NTNU
Norwegian University of Science and Technology

Department of Chemical Engineering

TKP4580 - Chemical Engineering, Specialization Project

Modelling of Offshore Blue Hydrogen Production

Author: Yoonsik Oh

Supervisor: Johannes Jäschke

Co-supervisor: Evren Mert Turan

October 23, 2022

Abstract

Contents

List of Figures

List of Tables

1 Introduction

1.1 Background and motivation

The world is in a desperately need for a new energy solution. Everything around us is heavily dependent on energy generated on CO_2 emitting sources, such as a coal power plant. Even though the majority of western industry is shifting towards "The green change", the rate of the shift is not enough. Europe is especially suffering the consequences of the gas dependent infrastructure as Russia stopped supplying Europe with gas for energy and heating. People in Europe can't afford to heating and food. Inflation has never been higher in Eurozone as for the last decades. Electricity generated from various renewable energy sources such as hydro power, wind mills and solar panels is not enough to replace the huge demand of energy that the current global infrastructure requires. But there is a rising interest and research for an another type of fuel; hydrogen.

Hydrogen is widely used for various purposes around the world and the industry. Hydrogen is also considered to be a fuel source without greenhouse gas emissions as the only emission is water vapour. Even though hydrogen as fuel is without emission when used, the production is still too harmful to the environment due to all the emission and the energy required. There are three ways to produce hydrogen, but the most used method of production around the globe is "grey hydrogen". Grey hydrogen is produced via steam-methane reforming, which uses methane and water to produce hydrogen. Grey hydrogen also emits a relatively high amount of CO_2, which is the main downside of grey hydrogen. Blue hydrogen, which also uses steam-methane reforming, but instead of letting the CO_2 emit into the atmosphere, the $> 95\%$ of CO_2 is captured and stored. The last method is green hydrogen, which is produced by splitting water molecule to hydrogen and oxygen via electrolysis.

Even though grey hydrogen is widely used around the world to produce hydrogen, but its more environmental counterpart, blue hydrogen is not used widely. Economy and the extra need for units is the main reason why blue hydrogen is less used than grey hydrogen. Norway is the country with the most carbon capture in its offshore rigs, but with today's technology, it requires the natural gas to be transported to onshore, process the gas, capture the CO_2 and transport it back to the offshore platform, where the CO_2 gas is transported and stored in the oil reservoir where the natural gas originated from. This project will look at the feasibility of an offshore blue hydrogen production where the natural gas from the oil reservoir will be extracted and reform into mainly hydrogen and CO_2 gas on the same unit, either on a ship or a platform. The CO_2 will be captured on the same unit and transported and stored in the oil reservoir. The hydrogen gas will be transported to an onshore plant. If a such plant is feasible, where hydrogen can be produced without large amounts of emission, this project could be a relatively large step towards the green change.

There is a lot of research needed to study if a project of this scale is feasible. There is the model feasibility and the economic feasibility. This project is a part of the SUBPRO Zero Blue Hydrogen project, which cooperating with the oil and gas industry in Norway. The goal is develop the exiting steady-state model at SUBPRO by implementing aspects that

reflects more to a real-life plant that can be realized.

1.2 Scope of the project

The goal of this projects is to develop further an existing model by SUBPRO and as the existing model is still under development. Different aspects will be implemented to the process, such as pressure drop, designing the plant such that the resulting CO_2 purge stream is within the regulations for CO_2 storage and adding more accurate oxygen combustion reactions in the reactor. The model will not take the physics and the complexity behind the transport and storage of CO_2, and will only focusing on improving the model without not considering what is happening with the product outflow.

The model will be optimized for each implementation made with a simple objective function and the resulting variables will be observed and studied for each optimization. In the project, theory around the process and optimization will be presented, and how the system and the model is built. Lastly, the results will be presented and discussed before concluding the project.

