Ammonia Production plant: Recycle load optimization and effect on process energy consumption and product through-put

DISERTATION

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CERTIFICATE OF APPROVAL

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A project dissertation submitted to the Chemical Engineering Programme, Universiti Teknologi PETRONAS, in partial fulfillment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

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Approved by,

_____

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CERTIFICATE 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.

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Samuel Dhukpuou Makhoi 11748

ABSTRACT

Commercial scale NH_3 production began in the 20th century, peaking at 131,000,000 metric tons in 2010. The running challenge pertains to optimizing raw material use, energy consumption and environmental pollution as well as. Current industrial ammonia production processes have a 25% [3] feed conversion. The first challenge in this project is minimizing raw material wastage by finding optimal recycle load. Being a very energy intensive process the second challenge is energy efficiency. This study therefore aims at finding an optimal operating mode that looks at using recycle stream to model, simulate and study general plant performance. Operating variables are carefully monitored using Icon simulation software and the results obtained are further analyzed to reach the most economical and energy-efficient operation. By comparing current ammonia production technologies with this process model and simulation, a conclusion is drawn with regard to energy saving potentials and optimal raw material utilization in ammonia production. Included are an outline of the methodology to reach the objectives, the process model and simulation, data, discussion, conclusions and recommendations.

Keywords: Optimization, product throughput, recycle load, ammonia production loop.

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To God the almighty I give thanks for giving me the strength to reach this point of my student life.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Ammonia is one of the most industrially significant and versatile chemicals. Commercial scale ammonia production started in 1913 and has since risen to become a very large industry by chemical standards. As of 2005, the world production stood at around 143 million metric tons. Commercial ammonia synthesis chemistry and catalyst are still based directly on the original developments by Haber and Bosch; variations in reaction equipment, operating conditions, and process schemes, however, have multiplied through the years.

With an aim being optimization, this study looks at the following ammonia production related issues:

- ❖ Ammonia production process is very energy intensive.

- ❖ There is global need for both energy efficiency and reduction in raw material wastage.

- ❖ Recycling has both merits and demerits

- ❖ Cost-wise (there is need for feasible investment)

- ❖ Environmental impact

    - ❖ Environment-friendliness & optimal production are achievable through careful investigation of other factors

    - ❖ Environmental impact

Given that backdrop, this project aims to investigate how the current industrial scale ammonia production can be optimized. Being a very energy intensive process; coupled with the fact that current production operates within 20-25% reactor conversion of the raw material into product(s)-the base feedstock in this study is natural gas-the study will has as its target minimization of energy consumed without sacrificing product throughput and plant economic feasibility.

A simulation of the whole plant mirroring current industrial operation will be conducted using Icon soft-ware. The variables of interest manipulated and observations are made. The main investigation surrounds the effect of recycle load on general plant performance as stipulated in the preceding paragraph.

Once the results are obtained, they will be analyzed and optimal plant operation drawn.

1.2 Problem Statements

The current ammonia production process wastes a lot of raw material (20% conversion) and is very energy intensive. To optimize the process, Icon simulation soft-ware is used to investigate the effect of employing recycle stream on the Performance of an Ammonia production plant with regard to:

3. Raw material optimization

II. Energy consumption

III. Product stream throughput

IV. Cost both in time and equipment e.g. extra compression

1.3 Objectives

THE OBJECTIVES ARE:

- To investigate the effect of recycling on

    - the energy consumption

    - Plant throughput

    - environmental impact

- To identify the optimal recycle stream ratio by plant simulation

1.4 Scope of Works

By doing this project, the topics to be covered are:

- ➢ Literature reviews

- ➢ Learn software for Chemical process simulations: Icon and HYSIS

- ➢ Selecting process units

- ➢ Developing a Process Flow Diagram (PFD) using Icon simulation soft-ware

- ➢ Defining and setting system variables and parameters

- ➢ Running case studies

- ➢ Solve, compare and simulate the model with actual data

- ➢ Analysis, prediction ,calculate and determine the parameters under investigation

- ➢ Process optimization

1.5 The Significance and Relevance of the Project

This project will assist in:

- ▪ Developing an optimum recycle load that balances:

  - ✓ energy efficiency

  - ✓ product throughput

  - ✓ general investment and costs

  - ▪ Having considered pertinent factors, industrialist will choose recycle ratios that result in optimal plant use.

1.6 Feasibility of the Project within the Scope and Time frame

In the FYP I, thorough literature review on ammonia production processes as well as use of simulation of chemical processes was conducted. Also reviewed were publications on energy efficiency strategies employed in the chemical industry.

The second phase of this project started by developing a Process Flow Diagram (PFD) as well as conducting a model simulation of real site data regarding the topic. The results obtained should be reliable enough to proceed with analysis and drawing an optimal recycle load that will yield profitable product throughput at minimal energy input.

As such, the project can be declared feasible on the following basis:

- ❖ Time allocated approximately 20 weeks which is enough

- ❖ Sufficient, for data acquisition and analysis on each procedures & compilation

- ❖ No equipment or lab experiment needed

- ❖ Computer lab –Icon/HYSIS available

- ❖ Sufficient research materials :Max Appl, Ammonia: principles and industrial practice, research publications from http://www.sciencedirect.com/

- ❖ Reference books & manual available : UTP IRC

All the necessary equipment and the information are available for the study and the project is expected to be finished within the time frame.

CHAPTER 2

2. LITERATURE REVIEWS AND THEORY

This section covers material on all process leading up to the final ammonia production. It also covers works on optimization of chemical processes, simulation of chemical processes, as well as energy efficiency in the chemical industry.

Three types of processes are mainly used for ammonia production

1. Steam reforming of natural gas or other light hydrocarbons;

2. Partial oxidation of heavy fuel oil or vacuum residue;

3. Coal gasification.

In this project only the steam reforming of natural gas is considered due to the shortcomings associated with the other two. The coal gasification process is neither economically nor environmentally friendly.

Ammonia is produced by reacting nitrogen with hydrogen as represented in the following equations.

Ammonia synthesis loop: $3H_2 + N_2 \rightarrow 2NH_3$

Catalytic Hydrogenation: $H_2 + RSH \rightarrow RH + H_2S\ (g)$

Hydrogen sulfide removal: $H_2S + ZnO \rightarrow ZnS + H_2O$

Catalytic steam reforming: $CH_4 + H_2O \rightarrow CO + 3H_2$

Catalytic shift conversion: $CO + H_2O \rightarrow CO_2 + H_2$

Catalytic methanation: $CO + 3H_2 \rightarrow CH_4 + H_2O$

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$
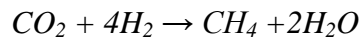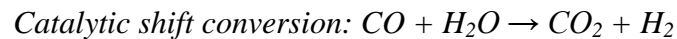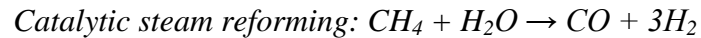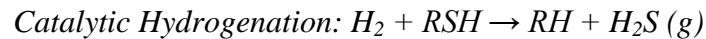
The process proceeds in the following sequence:

Feedstock	
Ammonia is produced basically from water, air and energy. The energy source is usually hydrocarbons, thus providing hydrogen as well. Steam reforming of light hydrocarbons is the most efficient route, with about 77% of world ammonia capacity being based on natural gas.	
Desulphurization	Sulphur is removed from natural gas through a zinc-oxide catalyst.
Primary & Secondary Reformer	Natural gas reforming with steam and air is the simplest and most efficient way of ammonia synthesis gas production.
Shift Conversion	Remaining carbon monoxide from the secondary reformer is converted into carbon dioxide.
CO_2 Removal and Methanation	The small amounts of CO and CO_2, remaining in the synthesis gas after CO_2 removal, are poisonous for the ammonia synthesis catalyst and must be removed by conversion to CH_4 in the methanator.
Compression and Ammonia Synthesis	Compressed Syngas reacts with nitrogen to form ammonia

Figure 1: Process sequencing

2.1 SYNTHESIS GAS (STEAM REFORMING OF NATURAL GAS)

Synthesis gas may be produced from a variety of feedstock. Natural gas is the preferred feedstock when it is available from gas fields (non-associated gas) or from oil wells (associated gas). The first step in the production of synthesis gas is to treat natural gas to remove hydrogen sulfide. The purified gas is then mixed with steam and introduced to the first reactor (primary reformer. The steam to natural gas ratio varies from 4–5 depending on natural gas composition (natural gas may contain ethane and heavier hydrocarbons) and the pressure used.

A promoted nickel type catalyst contained in the reactor tubes is used at temperature and pressure ranges of 700–800°C and 30–50 [1] atmospheres, respectively. The reforming reaction is equilibrium limited. It is favored at high temperatures, low pressures, and a high steam to carbon ratio.

These conditions minimize methane slip at the reformer outlet and yield an equilibrium mixture that is rich in hydrogen. The product gas from the primary reformer is a mixture of H2, CO, CO_2, unreacted CH_4, and steam.

The main steam reforming reactions are:

$$CH_4 (g) + H_2O (g) \rightarrow CO (g) + 3H_2 (g) \quad \Delta H ° = +206 \ KJ$$

$$\Delta H °800°C = +226 \ KJ$$

$$CH_4 (g) + 2H_2O (g) \rightarrow CO_2 (g) + 4H_2 (g) \quad \Delta H° = +164.8 \ KJ$$
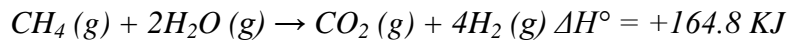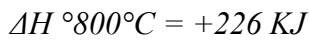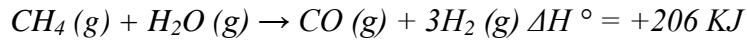
For producing hydrogen for ammonia synthesis, however, further treatment steps are needed. The required amount of nitrogen for ammonia must be obtained from atmospheric air by partially oxidizing unreacted methane in the exit gas mixture from the first reactor in another reactor (secondary reforming).

