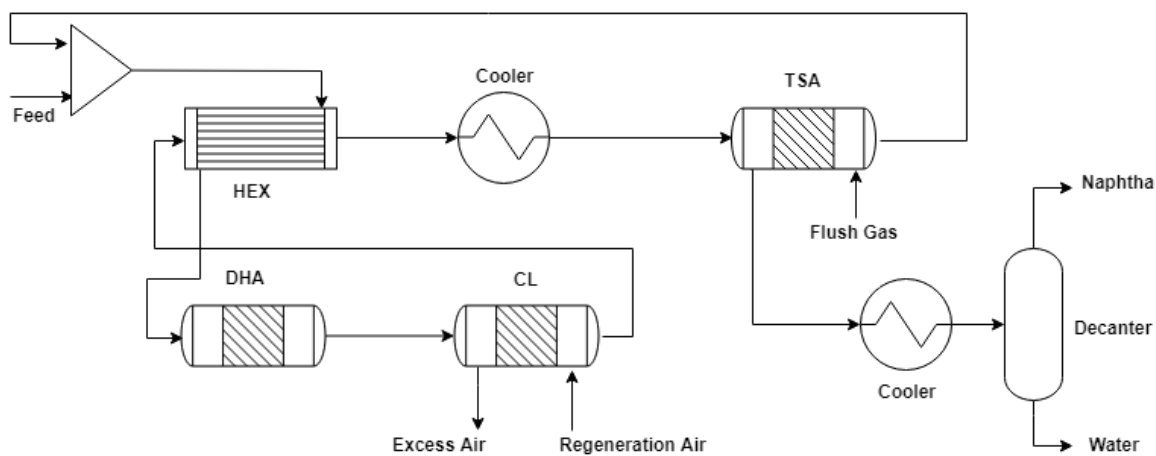


Figure 4.3: Process flow diagram of the plant without hydrogen production or hydrocarbon separation (Design 2)

Table 4.3: Operating conditions of the plant without hydrocarbon separation and without hydrogen production

Process equipment	Temperature ($^{\circ}C$)	Pressure (<i>bar</i>)
DHA	800	1
CL		
Reduction	750	1
Oxidation	850	1
TSA		
Adsorption	50	1
Regeneration	500	1
Decanter	10	1

regenerate the oxides in the CL reactor. Even though this regeneration process would probably be a lot slower than re-oxidizing with oxygen, it was assumed that steam re-oxidation has similar kinetics to oxygen re-oxidation. This was done in an attempt to capture potential advancements in chemical looping technologies. Because oxygen is no longer used to regenerate the CL oxide beds, but instead a reversible reaction occurs where H_2 is converted to H_2O and back, the CL reactors are no longer a net provider of heat. The additional heat exchanger network from section 4.1 is therefore no longer useful. Instead, additional heat, using fired heaters, has to be provided to the DHA, TSA and CL units. Similarly to the plants without hydrogen production, versions with (Design 3) and without (Design 4) hydrocarbon separation have been designed. These designs are completely similar to the designs from section 4.1, with the one notable difference being that the water produced in figures 4.1 and 4.3 is fed to the CL units as steam. Their flow sheets and operating conditions can be found in appendix B.

Chapter 5

CAPITAL AND OPERATING COSTS

The plant designs as discussed in the previous thesis chapter have been costed according to the procedures outlined in chapter 2. A rigorous, detailed overview of all equations, parameters and assumptions used to obtain these cost estimates can be found in appendix C. What follows is an overview of all capital and operating costs of all plant designs for a 50 MSCFD and a 175 MSCFD methane feed. All reported costs are pioneer plant costs.

5.1 Plants without Hydrogen Production

5.1.1 Full Hydrocarbon Separation

Since the idea behind this plant design was to have multiple reactor stages in series, all costs in this section will be reported for designs with one to four reactor stages. By increasing the amount of reactor stages, methane conversion increases, which lowers the recycle flow rate and therefore the capacity of the individual units. This causes the units in the reactor and separation section to have different installed costs, depending on the amount of stages and the feed size. However, the relative cost contribution of each individual unit with respect to the total cost of the section to which it belongs, stays approximately constant. It was therefore chosen to report the individual unit cost as a percentage of the overall reactor stage or separation section cost.

Figure 5.1 clearly shows that most of the reactor section cost comes from the DHA, CL and TSA units. This was expected, since these represent the three main processing steps. The TSA unit is responsible for a surprisingly large portion of the overall reactor section cost, because it requires large beds to operate efficiently. This is

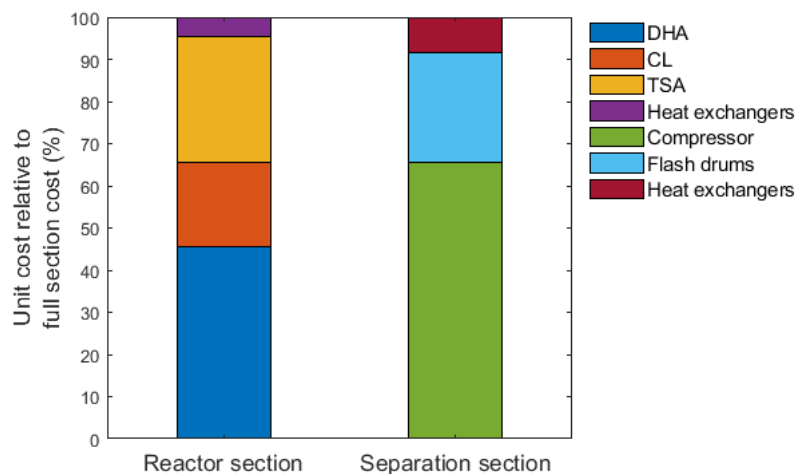


Figure 5.1: Installed unit costs relative to total installed reactor or separation section costs for design 1

due to three main reasons. The first being the long cycle time inherent to TSA, which requires the bed to be on-stream for an hour (see appendix C). It must therefore be able to adsorb the incoming water stream for at least an hour. The second reason is that the water adsorption capacity of the beds at 250°C is only 4wt%, which combined with the third reason, the relatively high water content of the TSA feed stream (16wt%-30wt%), results in large beds. The contribution of the gas compressor to the separation section cost is also striking. This compressor is required to maintain high enough pressures to efficiently separate the volatile benzene from the methane going to the recycle. If the pressure is not maintained sufficiently high, the benzene recovery and purity drops significantly. These high pressure compressors are known to be highly expensive and usually make up a large fraction of the plant cost.⁶

When looking at the total plant ISBL costs (figure 5.2), it is clear that the intended effect of lowering the cost of the separation section, by increasing the amount of reactor sections in series does not materialize. The cost of the separation section stays approximately constant, even when adding four reactor stages in series. This is due to the small scale of the plants. Operating at these scales implies that a further capacity reduction does not have a substantial effect on the equipment cost. In other words:

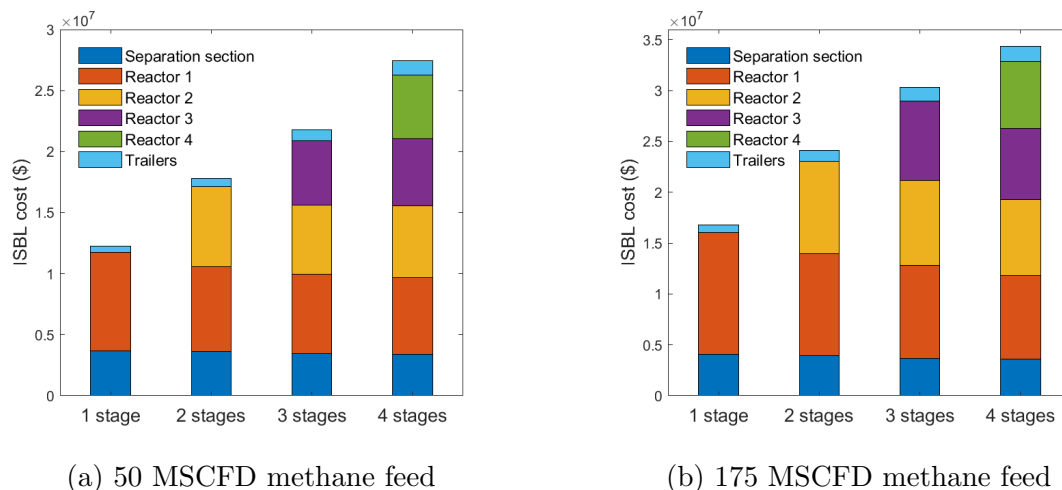
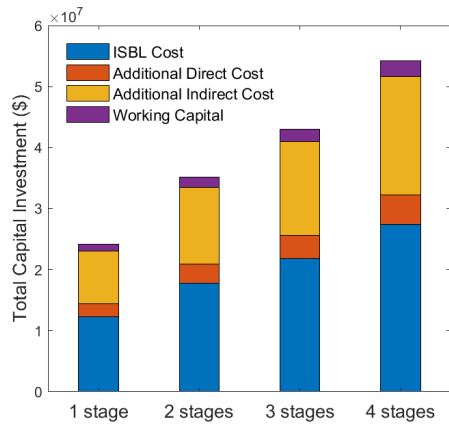


Figure 5.2: Total ISBL costs for plant design 1

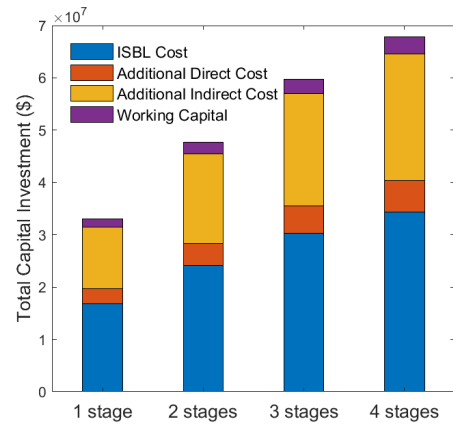
the separation section is already as cheap as it can get. Note that the reactor sections do get cheaper every time a stage is added, due to the lower required capacity. This is, however, not sufficient to decrease the overall cost. It is also worth mentioning that the classical chemical plant cost scaling effects are clearly taking place: by increasing plant capacity from 50 MSCFD to 175 MSCFD, the production rate has more than tripled, the costs, however, have only gone up by about 30%. Since the TCI (figure 5.3) is based completely on the ISBL costs, they show the same trend.

