Optimization Of Nitrogen Wash Column Operation

by

Ahmad Helmi Bin Abdul Rahman

Dissertation submitted in partial fulfilment
of the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Chemical Engineering Programme
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Approved by,

____
(Assoc. Prof. Dr Marappa Gounder Ramasamy)

Universiti Teknologi PETRONAS

Tronoh, Perak

September 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AHMAD HELMI BIN ABDUL RAHMAN

ABSTRACT

Nitrogen wash column is being used in the production of ammonia process. It is usually the purification step of H_2 in the ammonia synthesis. The liquid nitrogen wash column has the function to remove residual impurities like CO, Argon and CH_4 from a crude hydrogen stream and to establish a stoichiometric ratio H_2 / N_2 = 3:1. The outlet stream of the column is product gas containing of nitrogen and hydrogen mixture and another outlet stream is off gas. A high pressure liquid nitrogen is used to accomplish its process. Small quantities of H_2 with other impurities leave through the bottoms as off gas. Since H_2 is expensive, a reduction in H_2 loss through off gas is required. In this study, a simulation study to determine optimum operating condition with minimum H_2 loss is proposed. By simulate the parameter such as pressure, temperature and flowrate of the inlet nitrogen wash column, it will give several result in the amount of hydrogen loss at the bottom product. By using Design of Experiment (Box-Behnken design type) method, we can setup the exepriment to undergo the optimization of the Nitrogen Wash Column and it also can analyze the result to determine the optimum operating condition for this column. The whole simulation study will undergo by using iCON simulation software.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Nitrogen wash column is one of the equipment that helps in the production of ammonia. This equipment usually and mainly used to purify and prepare ammonia synthesis. Nitrogen wash column basically a column for separation in order to remove residual impurities like methane, argon and carbon monoxide from a crude hydrogen stream and to establish a stoichiometric ratio Hydrogen : Nitrogen = 3 : 1. Carbon monoxide must be completely removed, since it is poisonous for the ammonia synthesis catalyst. Argon and methane are inert components enriching in the ammonia synthesis loop and if not removed, a syngas purge or expenditures for purge gas are required then it will add some cost. Nitrogen wash column also operate in cryogenic condition means in a very low temperature and being installed in the coldbox, which is covered with a metal shell. Besides, the coldbox voidage is filled with insulation material (Perlite) to prevent heat input. Raw hydrogen and high pressure nitrogen are fed to the liquid nitrogen wash column. Both streams are cooled down against product gas. Feeding raw hydrogen to the bottom of the nitrogen wash column and condensed nitrogen liquid to the top. Furthermore, to establish the desired H_2/N_2 ratio, high pressure nitrogen is need to the process stream.

How Nitrogen Wash Column process:

Based on Lurgi Ammonia synthesis system, since this operation consumes hydrogen and forms an inert gas which will require to be purged from the ammonia synthesis loop, it is clear that it can only be applied to gas stream with content of carbon dioxide already reduced to a low level. Advantage can be taken of this to introduce nitrogen into the synthesis gas by the rather elegant nitrogen wash technique. In this type of operation, nitrogen is introduced after the hydrogen stream has been largely purified by the Rectisol process. The main purpose of this Rectisol process area is to remove the bulk amount of carbon dioxide generated from water-gas shift conversion. In addition, the Rectisol process uses liquid methanol to remove carbon dioxide and other impurities. But then, the feed gas that contains raw hydrogen still have a little amount of other impurities likes carbon dioxide, argon and carbon monoxide coming from the Rectisol process enters the liquid nitrogen wash process area shown in the **Figure 1.1**. The nitrogen is fed to a liquid nitrogen wash column where traces of carbon monoxide, argon and methane are removed in the solution of liquid nitrogen from the bottom of the column. The purified hydrogen stream together with evaporated nitrogen passes out at the top of the column. Furthermore, nitrogen is added to the stream to make up to the appropriate proportion for ammonia synthesis. Since Nitrogen wash column operate in such a low temperature that is about -190^{o}C called cryogenic condition, the feed gas need to enter the heat exchanger first that represents as a cooler to provide additional cool duty to make it reach the specified temperature before entering the liquid nitrogen wash column. The removal of inert gases by the nitrogen wash column is an advantage in the synthesis step that need for a purge with consequent loss of useful material is reduced to a minimum.

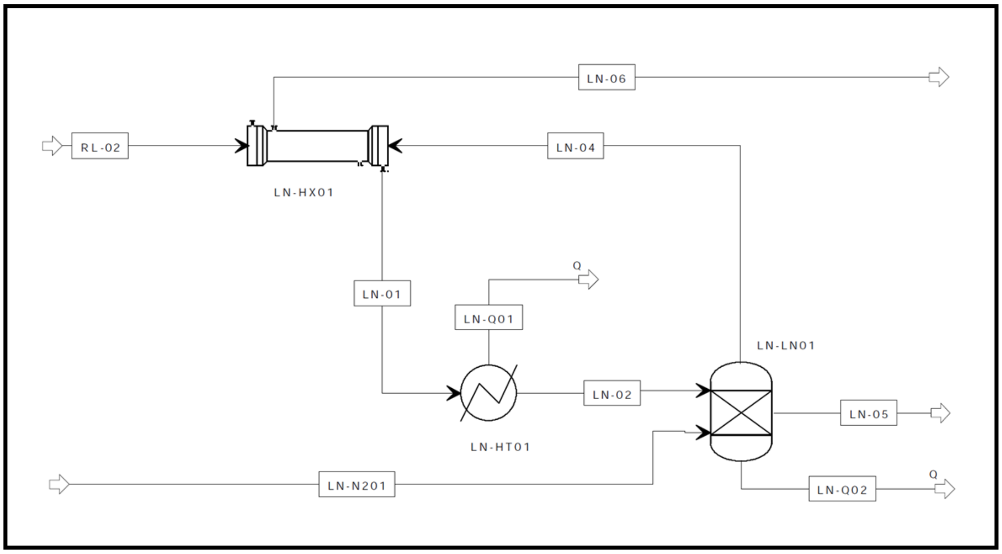


Figure 1.1: ASPEN Flow diagram of Nitrogen wash column for the design basis. (CHI XIE, 2001)

Block ID	Block Type	Block Parameter	Description
LN-LN01	Nitrogen wash column (Separation column)	**LN-02:** Pressure = 3000 KPa Temperature = -190^oC Composition = H_2, CH_4,CO & N_2 **LN-N201:** Pressure = 3000 KPa Temperature = -187oC Composition = N_2 **LN-05:** Pressure = 3000 KPa Composition = H_2, CH_4,CO & N_2 **LN-04:** Pressure = 3000 KPa Compositon = H_2 & N_2 **LN-Q02:** -Dummy cool duty	Remove impurities from the hydrogen and nitrogen mixture
LN-HX01	Heat Exchanger	Cold stream outlet temperature approach = -50^oC	Cool incoming syngas by product gas
LN-HT01	Cooler	Temperature = -190^oC	Cool incoming syngas by refrigeration duty

Table 1.1: Design parameter and composition of Nitrogen wash column.

1.2 Problem Statement

The concern is to optimize the production of the nitrogen wash column by minimise the loss of hydrogen in the off gas at the bottom stream since it is very expensive. It is a waste if the flow rate of hydrogen in the off gas is high.

1.3 Objective

1. To minimise the loss of hydrogen in the off gas at the bottom stream of the nitrogen wash column.

1.4 Scope of Study

In this project, the author will focuses on the optimization of the Nitrogen Wash column operation in the aspects of process simulation. All related parameters that involved will be considered and need to be determining in order to achieve the objective of this project that is to minimise the hydrogen loss at the off gas. The major scope of this study is to come out with the best evaluate and analysing data of the parameter for the Nitrogen Wash column to operate it in an optimum condition. All data gained from studies and the iCON simulation software will be recorded and tabulated to be analysing as a result of this project.

1.5 The Relevancy of the Project

Loss of hydrogen in the off gas from the nitrogen wash column is very costly. Minimisation of H2 in the off gas will increase ammonia production and also increase the profit margin of the operating unit.

1.6 Feasibility of Study

Throughout this study there are several phases that will be done throughout completing the project:

i. Research based on literature review on Nitrogen Wash Column operation from multiple types of references and sources. *This phase involved doing researches within the limit of scopes of the project in order to built strong foundation on the theoretical part before proceeding with the next phases of the project.*

ii. Identifying related data used for the Simulation Process. *This phase involved collecting all the required data needed before proceed with the simulation process of the respective natural gas dehydration process. These will involve all the related parameters needed in the process flow diagram of the respective processes.*

iii. Testing, Comparing and Modifying of all collected data. *This data that are previously collected from various trusted sources and references will be used as the input data in executing the simulation process in determining the best possible methods that can be used. Based on these data, certain criteria will be modified in order to optimise and to increase the effectiveness on the process.*

iv. Determining the most optimize process parameters. *Based on the result of testing and analysing of each data collected, the best process parameters will be determined. Then the best modified process best on the existence process will be proposed as the final outcome of this project.*

CHAPTER 2

LITERATURE REVIEW

2.1 Process Flow of Ammonia Production

There are several important types of commercial ammonia synthesis processes. It divides into two parts that are classic system and modern system. Nowadays, many of technology of gas purification and gasification created to produce syngas for ammonia synthesis but it still refer to the classic model of ammonia process.