2 Theory

2.1 Introduction to optimization

2.2 Nonlinear programming

2.3 Reaction

2.4 Conservation law

2.4.1 Mass balance

2.4.2 Energy balance

3 Process Description

Even though there are many ways that are well studied for blue hydrogen production, there are other circumstances when designing a plant on offshore. There are smaller constraints for space and weight, and the building cost will be greater. An ordinary blue hydrogen production plant uses a large furnace to perform the steam methane reforming, which takes up a lot of space. Since on a platform or on a ship where the plant will be based on, there will be additional constraints like for weight and space. The columns can't be too high either due to the waves will make the ship sway. Instead of taking basis on a regular steam methane reformer, the project will take basis on a method from the company *Johnson Matthey* has designed. This method replaces the large furnace with an autothermal reformer (ATR)

combined with the gas heated reformer (GHR) with pure oxygen stream into the ATR. This method has reported high hydrogen purity with a low carbon emission. A detailed description of the process will be broken down into parts and described in the next subsection.

3.1 Flowsheet

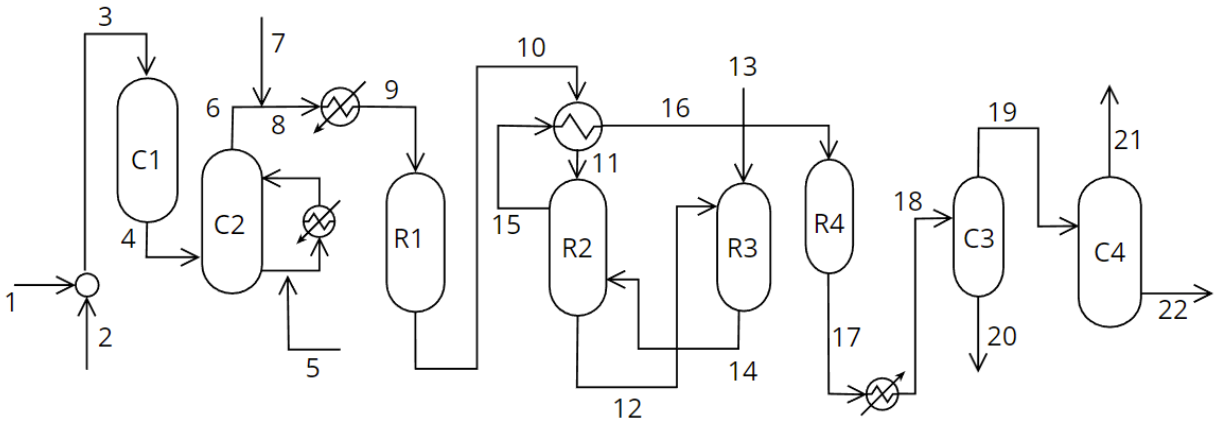

Figure 1: Flowsheet of the blue hydrogen production plant

The entire flowsheet which the modelling in this project takes basis on, is shown in fig. 1. The initial flow, or stream 1, which is the natural gas extracted from the North Sea oil and gas reservoir. It consists mainly of methane, CO_2 and other heavier organic compounds like ethane and propane. It also has traces of other inorganic compounds like sulphuric and nitric compounds. The model assumes that all heavier compounds than pentane will be considered as a collective term, C_{5+}. The composition of stream 1 is an average composition from a typical natural gas in the North Sea. A table of composition of different compounds are shown in table 1. Stream 2 consists of pure hydrogen. Inlet stream needs to undergo a purification step, where some hydrogen is mixed into the inlet stream to turn all sulfuric compounds into H_2S, which is removed in the purification step. H_2S is captured by pellets inside the column which will later be removed to repeat the process. This step is occurring where stream 3 entering the first column, C1, in the flowsheet. This is important as even though there are only traces of sulfuric compounds, sulfur is often the main cause for catalyst damages in the reactors which causes loss in profit and yield in the product stream.