The fixed costs dominate the operating costs (figure 5.4), with the raw materials and utility costs only making up a small fraction of the total operating cost. The raw material and utility costs scale almost linearly with plant capacity, whilst at these small scales the capital cost is almost independent of plant capacity. Since the fixed costs scale with the TCI through insurance and maintenance, the fixed costs end up being much larger than the variable costs. This results in an operating cost with a makeup almost completely opposite to that of large scale chemical plants.⁷

The amount of trailers needed to transport the plants ranges from five for the single stage 50 MSCFD capacity plant to 15 for the four stage 175 MSCFD capacity plant (figure 5.5). The latter is clearly not easily transportable. The fact that costs do not decrease by adding reactor stages to the plant and the added logistical problems

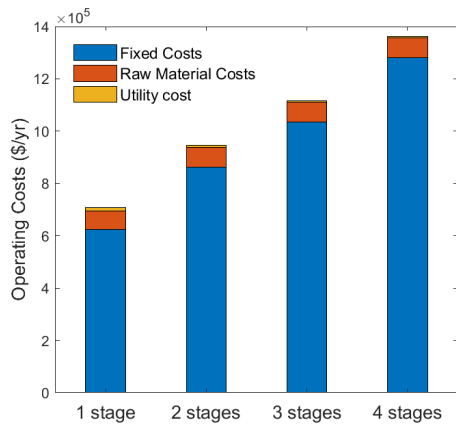


(a) 50 MSCFD methane feed

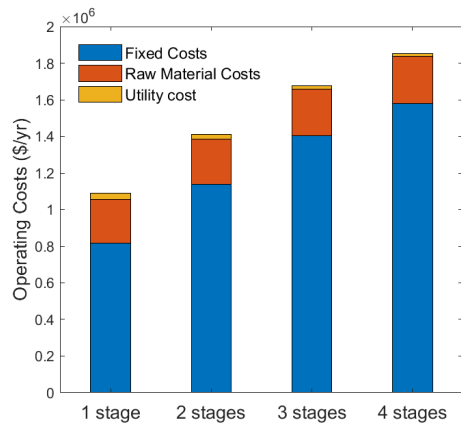


(b) 175 MSCFD methane feed

Figure 5.3: Total capital investment for plant design 1



(a) 50 MSCFD methane feed



(b) 175 MSCFD methane feed

Figure 5.4: Total operating cost for plant design 1

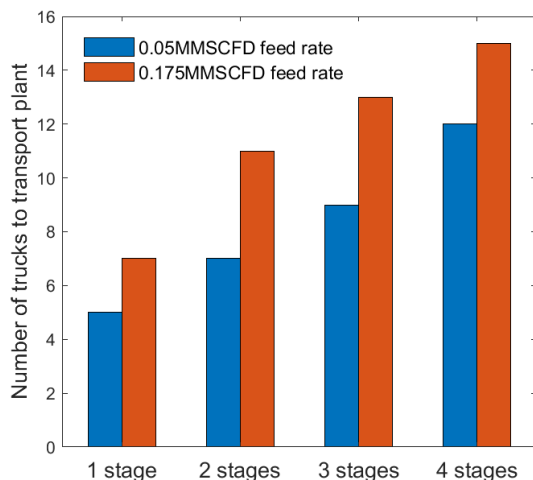


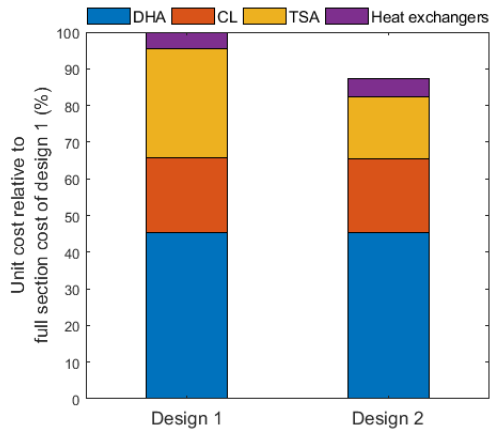
Figure 5.5: Number of trucks necessary to transport the plant for design 1

associated with the growing number of trucks, leads to the conclusion that the single stage designs are the most economically promising. It was therefore decided to only focus on single stage designs for all further discussions.

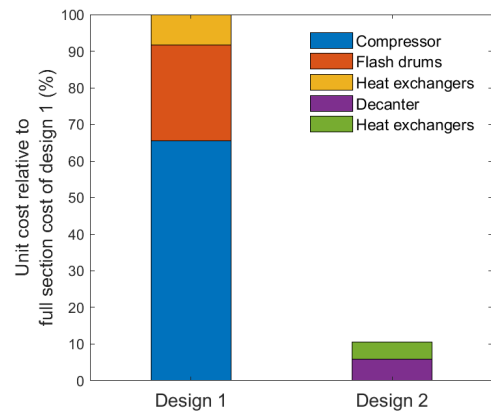
5.1.2 No Hydrocarbon Separation

Design 2 lowers the cost of the TSA unit substantially, by lowering its adsorption temperature to 50°C, thereby increasing its adsorption capacity, resulting in a smaller unit. On top of this, the design also does away with almost the entire separation section, replacing it with a decanter. Figure 5.6 clearly shows that the resulting cost reductions to both the reactor and separation sections are significant, with the reactor and separation section cost dropping by almost 15% and 90% respectively.

This also results in lower ISBL costs and lower TCI for both the 50 MSCFD and 175 MSCFD capacity plants (figure 5.7). Due to the removal of most of the separation section, the ISBL cost is almost fully comprised of the reactor section cost. By changing design 1 to design 2, a TCI reduction of almost 40% was achieved. The amount of trucks necessary for the transportation of the plant has also decreased from five to four and seven to five for the 50 MSCFD and 175 MSCFD capacity plants respectively.

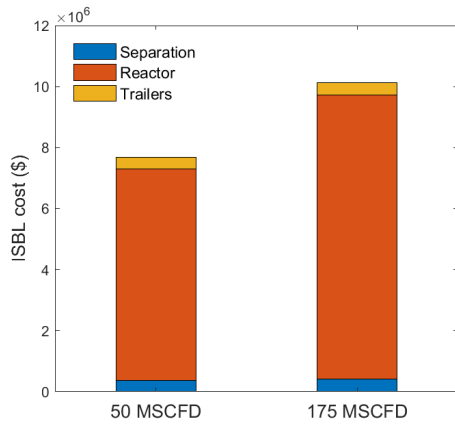


(a) Reactor section

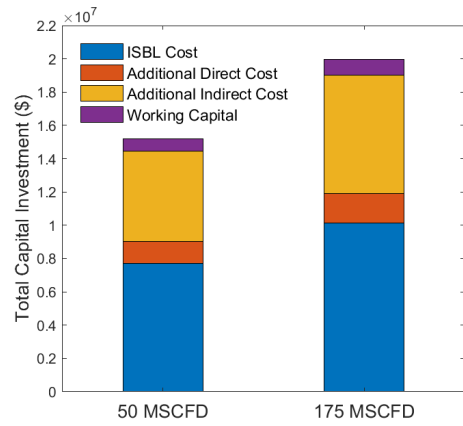


(b) Separation section

Figure 5.6: Installed unit costs relative to total installed section costs for design 2 compared to design 1



(a) ISBL costs



(b) Total capital investment

Figure 5.7: ISBL costs and TCI of design 2

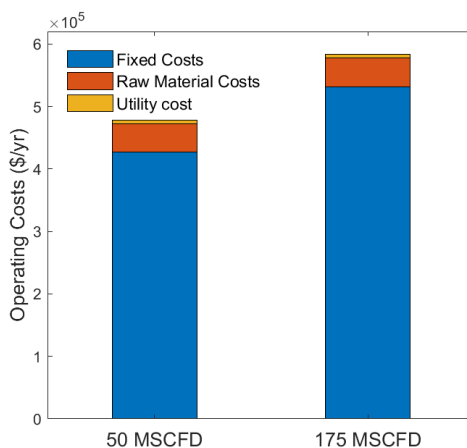


Figure 5.8: Operating costs of design 2

Since the capital costs have gone down significantly compared to design 1, and most of the operating costs scale with the capital costs through maintenance and insurance, the operating costs (figure 5.8) have also decreased significantly. Though there is also a slight decrease in utility cost, because of a lower electricity demand due to the process no longer requiring high pressure compression, most of the cost reduction can be found in the fixed costs. Overall, the operating costs of design 2 are almost 30% lower than those of design 1.

5.2 Plants with Hydrogen Production

Since the differences between designs 1 and 2 and designs 3 and 4 are only minor, the capital and operating costs are virtually the same. Therefore the conclusions that can be drawn from them are also similar: additional stages do not decrease plant cost, instead they cause a significant increase in size and cost. All further analysis for these plants will therefore only be carried out on the single stage designs. Design 4 compares to design 3 as design 2 compares to design 1: the TSA unit is cheaper, because it is smaller, and the separation section has been eliminated in favor of a decanter, reducing costs even further. The number of trucks required for the transportation of these plants is also the same as the number required for plant designs 1 and 2. Since the costs are so similar to those discussed in previous sections, they have not been added to the main text. Instead, they can be found in appendix D.

Chapter 6

ECONOMIC ANALYSIS

This chapter presents the findings of a detailed economic analysis of the chemical processes as presented in chapter 4 and costed in chapter 5. Two investment parameters have been investigated. The first being the NPVs of designs 1 and 2 and the second being the cost of manufacturing hydrogen gas for designs 3 and 4. Because capital and operating costs always increased when additional reactor sections were placed in series, the analyses have only been performed for the single reactor stage plant designs, as these had the lowest costs and were therefore more likely to be economically viable.