The main reaction occurring in the secondary reformer is the partial oxidation of methane with a limited amount of air. The product is a mixture of hydrogen, carbon dioxide, carbon monoxide, plus nitrogen, which does not react under these conditions. The reaction is represented as follows:

$$CH_4 + \tfrac{1}{2} (O_2 + 3.76 \ N_2) \rightarrow CO + 2H_2 + 1.88 \ N_2 \quad \Delta H ° = -32.1 \ KJ$$
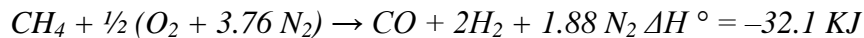
The reactor temperature can reach over 900°C in the secondary reformer due to the exothermic reaction heat. The second step after secondary reforming is removing carbon monoxide, which poisons the catalyst used for ammonia synthesis, done in three further steps, shift conversion, carbon dioxide removal, and methanation of the remaining CO and CO2.

2.2 Shift Conversion

In the shift converter, carbon monoxide is reacted with steam to give carbon dioxide and hydrogen. The reaction is exothermic and independent of pressure:

$$CO\ (g) + H_2O\ (g) \rightarrow CO_2\ (g) + H_2\ (g)\ \Delta H° = -41\ KJ$$
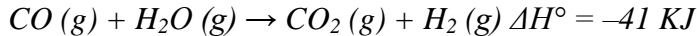
The feed to the shift converter contains large amounts of carbon monoxide which should be oxidized. An iron catalyst promoted with chromium oxide is used at a temperature range of 425–500°C to enhance the oxidation.

2.3 Methanation

Catalytic methanation is the reverse of the steam reforming reaction, an exothermic reaction in which in and methane yield is favored at lower temperatures:

$$3H_2(g) + CO(g) \rightarrow CH_4(g) + H_2O(g)\ \Delta H° = -206\ KJ$$
$$4H_2(g) + CO_2\ (g) \rightarrow CH4(g) + 2H_2O(g)\ \Delta H° = -164.8\ KJ$$
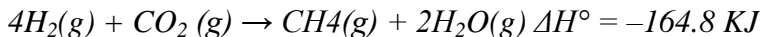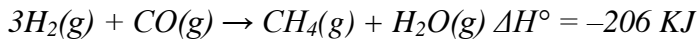
2.4 Syngas purification

Synthesis Gas Purification

The raw syngas leaving the hydrogen production section must be purified before it is suitable as feed to an ammonia synthesis reactor. The impurities in the syngas include carbon dioxide, carbon monoxide, water, methane, and argon. Carbon dioxide removal is accomplished through one of a variety of processes that are available, such as Benfield and activated MDEA. This is done by contacting the syngas with a liquid that either chemically reacts with, or physically dissolves, the carbon dioxide.

Catalytic methanation: $CO + 3H_2 \rightarrow CH_4 + H_2O$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
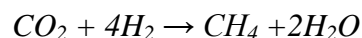
2.4 Industrial uses for Ammonia

As mentioned earlier in this paper, ammonia is one of the most industrially useful chemicals; serving as a raw material for most processes and as utility in others. The table below covers some of the industrial uses of ammonia.

Table 8: Industrial uses of Ammonia

Industry	Use
Circuit Board Manufacture	Printed circuit board wire materials
Heat Transferring Agents	Low-level Heat-transfer Media
Laboratory Chemicals	Bases
Machinery and Repair	Clean wash agents
Paper Coatings	Process Regulators – Paper Coating
pH Regulation Agents	pH Adjustors for Wastewater
Pharmaceuticals	Solvents – Pharmaceuticals
Photochemicals	Oxidizing Agents – Thiosulfate
Pulp and Paper Manufacture	Digesting agents
Rubber Manufacture	Solvents – Rubber Manufacture

2.5 Energy efficiency improvements in ammonia production

As mentioned earlier, ammonia production is a very energy-intensive process. This study has as its main objective improving energy efficiency by discussing and comparing the energy consumption and energy saving potential based on technologies currently in use and possible process improvements.

Since steam reforming of hydrocarbons for ammonia production started in the 1930, the technology has been gradually improved and energy consumption decreased from more than 80 GJ/t to a BAT level of about 28 GJ/t within the last decade [1].

The following table [1] shows energy consumption with regard to technology used.

Table 9: Energy consumption in Ammonia production according to production technology used

Unit operation	US ammonia manufacturing (1996)				Low energy ammonia plant	
	Gas	Steam	Losses	Electricity	Gas	Losses
Reformer feed	20.4				22.3	
Reformer fuel	9.9				6.8	
Primary reformer		4.8				0.7
Secondary reformer		0.0				
Waste heat boiler		−5.6				
Shift+CO$_2$ removal		1.2		0.2		1.3
Methanator			0.3			
Synthesis loop		−2.0		0.2		1.7
Aux. boiler	4.5	−3.9			0.3	
Turbines/compressor		5.5				6.5
Miscellaneous			0.3	0.1		0.7
Flare	0.3					
Total	35.0	0.0	0.6	0.5	29.3	10.9

This shows that there is actually a greater chance to improve on energy saving by further investigating effects of using recycle load in the ammonia production loop with is the main target of this research.

2.7 chemical process modeling

Dynamic simulation of chemical processes relies on intrinsic dynamic operation and synchronization of all units and processes afforded by a reliable dynamic simulator. Lately, several simulation programs have been developed for combined systems. These offer platforms capable of simulating the dynamic behavior of multiple-unit a systems and packages developed for simulation of chemical processes. By using predictive kinetic models, each process is run based its in-build formation function in the simulator. The results of the simulator are obtained and validated using two-unit experimental data, where available, or using published figures from the literature.

The simulator can also be employed to control and optimize the performance of the specific operations, termed as case studies.

The advantages of process simulation are obvious if one considers performing and experiments on such a scale as undertaken in this research. It would become unfeasible both in resources and time.

For this project iCON simulation soft-ware is used.

CHAPTER 3

3.0 Methodology

3.1 RESEARCH METHODOLOGY FLOW

Title Selection: Selection of the most appropriate final year project title
Prelim Selection: Understanding fundamental theories and concepts, performing a literature review, tools identification
Software/ Experimental Setup: Selection and design of experimental apparatus, materials, and procedures and learn how to operate hardware
Software/ Experimental Work: Conduct experiment and collect results
Analysis of Results: Correlate the result with the possibility of modification
Discussion of Analysis: Discuss the findings from the results and make a conclusion out of the study to determine if the objective has been met
Report Writing: Compilation of all research findings, literature reviews and outcomes into final report

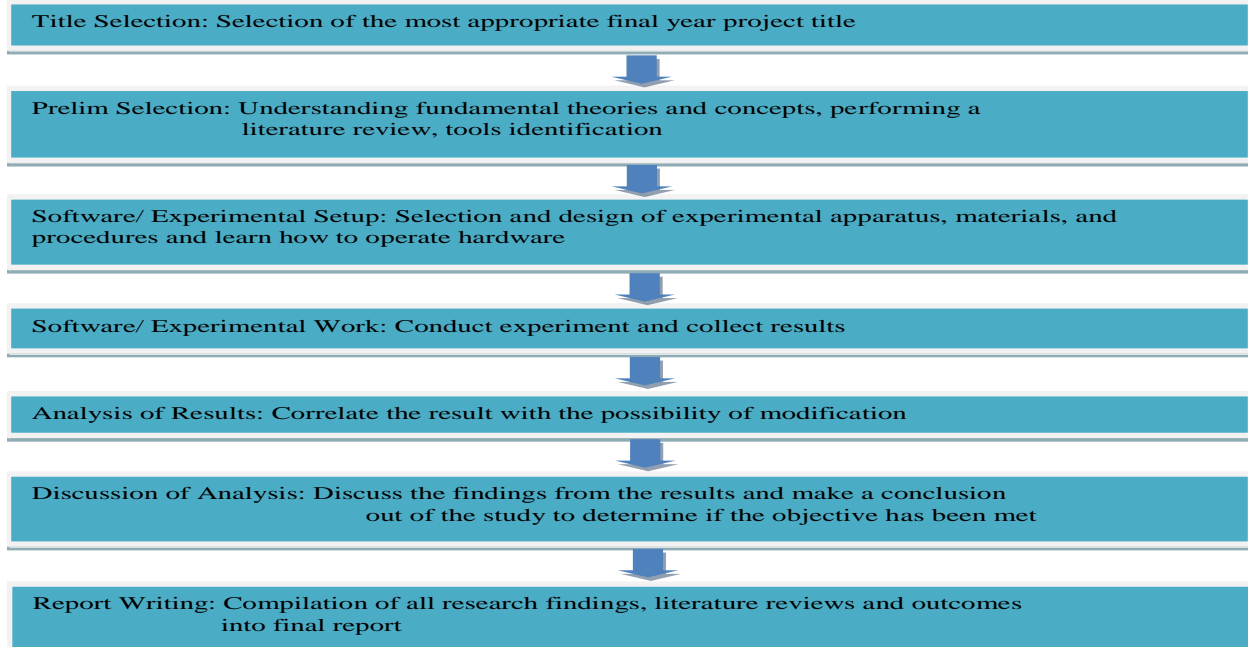Figure 2: Research methodology flow

3.2 PROJECT ACTIVITIES

- 1st ANALYTICAL APPROACH involves researching basic and fundamental procedures, materials and equipment

- 2nd, SIMULATION APPROACH. Simulation conducted using data from the literature and field data obtained with help from Dr. Lemma.