Several types of commercial systems:

2.1.1 Haber-Bosch Process

The classic Haber-Bosh plant uses coke as the feedstock for the synthesis gas generation. In the gas generator, coke reacts with water to produce carbon monoxide and hydrogen. Then, the raw syngas leaving the gasification part will be first desulphurized by oxidation and being extracted by ammonium sulphide solution. After desulphurization, CO shift conversion on syngas can form more hydrogen. Water scrubber can remove bulk amount of carbon dioxide generated from shift reaction and the copper liquid scrubber can remove trace carbon monoxide. After all of the pre-treatment procedure and syngas compression, the purified hydrogen-nitrogen mixture has been collected and proceeds to ammonia synthesis loop.

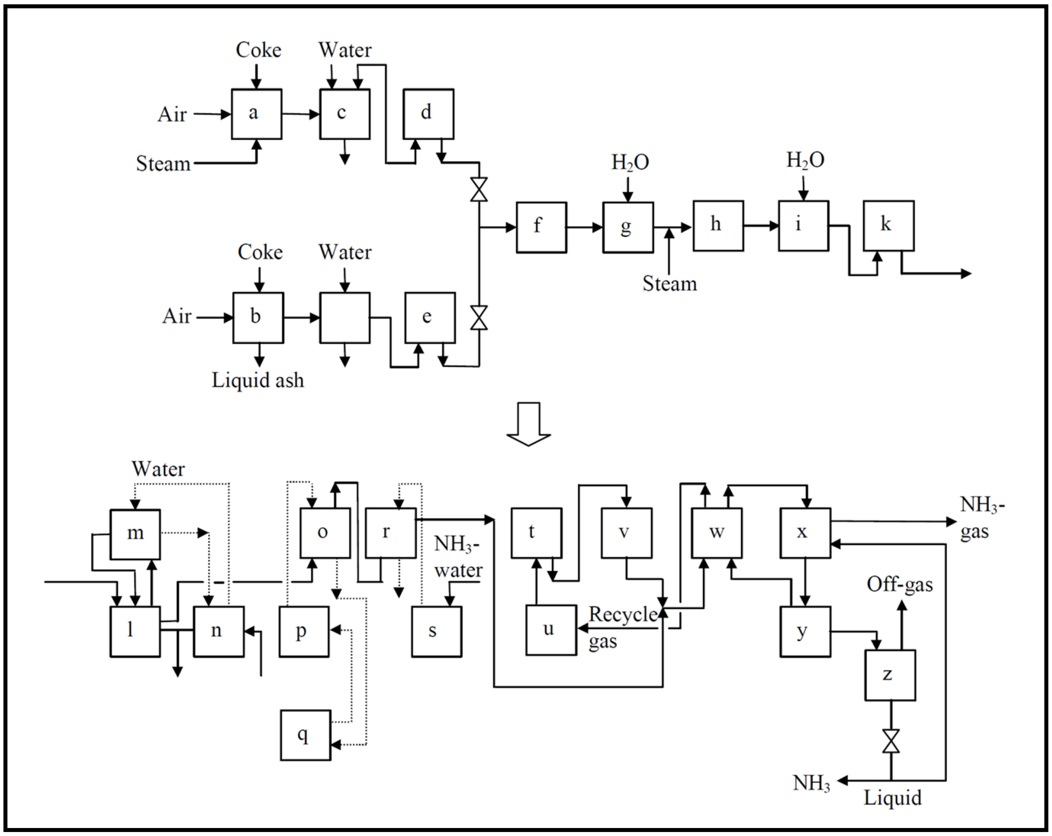


Figure 2.1.1 Simplified Process Flow Diagram of the Haber - Bosch process (Appl, 1976)

2.1.2 The Braun Purifier Process

Braun Purifier Process was a conventional and highly commercialized process based on natural gas. This process depends on steam-reforming reaction to generate syngas. It got its name because a special cryogenic purifier is installed to remove any trace impurities before the syngas enters the synthesis loop. The steam reforming reaction proceeds in two reactors - the primary reformer and the secondary reformer. Then, the syngas produced in steam reformers goes through CO shift converters, carbon dioxide removal column, methanator and cryogenic purifier before it enters the ammonia converter.

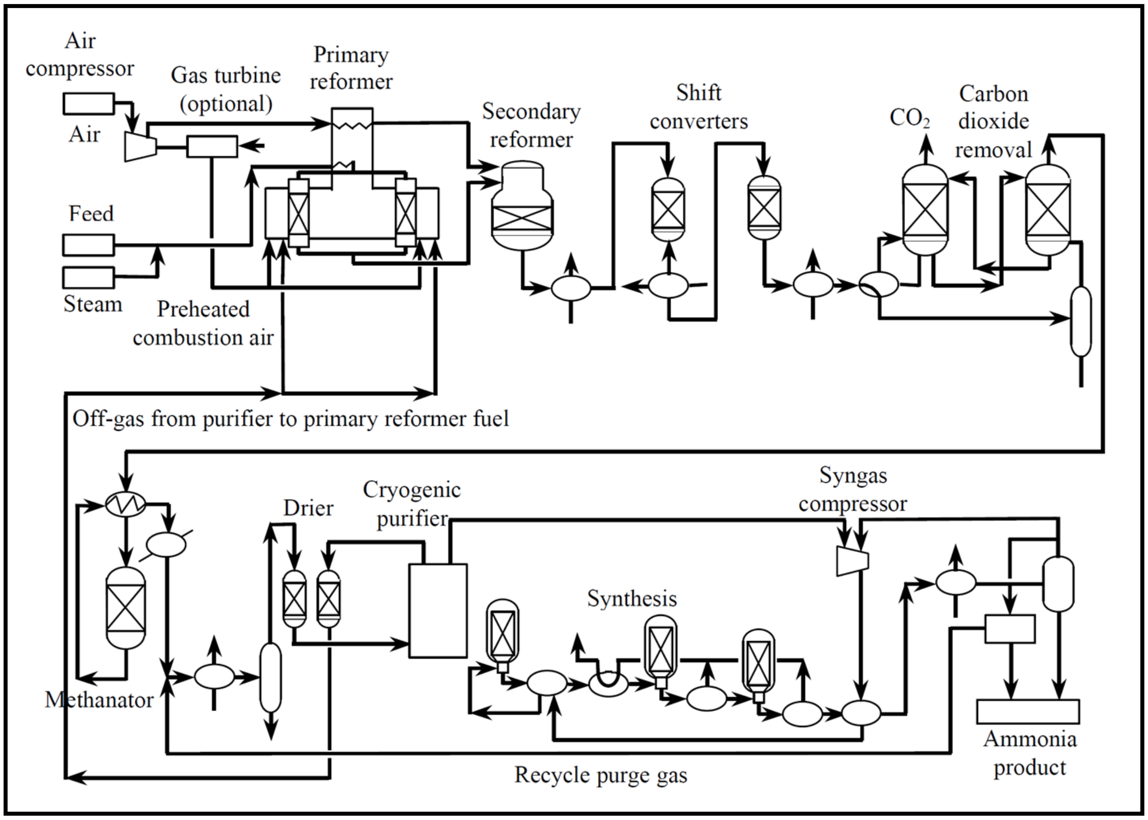


Figure 2.1.2 Simplified Process Flow Diagram of the Braun purifier process (Kroschwitz *et al*, 1992)

2.1.3 The Lurgi Process

Lurgi process introduces coal as a feedstock for ammonia synthesis. The coal, heavy residual oil or solid waste feed combined with steam and pure oxygen obtained from an air separation plant react in the gasifier to generate syngas. The raw syngas from gasifier contains methane, higher hydrocarbons, troublesome phenolic material and tars. After ash removal, gas cooling and some other process steps to recover tar, phenols and some ammonia from gas liquor, cleaned syngas can be further treated by shift conversion; Rectisol process and liquid nitrogen wash to form make-up gas.

The Rectisol process is a widely used CO2 and sulfur removal approach. In a typical Lurgi ammonia synthesis including syngas generation, two Rectisol processes are used, the first one focuses on desulfurization, and the second one removal CO2 generated from water gas shift. The liquid nitrogen wash process can remove any trace impurities in the syngas, especially methane, and input necessary nitrogen for final synthesis. The methane enriched tail gas from liquid nitrogen wash will be recycled to recover more hydrogen for ammonia synthesis.