After the purification step, the purified natural gas (stream 4) enter the second column, the saturator. Stream 5 consists of pure water and will enter the column together with the purified natural gas after being heated. It's purpose is to saturate the natural gas stream with steam for different stages later like pre-reforming, methane steam reforming, and water gas shift reaction. The steam amount is set to a carbon to steam ratio to 2.5, where carbon is the sum of all the hydrocarbons in the inlet stream. After the saturator process, outlet (stream 6) will mix with a stream consisting of pure steam to maintain the 2.5 carbon to steam ratio. The saturated, purified natural gas stream (stream 8) will be heated before entering the first reactor, the pre-reformer (R1). The pre-reformers task is to remove all

Compound	%mol
CH_4	78.24
C_2H_6	6.10
C_3H_8	6.70
n-C_4H_{10}	2.48
i-C_4H_{10}	1.41
C_5H_{12}	3.70
H_2O	≈ 0
H_2	≈ 0
CO	≈ 0
CO_2	1.34
H_2S	≈ 0

Table 1: Average composition of natural gas in the north sea

the hydrocarbons heavier than methane into methane. The model takes the assumption that all heavy hydrocarbons converts to methane, such that the first equilibrium is heavily shifted towards right, and the second equilibrium is heavily shifted towards left due to the reactor conditions. The first and second equilibrium reactions are shown in eq. (3.1.1) and eq. (3.1.2). These equilibrium equations are also called the steam reforming equations. The conditions are the main reason why the inlet stream before the reformer is heated up. In summary, in the pre reformer step, hydrocarbons and water is being converted to CO and H_2, and CO and H_2 will convert back to methane and water.

$$\mathrm{C}_n\mathrm{H}_m + \mathrm{nH_2O} \rightleftharpoons \mathrm{nCO} + (\mathrm{n} + \mathrm{m}/2)\,\mathrm{H}_2, \quad \Delta H > 0 \tag{3.1.1}$$

$$\mathrm{CH_4} + \mathrm{H_2O} \rightleftharpoons \mathrm{CO} + 3\,\mathrm{H}_2, \quad \Delta H > 0 \tag{3.1.2}$$

After the pre reformer step, stream 10 will enter a heat exchanger which exchanges heat with outlet stream of the main reforming part which will be explained later. The heated stream will enter the second reactor, R2, which is the gas heated reformer (GHR). The GHR consists of catalyst filled pipes where the inlet stream passed through and steam methane reforming and water gas shift reaction will take place. These equations are shown in eq. (3.1.2) and eq. (3.1.3). The outlet of the GHR will enter the next reactor, R3, which is the autothermal reformer (ATR). In the ATR, pure oxygen (stream 13) is fed into the reactor such that the heat from combusting oxygen gives higher conversion of H_2 and CO_2, since the reaction is endothermic (eq. (3.1.2)). Oxygen can combust with mainly two components; methane and hydrogen. It is found from a study that hydrogen combust with oxygen 10 times faster than the methane combustion. Due to this reason, it is assumed that the oxygen will only combust with hydrogen and the methane combustion will not be modelled.

The GHR is designed such that outlet of the next reactor is exchanging heat with the pipelines. This is preferred as the heat from the ATR is high, and the outlet from ATR can exchange satisfying amount of heat such that the reactions occurring in the pipelines in the GHR gives greater conversion of H_2 and CO from eq. (3.1.2). This technology is similar to a tube and shell heat exchanger, only that there are reactions occurring in the pipes. After the ATR and GHR process, almost all methane has converted. After the outlet stream of ATR has exchanged heat with the pipelines inside GHR, the stream will again exchange heat with the stream 10, which was mentioned earlier.