3.3 PROJECT METHODOLOGY FLOW
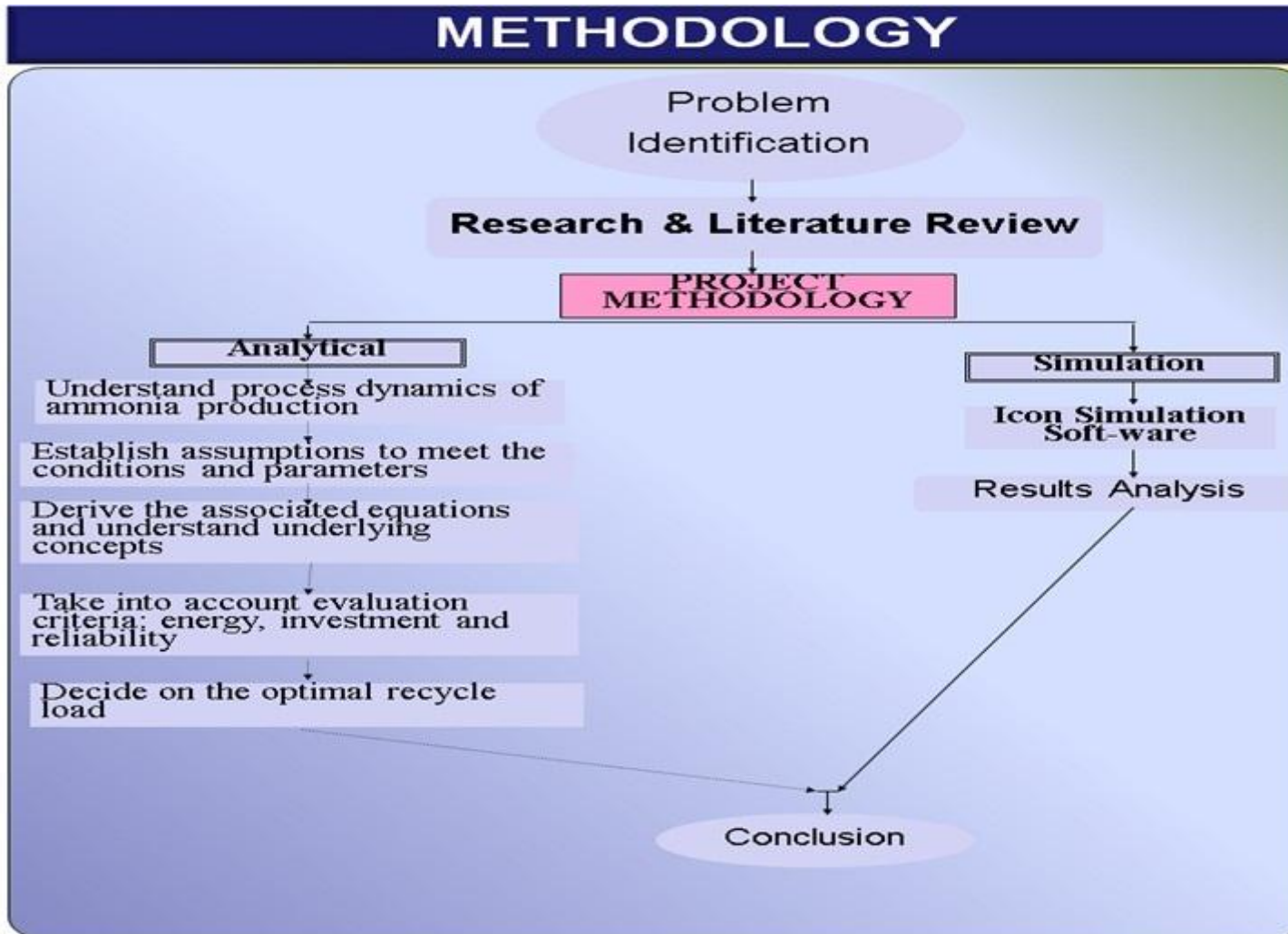
Figure 3: Project flow
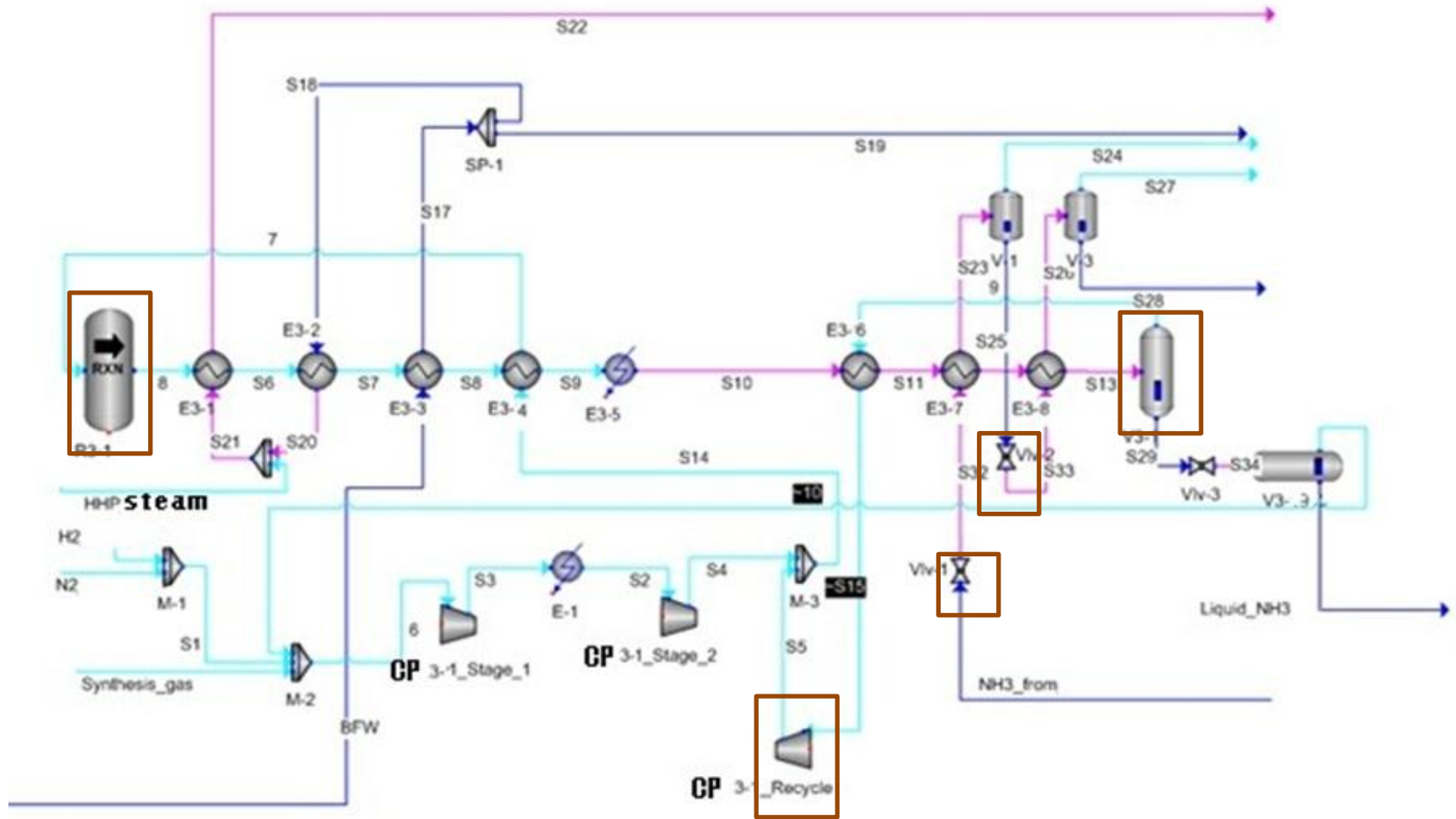
Figure 4: Process Flow Diagram (PFD)

The Process is modeled using iCON soft-ware. From the PFD above, it can be seen that all unit operations and streams in the model were able to converge; a proof to the success of replicating the process in real industry under similar parametric conditions.

With that achieved, the next phase of the project is to run a number of case studies aimed investigating ways to meet the objectives outlined earlier. The results of the case studies are presented and discussed in the next chapter.

CHAPTER 4

4.0 RESULT AND DISCUSSION

These results are presented in cluster of case studies. Each case study takes a set of certain parameters; some set to be independent while others are dependent. While independent variables are changed, resulting changes are observed and interpreted on the dependent variables.

Since the aim of the project is to find optimal solutions to the problems, operational of productive, each case study concludes by finding an optimal solution of the objective.

All the case studies were performed with iCON simulation software.

4.8 CASE STUDIES

CaseStudy1: *Finding optimal reactor pressure-temperature combination*

Independent variables:

- ✓ Convertor feed temperature (fixed)
- ✓ Convertor internal pressure(variable)

Dependent variable:

- ➤ Convertor OutPut [NH$_3$ MassFlow]