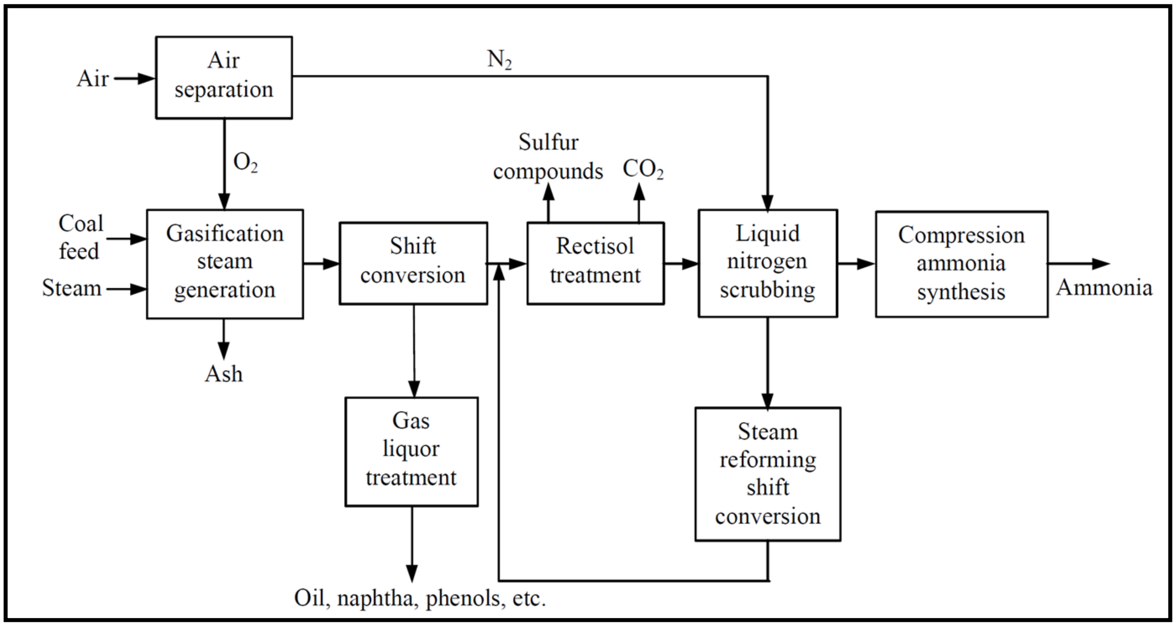
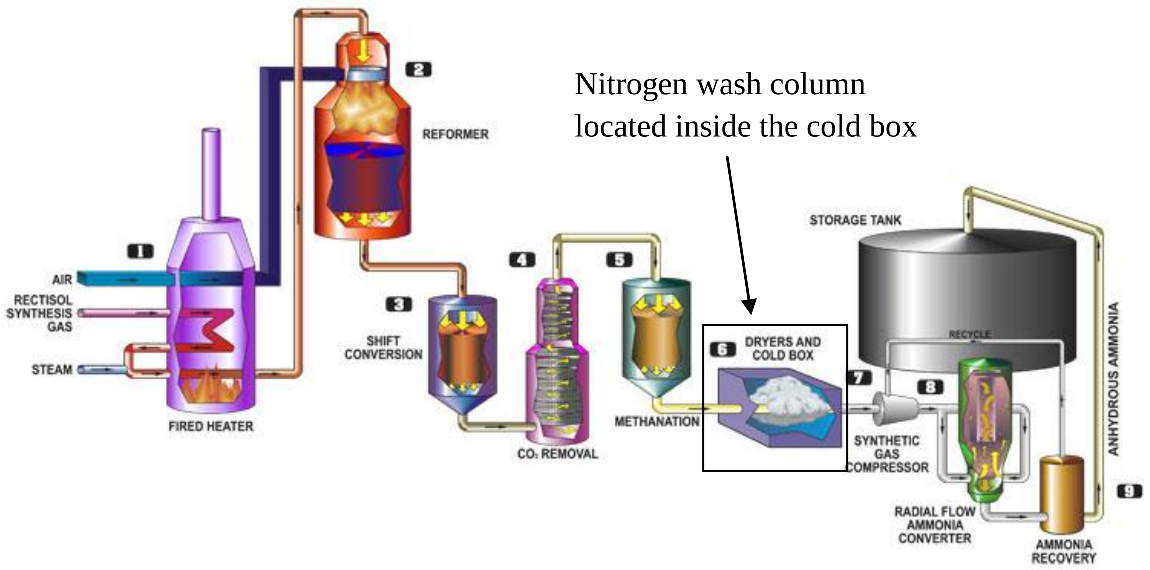


Figure 2.1.3 Flow sheet for ammonia production from Lurgi coal gasification (Kroschwitz *et al*, 1992)

2.2 Location of nitrogen wash column in the Ammonia production process.

Based on Chemenginering.com 2012, production of ammonia process flow start by converting natural gas (methane) or petroleum naphtha into gaseous hydrogen. The method for producing hydrogen from hydrocarbon is referred to as Steam Reforming. Then, the hydrogen is combined with nitrogen to produce ammonia. **Nitrogen wash column** is located inside the ammonia (NH3) synthesis unit.



Nitrogen wash column located inside the cold box

Figure 2.2: Process flow diagram of ammonia production process (dakotagas.com-2012)

Step by step of ammonia production:

1) Rectisol synthesis gas, air and steam are heated by a fired heater using synthetic natural gas as a fuel. These heated gases are introduced into
2) The reformer where the methane is converted to carbon monoxide, carbon dioxide and hydrogen. The exit gases from the reformer enter
3) Shift conversion where the carbon monoxide and water react to form hydrogen and carbon dioxide. In the

4) Carbon dioxide removal vessel, an absorption process is used to remove the carbon dioxide. The stream from the carbon dioxide removal system still contains small amounts of carbon monoxide and carbon dioxide so it is sent through
5) The methanator where they react with hydrogen to form methane. Before the stream can be introduced to the ammonia synthesis loop,
6) **The dryers and nitrogen wash column inside the cold box remove water and methane along with excess nitrogen so that the hydrogen and nitrogen ratio equals three to one.**
7) The synthetic gas compressor takes the fresh feed from the cold box plus the ammonia loop recycle stream and compresses it to 2500 psig. As the stream travels through
8) The radial flow ammonia converter, the hydrogen and nitrogen react to form ammonia.
9) The ammonia recovery unit then cools the stream and the liquid ammonia is sent to the 30,000 ton ammonia tank where it is stored until it is sold. The recycle gases are then returned to the synthetic gas compressor for reintroduction into the ammonia converter.

Nitrogen wash column will take place after methanation process means after removing all the carbon dioxide from the stream. In the nitrogen wash unit, the feed inlet that is nitrogen being purify to get the stoichiometric of nitrogen/hydrogen ratio to a value 1:3. Therefore, purification of nitrogen to generate the 3:1 ratio of hydrogen : nitrogen is needed before entering the last part of the unit that is ammonia synthesis.

2.3 Nitrogen wash column

Based on Linde-Engineering.com 2012, after CO2 removal the cold gas enters the Nitrogen Wash section. Remaining traces of CO2 are removed by a molecular sieve while the CO, CH4 and most of the argon are removed cryogenically by condensation and washing with liquid nitrogen. CO and methanol is been removed in the adsorbers section before entering the coldbox for the next step of purification. The feed is being cooled to the very low temperature in coldbox about -190 C^{o}. It will enter the nitrogen wash column at the bottom part of the column which is nitrogen liquid. This tower consists of sieve trays and on these undesired components i.e. CO and CH$_4$ are carried along by the downward flow of liquid nitrogen. The desire product that is purified gas of nitrogen and hydrogen is flow up to the top outlet. After frigony recovery of the gases in exchangers of rectisol section, where the incoming gases to CO$_2$ absorber are cooled, and this gas goes to synthesis compressor suction as make up gas for synthesis section. Production of waste is formed at the bottom of the column in being heated by superheater. Cold requirement of Nitrogen wash unit is fulfilled by sending a partially cooled nitrogen stream to Adsorber Unit for liquification and super cooling. In the course of operation of adsorbers, due to attrition, fine dust of molecular sieve is formed.

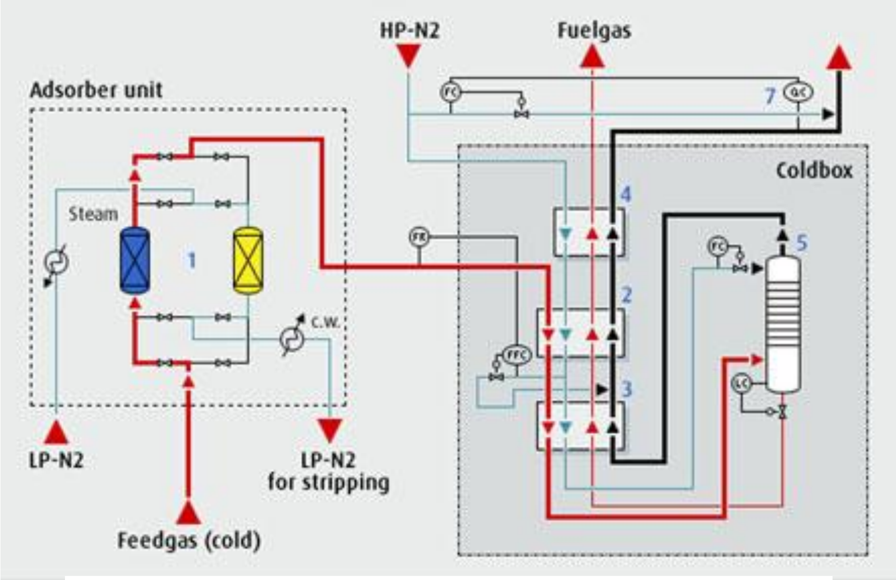


Figure 2.3: Process flow of Liquid Nitrogen Wash
(Linde Engineering.com – 2012)

2.4 Design of the Nitrogen Wash Column

Nitrogen wash column is a separation column that using absorption method to get the desire product. This type of separation method required two inlets stream that in different state. One will be in gas (syngas or feed gass) and another one is liquid (nitrogen liquid). Both stream will enters the absorption column and produce also two different in state of outlet stream that are vapour (desire product – syngas mixture of nitrogen and hydrogen) and liquid (off gas contain impurities and a little amount of hydrogen).

During the absorption process, in the absorption column components distribute themselves between the vapour and liquid until their fugacities in both phases are equal or until

$Yi = KiXi$, where;

Ki: the vapour-liquid equilibrium distribution coefficient
Yi: mole fractions in the vapour of component i and
Xi: mole fractions in liquid of component i.