$$CO + H_2O \rightleftharpoons CO_2 + H_2, \quad \Delta H < 0 \tag{3.1.3}$$

Stream 16 will then enter the last reactor, R4, which is the isothermal shift reactor (ITSR). The purpose of this step is to convert CO into H_2 and CO_2 to a maximum achievable amount. As GHR and ATR in previous steps has a such high temperature, the steam methane reforming reaction is preferred and the outlet stream of ATR mainly consists of H_2O, CO, CO_2 and H_2. Due to the catalysts and other conditions in the ITSR, only water gas shift reactor will occur. Outlet stream of ITSR (stream 17) will now mainly consist of H_2O, CO_2 and H_2. Stream 17 will enter a cooler such that the steam will condensate and can be removed in the condensator (C3). Outlet stream of the condensator will now mainly consist of H_2 and CO_2. The water removed from the condensator can be recycled for either stream 5 or stream 7. The last step is the pressure swing adsorption (PSA). When operating in high temperature, CO_2 is being adsorbed by particles and H_2 is passed through. When lowering the pressure, CO_2 is desorbed from the particles by flushing it with pure H_2. This technique is similar to a batch reactor, where the process needs to wait until the tank has an saturated amount of CO_2 adsorbed particles and then lowering the pressure to flushing it out. To model this to a more continuous process, PSA consists of two tanks, where one tank is adsorbing with high pressure while the other tank is lowering pressure and desorbing the particles. Stream 22 is the product hydrogen stream, which is reported to be almost pure H_2, while stream 21 is the CO_2 stream with other unreacted components and other impurities which is being transported back to the reservoir to complete the enhanced oil recovery. The almost pure H_2 stream will be transported back to onshore where it can be applied for different purposes.

4 Model Description

When modelling the process, there were several assumptions made in addition to the ones explained in section 3.1. First and most important one to mention, the model assumed to be in steady state. In other words, no dynamics were implemented. This is to simplify the model when developing and testing the model. The optimization problem is formulated as algebraic nonlinear equations. It is also assumed that the model's initial flow is stream 6 in the flowsheet shown in fig. 1, specifically the purified natural gas stream. The composition in the inlet stream is assumed to be the same from table 1. To estimate the size of the initial mole stream, natural gas stream data from *Norsk Petroleum* was used, where the platform

Troll in the North Sea was chosen. *Troll* is producing an average of 35 million Sm^3/year, which is calculated to approximately 4000 Sm^3/h. When converting from unit Sm^3 to kg, it is assumed to be 0.829 kg/Sm^3. The final initial mole was then calculated to be 145.4 kmol h^{-1}.

To model the connection between the GHR and ATR, an additional cooler is introduced to cool down the outlet stream from ATR. The amount of heat released from the cooler is modelled to be the same as a new Q_{GHR} variable which is the heat GHR receives from the ATR. The temperature of the stream after the cooler is modelled to be the same as the outlet temperature of the ATR in the flowsheet shown in fig. 1. The new flowsheet which the model takes basis on is shown in fig. 2.

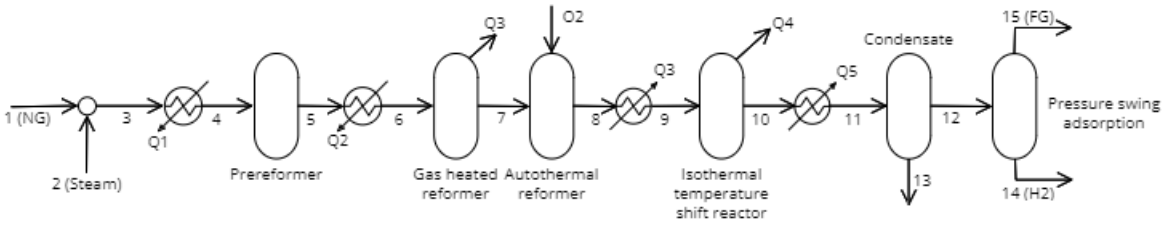

Figure 2: Flowsheet of the process used in the model

4.1 JuMP Julia Model

To build the model in JuMP Julia, there were first built 11 models, which is assembled to a final model at the end. Each model is a control volume of the process. After the 11 models are assembled, some additional constraints were added to implement connection between the flows of each model, initial value and an extra variable which is being optimized in the objective function. And also a function to print out the mole stream table and other relevant variables and another function for mass stream table to check that the mass is balanced for every stream. A summary of description of each model is shown in table 2. At the end, there were total of 184 variables with 183 equality constraints, where 181 variables had a lower bound and 3 variables with an upper bound. This means that the system has 1 degree of freedom, which is used for the objective function.