From the results it is evident that more ammonia is produced at lower feed temperature and reaction pressure.
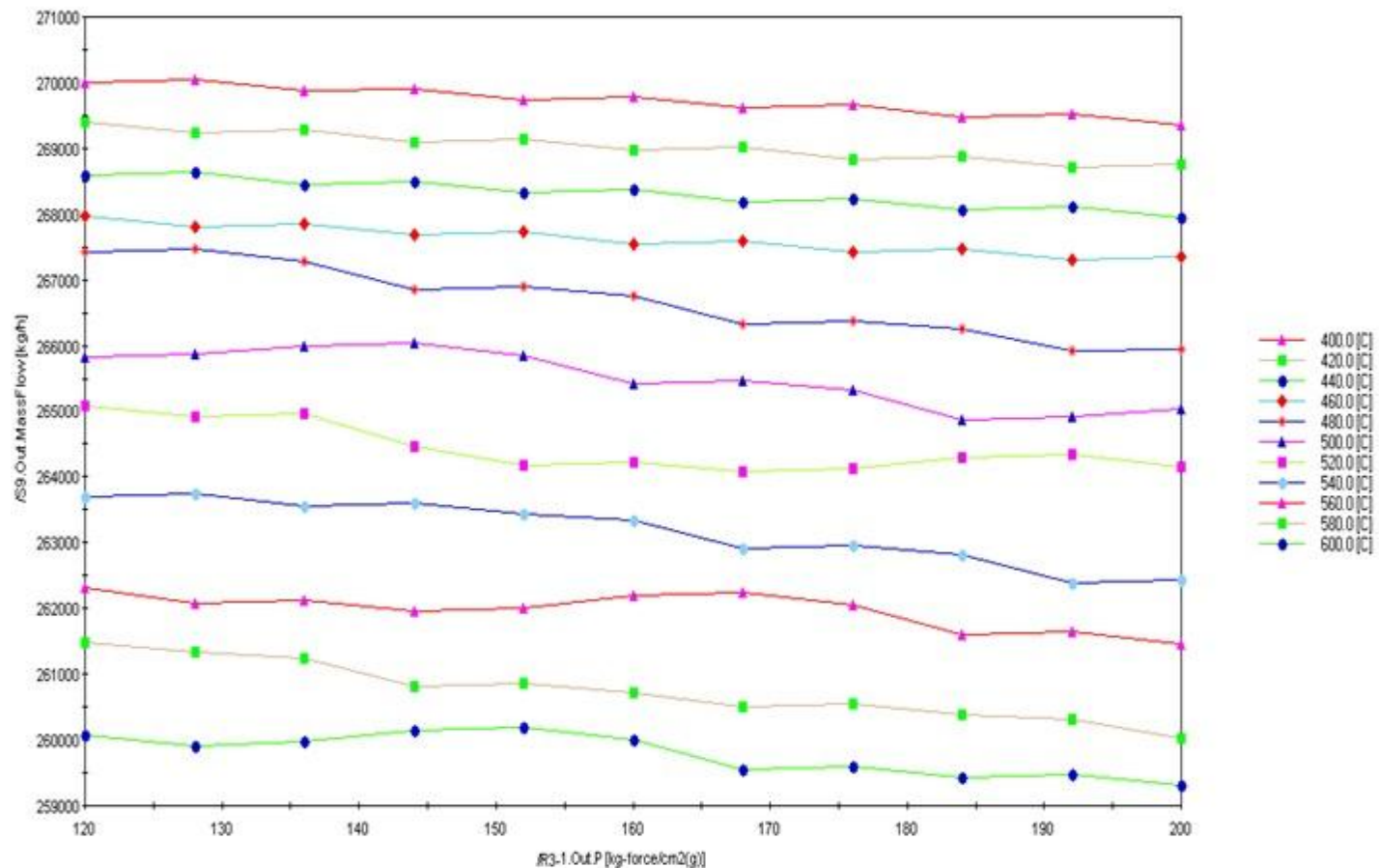
Figure 5: graph of MassFlow_Ammonia (fixed T) against P[kg-force/cm2(g)]
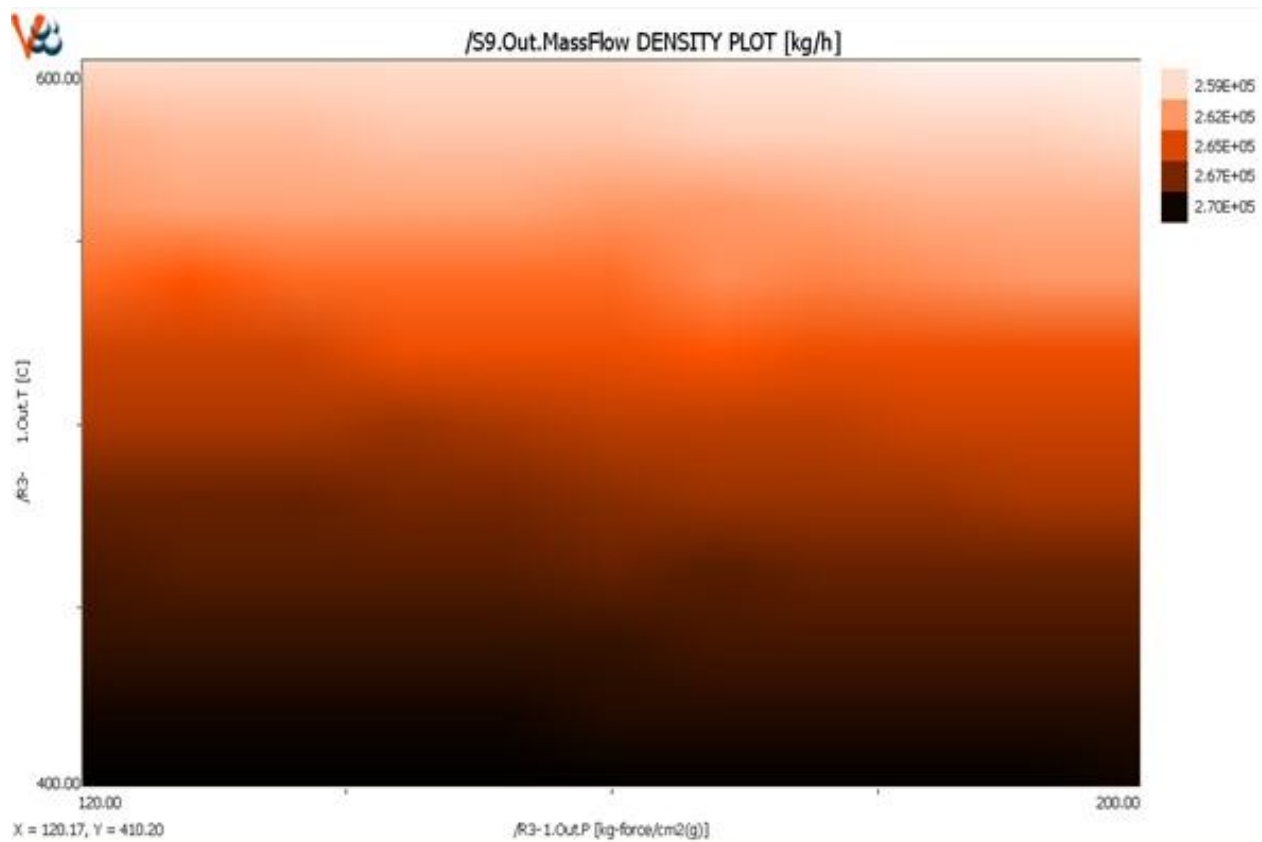
Figure 6: graph of MassFlow_Ammonia (fixed T) against P[kg-force/cm2(g)]: Density

OBSERVATIONS:

On the other hand pressure, though having a fluctuation relationship to yield, seems to also have inverse impact on yield. It should be expected that equilibrium should shift in such a way that pressure increase should lead to higher yield (le Chatelier principle).

CaseStudy2: Effect of convertor Temperature on heat exchanger *E3-1* duty.

Independent variable:

> ➢ R3-1 Out.T [C]

Dependent variable:

> ➢ E3-1 OutShell.Energy [MW]

Table 10: Results_CaseStudy3

Run	/R3-1 Out.T [C]	/E3-1 OutShell.Energy [MW]
1	450	39.6083
2	455	40.86465
3	460	42.12193
4	465	43.38014
5	470	44.63931
6	475	45.89943
7	480	47.16053
8	485	48.42262
9	490	49.6857
10	495	50.94978
11	500	52.21489
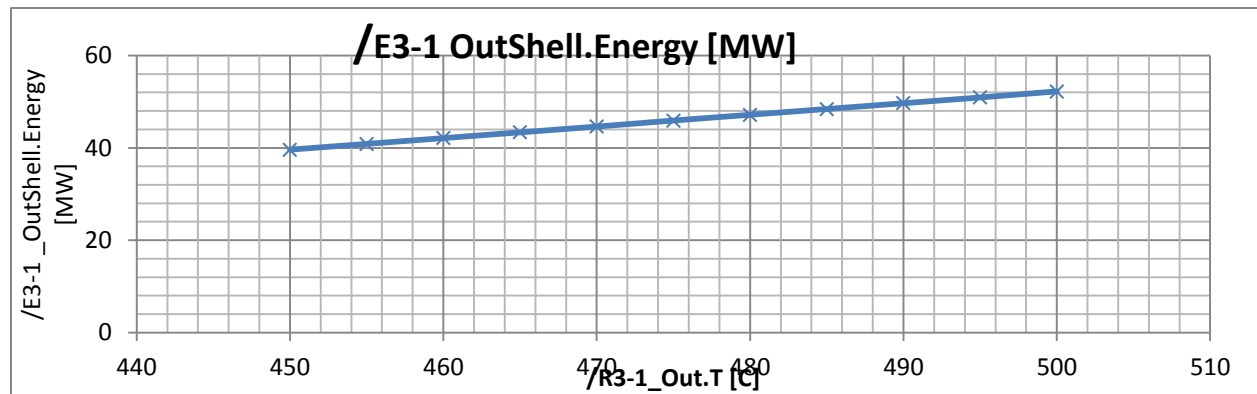
Figure 7: graph of E3-1 _OutShell.Energy against R3-1_Out.T [C]

OBSERVATIONS:

The trend that can be seen in this case study is that reactor performance is very dependent on pressure and temperature. Temperature increase is seen to have inverse proportional relation to yield. At higher temperatures, the convertor product yield decreases and increases with temperature decrease. It is not surprising as this reaction is exothermic and therefore heat is a product (more about this later in the paper).

CaseStudy3: Separator_conditions_T

Independent variable:

✓ Separator V1 feed temperature /E3-8 OutTube.T [C]

Dependent variables:

➢ Ammonia Mass in the recycle stream /MassFlow_AMMONIA [kg/h]

➢ Recycle composition /MolFrac_AMMONIA [Fraction]

➢ Compressor power consumption /CP-1_Recycle Out.Energy [W]

➢ Steam energy content /S22 In.Energy [W]