In ideal solutions this relationship simplifies to Raoult's law;

$PYi = pi^{o}Xi$, where;

P: the stage pressure
Pi: vapour pressure of component i at the stage temperature

Referring to Raoult's law, the vapour pressure of the light components is too high to allow them to move in any appreciable amounts to the liquid. (*If pi is large, Xi must be small to keep their product equal to the partial pressure of i, PYi*) Conversely, the vapour pressure of the heavy components is too low to allow it to be transferred significantly to the vapour. Hence, in absorption, net mass is transferred from one phase to the other and as for the case of natural gas dehydration the mass transfer of water vapour is from gas phase (natural gas) to liquid phase (absorbent).

The limiting condition of total reflux in distillation is approached when most of the overhead is refluxed back to the top of the column and most of the bottoms is reboiled and sent back to the bottom of the column. In absorbers and strippers the concept of total reflux does not apply since the liquid reflux (solvent) or stripping gas are external feeds. This is because absorption processes involve one way mass transfer from one phase to the other, the liquid:vapour ratio (L/V) in absorbers varies considerably from stage to stage. In absorbers the L/V ratio usually varies most appreciably in the bottom stages where most of the absorption takes place. Any thermal effects causing a temperature rise are also most noticeable in these stages where most of the absorption takes place. Obviously, the column size sets practical limitations on the allowable flow rate ranges. Moreover, as the liquid solvent or stripping gas rates are increased, larger quantities of the gas or liquid feeds get carried along with the intermediate components to be recovered. This translates into poor separation with the existing number of stages, and a larger number may be required.

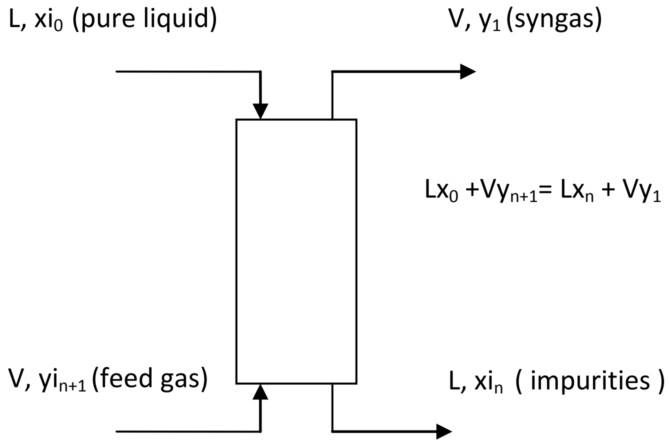


Figure 2.4: Schematic diagram of an absorption column

As for the material balance, since the liquid and gas components do not change phases, their flow rates will remain constant in the column.

$$Lx_0 + Vy_{j+1} = Lx_j + Vy_1$$

Thus from the formula above, the composition of the respective component in the vapour phase or liquid phase coming out from the absorption column can be determine if the balance amount of liquid and vapour entering the absorption column are given.

2.5 Vapour Liquid Equilibrium of Hydrogen and Nitrogen

Nitrogen Wash column will having two outlet streams that will be in vapour and liquid state. Top product of the column will be composition of hydrogen and nitrogen in the vapour state. Meanwhile, the bottom product of the column will be the others impurities such as carbon monoxide, argon and a little amount of nitrogen and hydrogen.

In order to get such good composition of hydrogen and nitrogen at the top product since it is our desire product for ammonia production, we need to study about the vapour liquid equilibrium. From this study, we can get several information regarding main parameters that will be used to operate this separation unit column such as temperature and pressure. In addition, to determine the equilibrium compositions of mixtures of hydrogen and nitrogen we can determined at very low temperature (-190^{o}C or -310F) that will be known as cryogenic condition. Based on Eubanks L. Stanley (May, 1957) on his thesis about “Vapor-Liquid Equilibria In The System Hydrogen-Nitrogen-Carbon Monoxide” said that, in a system consisting of two or more phase, the criteria for equilibrium existing between the phases is that the chemical potential of each component will be equal in all phase in which that component is present. Therefore the Vapor-Liquid equilibrium data can be done based on the chemical potential of each component.

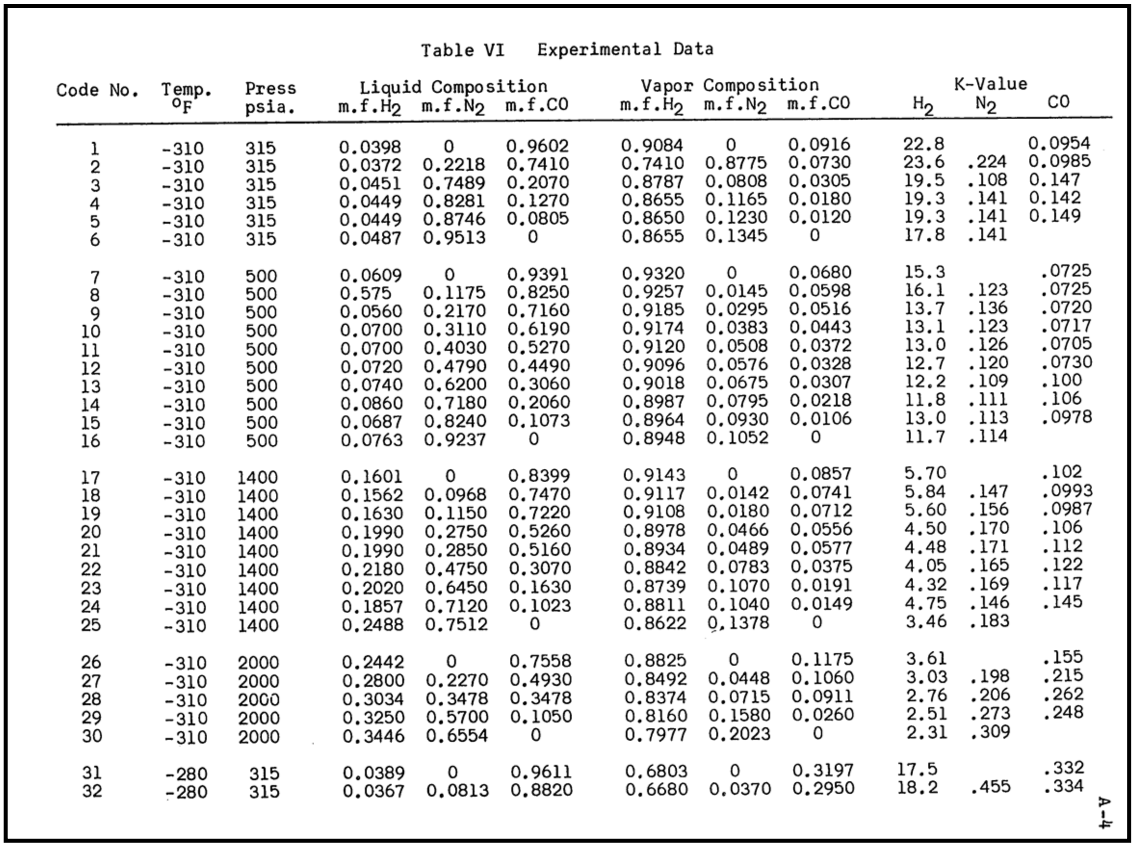


Table VI Experimental Data

Code No.	Temp. °F	Press psia.	Liquid Composition m.f.H_2	m.f.N_2	m.f.CO	Vapor Composition m.f.H_2	m.f.N_2	m.f.CO	K-Value H_2	N_2	CO
1	-310	315	0.0398	0	0.9602	0.9084	0	0.0916	22.8		0.0954
2	-310	315	0.0372	0.2218	0.7410	0.7410	0.8775	0.0730	23.6	.224	0.0985
3	-310	315	0.0451	0.7489	0.2070	0.8787	0.0808	0.0305	19.5	.108	0.147
4	-310	315	0.0449	0.8281	0.1270	0.8655	0.1165	0.0180	19.3	.141	0.142
5	-310	315	0.0449	0.8746	0.0805	0.8650	0.1230	0.0120	19.3	.141	0.149
6	-310	315	0.0487	0.9513	0	0.8655	0.1345	0	17.8	.141	
7	-310	500	0.0609	0	0.9391	0.9320	0	0.0680	15.3		.0725
8	-310	500	0.575	0.1175	0.8250	0.9257	0.0145	0.0598	16.1	.123	.0725
9	-310	500	0.0560	0.2170	0.7160	0.9185	0.0295	0.0516	13.7	.136	.0720
10	-310	500	0.0700	0.3110	0.6190	0.9174	0.0383	0.0443	13.1	.123	.0717
11	-310	500	0.0700	0.4030	0.5270	0.9120	0.0508	0.0372	13.0	.126	.0705
12	-310	500	0.0720	0.4790	0.4490	0.9096	0.0576	0.0328	12.7	.120	.0730
13	-310	500	0.0740	0.6200	0.3060	0.9018	0.0675	0.0307	12.2	.109	.100
14	-310	500	0.0860	0.7180	0.2060	0.8987	0.0795	0.0218	11.8	.111	.106
15	-310	500	0.0687	0.8240	0.1073	0.8964	0.0930	0.0106	13.0	.113	.0978
16	-310	500	0.0763	0.9237	0	0.8948	0.1052	0	11.7	.114	
17	-310	1400	0.1601	0	0.8399	0.9143	0	0.0857	5.70		.102
18	-310	1400	0.1562	0.0968	0.7470	0.9117	0.0142	0.0741	5.84	.147	.0993
19	-310	1400	0.1630	0.1150	0.7220	0.9108	0.0180	0.0712	5.60	.156	.0987
20	-310	1400	0.1990	0.2750	0.5260	0.8978	0.0466	0.0556	4.50	.170	.106
21	-310	1400	0.1990	0.2850	0.5160	0.8934	0.0489	0.0577	4.48	.171	.112
22	-310	1400	0.2180	0.4750	0.3070	0.8842	0.0783	0.0375	4.05	.165	.122
23	-310	1400	0.2020	0.6450	0.1630	0.8739	0.1070	0.0191	4.32	.169	.117
24	-310	1400	0.1857	0.7120	0.1023	0.8811	0.1040	0.0149	4.75	.146	.145
25	-310	1400	0.2488	0.7512	0	0.8622	0.1378	0	3.46	.183	
26	-310	2000	0.2442	0	0.7558	0.8825	0	0.1175	3.61		.155
27	-310	2000	0.2800	0.2270	0.4930	0.8492	0.0448	0.1060	3.03	.198	.215
28	-310	2000	0.3034	0.3478	0.3478	0.8374	0.0715	0.0911	2.76	.206	.262
29	-310	2000	0.3250	0.5700	0.1050	0.8160	0.1580	0.0260	2.51	.273	.248
30	-310	2000	0.3446	0.6554	0	0.7977	0.2023	0	2.31	.309	
31	-280	315	0.0389	0	0.9611	0.6803	0	0.3197	17.5		.332
32	-280	315	0.0367	0.0813	0.8820	0.6680	0.0370	0.2950	18.2	.455	.334