6.1 Economic Viability of Plants without Hydrogen Production

In order for the plants without hydrogen production (designs 1 and 2) to be economically viable, the NPVs of these designs must be larger than those of flaring, since this would indicate that the current value of investing in one of these plants is greater than the value of investing in a flare. The process would then be profitable compared to flaring. As such, the plant is viable when $NPV_{CL} > NPV_{flare}$ or, in other words, when $NPV_{CL} - NPV_{flare} > 0$.

All NPVs have been calculated assuming a 30 year plant life time,¹⁸ the MACRS depreciation method over 7 years,⁷ a 25.7% tax rate¹¹ and a 10% discount rate,¹¹ according to the method outlined in chapter 2. The same assumptions have been made to determine the NPV of flaring.²⁸ To increase the scope of the economic assessment, the effects of external market conditions were taken into account by calculating the NPVs for a variety of product prices and carbon taxes.

6.1.1 Pioneer Plant

Figures 6.1 and 6.2 clearly show that the pioneer plant process is never viable, even under the market conditions of 2008 and 2013, when product prices were at an all time high of approximately $1.3 \frac{\$}{kg}$ for naphtha and $1.8 \frac{\$}{kg}$ for benzene (adjusted for inflation).^{29,30} In order to achieve a viable plant, the product prices would have to increase by at least a factor of 8 compared to the current market prices ($0.5 \frac{\$}{kg}$ for naphtha and $0.6 \frac{\$}{kg}$ for benzene).³¹ Even then, only plant design 2 with a 175 MSCFD methane capacity would be viable.

The biggest factors affecting the process viability, apart from the product prices, are clearly the plant design and scale. The capital and operating costs of design 2 are lower than those of design 1, which translates into the black line, marking where $NPV_{CL} = NPV_{flare}$, moving to the left, increasing the viability of the process. The scale of the process clearly also has a large effect, with the 'viability' lines shifting dramatically to the left for the larger scale plants. The scaling laws, dictating that larger scale plants are more economically viable, are in full effect here. By increasing the plant capacity from a 50 MSCFD methane feed to a 175 MSCFD methane feed, the potential revenue of the plants more than triples. However, the capital costs only increase by roughly 30% (see chapter 5). This results in the 175 MSCFD pioneer plants being closer to viable, than the 50 MSCFD plants.

The lines marking where $NPV_{CL} = NPV_{flare}$ are rather steep, indicating that a proposed carbon tax would only have a limited effect. This is due to the fact that natural gas does not emit large amounts of CO_2 when burned, especially compared to other fossil fuels. For every thousand standard cubic feet of natural gas burned, only $54kg$ of CO_2 is emitted into the atmosphere.³² In order to significantly effect the cost of flaring, the carbon tax would therefore have to be excessively high. Considering the highest effective cost of carbon emission in the world is only $62 \frac{\$}{tonne}$, it is highly unlikely a carbon tax will be signed into law, that is sufficiently high to make the pioneer chemical looping process viable.

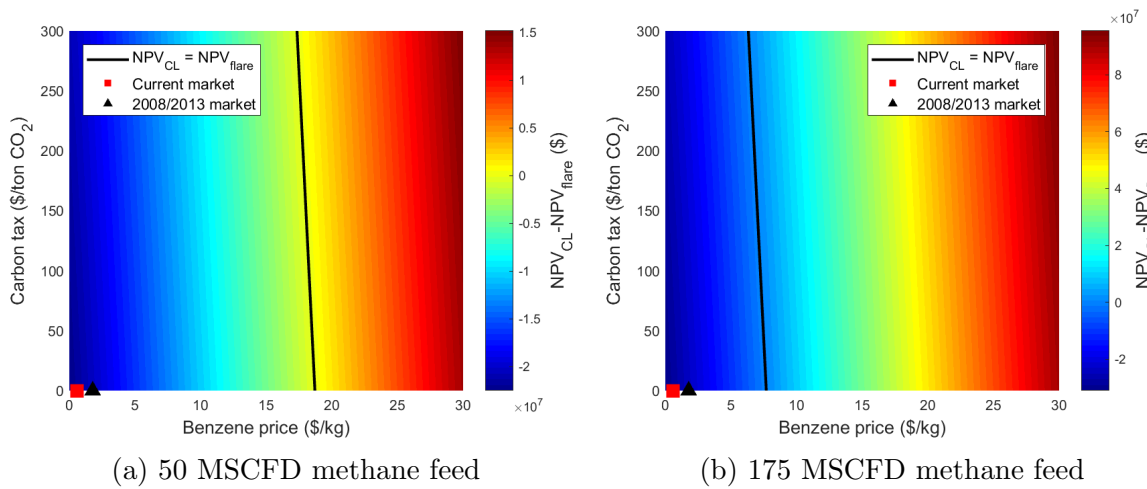


Figure 6.1: Difference in the NPV of the pioneer plant (design 1) and the NPV of flaring as a function of product price and carbon tax

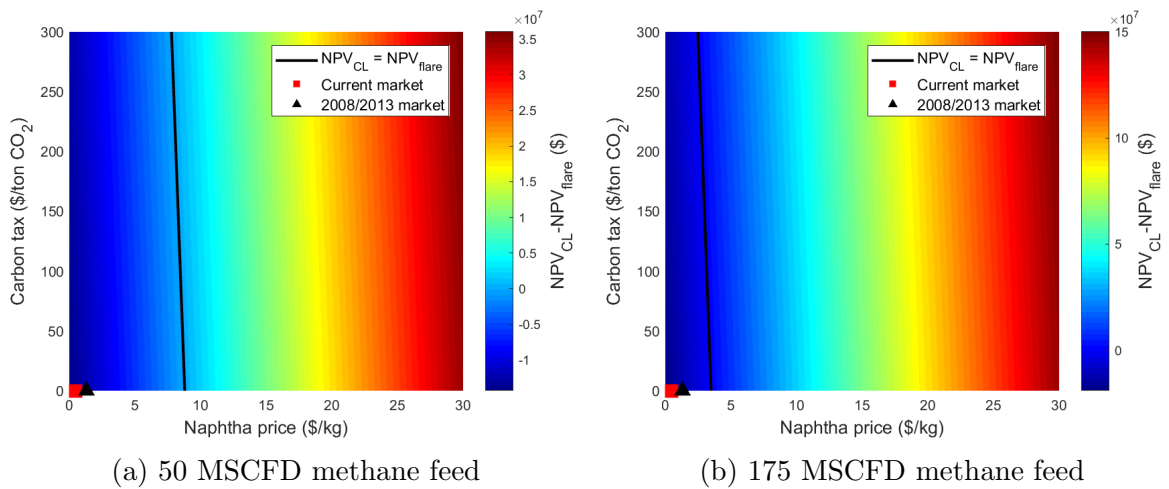


Figure 6.2: Difference in the NPV of the pioneer plant (design 2) and the NPV of flaring as a function of product price and carbon tax

Table 6.1: Parameters of the experience learning curve: improvement slope and 2029 market potential

Design	Improvement slope (%)
1 & 3	86.3
2 & 4	89.5
Capacity (MSCFD)	2029 market potential
50	13500
175	3600

6.1.2 Final Plant

A scenario in which a pioneer plant would turn a profit seems unlikely, barring major market or policy changes. However, it is not because the pioneer plant cannot be profitable, that subsequent plants also have to make a loss. Although, it has to be admitted that a non-profitable pioneer process is a significant economic hurdle, there are examples of processes and products that were originally loss-making, but turned profitable due to further investment and a willingness to learn in order to reduce costs. The most famous among them being the Ford Model T.¹⁶ All used the principle known as experience learning. As described in chapter 2, this principle predicts cost reductions due to increased knowledge of the process. As this type of cost reduction is a function of the cumulative amount of produced units, mass produces units, such as the proposed small scale plants, benefit most from this experience effect. In order to quantify the expected cost reductions, the improvement slope f and the market potential have to be known. Table 6.1 shows these parameters. Their derivation can be found in appendix E.

Using these parameters to estimate cost reductions for the final plant leads to figures 6.3 and 6.4. The capital and fixed operating costs of the final plants have dropped by more than 75% for the 50 MSCFD capacity plants and 70% for the 175 MSCFD capacity plants. This, of course, has big effects on the viability of the plants. Although, none of the designs or scales of the final plants are viable under the current

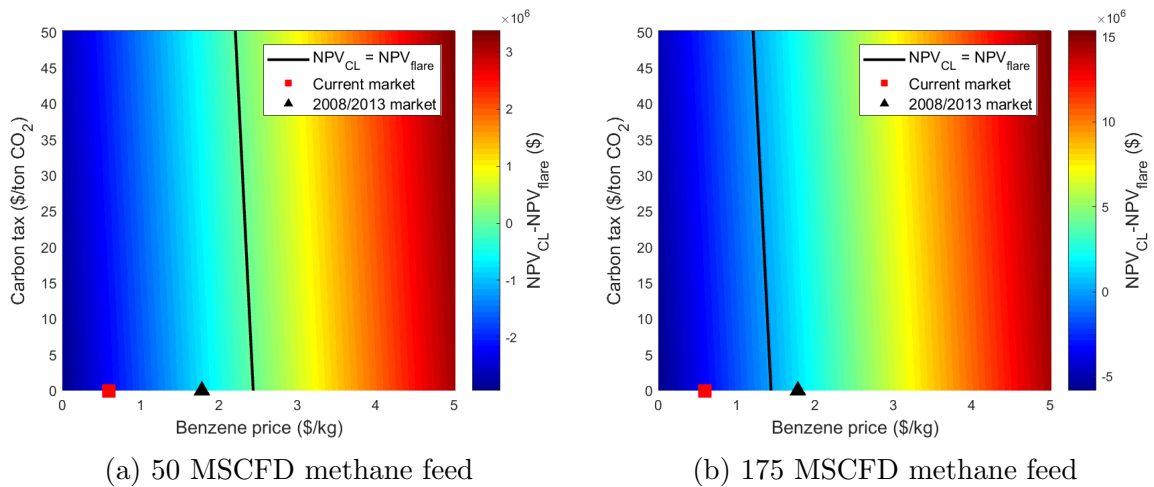


Figure 6.3: Difference in the NPV of the final plant (design 1) and the NPV of flaring as a function of product price and carbon tax