Table 11: Results_CaseStudy4

Points	/E3-8 OutTube.T [C]	MassFlow_AMMONIA [kg/h]	Frac_AMMONIA [Fraction]	/CP-1_Recycle Out.Energy [W]	/S22 In.Energy [W]
1	-4	22,617.97	0.058713	53,200,634	40,749,988
2	-3.5	23,029.16	5.97E-02	53,332,462	40,807,164
3	-3	23,446.75	6.07E-02	53,469,738	40,865,638
4	-2.5	23,864.02	6.18E-02	53,603,250	40,918,733
5	-2	24,294.08	6.28E-02	53,737,996	40,978,895
6	-1.5	24,723.86	0.063846	53,872,566	41,033,813
7	-1	25,166.73	6.49E-02	54,009,715	41,095,754
8	-0.5	25,609.26	0.06599	54,146,937	41,152,475
9	0	26,065.25	6.71E-02	54,283,720	41,216,243
10	0.5	26,520.86	6.82E-02	54,423,979	41,274,792
11	1	26,990.31	6.93E-02	54,563,710	41,340,435
12	1.5	27,459.29	7.04E-02	54,704,759	41,400,844
13	2	27,942.55	7.16E-02	54,846,288	41,468,409
14	2.5	28,425.24	7.27E-02	54,989,089	41,530,719
15	3	28,922.65	7.39E-02	55,132,577	41,600,255
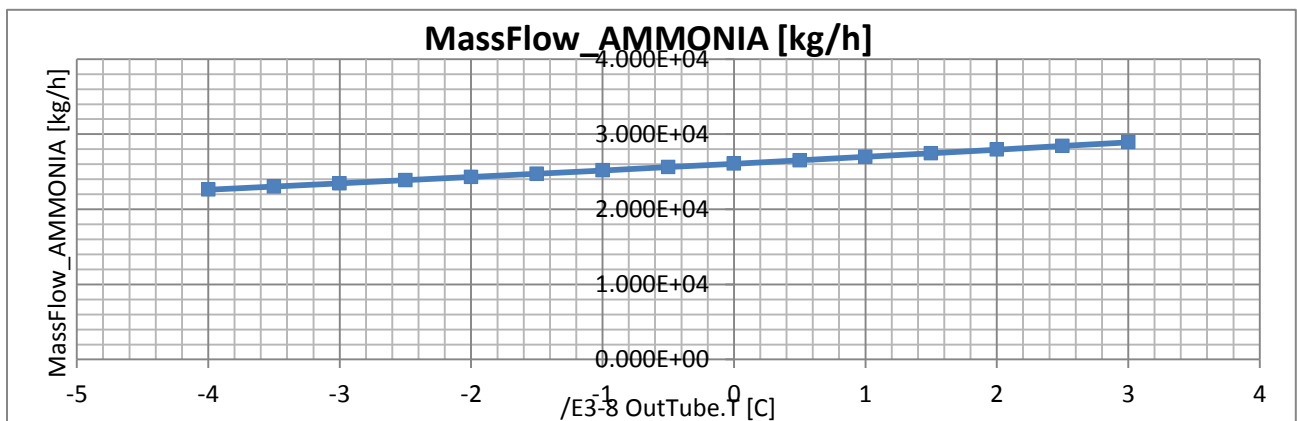
Figure 8: graph of MassFlow_AMMONIA [kg/h] against E3-8 OutTube.T [C]
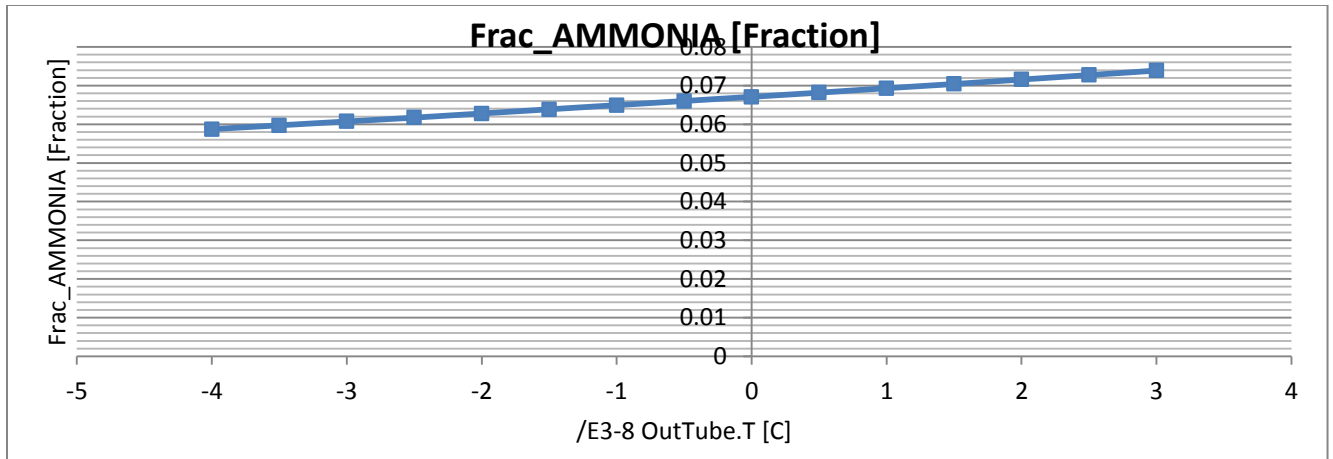
Figure 9: graph of Frac_AMMONIA [Fraction] against E3-8 OutTube.T [C]

OBSERVATIONS:

The amounts of ammonia in the separator recycle stream increases with increase in separator temperature. This is consistent with flash condition predictions that at higher temperatures, the volatile components of a mixture will be higher in the gaseous phase than in the liquid phase.
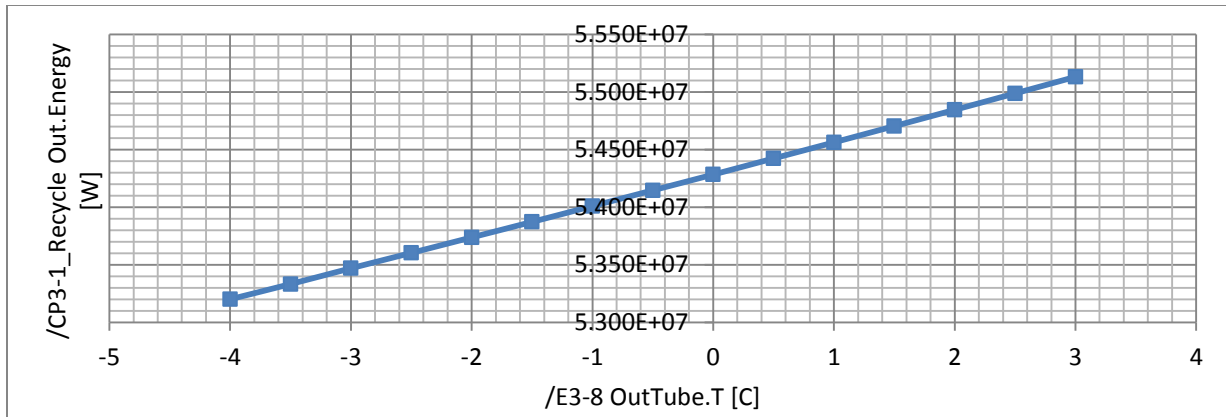
Figure 10: graph of CP3-1_Recycle Out.Energy [W] against E3-8 OutTube.T [C]

OBSERVATION:

Recycle stage 1 compressor power consumption increases with separator temperature increase. As separator temperature increase the gases expand and more work is done to compress them.

CaseStudy4: Separator_conditions_P

Independent variable:

- ✓ Separator V1 feed pressure /E3-8 OutTube.P [bar]

Dependent variables:

- ➢ Ammonia Mass in the recycle stream /MassFlow_AMMONIA [kg/h]
- ➢ Recycle composition /MolFrac_AMMONIA [Fraction]
- ➢ Compressor power consumption /CP-1_Recycle Out.Energy [W]
- ➢ Steam energy content /S22 In.Energy [W]