A-4

Figure 2.5: Experimental Data for vapour-liquid equilibrium of Hydrogen, Nitrogen and Carbon Monoxide. (Eubanks L. Stanley, 1957)

From **Figure 2.5**, we can observe and determine that the composition of hydrogen and nitrogen by using mole fraction in both liquid and vapour phase at temperature -310F (-190^{o}C). The mole fraction show how the composition of hydrogen and nitrogen is determining in which vapour or liquid state. It showed that at very low temperature (-190^{o}C), composition of hydrogen is higher in the vapour state compare to liquid state. Therefore, that the good proof why we need to operate this Nitrogen Wash Column in such a low temperature or else known as cryogenic condition.

2.6 Design of Experiment (Optimization method)

Design of Experiments (DOE) techniques enables to determine simultaneously the individual and interactive effects of many factors that could affect the output results in any experiment. DOE also provides a full insight of interaction between design elements therefore; it helps turn any standard design into a robust one. Simply put, DOE helps to pin point the sensitive parts and sensitive areas in designs that cause problems in yield. Designers are then able to fix these problems and produce robust and higher yield designs prior going into production.

There are several types of DOE but for this optimization project, Box-Behnken type has been chosen to undergo the analysis step in this project. Box-Behnken designs are not built on a factorial basis, but they are nevertheless good optimization designs with simple properties. Besides, it is an alternative to central composite designs, when the optimum response is not located at the extremes of the experimental region or does not use previous results from a fractional design. All design variables must vary continuously. In a Box-Behnken design, all design variables have exactly three levels there are low cube, centre, and high cube. Each experiment crosses the extreme levels of two or three design variables with the mid-levels of the others. In addition, the design includes a number of centre samples.

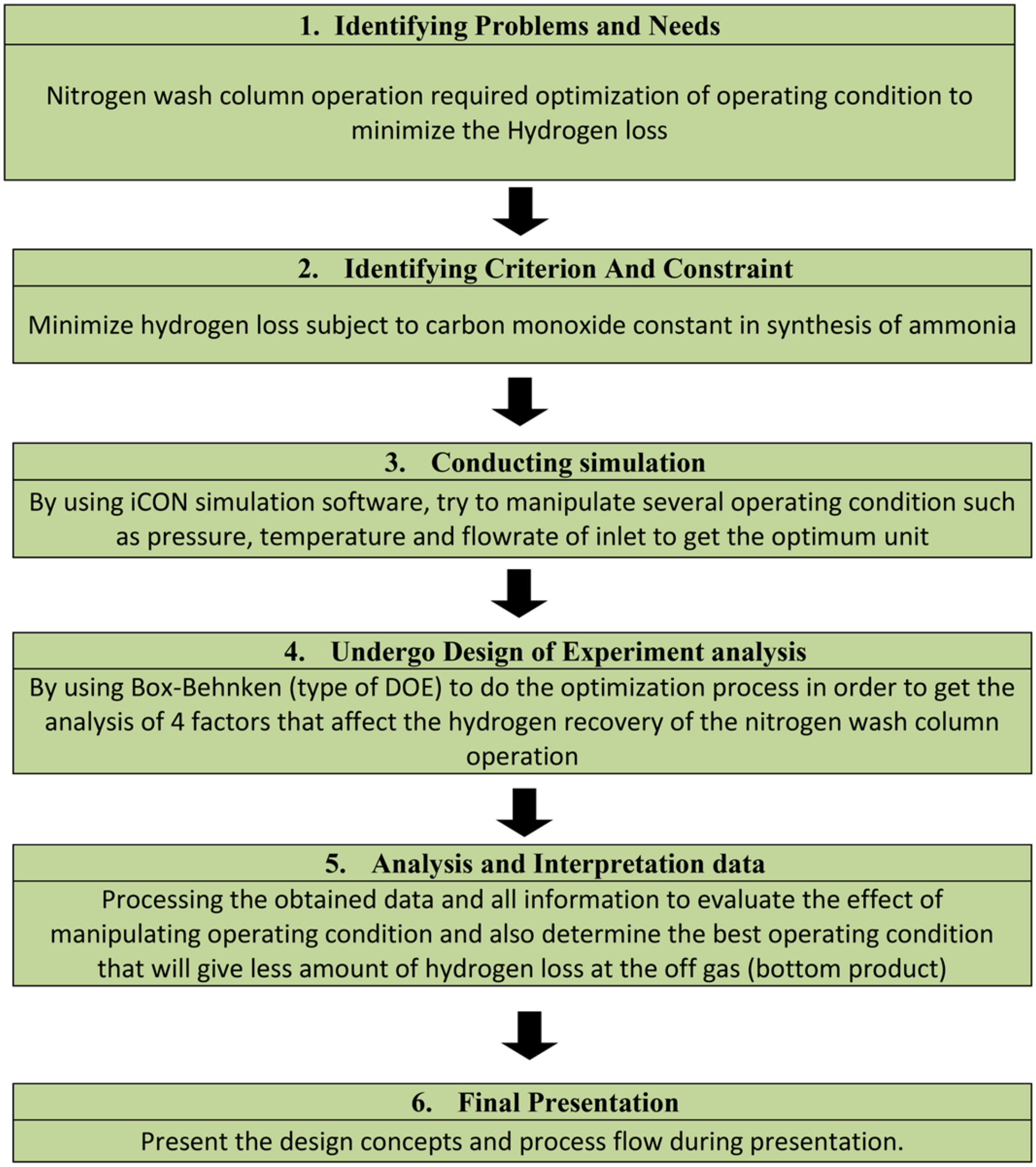
The properties of Box-Behnken designs are the following:

- The actual range of each design variable is low cube to high cube, which makes it easy to handle
- All non-centre samples are located on a sphere, thus achieving the property of rotatability

CHAPTER 3

METHODOLOGY

3.1 Process work flow for FYP 1



1. Identifying Problems and Needs

Nitrogen wash column operation required optimization of operating condition to minimize the Hydrogen loss

2. Identifying Criterion And Constraint

Minimize hydrogen loss subject to carbon monoxide constant in synthesis of ammonia

3. Conducting simulation

By using iCON simulation software, try to manipulate several operating condition such as pressure, temperature and flowrate of inlet to get the optimum unit

4. Undergo Design of Experiment analysis

By using Box-Behnken (type of DOE) to do the optimization process in order to get the analysis of 4 factors that affect the hydrogen recovery of the nitrogen wash column operation

5. Analysis and Interpretation data

Processing the obtained data and all information to evaluate the effect of manipulating operating condition and also determine the best operating condition that will give less amount of hydrogen loss at the off gas (bottom product)

6. Final Presentation

Present the design concepts and process flow during presentation.

3.2 Hardware/Tools and Software

No	Name	Description
1	iCON	It is simulation software of a designing plant.

3.2.1 iCON Simulation Methodology

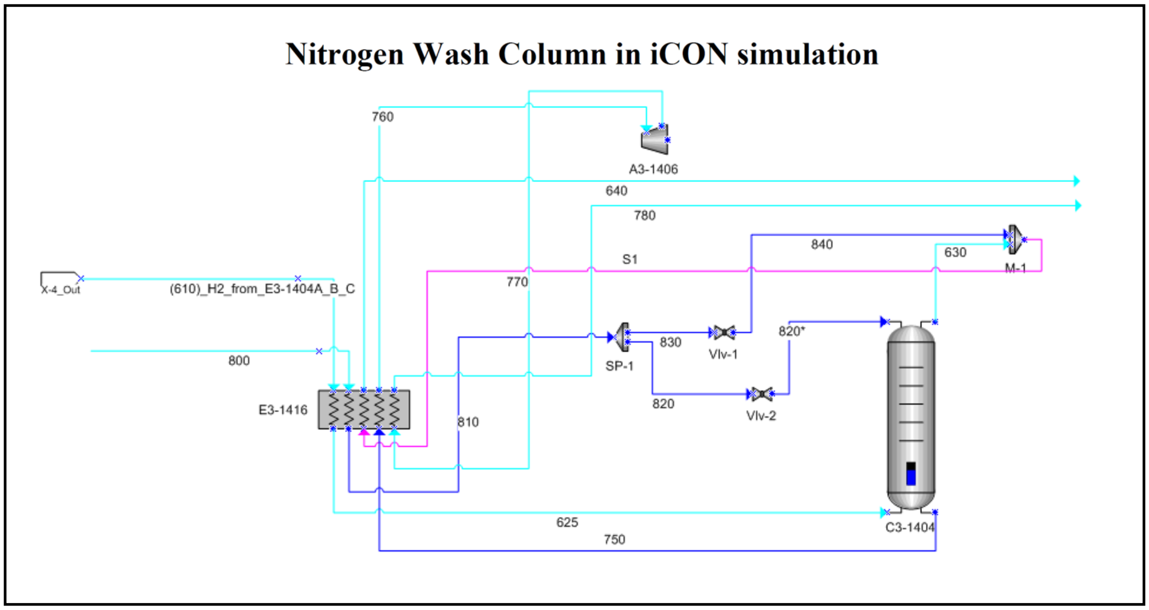


Figure 3.2: Screenshot of Nitrogen Wash Column in iCON

1) Changing data parameters of the nitrogen wash column and flow lines in the simulation.