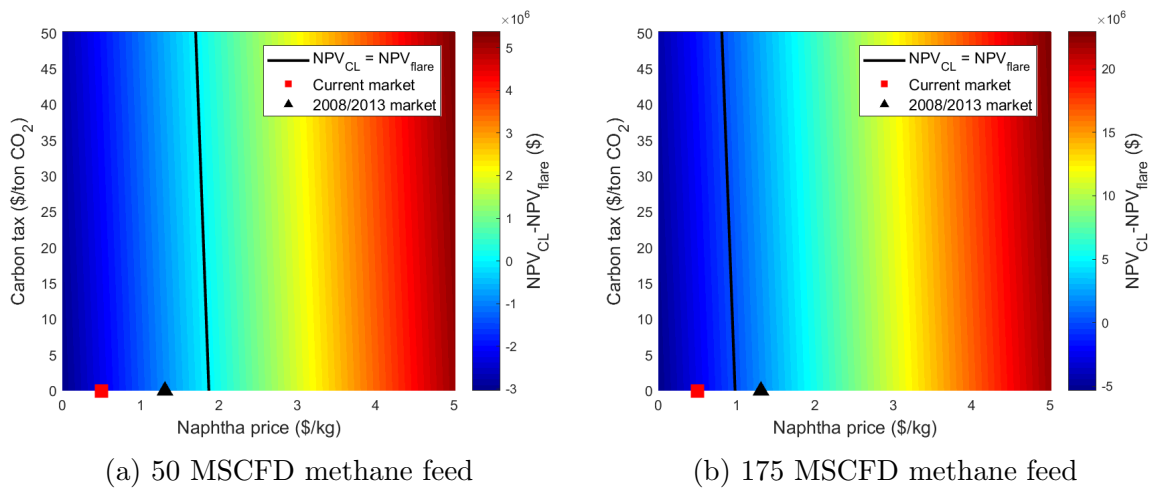


Figure 6.4: Difference in the NPV of the final plant (design 2) and the NPV of flaring as a function of product price and carbon tax

market conditions, the market conditions of 2008 and 2013 would lend themselves to viable final plants, where $NPV_{CL} > NPV_{flare}$. In order for the final plants to be viable under the current market conditions, steeper improvement slopes than those predicted by equation 2.9 are necessary. As most improvement slopes lie between 70% and 90%, the required values shown in table 6.2 are not unreasonable, but they are significantly lower than the predicted values in table 6.1.

Table 6.2: Improvement slopes required for plant designs 1 and 2 to become viable under the current market conditions when mass-produced

Design	Required improvement slope (%)	
	50 MSCFD	175 MSCFD
1	77.5	78
2	81.0	82.9

Again, the larger scale 175 MSCFD capacity plants perform the best, since they are the only plants that would become viable under the 2008/2013 market conditions with the predicted improvement slopes. These plants seem to have the optimal combination of scale and mass production cost benefits. Even though the cost reduction due to mass production is lower for the 175 MSCFD capacity plants, since the market potential is lower compared to the 50 MSCFD capacity plants, this is offset by the cost advantage that comes with a larger scale. This causes them to have an overall higher NPV than the smaller scale plants.

In short, the small scale 50 MSCFD capacity plants seem unlikely to become economically viable under any circumstance. Neither the pioneer plants, nor the predicted final plants come close to being profitable, or to a point where a reasonable carbon tax might make them viable. The larger scale, final 175 MSCFD capacity plants, however, have a chance of becoming an economically attractive alternative to flaring. Although the pioneer process is also unlikely to out compete flaring, historical conditions exist under which the final plants are profitable with the predicted improvement slopes. A combination of legislative action, through carbon pricing, and external market effects,

in the form of increased product prices, might reasonably cause the economic balance to tip in favor of the modular, mass-produced plants for methane dehydroaromatization through chemical looping with a 175 MSCFD methane capacity.

6.2 Economic Viability of Plants with Hydrogen Production

The economic viability of the plants with hydrogen production (design 3 and 4) will not be based on a comparison between the plant NPV and the NPV of flaring because of two reasons. The first being that the capital and operating costs of these plants are almost exactly the same as those of designs 1 and 2. The only difference between designs 3 and 4 and designs 1 and 2 is that the former also create hydrogen as a product. However, since hydrogen is a gas, it would be difficult to transport it away from the well to be sold, causing its value to be close to zero. The plants would therefore be viable under the exact same conditions as those specified in the previous sections. The second reason is that this thesis is not interested in the overall economic viability of these plant designs, but in their ability to produce hydrogen gas under $2\frac{\$}{kg}$, as the US Department of Energy has expressed interest in technologies that could do so. The cost of manufacturing (COM), as described in chapter 2, is therefore a much better suited investment parameter. The COM has been calculated assuming a 30 year plant lifetime, a 10% discount rate and a linear amortization of the capital costs.

6.2.1 Pioneer Plant

The COM (figure 6.5) of the pioneer plants is dominated by the capital costs, amortized as depreciation, followed distantly by the fixed costs, which scale with the capital cost through maintenance and insurance. The raw material costs and the utility costs make up only a tiny fraction of the cost of manufacturing. The pioneer plants clearly do not come close to the target of $2\frac{\$}{kg}$, although the larger scale 175 MSCFD capacity plants clearly outperform the smaller 50 MSCFD capacity plants again. This is another good representation of scaling effects: capital costs do not increase nearly as much as capacity, causing the produced amount of hydrogen gas, and the revenues of

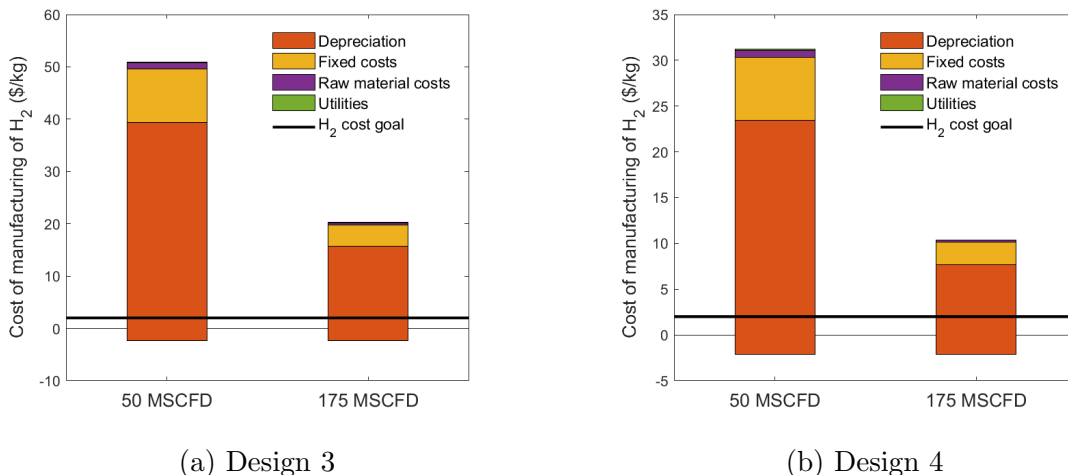


Figure 6.5: Cost of manufacturing of hydrogen gas for pioneer plants

the produced benzene and naphthalene, to increase much more than the costs, which results in a lower COM. Design 4 also performs much better than design 3, due to having a cheaper TSA unit and separation section (see chapter 5). In order for the pioneer plants to reach the cost target, the revenues generated by the byproducts would have to increase by a factor of 8 or more.

6.2.2 Final Plant

The pioneer plants will clearly not reach the desired cost target. However, the final plants, which can take advantage of experience learning effects to reduce costs, might still prove capable of reaching the target. The parameters used to quantify the experience learning cost reduction can be found in table 6.1, while their derivations are located in appendix E. Figure 6.6 shows the COM of the final plants. Note that these costs are no longer divided into different categories, as it is impossible to predict how much each individual cost will decrease through experience learning.

Even though experience learning effects significantly decrease the cost of manufacturing, only the mass-produced 175 MSCFD capacity plants are capable of producing hydrogen sufficiently cheaply to reach the $2 \frac{\$}{kg}$ cost target under the current market conditions. However, given the market conditions of 2008 and 2013, it would also

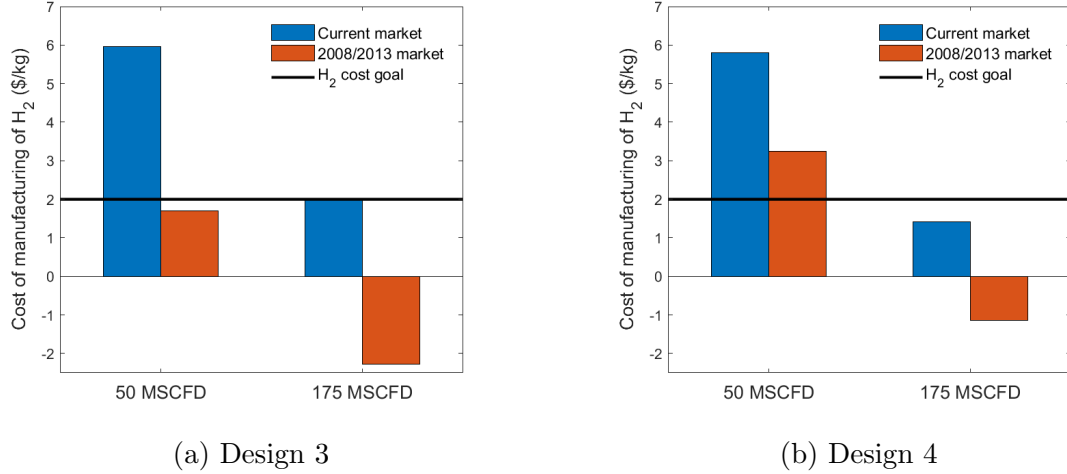


Figure 6.6: Cost of manufacturing of hydrogen gas for final plants

become possible for the mass-produced 50 MSCFD capacity plants with hydrocarbon separation (design 3) to produce hydrogen at a cost lower than $2 \frac{\$}{kg}$. In order for the 50 MSCFD capacity plants to reach the cost target under the current market conditions, steeper improvement slopes than those predicted by equation 2.9 are necessary. The required values of the improvement slopes, as shown in table 6.3, all lie between 70% and 90% and are therefore reasonable. However, these values are still significantly lower than those predicted in table 6.1.