Table 12: Results_CaseStudy4

| Points	/E3-8 OutTube.P [bar]	MassFlow_AMMONIA [kg/h]	Frac_AMMONIA [Fraction]	/CP-1_Recycle Out.Energy [W]	/S22 In.Energy [W]
1	110	27171.292	6.97E-02	57648424	41378539
2	112	26928.059	6.91E-02	57241950	41345747
3	114	26675.64	6.85E-02	56814178	41297688
4	116	26451.837	6.80E-02	56423683	41266487
5	118	26237.777	6.75E-02	56041335	41237317
6	120	26032.863	6.70E-02	55668917	41209939
7	122	25814.171	6.65E-02	55275963	41164066
8	124	25624.825	6.61E-02	54918958	41137646
9	126	25443.5	6.56E-02	54569895	41113018
10	128	25269.724	6.52E-02	54228931	41089958
11	130	25082.176	6.48E-02	53868817	41049246
12	132	24921.151	0.064404	53542465	41026880
13	134	24766.806	6.40E-02	53222402	41006088
14	136	24608.352	6.37E-02	52896151	40977579
15	138	24465.507	6.33E-02	52589644	40958081
16	140	24328.493	6.30E-02	52287440	40939953
17	142	24182.235	6.27E-02	51975332	40909594
18	144	24055.074	6.24E-02	51685943	40892185
19	146	23933.094	6.21E-02	51401752	40876079
20	148	23803.024	6.18E-02	51107252	40849294
21	150	23689.777	6.15E-02	50833541	40833894
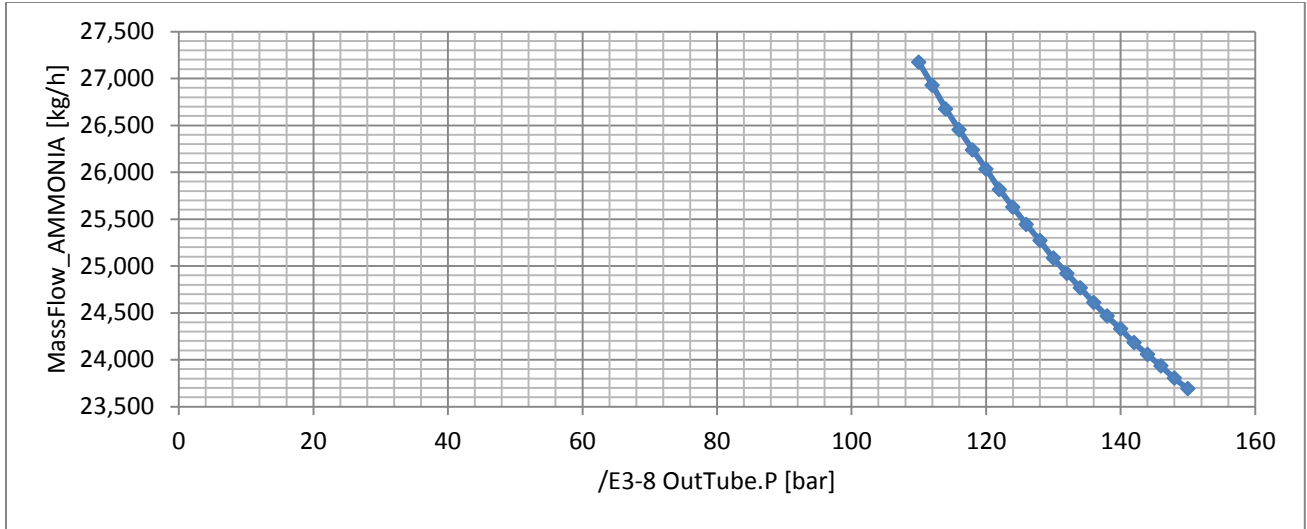
Figure 11: graph of MassFlow_AMMONIA [kg/h] against E3-8 OutTube.P [bar]
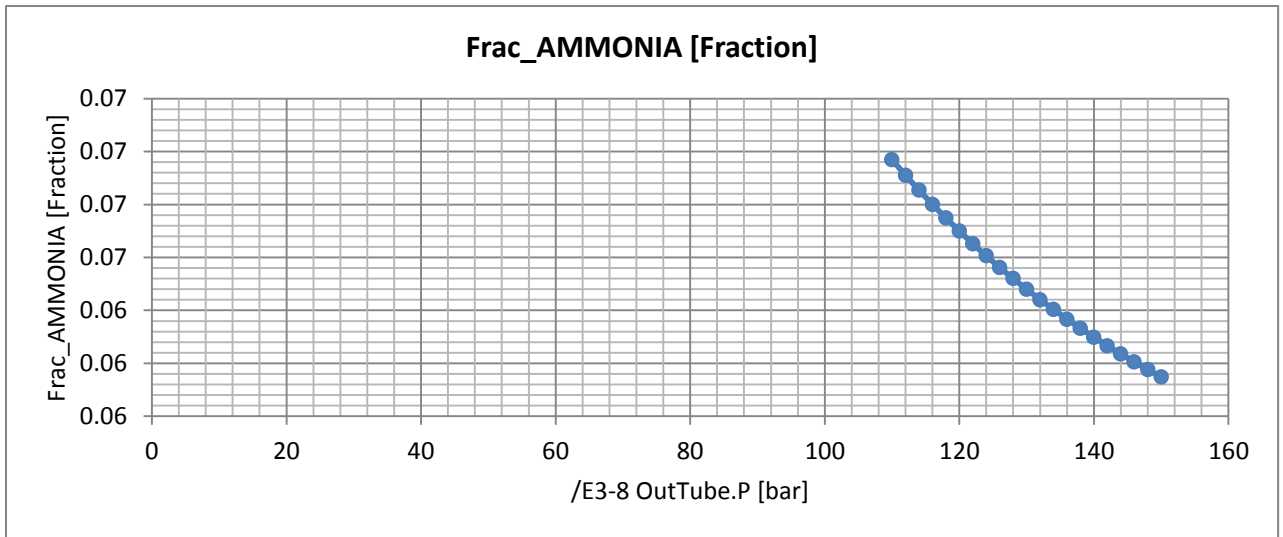
**Figure 12:** graph of Frac_AMMONIA [Fraction] against E3-8 OutTube.P [bar]
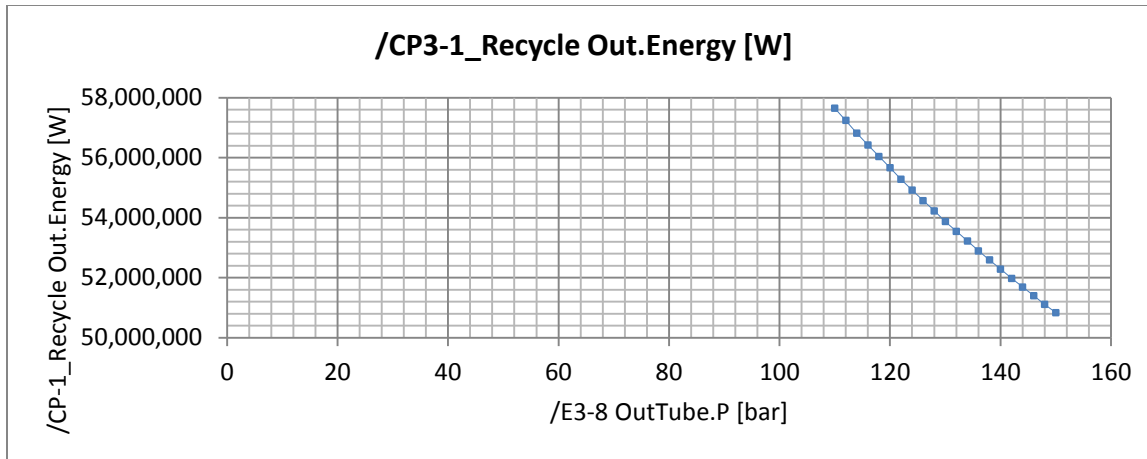
Figure 13: graph of /CP-1_Recycle Out.Energy [W] against E3-8 OutTube.P [bar]

Observation:

Both the amount of ammonia in the recycle stream and the compressor power consumptions decrease with increase in separator pressure.

At higher pressures, the vapor partial pressure at which molecules will be released from liquid to gas phase increases hence confining most of the component to the liquid phase.

CaseStudy5: EFFECT OF VALVE_1_PRESSURE VARIATION

Independent variable:

- ✓ Vlv-1 Out.P [bar]

Dependent variables:

- ➢ Separator V1 feed temperature /S13 Out.T [C]
- ➢ Separator V1 feed pressure /S13 Out.P [bar]
- ➢ Recycle Ammonia MassFlow_AMMONIA [kg/h]
- ➢ LP separator V3 recovered chiller ammonia energy content /S23 In.Energy [W]
- ➢ LP separator V3 recovered chiller ammonia energy content /S24 In.Energy [W]
- ➢ LP separator V3 recovered chiller ammonia energy content /S24 In.MassFlow [kg/h]
- ➢ LP separator V4 recovered chiller ammonia energy content /S27 In.Energy [W]
- ➢ Separator V1 feed energy content /S13 In.Energy [W]

**Table 13: Results_CaseStudy5**

| Points	/Vlv-1 Out.P [bar]	/S13 In.T [C]	/S13 In.P [bar]	MassFlow_ammonia [kg/h]	/S23 In.Energy [W]	/S24 In.Energy [W]	/S27 In.Energy [W]	/S24 In.MassFlow [kg/h]	/S13 In.Energy [W]
1	4	-1	129.4804	85377.345	-2360627	4858052	3349087	33809.93	33948608
2	4.5	-1	129.4804	85377.345	-2360627	4830237	3406602	33273.79	33948608
3	5	-1	129.4804	85377.345	-2360627	4801502	3460813	32780.02	33948608
4	5.5	-1	129.4804	85377.345	-2360627	4772127	3512299	32320.68	33948608
5	6	-1	129.4804	85377.345	-2360627	4742298	3561492	31889.91	33948608
6	6.5	-1	129.4804	85377.345	-2360627	4712147	3608726	31483.24	33948608
7	7	-1	129.4804	85377.345	-2360627	4681765	3654266	31097.21	33948608
8	7.5	-1	129.4804	85377.345	-2360627	4651220	3698322	30729.06	33948608
9	8	-1	129.4804	85377.345	-2360627	4620561	3741070	30376.54	33948608
10	8.5	-1	129.4804	85377.345	-2360627	4589824	3782654	30037.83	33948608
11	9	-1	129.4804	85377.345	-2360627	4559037	3823196	29711.38	33948608
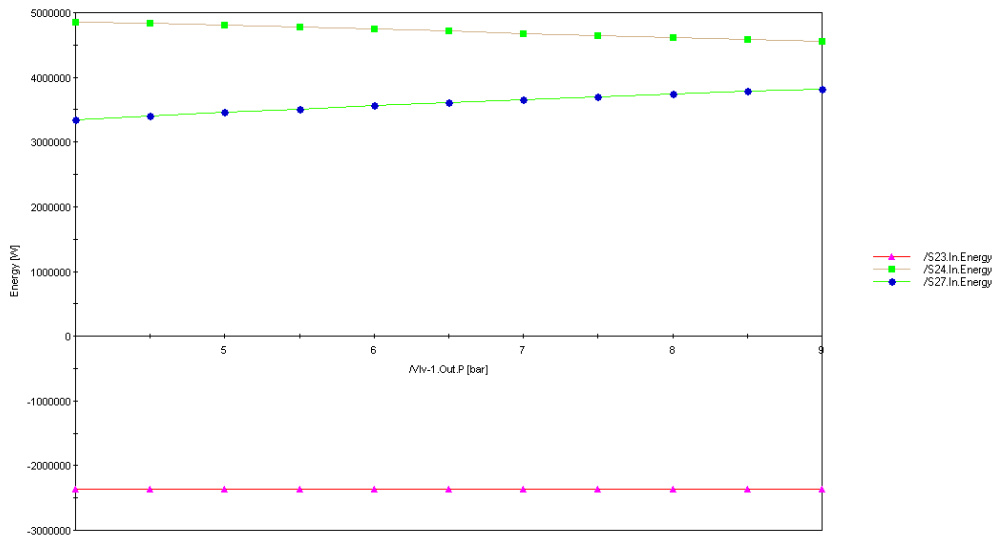
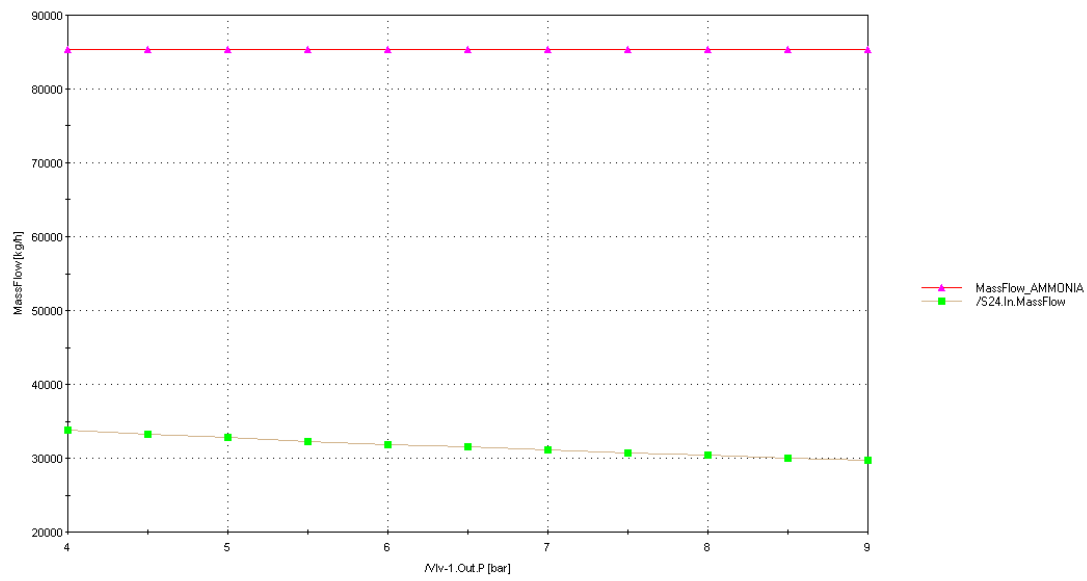**Figure 14:** graph of Energy [W] against Vlv-1 Out.P [bar]