- Simulate the pressure, temperature and flowrate for both inlet of the column
- Study the variation of each change for each parameter by tabulating table and constructing graph.

2) Analysing data gained from simulations

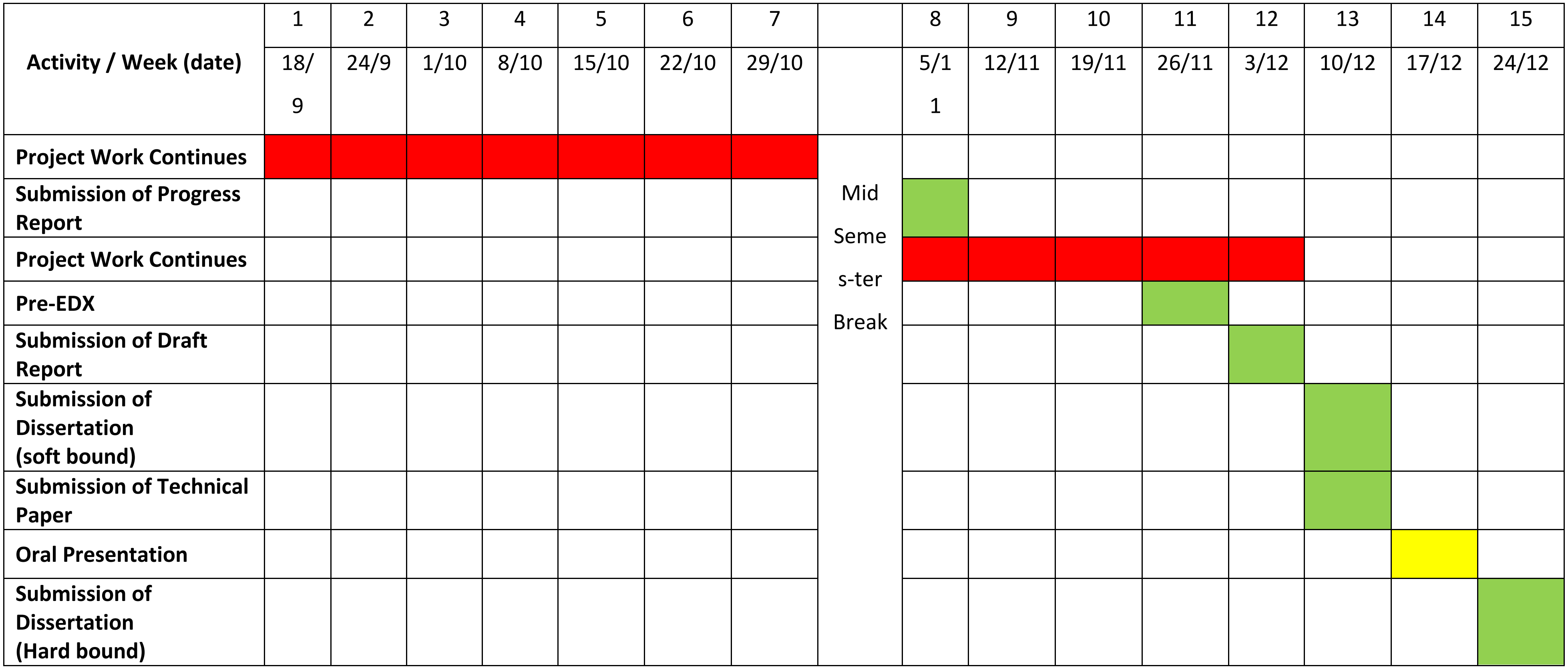
- To identify the parameter that affect most of the outlet composition
- To optimize the Nitrogen Wash Column by reducing the hydrogen loss at the off gas

3) Perform DOE (Box-Behnken Design) by manipulate simultaneously the 4 factors that clearly affect the result of hydrogen recovery for the nitrogen wash column. The 4 factors are:

i. Temperature of H_2 inlet stream into the nitrogen wash column (^oC)
ii. Temperature of lin N_2 inlet stream into the nitrogen wash column (^oC)
iii. Flowrate of H_2 inlet stream into the nitrogen wash column (Nm^3/h)
iv. Flowrate of N_2 inlet stream into the nitrogen wash column (Nm^3/h)

These 4 factors will be simultaneously varied in each experiment to get the analysis for the optimization purpose.

3.3 Gantt Chart



Activity / Week (date)	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
	18/9	24/9	1/10	8/10	15/10	22/10	29/10		5/11	12/11	19/11	26/11	3/12	10/12	17/12	24/12
Project Work Continues	🟥	🟥	🟥	🟥	🟥	🟥	🟥	Mid Semester Break								
Submission of Progress Report									🟩							
Project Work Continues									🟥	🟥	🟥	🟥	🟥			
Pre-EDX												🟩				
Submission of Draft Report													🟩			
Submission of Dissertation (soft bound)														🟩		
Submission of Technical Paper														🟩		
Oral Presentation															🟨	
Submission of Dissertation (Hard bound)																🟩

CHAPTER 4

RESULT AND DISCUSSION

A four-factors, three level of Box-Behnken design is use to determine the optimal factors that affect the amount of hydrogen recovery for the nitrogen wash column operation. The Box-Behnken design with a quadratic model was employed. Four independent variables namely temperature of H_2 inlet stream, temperature of lin N_2 inlet stream, flowrate of H_2 inlet stream and flowrate of lin N_2 inlet stream. Each independent variable has 3 levels which were -1, 0 and +1. A total of 27 different combinations were chose in random order according to a Box-Behnken configuration for four factors. The coded values of independent variables are tabulated in **Table 4.1**.

Independent Variable	Coded levels		
	-1	0	+1
Effect of Temp (H2 stream to N2 Column)	-165	-168	-176
Effect of Temp (Lin N2 stream to N2 Column)	-170	-176	-180
Effect of Flowrate (H2 Stream to N2 Column)	67653.130	75170.150	82687.165
Effect of Flowrate (Lin N2 Stream to N2 Column)	14448.645	16054.050	17659.450

Table 4.1: Coded and Uncoded levels of the independent variables.

Effects of temperature of H_2 inlet stream, temperature of lin N_2 inlet stream, flowrate of H_2 inlet stream and flowrate of lin N_2 inlet stream on hydrogen recovery of nitrogen wash column were investigated by response surface plotting methodology. The experimental values for hydrogen recovery and nitrogen recovery under different treatment conditions are presented in **Table 4.2**. The coefficients of the response surface equation were determined by using Statgraphics *Centurion XVI* software (Statgraphics *Centurion XVI*, was released in October 2009).

$$\text{Hydrogen Recovery (\%)} = \frac{\text{Hydrogen Flowrate in syngas } (\frac{\text{Nm3}}{\text{h}})}{\text{Hydrogen Flowrate in feed gas } (\frac{\text{Nm3}}{\text{h}})}\ x\ 100\%$$

Exp No.	Temp (H2)	Temp (N2)	Flowrate (H2)	Flowrate (N2)	Result (flowrate at top outlet)	
	x1	x2	x3	x4	Hydrogen Recovery	Carbon Monoxide
					%	PPM
1	0	0	-1	-1	99.73494	0.017
2	0	+1	-1	0	99.50556	0.000
3	0	-1	0	-1	99.94313	13.363
4	0	+1	+1	0	99.81103	0.084
5	0	0	-1	+1	99.40921	0.000
6	-1	0	+1	0	99.94332	15.642
7	+1	0	0	+1	99.35608	0.000
8	0	0	0	0	99.73488	0.017
9	0	-1	-1	0	99.68105	0.006
10	0	-1	0	+1	99.69619	0.008
11	-1	0	-1	0	99.67008	0.009
12	+1	0	+1	0	99.62313	0.000
13	+1	-1	0	0	99.58476	0.000
14	+1	0	-1	0	99.34049	0.000
15	0	0	0	0	99.73488	0.017
16	0	0	+1	+1	99.73487	0.017
17	-1	+1	0	0	99.7715	0.056
18	0	+1	0	-1	99.82424	0.112
19	-1	0	0	+1	99.68659	0.011
20	0	0	0	0	99.73488	0.017
21	0	-1	+1	0	99.93533	2.605
22	+1	0	0	-1	99.6358	0.000
23	-1	0	0	-1	99.95115	29.079
24	0	0	+1	-1	99.96087	4.642
25	0	+1	0	+1	99.52204	0.000
26	+1	+1	0	0	99.44104	0.000
27	-1	-1	0	0	98.55985	1.447

Table 4.2: Show the Box-Behnken design with four independent variables and experimental amount of hydrogen recovery and amount of CO in PPM.