Table 6.3: Improvement slopes required for plant designs 3 and 4 with a 50 MSCFD methane capacity to reach the $2 \frac{\$}{kg}$ cost target under the current market conditions when mass-produced

Design	Required improvement slope (%)
3	81.2
4	84.5

Yet again, the 175 MSCFD capacity plants prove to have the best combination of scaling and mass production effects, with the larger scale offsetting the smaller cost reduction through mass production. The final 175 MSCFD capacity plants, with the predicted improvement slopes, even exhibit negative COMs under the market conditions of 2008 and 2013, indicating that a profit could be made even without hydrogen

production. This is in agreement with the NPV analysis performed in section 6.1, which showed that the mass-produced 175 MSCFD capacity plants were economically viable under the 2008/2013 market conditions.

Here too, the small scale 50 MSCFD capacity plants seem unlikely to reach the cost target for hydrogen production under the current market conditions. The costs of manufacturing for both the pioneer and predicted final plants are simply too high, with revenues obtained through the sale of byproducts (benzene and naphthalene) unlikely to reduce the overall cost sufficiently. However, historical conditions do exist under which one of the mass-produced 50 MSCFD capacity plants reaches the cost target with the predicted improvement slope. The larger scale 175 MSCFD capacity plants have a higher chance of reaching the $2 \frac{\$}{kg}$ target. Although the pioneer plants are clearly never close to reaching this target, the final plants, with the predicted improvement slopes, might be able to produce hydrogen gas sufficiently cheaply, even under the current market conditions.

Chapter 7

CONCLUSION

A novel approach for natural gas to liquids conversion was proposed, to reduce the amount of stranded gas and its associated flaring in the United States. This process uses a dehydroaromatization reaction to convert methane to benzene and naphthalene. Because the reaction is thermodynamically limited by the produced hydrogen, the hydrogen has to be converted to water in a chemical looping unit using metal oxides. The water can subsequently be removed, breaking the equilibrium and increasing conversion.

Four plants were designed to achieve this process on a modular, small scale, with methane gas feed rates of 50 MSCFD and 175 MSCFD. These capacities were chosen because wells producing those amounts of natural gas are responsible for almost 50% of all flaring in the US. Two of these plants were designed to have only liquid products, with the intent of competing directly against flaring as a natural gas processing unit. Several chemical looping reactor stages were put in series in an effort to increase overall conversion and decrease separation costs. One of these plants separates the produced benzene/naphthalene mixture to sell the higher value benzene independently of the naphthalene. The second plant does not separate this mixture, instead selling it as cheaper virgin naphtha. The other two plants use steam instead of oxygen to re-oxidize the chemical looping beds, with the goal of producing pure hydrogen gas under $2\frac{\$}{kg}$. These plants also have one version that separates the hydrocarbons and one that does not.

An analysis of the capital and operating costs showed that adding reactor stages in series did not decrease overall costs. At the small capacities at which these plants operate, their cost is largely independent of capacity. This is especially true for the

separation section of the plant, causing the decrease in flow rate, due to a higher conversion, to only have a minimal effect on separation costs. Instead, adding reactor stages increased overall costs, which is why this approach was abandoned and all economic analyses were performed on plants with only one reactor section. The scaling effect inherent to chemical process economics could be readily seen here. Comparing the 50 MSCFD plants to the 175 MSCFD plants, capital costs increased by approximately 30%, while capacity increased by more than threefold. Indicating that the larger scale 175 MSCFD pioneer plants would be more viable. The designs without hydrocarbon separation had capital costs that were roughly 40% lower than the designs with hydrocarbon separation. This was due to a decrease in the TSA bed sizes and a significant simplification of the separation section of the plants, going from two flash drums, a high pressure compressor and a turbine, to a simple decanter. The operating costs for all designs were dominated by the fixed costs, which is the opposite cost make-up of large scale plants. Fixed costs scale with capital costs through maintenance and insurance and, since capital costs are relatively high at these small scales, the fixed costs were high too.

An NPV calculation for the designs using oxygen as the re-oxidizer in the chemical looping reactors was performed to compare it to the NPV of flaring. The small scale 50 MSCFD capacity plants proved unlikely to ever become viable. Neither the pioneer plants, nor the final plants, which had lower costs due to experience learning effects, came close to being profitable. Due to natural gas being relatively clean to flare, a carbon tax also had a limited effect on the viability of the plants. The final 175 MSCFD capacity plants, however, seemed to benefit from an ideal combination of scaling and experience learning effects, with a lower experience learning cost reduction being offset by traditional chemical plant cost scaling laws favoring larger plants. Under the market conditions of 2008 and 2013, these final 175 MSCFD capacity plants proved capable of out competing flaring as they had a larger net present value than a flaring installation. This conclusion was true for the plants with and without hydrocarbon separation, although the plants without hydrocarbon separation performed slightly better.

A similar conclusion followed from the cost of manufacturing analysis performed on the hydrogen gas producing plants. Although the 50 MSCFD capacity plants proved incapable of reaching the $2\frac{\$}{kg}$ cost target under the current market conditions, the final 50 MSCFD capacity plant with hydrocarbon separation and both mass-produced plants with a 175 MSCFD methane capacity were capable of reaching the hydrogen production cost target under favourable market conditions, such as those in 2008 and 2013.

None of the proposed plants, using chemical looping and dehydroaromatization to convert methane to liquid hydrocarbons, were viable as pioneer plants. This poses a significant hurdle to achieving widespread commercialisation, as investors must be willing to operate at an initial loss. However, an experience learning analysis, simulating the cost reducing effects of mass production, has shown that mass-produced plants with a 175 MSCFD methane feed rate, can become sources of cheap hydrogen gas or viable alternatives to stranded natural gas flaring, under the right market conditions.

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Appendix A

FEED AND PRODUCT FLOW RATES

This appendix provides a complete overview of the feed and product flow rates of all plant designs as discussed in chapter 4. These flow rates have been calculated using Aspen Plus and can be found in table [A.1](#).

Table A.1: Feed and product stream flow rates for all plant designs

Stream	Flow rate ($\frac{kg}{hr}$)	
Design 1		
1 stage		
	50 MSCFD feed	175 MSCFD feed
Benzene	24.8	82.8
Naphthalene	7.7	25.7
2 stages		
	50 MSCFD feed	175 MSCFD feed
Benzene	22.0	73.5
Naphthalene	11.0	36.7
3 stages		
	50 MSCFD feed	175 MSCFD feed
Benzene	19.0	63.5
Naphthalene	14.2	47.4
4 stages		
	50 MSCFD feed	175 MSCFD feed
Benzene	16.1	53.8
Naphthalene	17.2	57.4
Design 2		
	50 MSCFD feed	175 MSCFD feed
Naphtha	32.4	108.2
Design 3		
	50 MSCFD feed	175 MSCFD feed
Benzene	24.8	82.8
Naphthalene	7.7	25.7
Design 4		
	50 MSCFD feed	175 MSCFD feed
Naphtha	32.4	108.2

Appendix B

FLOW SHEETS AND OPERATING CONDITIONS FOR PLANT DESIGNS WITH HYDROGEN PRODUCTION

This appendix contains the process flow diagrams of the plants with hydrogen production (designs 3 and 4), as discussed in section 4.2, as well as the operating conditions of all their units. The process flow diagram for the plant with full hydrocarbon separation can be found in figure B.1, whilst figure B.2 shows the process flow diagram of the plant design without hydrocarbon separation. Table B.1 contains the operating conditions of both designs.

Table B.1: Operating conditions of the hydrogen producing plants

Process equipment	Temperature ($^{\circ}C$)	Pressure (<i>bar</i>)
Design 3		
DHA	800	1
CL		
Reduction	750	1
Oxidation	800	1
Water removal - TSA		
Adsorption	250	1
Regeneration	500	1
Flash Drum 1	28	1
Flash Drum 2	10	30
Design 4		
DHA	800	1
CL		
Reduction	750	1
Oxidation	800	1
TSA		
Adsorption	50	1
Regeneration	500	1
Decanter	10	1

Appendix C

DETAILED OVERVIEW OF COST ESTIMATION CALCULATIONS

This appendix provides a detailed overview of all equations and assumptions used in estimating the capital and operating costs associated with the plant designs as discussed in chapter 4.

C.1 Capital Cost Estimates

The capital costs have been estimated following the procedure outlined in section 2.1.1. What follows is a detailed overview of all the equations and parameters used to obtain these estimates.

C.1.1 ISBL Cost Estimates

Since all the plants are similar in design, the cost estimation techniques will be discussed on a process unit basis, instead of for each plant individually. The total plant ISBL costs are obtained by adding the installed costs of all equipment together, as was explained in section 2.

C.1.1.1 Separation Section

Since all the units present in the separation sections of the plant are heat exchangers, flash drums, compressors, expanders or decanters they could be modelled and priced directly by Aspen Plus and its built in cost estimation program Aspen Process Economic Analyzer (APEA). This software simply requires the user to map units to certain equipment templates (table C.1) and subsequently calculates equipment weight, installed equipment weight, purchased equipment cost and installed equipment cost.

Table C.1: APEA equipment mappings

Unit	Mapping
Heat exchanger	Shell and tube
Flash drum	Jacketed vertical vessel Shell and tube heat exchanger Light liquid recycle pump
Compressor	Horizontal centrifugal compressor
Expander	Non-condensing turbine
Decanter	Vertical process vessel

C.1.1.2 Chemical Looping Reactor

The chemical looping reactor was modelled as a collection of parallel SS321 horizontal vessels containing fixed beds of Fe_3O_4/FeO . The vessels also contain inter-coolers to ensure isothermal operation. Compressors are present outside of the reactor vessels to provide regeneration gas flow.