Figure 15: graph of MassFlow [kg/h] against Vlv-1 Out.P [bar]

CaseStudy6: effect of valve_2_pressure variation

Independent variable:

- ✓ Valve_2_Pressure

Dependent variables:

- ➢ Separator V1 feed pressure /S13 Out.P [bar]
- ➢ Separator V1 feed pressure /S13 Out.P [bar]
- ➢ Recycle Ammonia MassFlow_AMMONIA
- ➢ LP separator V3 recovered chiller ammonia energy content /S26 In.Energy [W]
- ➢ LP separator V4 recovered chiller ammonia energy content /S27 In.Energy [W]
- ➢ Separator V1 feed energy content /S13 In.Energy [W]

Table 14: Results_CaseStudy6

| Points	/Vlv-2 Out.P[bar]	/S13 Out.T[C]	/S13 Out.P[bar]	MassFlow_ammonia [kg/h]	/S26 In.Energy[W]	/S27 In.Energy[W]	/S13 In.Energy[W]
1	0.5	-1	129.4804	85377.345	1381573.3	3437853	33948608
2	1	-1	129.4804	85377.345	1381573.3	3529960	33948608
3	1.5	-1	129.4804	85377.345	1381573.3	3575953	33948608
4	2	-1	129.4804	85377.345	1381573.3	3603817	33948608
5	2.5	-1	129.4804	85377.345	1381573.3	3621967	33948608
6	3	-1	129.4804	85377.345	1381573.3	3634082	33948608
7	3.5	-1	129.4804	85377.345	1381573.3	3642097	33948608
8	4	-1	129.4804	85377.345	1381573.3	3647155	33948608
9	4.5	-1	129.4804	85377.345	1381573.3	3649986	33948608
10	5	-1	129.4804	85377.345	1381573.3	3651085	33948608
11	5.5	-1	129.4804	85377.345	1381573.3	3650801	33948608
12	6	-1	129.4804	85377.345	1381573.3	3649389	33948608
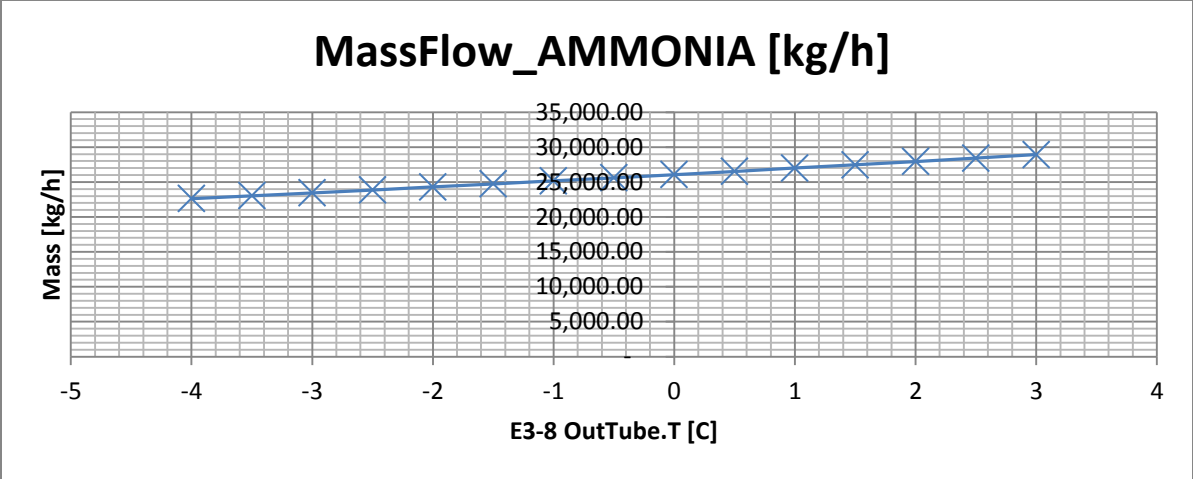
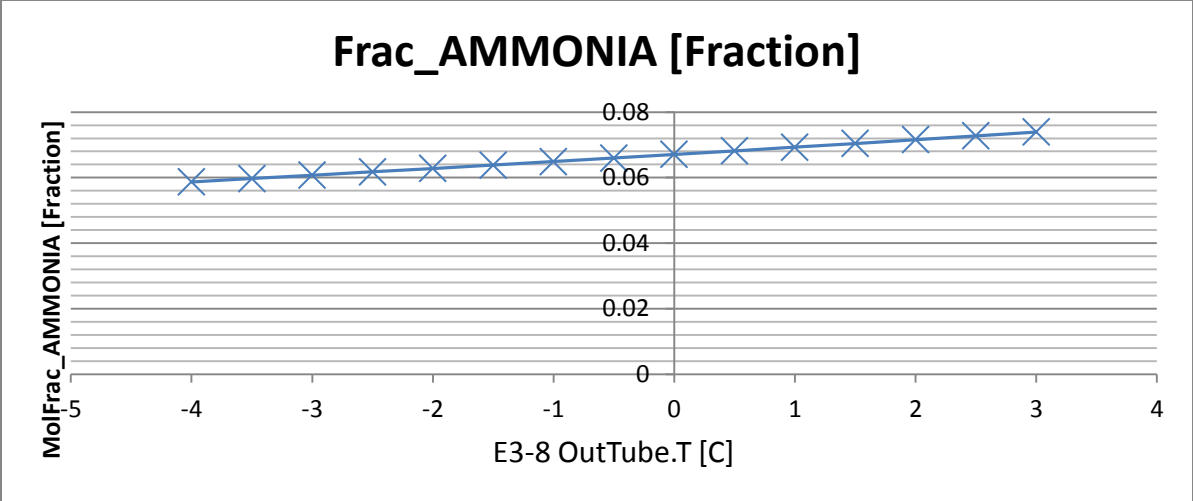**Figure 16:** graph of MassFlow [kg/h] against Vlv-2 Out.P [bar]

Figure 17: graph of Frac_AMMONIA [Fraction] against Vlv-2 Out.P [bar]

CaseStudy-7: *Effect of Separator conditions on the ammount of NH_3 in the recycle load, Chiller_NH3 flow-rate and CP- 1_Recycle energy consumption.*

Independent variable:

- E3-8 OutTube.T [C]

Dependent variables:

- AMMONIA MassFlow [kg/h] in in the recycle stream after separation stage1
- Compressor CP3- 1_Recycle energy consumption (Out.Energy [MW])
- Chiller_NH3 MassFlow [kg/h]

It is observed that the higher the temperature of the OutTube stream, the more there will be ammonia in the recyle and consequently the more the compressor power consumption.

However there will be less chiller_NH_3 mass flow (less cooling required).

The results are presented in the table below and the acompanying graphs.

Table 15: Results_CaseStudy7

|	/E3-8 OutTube.T [C]	MassFlow_AMMONIA [kg/h]	/ CP- 1_Recycle Out.Energy [MW]	Chiller_NH3 In.MassFlow [kg/h]
1	-4	82801.85	53.20078	35857.93
2	-3.5	83211.6	53.33246	35838.94
3	-3	83628.72	53.46975	35819.43
4	-2.5	84049.92	53.60325	35804.41
5	-2	84479.29	53.738	35784.36
6	-1.5	84913.08	53.87336	35768.71
7	-1	85355.33	54.00956	35748.08
8	-0.5	85801.99	54.14599	35731.83
9	0	86257.44	54.28454	35710.61
10	0.5	86717.31	54.42399	35693.77
11	1	87186.31	54.56371	35671.93
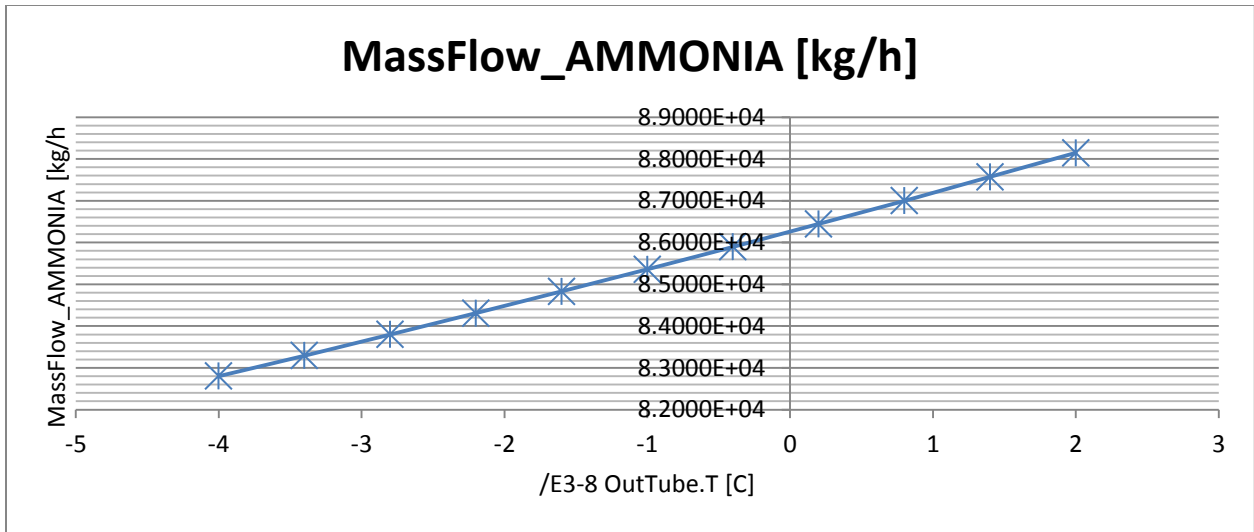
Figure 18: graph of MassFlow_Ammonia against E3-8 OutTube.T[C]
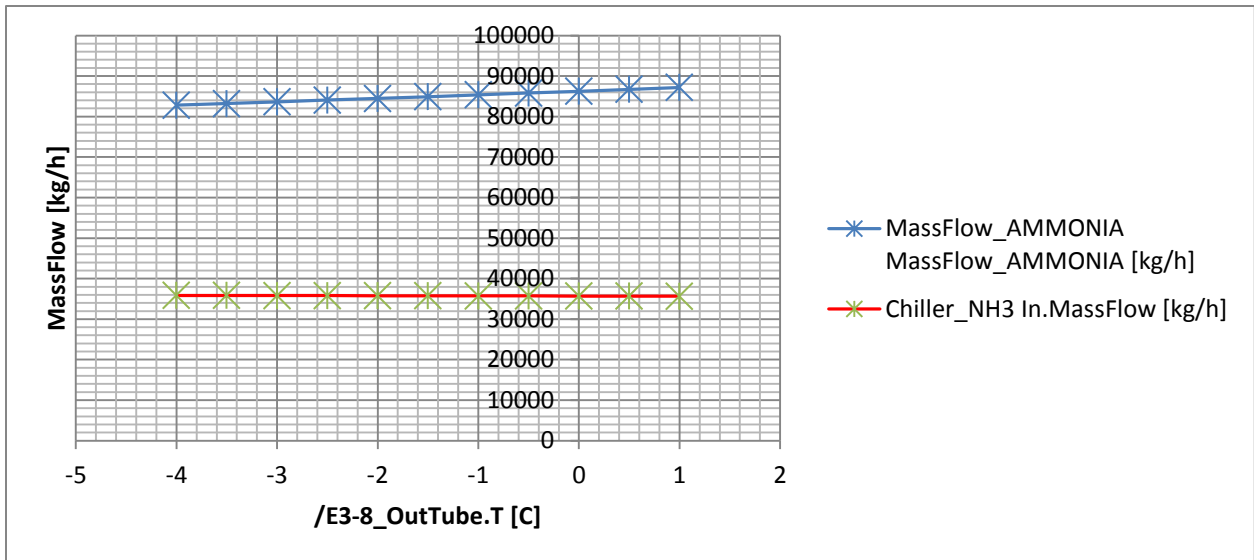