From **Table 4.2,** it shows the overall result for the hydrogen recovery that obtains after running the simulation at different numbers of condition. Each number of experiments gives different result since those 4 factors are the most affecting factor to the result. The regression coefficients for the second order polynomial equation and results for linear, quadratic and interaction term are presented in **Table 4.3.** The statistical analysis indicates that the model was adequate, possessing no significant lack fit and with very satisfactory of the R^2.

Source	*Sum of Squares*	*Df*	*Mean Square*	*F-Ratio*	*P-Value*
A:Temp H2	0.0301192	1	0.0301192	0.47	0.5052
B:Temp N2	0.0188095	1	0.0188095	0.29	0.5972
C:Flowrate H2	0.231635	1	0.231635	3.63	0.0810
D:Flowrate N2	0.225542	1	0.225542	3.53	0.0846
AA	0.18331	1	0.18331	2.87	0.1159
AB	0.459262	1	0.459262	7.20	0.0199
AC	0.0000220884	1	0.0000220884	0.00	0.9855
AD	0.0000573734	1	0.0000573734	0.00	0.9766
BB	0.0495648	1	0.0495648	0.78	0.3955
BC	0.000654908	1	0.000654908	0.01	0.9210
BD	0.000763192	1	0.000763192	0.01	0.9147
CC	0.00764829	1	0.00764829	0.12	0.7352
CD	0.00248686	1	0.00248686	0.04	0.8468
DD	0.0138851	1	0.0138851	0.22	0.6493
Total error	0.765938	12	0.0638282		
Total (corr.)	2.06729	26			

R^2 = 62.9496 %
R^2 (adjusted for d.f.) = 19.7242 %
Standard Error of Est. = 0.252642
Mean absolute error = 0.125533
Durbin-Watson statistic = 2.10279 (P=0.5479)
Lag 1 residual autocorrelation = -0.267886

Table 4.3: Analysis of Variance for Hydrogen Recovery

The ANOVA table partitions the variability in Hydrogen Recovery into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, one effect have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level. The R^2 statistic indicates that the model as fitted explains 62.9496% of the variability in Hydrogen Recovery. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 19.7242%. The standard error of the estimate shows the standard deviation of the residuals to be 0.252642. The mean absolute error (MAE) of 0.125533 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 5.0%, there is no indication of serial autocorrelation in the residuals at the 5.0% significance level.

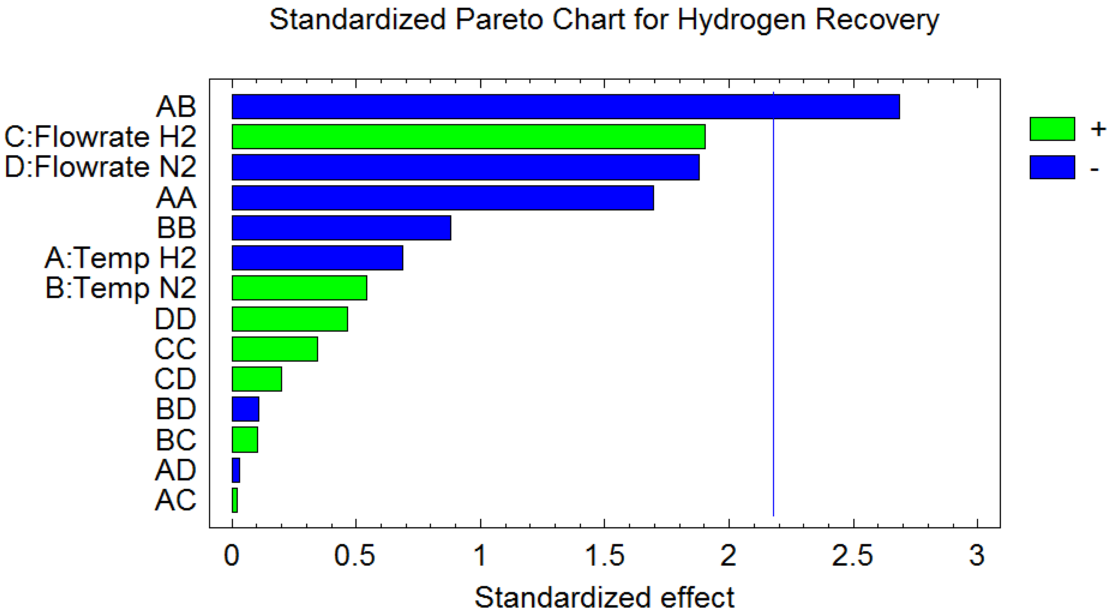


Figure 4.1: Standardized Pareto Chart for Hydrogen Recovery

The main factor that affects the value of hydrogen recovery can be determined by using Standardized Pareto Chart. The Standardized Pareto Chart contains a bar for each effect, sorted from most significant to least significant. The length of each bar is proportional to the standardized effect, which equals the magnitude of the t-statistic that would be used to test the statistical significance of the effect. A vertical line is drawn at the location of the 0.05 critical value and any bars that extend to the right of that line indicate effects that are statistically significant at the 5% significant level. From **Figure 4.1**, determine that the main factor that affects the hydrogen recovery is interaction between Temperature H_2 and N_2 inlet stream **(AB)** followed by H_2 inlet flowrate **(C)** and then N_2 inlet flowrate **(D)**.

The effect of interaction for both inlet H_2 and N_2 stream temperature is also well displayed by response surface plot and also contour plot.

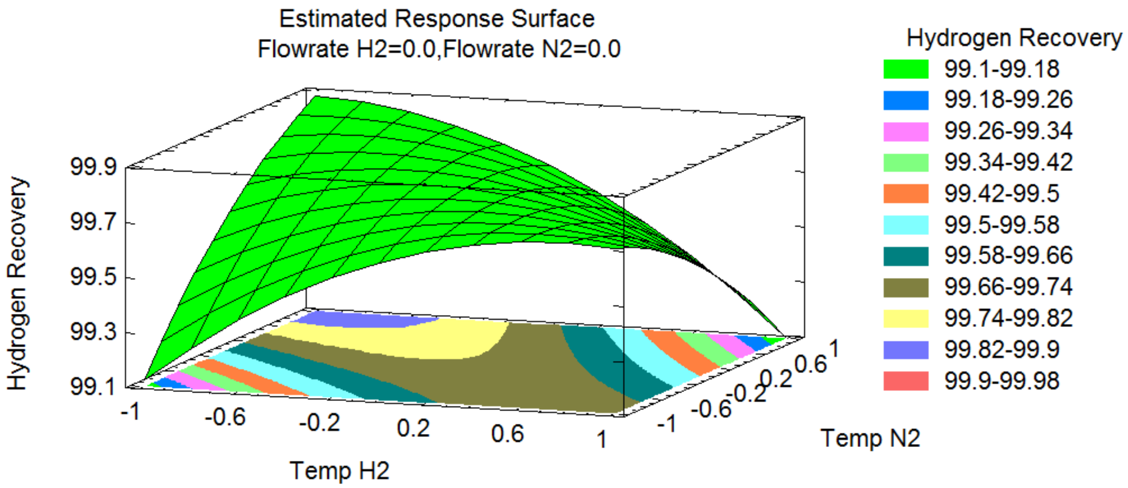


Figure 4.2: Response Surface Plot for Hydrogen Recovery against both H_2 and N_2 inlet stream temperature.

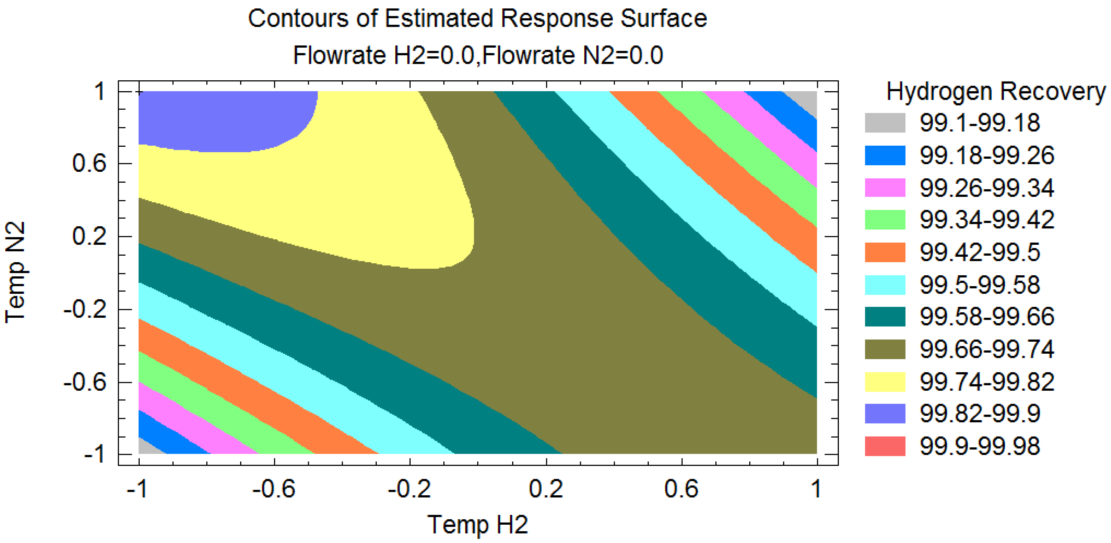


Figure 4.3: Contour plot for Hydrogen Recovery with effect of both H_2 and N_2 inlet stream temperature.