Metal Oxide Beds

First the amount of fixed beds in parallel N_{bed} has to be determine. Using equation C.1 ensures that at least one bed is always on-line.

$$N_{bed} \geq \frac{t_{oxi}}{t_{oxi} + t_{red} + t_{switch}} \quad (C.1)$$

Knowing this, the individual bed mass m_{bed} can be calculated using equation C.2 as well as the total purchasing cost of all beds (equation C.3) with the molar flow rate of hydrogen Fl_{H_2} ($\frac{mol}{s}$) as the size determining parameter.

$$m_{bed} = \frac{Fl_{H_2} M_{Fe_3O_4}}{x_{ox}} t_{oxi} \quad (C.2)$$

$$C_{bed} = m_{bed} C_{Fe_3O_4} N_{bed} \quad (C.3)$$

Reactor Vessel

Vessel cost correlations exist in the form of equation C.4. The cost scaling parameter is equal to the vessel mass m_v (kg).⁷ Since the CL reactors operate at high temperatures, SS321 is used as the construction material.³³ Since the correlation dates from 2010, a CEPCI correction has to be made. The vessel mass and cost was calculated using equations C.4 to C.7.³⁴

$$C_v = (10200 + 31m_v^{0.85}) \frac{CEPCI_{2018}}{CEPCI_{2010}} N_{bed} \quad (C.4)$$

$$V_{bed} = \frac{m_{bed}}{\rho_{Fe3O4}} \epsilon \quad (C.5)$$

$$V_{bed} = \frac{\pi LD^2}{4} \quad (C.6)$$

$$m_v = \rho_v(\pi D(L + L_{int})t_w + \pi D^2 t_w) \quad (C.7)$$

Compressor

The equipment cost scaling parameter for the compressor is the air flow rate Fl_{air} ($\frac{m^3}{s}$) for designs 1 and 2. The costing equation itself takes the form of equation C.9.³⁵ Carbon steel has sufficiently high temperature resistance, so a higher grade alloy is not necessary.³³ CEPCI indexing is required, since the cost equation dates from 2002. The air flow rate was obtained from the overall oxidation-reduction reaction stoichiometry and the ideal gas law, which results in equation C.8.

$$Fl_{air} = 2.38 Fl_{H_2} \frac{RT}{2P} \quad (C.8)$$

$$C_{comp} = 44700 Fl_{air}^{0.67} \frac{CEPCI_{2018}}{CEPCI_{2002}} \quad (C.9)$$

Designs 3 and 4 do not use oxygen as the re-oxidizer, but steam. It is therefore the steam flow rate, Fl_{steam} , that determines the compressor cost, according to equations C.10 and C.11.

$$Fl_{steam} = Fl_{H_2} \frac{RT}{P} \quad (C.10)$$

$$C_{comp} = 44700 Fl_{steam}^{0.67} \frac{CEPCI_{2018}}{CEPCI_{2002}} \quad (C.11)$$

Heat Exchanger

The heat exchangers are used to remove the heat generated in the exothermic CL reaction when oxygen is used as the re-oxidizer (design 1 and 2) or to divert the heat from the exothermic reaction to the oxidation reaction when steam is used as the re-oxidizer (design 3 and 4). Their cost is determined by their heat exchange surface area A (m^2). Large heat exchangers ($> 10m^2$) were costed using equation C.12,⁷ whilst the cost of smaller heat exchangers was determined with equation C.13.¹⁰ The heat exchange surface area was calculated using equation C.14, in which the produced heat of reaction Q (W) is the size determining parameter. Like the reactor vessels, they have to be made out of SS321.

$$C_{hex} = (2800 + 54A^{1.2}) \frac{CEPCI_{2018}}{CEPCI_{2010}} \quad (C.12)$$

$$C_{hex} = 9800A^{0.13} \quad (C.13)$$

$$A = \frac{Q}{h\Delta T_{LM}} \quad (C.14)$$

Fired Heaters

Since designs 3 and 4 lack the CL reaction as a heat source, the heat to warm up the steam to reaction temperatures for re-oxidation has to be provided by fired

heaters. The cost determining parameter for a fired heater is its heat duty Q (W), as calculated by equation C.15 and C.16. The heat duty was used to calculate the heater cost with equation C.17.³⁵ SS321 has to be used as the construction material.

$$\dot{m}_{steam} = Fl_{steam} \frac{P}{RT} M_{fg} \quad (C.15)$$

$$Q = \dot{m}_{steam} C_{p,steam} \Delta T \quad (C.16)$$

$$C_{fh} = 0.62Q^{0.85} \frac{CEPCI_{2018}}{CEPCI_{2002}} \quad (C.17)$$

Parameters

The equations mentioned in the previous sections require parameters to generate numerical results. These parameters can be found in table C.2. Every parameter not explicitly mentioned in this table was an output of the plant model as solved by Aspen Plus.

Installed Equipment Cost

In order to determine the installed equipment cost of the CL reactor, all the individual equipment costs previously mentioned have to be multiplied by their respective Lang factors (table C.3) and summed together as in equation 2.4.

C.1.1.3 Temperature Swing Adsorption Unit

The TSA unit was modelled as a collection of parallel vessels containing a fixed zeolite 3Å bed. An additional compressor and heat exchanger or fired heater provide flush gas for bed desorption at the desorption temperature.

Zeolite Beds

The fixed bed size is based on the amount of material it has to adsorb. For designs 1 and 3 this is solely the amount of H_2O adsorption, for designs 2 and 4 this is

Table C.2: Parameters used in determining purchased equipment cost of the CL reactor

Parameter	Description	Value
t_{oxi}	Bed oxidation time	800s ³⁶
t_{red}	Bed reduction time	800s ³⁶
t_{switch}	Time it takes to switch reactors between oxidation and reduction	400s ³⁶
$M_{Fe_3O_4}$	Molar mass of Fe3O4	$0.2135 \frac{kg}{mol}$ ³⁷
x_{ox}	Maximum Fe3O4 conversion in bed	40%
$C_{Fe_3O_4}$	Cost of Fe3O4	$0.2 \frac{\$}{kg}$ ³⁸
$CEPCI_{2018}$	2018 Chemical engineering cost index	576.4 ¹³
$CEPCI_{2010}$	2010 Chemical engineering cost index	532.9 ⁷
$\rho_{Fe_3O_4}$	Density of Fe3O4	$5170 \frac{kg}{m^3}$ ³⁷
ϵ	Bed porosity	40% ³⁶
$\frac{L}{D}$	Bed ratio	2 ³⁶
ρ_v	SS321 density	$7850 \frac{kg}{m^3}$ ³⁴
L_{int}	Additional vessel length for vessel internals Design 1 and 2 Design 3 and 4	1.98L ³⁹ 0.84L ³⁹
t_w	Vessel wall thickness	0.05m ³⁴
R	Ideal gas constant	$8.31 \frac{J}{molK}$
T	Inlet re-oxidizer gas temperature Design 1 and 2 Design 3 and 4	25°C 500°C
$CEPCI_{2002}$	2002 Chemical engineering cost index	395.6 ⁷
h	Overall heat transfer coefficient	$150 \frac{W}{m^2K}$ ⁷

Table C.2: continued

Parameter	Description	Value
ΔT_{LM}	Log mean temperature difference between hot and cold side of heat exchanger	
	Design 1 and 2	
	Internal heat exchanger	$50^{\circ}C$
	External heat exchanger	$766^{\circ}C$
Design 3 and 4		
	Internal heat exchanger	$22^{\circ}C$
ΔT	Temperature difference before and after the fired heater	$300^{\circ}C$
M_{steam}	Molar mass of water	$0.018 \frac{kg}{mol}$ ¹⁷
$C_{p,steam}$	Heat capacity of steam	$2.15 * 10^3 \frac{J}{kgK}$ ¹⁷

Table C.3: Lang factors for the determination of the total installed cost of the CL reactor for carbon steel (CS) and SS321

Equipment	Installation factor	
	CS	SS321
Vessel	3^8	3.8^8
Compressor	2.5^7	2.8^8
Heat exchanger	3.5^7	4.1^8
Fired heater	2^7	2.2^8

the amount of H_2O and hydrocarbon adsorption. The incoming stream to be adsorbed is represented by Fl_{ad} ($\frac{kg}{s}$). Equations C.18 and C.19 are adaptations of equations C.2 and C.3 respectively.

$$m_{bed} = \frac{Fl_{ad}}{x_{zeo}} t_{ad} \quad (C.18)$$

$$C_{bed} = m_{bed} C_{zeo} N_{bed} \quad (C.19)$$

Adsorption Vessel

The equations used to cost the adsorption vessels are exactly the same as equations C.4 to C.7. The TSA unit operates at sufficiently low temperatures to allow for the use of carbon steel.³³

Compressor

The equation used to evaluate the equipment cost of the compressor, that maintains the regeneration flush gas flow rate, is the same as equation C.9, with Fl_{air} being replaced by Fl_{fg} , the flush gas flow rate in $\frac{m^3}{s}$. The flush gas flow rate is taken to be 20% of the feed flow rate.³⁴

Heat Exchanger

The heat exchangers are only used in designs 1 and 2 to heat the incoming flush gas stream. Similarly to the CL reactor, large heat exchangers ($> 10m^2$) were costed using equation C.12, whilst the cost of smaller heat exchangers was determined with equation C.13. Equations C.20 to C.22 were used to determine the heat exchange surface area A. The flush gas has properties similar to air.

$$\dot{m}_{fg} = Fl_{fg} \frac{P}{RT} M_{fg} \quad (C.20)$$

$$Q = \dot{m}_{fg} C_{p,fg} \Delta T \quad (C.21)$$

$$A = \frac{Q}{h\Delta T_{LM}} \quad (\text{C.22})$$

Fired Heaters

Since designs 3 and 4 lack the CL reaction as a heat source, the heat to warm up the incoming flush gas has to be provided by fired heaters. The cost determining parameter for a fired heater is its heat duty Q (W), as calculated by equation C.21. This heat duty was used to calculate the heater cost with equation C.17. The lower operating temperatures of the TSA unit do not require a high temperature resistant steel to be used.³³

Parameters

The equations mentioned in the previous sections require parameters to generate numerical results. These parameters can be found in table C.4. Every parameter not explicitly mentioned in this table was an output of the plant model as solved by Aspen Plus.