Each model first defines the variables with lower bounds and looping through the variables to give each variable an initial value when optimizing. The code for defining the variables and setting initial values will resemble the following pseudo code:

```
@variables(model, 0 <= inlet[1:10]);
@variables(model, 0 <= outlet[1:10]);

init_inlet = [...];
init_outlet = [...];

for i=1:10
    set_start_value(inlet[i], init_inlet[i]);
    set_start_value(outlet[i], init_outlet[i]);
```

Model	Inlet	Outlet	What
Mix.jl	$\dot{n}_1$, $\dot{n}_2$	$\dot{n}_3$	Mixer for stream 1 and 2 and calculate required amount of steam
PrePR.jl	$\dot{n}_3$	$\dot{n}_4$	Heater before pre reformer
PR.jl	$\dot{n}_4$	$\dot{n}_5$	Pre reformer
PreGHR.jl	$\dot{n}_5$	$\dot{n}_6$	Heater before GHR
GHR.jl	$\dot{n}_6$	$\dot{n}_7$	Gas heated reformer
ATR.jl	$\dot{n}_7$	$\dot{n}_8$	Autothermal reformer
PostATR.jl	$\dot{n}_8$	$\dot{n}_9$	Cooler after ATR
ITSR.jl	$\dot{n}_9$	$\dot{n}_{10}$	Isothermal shift reactor
PreCondensate.jl	$\dot{n}_{10}$	$\dot{n}_{11}$	Cooler before condensator
Condensate.jl	$\dot{n}_{11}$	$\dot{n}_{12}$, $\dot{n}_{13}$	Condensator
PSA.jl	$\dot{n}_{12}$	$\dot{n}_{14}$, $\dot{n}_{15}$	Pressure swing adsorption

Table 2: Summary of description of all models

```
    end

    @variable(model, 273 <= inlet_T, start = T_in);
    @variable(model, 273 <= outlet_T, start = T_out);
```

It is worth noticing the "model" variable inside the @variable function. This assigns the variables to the model, and when the final model is assembled with all the other models, this variable will be assigned as a variable to the final model at the end. Each model also has expression for enthalpy for its inlet and outlet stream. To introduce equations in the model and not constraints, the built-in function @NLexpression() is used. To introduce constraints in the model, @NLconstraint() is used. Every constraint should have one variable each assigned, for example in cases for component balance and energy balance. The constraint are set to equal 0 such that the constraints are an equality constraint. Expressions and constraints will resemble the following pseudo code:

```
    # creating variable x and y, which is being used for one of the constraints
    x = @NLexpression(model, equation1);
    y = @NLexpression(model, equation2);

    # Constraints
```

```
    @NLconstraint(model, x - y*inlet[1] == 0);

    # Mass balance
    @NLconstraint(model, inlet[i] - outlet[i] == 0);

    # Energy balance
    % This gives a vector of h [kJ/kmol] for each component in the stream
    inlet_enthalpy = build_enthalpy(model, T_in, par);
    outlet_enthalpy = build_enthalpy(model, T_out, par);

    @NLconstraint(model, sum(outlet_enthalpy[i]*outlet[i] - inlet_enthalpy[i]*
        inlet[i] for i = 1:10) == 0);
```

A final table of all variables and its initial values are shown in appendix. In the pseudo code for mass and energy balance, there were two things that occurred. the variable par and the build_enthalpy() function. The par variable is mutable struct which is a collection of all parameters used in the model. These parameters are initial values, split ratios and operating temperatures for the reactors. To define the par,

4.2 Model simulation

Word count:

2839 (errors:1) words