From **Figure 4.2 and Figure 4.3,** shows that the highest value of Hydrogen Recovery is approximately at +1 [-180 C^o] temperature of N_2 inlet stream with temperature of H_2 inlet stream at -0.8 [-165.6 C^o] (when fixed the flowrate of H_2 inlet stream at 75170.15 Nm^3/h and at 16054.05 Nm^3/h of N_2 inlet flowrate). By producing these two plots it will help the process of optimizing the nitrogen wash column and it can give out the overview that tell us how much the interaction between H_2 and N_2 inlet temperature can affect the hydrogen recovery of the nitrogen wash column.

Statgraphics *Centurion XVI* software also provides a regression equation which has been fitted to the data. The equation fitted to this model is:

Hydrogen Recovery = 99.7349 - 0.0500992*x1 + 0.0395911*x2 + 0.138935*x3 - 0.137096*x4 - 0.185393*x1^2 - 0.338844*x1*x2 + 0.00234991*x1*x3 - 0.00378726*x1*x4 - 0.0964023*x2^2 + 0.0127956*x2*x3 - 0.013813*x2*x4 + 0.0378689*x3^2 + 0.0249342*x3*x4 + 0.0510242*x4^2

Where:

x1 = Temperature of H_2 inlet

x2 = Temperature of N_2 inlet

x3 = Flowrate of H_2 inlet

x4 = Flowrate of N_2 inlet

From this equation it can calculate the value of hydrogen recovery that we want to analyse and from this equation also showed that the factor that effect the most is temperature of H_2 inlet and temperature of N_2 inlet. In conclusion, by manipulate the temperature for both inlet of this nitrogen wash column it can affect the most of the value of hydrogen recovery. The optimum value of operating condition for the nitrogen wash column is:

The Paramter	Value
Effect of Temp (H2 stream to N2 Column)	**-165.6 C^o**
Effect of Temp (Lin N2 stream to N2 Column)	**-180 C^o**
Effect of Flowrate (H2 Stream to N2 Column)	**75170.15 Nm^3/h**
Effect of Flowrate (Lin N2 Stream to N2 Column)	**16054.05 Nm^3/h**

Table 4.4: The optimum operating condition obtain from result of this DOE

Those data showed in **Table 4.4** is the approximately value that obtain from this statistical analyse and from these operating condition it will give the highest hydrogen recovery value that can be the result of this project. This project objective is to reduce the amount of hydrogen loss at the off gas by operate it at the optimum operating condition. Therefore, the objective has been achieved and the optimum parameter for this nitrogen wash column has been identified.

The amount of Carbon Monoxide at the syngas outlet.

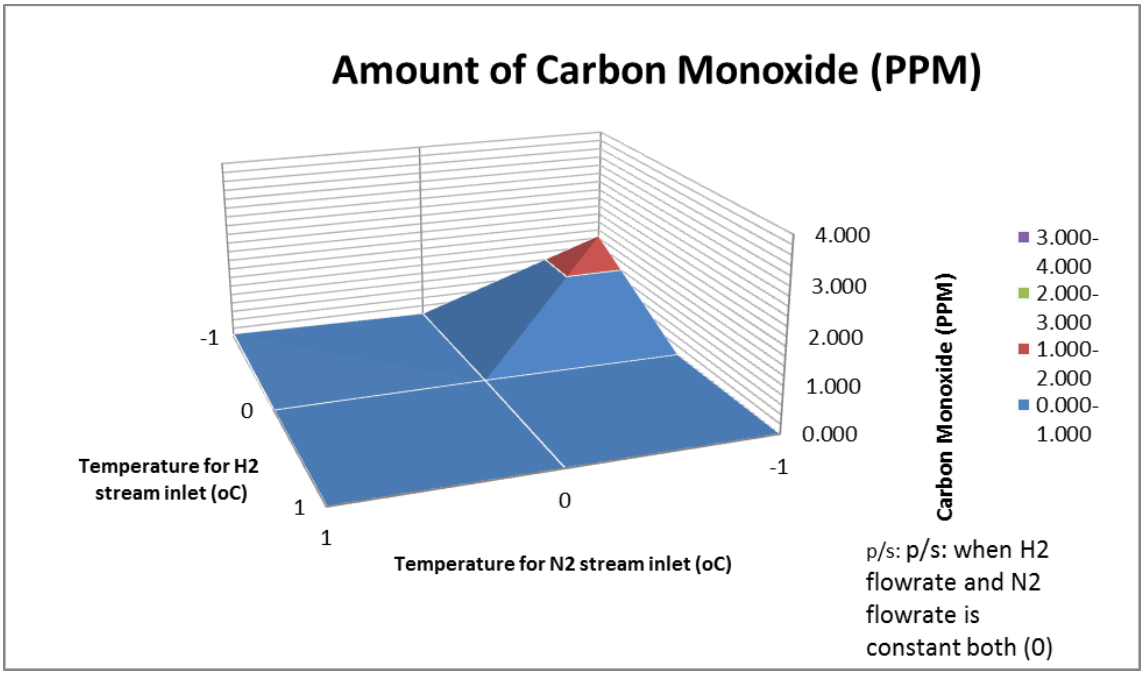
After we had known the optimum value of operating condition for hydrogen recovery, we might also need to ensure that the amount of carbon monoxide at the syngas outlet is not more than 5 ppm. CO is also one of the compositions at the syngas outlet but the amount is very little compare to nitrogen and hydrogen composition. Since, this is a nitrogen wash column that functions to purify the hydrogen for the ammonia synthesis, therefore the present of CO in the syngas outlet need to be less than 5 ppm in order to make sure the purification of H_2 is on a satisfaction level for ammonia synthesis.

As a conclusion, the analysis of amount of CO in the syngas outlet also needs to be done to ensure the amount is not exceeding 5 ppm. From the result we get for the hydrogen recovery, we determine that the optimum value of operating condition is when both flowrate H_2 and N_2 at the original value that is at 75170.15 Nm^3/h and 16054.05 Nm^3/h respectively. So, we have done an analysis focusing on that area which is at both constant value of the H_2 and N_2 inlet flowrate.

Temp (H2)	Temp (N2)	Flowrate (H2)	Flowrate (N2)	Result (flowrate at top outlet)					
x1	x2	x3	x4	Hydrogen	Nitrogen	Carbon Monoxide	Total	% CO in Total	CO in PPM
				Syngas	Syngas	Syngas			
0	0	0	0	73341.02	13864.99	0.15	87206	0.00000172006198	0.017
1	-1	0	0	73230.63	12201.26	0	85432	0.00000000000000	0.000
0	0	0	0	73341.02	13864.99	0.15	87206	0.00000172006198	0.017
-1	1	0	0	73367.95	14267.49	0.49	87636	0.00000559131397	0.056
0	0	0	0	73341.02	13864.99	0.15	87206	0.00000172006198	0.017
1	1	0	0	73124.94	10724.1	0	83849	0.00000000000000	0.000
-1	-1	0	0	72476.95	15879.76	12.79	88370	0.00014473319415	1.447

Table 4.5: The amount of Carbon Monoxide at the syngas outlet in PPM

The response surface plot also showed that the analysis of the amount of CO at the syngas outlet.



p/s: p/s: when H2 flowrate and N2 flowrate is constant both (0)

Figure 4.4: Response Surface Plot for Amount of CO against both H_2 and N_2 inlet stream temperature.

From both **Table 4.5** and **Figure 4.4** it is determine that the amount of Carbon Monoxide at the syngas is less than 5 PPM as required when both H_2 and N_2 inlet flowrate is constant and remain its original value. Therefore, we can conclude that when the hydrogen recovery increase, the amount of CO in the syngas outlet is still below 5 PPM.

CHAPTER 5
CONCLUSION

An optimization problem of nitrogen wash column operation has been identified. An iCON simulation modal is available for simulation study. Optimization will be performed by simulating the wash column at various operating condition such as temperature, pressure and flowrate. Since this wash unit operate in cryogenic condition therefore it need to be operate in coldbox in a very low temperature. In addition, this is the last stage of purification of nitrogen for ammonia synthesis and at this stage also we are removing the residual impurities likes carbon monoxide, argon and also methane. By removing those impurities we can get at the top stream of this column the desire product that is hydrogen and nitrogen in the ration 3:1 before continue the step of ammonia synthesis.

As far of conclusion the objective of this project is achieve that is to minimise the hydrogen loss at the off gas by operating this nitrogen wash column in an optimum operating condition in order to increase the hydrogen recovery. As shown in the result and discussion part, the main factor that affects the amount of hydrogen loss at the off gas is interaction between inlet temperatures of H_2 and N_2 stream. Moreover, from the result also shown that when both flowrate of H_2 and N_2 inlet stream is constant (at original value) and meanwhile the inlet temperature of N_2 stream is at +1 (-180 C^o) and inlet temperature of H_2 is at -0.8 (-165.6 C^o) it will produce the highest amount of hydrogen recovery and it mean that these parameter is the optimum value for this nitrogen wash column. Besides, the amount of CO at the syngas also needs to be below than 5 PPM. By using Design of Experiment (Box-Behnken) methodology, it will help to perform the optimization process and provide the best solution to get the result. Furthermore, Statgraphics *Centurion XVI* software it been used to analyse the DOE and also to determine the optimum operating condition for the nitrogen wash column with respect to the objective of this project that is to minimise the hydrogen loss in the off gas. This project is a simulation type to be implemented in the ammonia plant. Since it is a PETRONAS based project it is compulsory to use iCON as simulation software.

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