Installed Equipment Cost

The installed equipment cost of the TSA unit was calculated completely similarly to the method used to determine the CL installed costs, with the same installation factors as table C.3.

C.1.1.4 DHA Reactor

The DHA reactor cost scales with the reactor heat duty Q (MW), according to the scaling law in equation C.23. The installation factor for this unit is 1.5.¹³ Q is a direct output of the Aspen Plus model.

$$C_{DHA} = 100,380,00 \left(\frac{Q}{500} \right)^{0.67} \quad (\text{C.23})$$

However, if this equation is used, the DHA reactor cost behaves markedly different from the rest of the plant, as can be seen on figure C.1a. The equipment cost of the DHA reactor keeps going down, as the capacity of the plant decreases, even though

Table C.4: Parameters used in determining purchased equipment cost of the TSA unit

Parameter	Description	Value
N_{bed}	Number of vessels in parallel	4 ³⁴
t_{ad}	Adsorption time	3600s ¹⁹
x_{zeo}	Maximum Fe ₃ O ₄ conversion in bed Design 1 and 3 Design 2 and 4	4wt% 20wt%
C_{zeo}	Cost of zeolite 3Å	0.8 $\frac{\$}{kg}$ ⁴⁰
$CEPCI_{2018}$	2018 Chemical engineering cost index	576.4 ¹³
$CEPCI_{2010}$	2010 Chemical engineering cost index	532.9 ⁷
$\rho_{Fe_3O_4}$	Density of zeolite 3Å	700 $\frac{kg}{m^3}$ ¹⁷
ϵ	Bed porosity	40% ³⁴
$\frac{L}{D}$	Bed ratio	2 ³⁴
ρ_v	SS321 density	7850 $\frac{kg}{m^3}$ ³⁴
L_{int}	Additional vessel length for vessel internals	0.2L ³⁴
t_w	Vessel wall thickness	0.05m ³⁴
R	Ideal gas constant	8.31 $\frac{J}{molK}$
T	Inlet re-oxidizer gas temperature	25°C
$CEPCI_{2002}$	2002 Chemical engineering cost index	395.6 ⁷
h	Overall heat transfer coefficient	150 $\frac{W}{m^2K}$ ⁷
ΔT_{LM}	Log mean temperature difference between hot and cold side of heat exchanger	510°C
ΔT	Temperature difference before and after the fired heater	475°C
M_{fg}	Molar mass of flush gas	0.029 $\frac{kg}{mol}$ ¹⁷
$C_{p,fg}$	Heat capacity of the flush gas	1.08 * 10 ³ $\frac{J}{kgK}$ ¹⁷

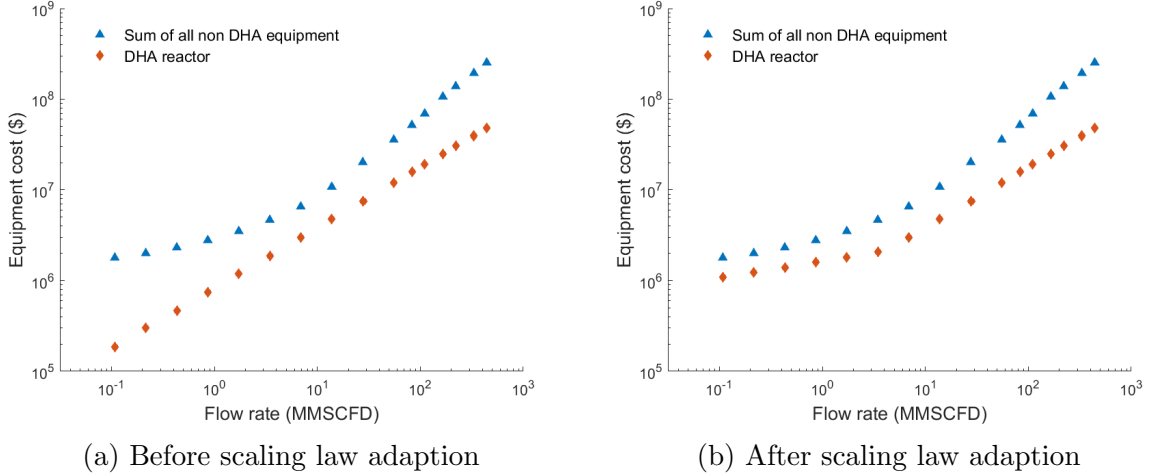


Figure C.1: Equipment cost of the DHA reactor compared to the sum of the cost of all other plant equipment as a function of plant capacity

the combined cost of all other units begins to decrease at a decelerated rate. This is due to the fact that equation C.23 was made for large scale installations and does not take small scale effects into account. That causes the DHA cost to keep decreasing as though it stays a large scale reactor.

Since this thesis concerns itself with small scale, modular plants, an adaption to equation C.23 was proposed to bring the DHA reactor cost in line with the rest of the plant. Equation C.24 shows this adapted scaling law, which was used for heat duties below $1.6MW$. Figure C.1b shows the effect of using this scaling law for smaller scales. This adaption clearly brings the cost behavior of the DHA reactor closer to that of the rest of the plant.

$$C_{DHA} = 2,150,000 \left(\frac{Q}{1.6} \right)^{0.19} \quad (C.24)$$

C.1.1.5 Trailers

After the installed cost of all equipment has been calculated, it becomes possible to estimate the weight of the plant. This can subsequently be used to estimate the amount of 18-wheelers necessary to transport the modular, movable plants to the well

sites. An 18-wheeler trailer costs on average \$50,000 and can legally carry at most 80,000 lbs.⁴¹

Since chemical plants are usually built on solid ground and the plant weight therefore does not tend to be a major concern, there are little to no correlations in literature that allow for the estimation of equipment weight. Only the Aspen Process Economic Analyzer software has been found to report installed equipment weight. This information was used to establish a relationship between installed cost and installed weight. Since vessel costing equations, like equation C.4 are based on the equipment mass and vessels generally account for much of the plant weight and cost,⁶ it was assumed that every plant scale has a particular installed weight to installed cost ratio. Based on the parts of the plant designs for which weight information was available through APEA, these ratios were determined to be $0.06 \frac{\text{lbs}}{\$}$ and $0.07 \frac{\text{lbs}}{\$}$ for the 50 MSCFD and 175 MSCFD capacity plants respectively.

C.1.2 Total Capital Investment

The total capital investment was based on the ISBL costs calculated in the previous section. The approach completely follows the methodology of section 2.1.1.3 and table 2.1.

C.1.2.1 Pioneer Plant Cost

The pioneer plant cost analysis was performed using equations 2.5 and 2.6 and was based on the costs determined in the previous sections. The parameter values for equation 2.5 can be found in table C.5.

C.2 Operating Costs

The operating costs have been calculated using the approach as outlined in section 2.1.2. What follows is a detailed overview of all the equations and parameters used to obtain the operating cost estimates.

Table C.5: Parameter values for the calculation of the pioneer plant cost growth using equation 2.5

Parameter	Value
PCT_new	Reactor section costs as a percentage of total ISBL costs (%)
IMP	2.3 ¹³
COMP	
Design 1 and 3	5
Design 2 and 4	4
INC	100% ¹³
PD	8 ¹³

C.2.1 Raw Material Costs

Since the process feedstock consists of methane from stranded natural gas that would otherwise be flared, it was assumed methane has no value. The only raw materials consumed during this process are therefore the DHA catalyst material, the CL oxide and the TSA zeolite 3Å. The purchasing costs ($C_{bed,i}$) of the beds are the basis of the raw material cost estimates. Equation C.27 gives the annual bed replacement cost estimate. The purchasing costs of the oxide and zeolite beds have already been determined in previous sections, with the material lifetime determined by equation C.25. The purchasing cost of the DHA catalyst bed has to be calculated with equation C.26, where the feed flow rate Fl_{Feed} ($\frac{l}{s}$) is an output of Aspen Plus. Table C.6 specifies the parameter values.

$$t_{life} = t_{cycle}N_{cycle} \quad (C.25)$$

$$C_{bed,cat} = \frac{Fl_{feed}}{l_{cat}}C_{cat} \quad (C.26)$$

$$C_{raw} = \sum_{i=1}^3 C_{bed,i} \frac{t_{life,i}}{t_{op}} f_{inst} \quad (C.27)$$

Table C.6: Parameters used in determining the raw material cost

Parameter	Description	Value
t_{cycle}	Total bed cycle time	
	CL oxide beds	2000s ³⁶
	TSA zeolite 3Å beds	14400s ¹⁹
N_{cycle}	The maximum amount of cycles the material can withstand before it needs to be replaced	
	CL oxide beds	1000
	TSA zeolite 3Å beds	450 ³⁴
$t_{life,cat}$	Lifetime of catalyst bed	$2.4 * 10^7 s$ ¹³
l_{cat}	Catalyst bed loading	$4.17 \frac{l}{kg_{cat} s}$ ¹³
C_{cat}	Catalyst cost	$275 \frac{\$}{kg}$ ¹³
t_{op}	Operating time per year	$7884hr (2.8 * 10^7 s)$ ¹¹
f_{inst}	Bed manufacturing and installation factor	1.5 ¹¹

C.2.2 Utility Costs

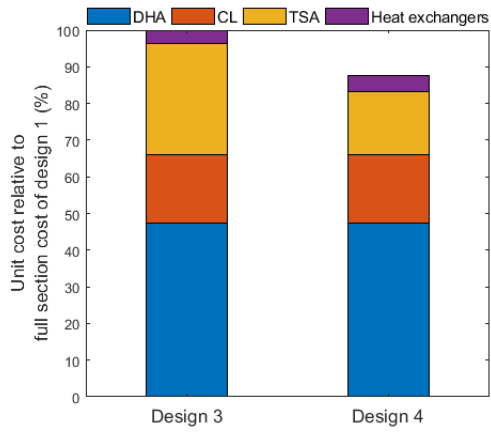
All utility cost estimates were obtained directly from the appropriate Aspen Plus models through the use of the Aspen Process Economic Analyzer software.