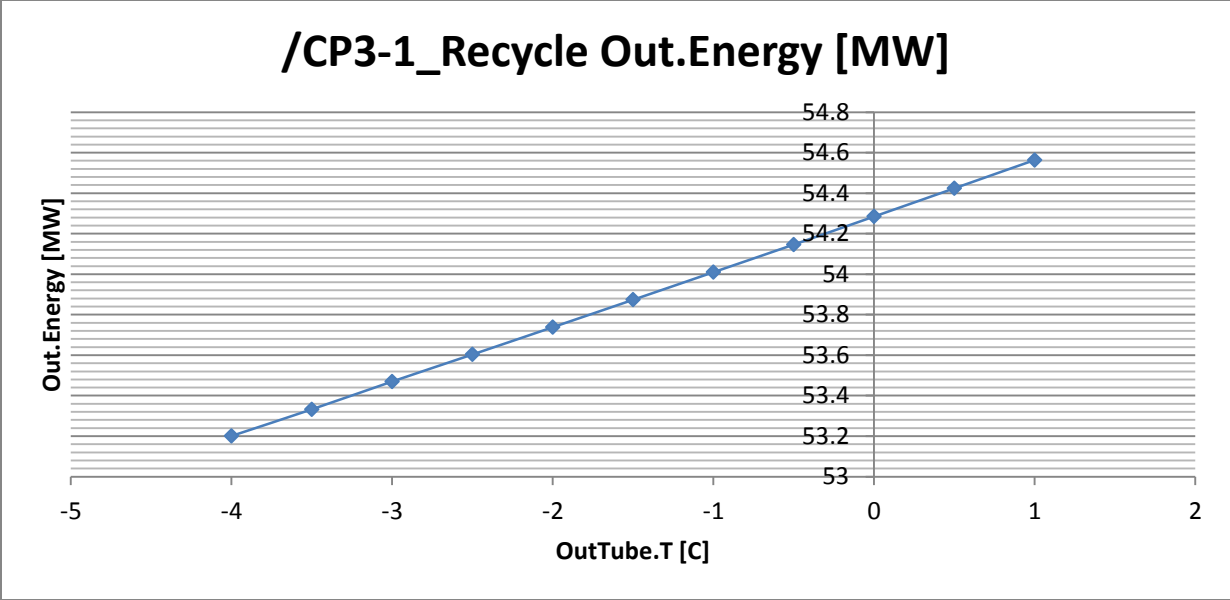**Figure 19:** graph of MassFlow as a function of OutTube T[C]

Figure 20: graph of Compressor energy consumption as a function of OutTube T[C]

4.2 DISCUSSION AND INTERPRETATION OF THE RESULTS

CONVERTER

Converter pressure and temperature affect product yield according to le Chatelier's principle.

> *If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change.*

> When a system momentarily deviates from equilibrium due to any of the three:

> (1) Changing the concentration of one of the components of the reaction

> (2) Changing the pressure on the system

> (3) Changing the temperature at which the reaction is run.

The system adjusts so as to change the conditions of a chemical reaction to restore equilibrium. High temperatures decrease yield while high pressures increase yield. In accord with le Chatelier's principle, a system in dynamic equilibrium will behave in such a way as to balance any change in operating conditions. Since increasing converter temperature is unfavorable to forward reaction; reaction being adiabatic exothermic and hence heat being a product, the reaction will slow in the forward reaction which explains the inverse relationship between converter temperature and its yield.

On the other hand, increasing converter pressure is favorable to the product formation as the system tries to reduce the pressure; it takes two molecules of the reactants to produce a molecule of ammonia. This is the basis of the proportional relationship between converter presser and its yield.

Determining the optimal temperature-pressure combination for the converter is partly guided by economic and safety considerations. Very high pressures, though favorable to this reaction are neither practical nor feasible economical. They also post safety risks to equipment and staff hence the need to operate within acceptable range.

Duhem's Theorem: *For any closed system, formed initially from given masses of prescribed chemical species, the equilibrium state is completely determined when any two independent variables are fixed.*

This is the logic behind jointly specifying converter pressure and temperature that produce better yield.

COMPRESSOR

Compressor power consumption increases with converter temperature increase and decreases with increase in converter pressure.

The relationship here can be attributed to the fact that it is much more difficult to compress gases at higher temperatures than it is for gases at lower temperature. More power is therefore consumed for the compressor to do work on the gases.

Energy (work) done by the compressor on the gas according to the first law of thermodynamics can be mathematically expressed as follows

$du = dq - dw$

du is the differential increase in internal energy of the system.

dq is the differential increment of heat added to the system,

dw is thedifferential element of work done by the system

Since the system is considered to be adiabatic,

$dq = 0 \text{ and } dW = \oint_{V1}^{V2} p \, dV$

The work done is equal to the pressure of the substance multiplied by its increase in volume and at higher temperatures gases expand increasing in volume and hence become more difficult to compress.

SEPARATOR.

Separator P and T are functions of Vlv-1 and Vlv-2 pressure.

Pressure changes in both valves determine the chiller ammonia flow rate. This in turn determines the temperature and pressure of the inlet stream to the separator.

Flash Calculations:

Specifying T, P and z_i, gives sufficient information for a flash calculation. Flash calculations show the phase equilibrium compositions of the components.

F zi = Lxi + V yi

Where a feed F (with composition z_i) is split into a vapor product V (with composition y_i) and a liquid product (with composition x_i)

Raoult's Law: $\quad x_i = \dfrac{y_i p_{total}}{p_{i,eqm}}$

Where x_i is the mole fraction of component *i* in the solution and y_i is its mole fraction in the gas phase.

CHAPTER 5

5.0 CONCLUSION AND RECOMMENDATION

This research project has met the objectives using the methodologies stipulated from the onset. It has generated reliable results quite comparable with current industrial practices and was completed within specified time. The following observations and conclusions were drawn from the synthesis of the simulation results.

Also included in this chapter are parametric recommendations once the model is implemented in the industry.

- At a fixed pressure, increasing converter temperature decreases yield: exothermic reaction.

- At fixed temperature, increasing converter pressure increases NH3 yield: le Chatelier's principle.

- The optimum condition for NH3 production occurs at 400˚C and 125bar

- The highest yield of NH3 obtained is 25.1812ton/h

- Industrial NH3 convertor conditions:400°C - 540°C and 120bar – 600bar

- Optimal recycle load at separation achieved at -1°C and 130bar (77.64 %).

It is recommended that any future research in this area would achieve much better recycle load by use of much lower separator temperatures and a bit higher pressures which cannot currently be pursued due to economic unfeasibility.

APPENDIX:

REFERENCES (LITERATURE REVIEW)

	REVIEWED MATERIALS			
No.	Author	Year	Title	Publisher
1	Islam Rafiqul*, Christoph Weber, Bianca Lehmann, Alfred Voss	2002	Energy efficiency improvements in ammonia production—perspectives and uncertainties	Energy
2	R. Zukerman et al	2009	Modeling and simulation of a smart catalytic converter combining NO_x storage, ammonia production and SCR	Chemical Engineering Journal
3	Yao Wang et al	2003	Application of total process energy-integration in retrofitting an ammonia plant	Elsevier Ltd
4	Shannon Page, SusanKrumdieck	2009	System level energy efficiency is the greatest barrier to development of the hydrogen economy	Energy Policy
5	Jeremy T. Kraemer and David M. Bagley	2005	Simulation of the Impact of Higher Ammonia Recycle Loads Caused by Upgrading Anaerobic Sludge digesters	Water Qual. Res. J. Canada
6	Francois Marechal, Boris alitventzeff	2003	Targeting the integration of multi-period utility systems for site scale process integration	Elsevier Ltd
7	By Max Appl	1999	Ammonia Principles and Industrial Practice	