C.2.3 Fixed Costs

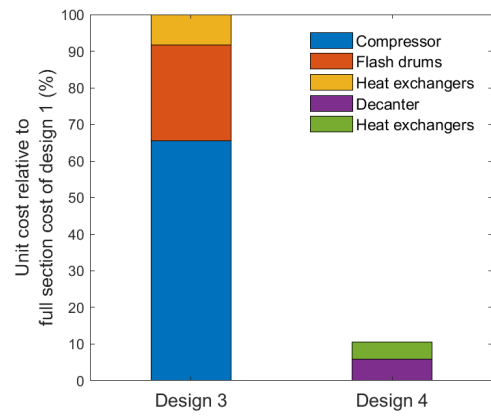
Maintenance and insurance costs were based on the capital cost estimates determined in previous sections of this appendix. The factors used to go from ISBL costs and FCI to maintenance and insurance costs respectively can be found in section 2.1.2. It is assumed that one additional operator is sufficient to safely run this plant. The \$50,000 salary of this operator forms the basis for the salaried and overhead fixed costs as previously defined.

Appendix D
CAPITAL AND OPERATING COSTS OF PLANTS WITH
HYDROGEN SEPARATION

This appendix contains all capital and operating cost estimates performed for the plant designs with hydrogen separation (designs 3 and 4). The conclusions that can be drawn from these costs are exactly the same as the conclusions of designs 1 and 2 as specified in chapter 5. Because the plant designs are slightly different from designs 1 and 2, the costs differ slightly too, which is why all costs were still included here. All reported costs are pioneer plant costs.

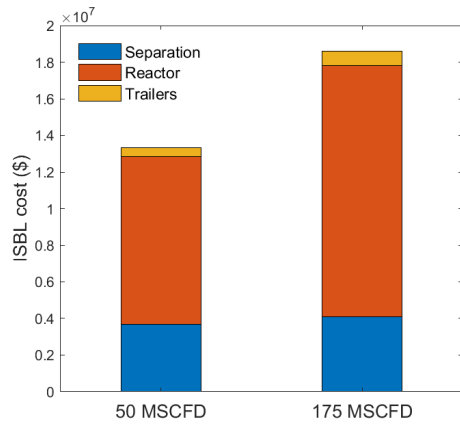


(a) Reactor section

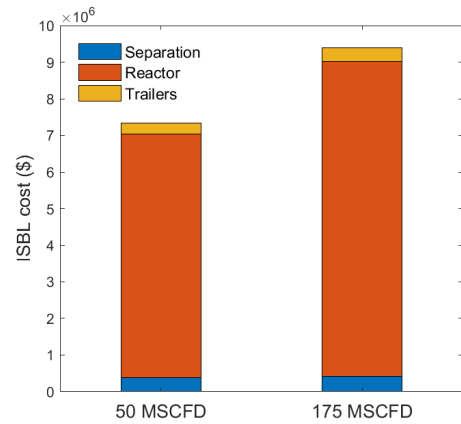


(b) Separation section

Figure D.1: Installed unit costs relative to total installed section costs for design 4 compared to design 3

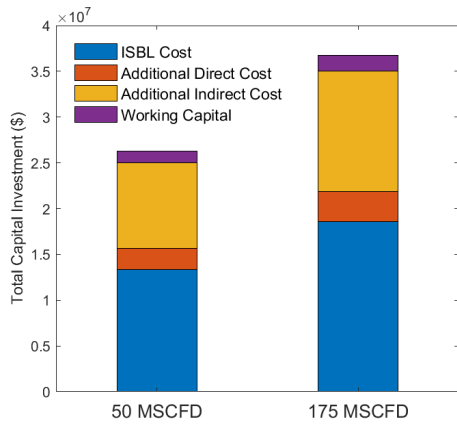


(a) Design 3

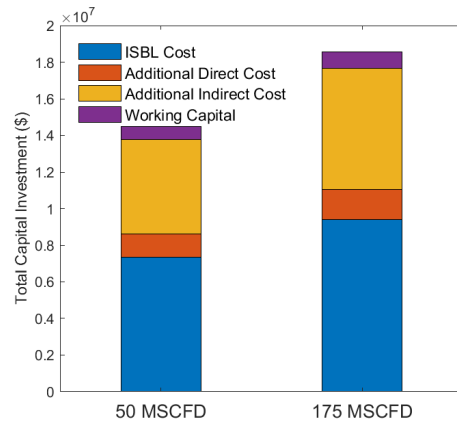


(b) Design 4

Figure D.2: Total ISBL cost of designs 3 and 4

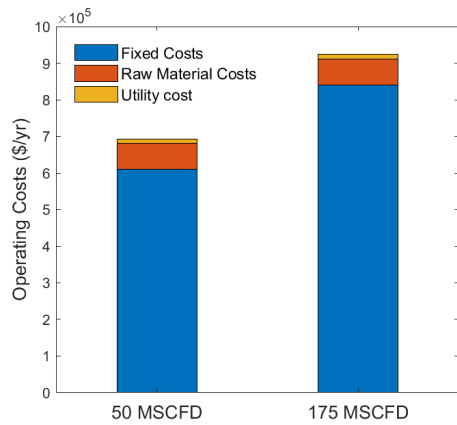


(a) Design 3

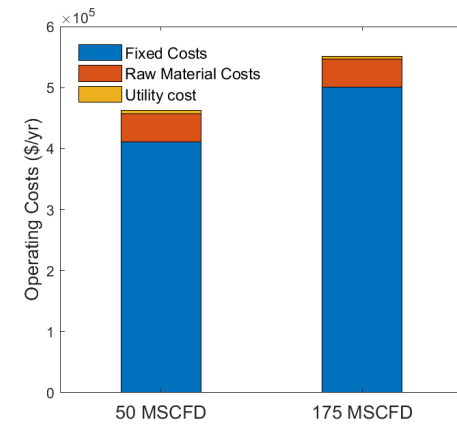


(b) Design 4

Figure D.3: Total capital investment of designs 3 and 4



(a) Design 3



(b) Design 4

Figure D.4: Operating cost of designs 3 and 4

Appendix E

DETAILED OVERVIEW OF EXPERIENCE LEARNING COST REDUCTION CALCULATIONS

In order to use the experience learning curve to predict capital and fixed operating cost reductions due to mass production, two parameters have to be known: the improvement slope and the cumulative production number. The former predicts how quickly the costs will decline, whilst the latter determines how much of that decline the product might be able to achieve. This appendix gives a detailed overview of the techniques used to estimate these parameter values.

E.1 Improvement Slope

The improvement slope quantifies how much costs will reduce with each doubling of cumulative production. For example, if the improvement slope is 90%, the costs will decrease by 10% every time cumulative production doubles. The methods to predict this slope have been outlined in chapter 2. The improvement slope can be quantified using equation 2.9 and the values in table E.1. The improvement slope is fully determined by the process design. Note that even though solid materials are present in the process, the SOLIDS value is set to zero. This parameter only has to be set to one if solid processing steps, e.g., milling, grinding, etc., are present, not if a processing step simply makes use of a packed bed.

The typical values of improvement slopes lie somewhere between 70% and 90%. As such, the calculated slopes of 86.3% and 89.5%, for designs 1 and 3 and designs 2 and 4 respectively, are reasonable. However, given their relatively high values, the expected cost reductions due to experience learning will not be excessively large.

Table E.1: Parameters used to estimate the improvement slopes of all plant designs

Parameters	Values	
	Design 1 & 3	Design 2 & 4
COMP	5	4
SOLIDS	0	0
PRIMARY	1	1
LIQUID	1	1

E.2 Market Potential

The market potential of the modular CL plants was estimated 10 years into the future, to better account for future wells for which this technology could also prove beneficial. This prediction was based on historical data from the past 30 years.¹ The total number of gas producing wells was used to obtain the shape of the prediction curve, as this data goes back further. An exponential curve proved to be the best fit, with an R^2 value of 0.97. Since not only gas producing wells, but all wells flare, the total amount of wells in the United States has to be predicted. This was done by fitting an exponential curve to the total amount of wells in the past 15 years ($R^2 = 0.98$) and extrapolating from there. The data, and the resulting predictions, can be found in figure E.1. It should be noted that the last 3 years of historical data have been neglected, since these years exhibited an overly sharp drop in the number of wells due to under reporting.¹

The total number of predicted wells in 2029 is approximately 1.5 million. Of these wells, roughly 3% flare because they are not connected to a gas distribution network, with 37% of these wells in the 50 MSCFD and 10% in the 175 MSCFD natural gas production range.⁴ This brings the total market potential in 2029 to 13500 and 3600 wells for the 50 MSCFD and 175 MSCFD methane capacity plants respectively. Plugging these market potentials, and the improvement slopes calculated in the previous section, into equation 2.7 allows for the quantification of the expected capital and fixed operating cost reductions through experience learning.

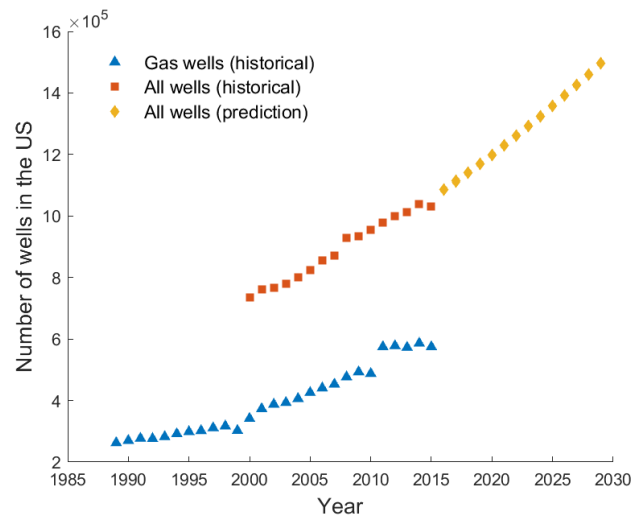


Figure E.1: The total number of gas producing wells, total number of all wells and predicted total number of all wells in the United States by year¹

Appendix F

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Publication: ACS Catalysis
Publisher: American Chemical Society
Date: Jun 1, 2017

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