IDENTIFICATION OF PERFORMANCE PARAMETERS, KINETIC MODELING AND OPTMIZATION OF LPG SWEETENING UNIT

By

K. JAYAKUMAR

COLLEGE OF ENGINEERING

(DEPARTMENT OF CHEMICAL ENGINEERING)

Submitted

IN PARTIAL FULFILLMENT OF THE REQUIREMENT OF THE DEGREE OF
DOCTOR OF PHILOSOPHY

TO

UNIVERSITY OF PETROLEUM AND ENERGY STUDIES
DEHRADUN
MAY 2018
Under the Guidance of

Dr. SANTOSH K GUPTA

Distinguished Professor

Chemical Engineering Department, UPES, Dehradun

Dr. ASHOUTOSH PANDAY

Professor

Chemical Engineering Department, UPES, Dehradun

Dr. RAMES C. PANDA

Principal Scientist, Chemical Engineering Department, CLRI, Chennai

UPES
www.upes.ac.in

This is to certify that the thesis entitled "Identification of Performance Parameters, Kinetic Modeling and Optimization of LPG Sweetening Unit", is being submitted by Krishnan Jayakumar in fulfillment for the Award of DOCTOR OF PHILOSOPHY in Chemical Engineering to the University of Petroleum & Energy Studies (UPES), Dehradun, India. The thesis has been corrected as per the evaluation reports dated 06/08/2018 and NIL, and all the necessary changes/modifications have been inserted/incorporated in the thesis.

APandey
Dr. Ashoutosh Panday
Chemical Engineering Department
UPES, Dehradun

SKGupta
09/10/18
Dr. Santosh K. Gupta
Chemical Engineering Department
UPES, Dehradun

Date: 09 Oct 2018

CORPORATE OFFICE: 210, 2nd Floor, Okhla Industrial Estate, Phase III, New Delhi - 110 020, INDIA, **T** +91 - 11 - 41730151-53, **F** +91 - 11 - 417301
CAMPUSES:
ENERGY ACRES: Bidholi Via Prem Nagar, Dehradun - 248 007 (Uttarakhand), INDIA, **T** +91 - 135 - 2770137, 2776053/54/91, 2776201
F +91 - 135 - 2776090/95
KNOWLEDGE ACRES: Kandoli Via Prem Nagar, Dehradun - 248 007 (Uttarakhand), INDIA, **T** +91 - 8171979021/2/3, 7060111775

CHEMICAL ENGINEERING DEPARTMENT
CENTRAL LEATHER RESEARCH INSTITUTE
(Council of Scientific & Industrial Research)
Adyar, Chennai-600 020, INDIA

Dr Rames C Panda, MTech & PhD (IITM), MIIChE, MIEAust, AMIChEM
Principal Scientist, Honorary Faculty, Anna University
Chemical Sciences/ Engg Area

This is to certify that the thesis entitled "Identification of Performance Parameters, Kinetic Modeling and Optimization of LPG Sweetening Unit" is being submitted by Krishnan Jayakumar in fulfillment for the Award of DOCTOR OF PHILOSOPHY in (Chemical Engineering) to the University of Petroleum and Energy Studies. Thesis has been corrected as per the evaluation reports dated 13/08/2018 and all the necessary changes / modifications have been inserted/incorporated in the thesis.

Panda
Scientist
Central Leather Research Institute
Adyar, Chennai-600 020

Panda
Dr Rames C. Panda
Principal Scientist & Faculty
Chemical Engineering Department
CSIR-CLRI, Adyar, Chennai – 600 020

Date: 24 Sept 2018

CHEMICAL ENGINEERING DEPARTMENT
CENTRAL LEATHER RESEARCH INSTITUTE
(Council of Scientific & Industrial Research)
Adyar, Chennai-600 020, INDIA

Dr Rames C Panda, MTech & PhD (IITM), MIIChE, MIEAust, AMIChEM
Principal Scientist, Honorary Faculty, Anna University
Chemical Sciences/ Engg Area

This is to certify that the thesis entitled "Identification of Performance Parameters, Kinetic Modeling and Optimization of LPG Sweetening Unit" is being submitted by Krishnan Jayakumar in fulfillment for the Award of DOCTOR OF PHILOSOPHY in (Chemical Engineering) to the University of Petroleum and Energy Studies. Thesis has been corrected as per the evaluation reports dated 13/08/2018 and all the necessary changes / modifications have been inserted/incorporated in the thesis.

Panda

Scientist
Central Leather Research Institute
Adyar, Chennai-600 020

Panda

Dr Rames C. Panda
Principal Scientist & Faculty
Chemical Engineering Department
CSIR-CLRI, Adyar, Chennai – 600 020

Date: 24 Sept 2018

THESIS COMPLETION CERTIFICATE

This is to certify that the thesis on "Identification of performance parameters, kinetic modeling and optimization of LPG sweetening unit" submitted by Krishnan Jayakumar in partial completion of the requirements for the award of the Degree of Doctor of Philosophy (Engineering) is an original work carried out by him under our joint supervision and guidance. It is certified that the work has not been submitted anywhere else for the award of any other diploma or degree of this or any other university.

APandey

Dr.Ashoutosh Panday

Date: 21 May 2018

Place: UPES Dehradun

SKGupta

Dr.Santosh K. Gupta

Date: 21 may 2018

Place: UPES Dehradun

CHEMICAL ENGINEERING DEPARTMENT
CENTRAL LEATHER RESEARCH INSTITUTE
(Council of Scientific & Industrial Research)
Adyar, Chennai-600 020, INDIA

Dr Rames C Panda, MTech & PhD (IITM), MIIChE, MIEAust, AMIChEM
Principal Scientist, Honorary Faculty, Anna University
Chemical Sciences/ Engg Area

THESIS COMPLETION CERTIFICATE

This is to certify that the thesis entitled "Identification of performance parameters, kinetic modeling and optimization of LPG sweetening unit" submitted by Krishnan Jayakumar to UPES (Full) for the award of the degree of Doctor of Philosophy (Engineering) is a bona fide record of the research work carried out by him under our supervision and guidance. The content of the thesis, in full or parts have not been submitted to any other institute or University for the award of any other degree or diploma

Panda

Dr Rames C. Panda
(Co-Supervisor)
Place: Chennai
Date: 12 January 2018

Scientist
Central Leather Research Institute
Adyar, Chennai-600 020

Dr. Rames C. Panda
Principal Scientist (DAAD Fellow & Ex-Faculty, Curtin University of Tech, Australia)
Department of Chemical Engineering (Process Control)
CSIR-CLRI, Adyar, Chennai - 600 020, India
Ph: 044-24437115, Fax: 044-24911589

DECLARATION

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, except where due acknowledgment has been made in the text.

Krishnan Jayakumar

Date: 11-10-2018

Place: UPES, DEHRADUN

DECLARATION

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, except where due acknowledgment has been made in the text.

Krishnan Jayakumar

Date:

Place:

THESIS COMPLETION CERTIFICATE

This is to certify that the thesis on “Identification of performance parameters, kinetic modeling and optimization of LPG sweetening unit” submitted by Krishnan Jayakumar in Partial completion of the requirements for the award of the Degree of Doctor of Philosophy (Engineering) is an original work carried out by him under our joint supervision and guidance. It is certified that the work has not been submitted anywhere else for the award of any other diploma or degree of this or any other University.

Dr. Ashoutosh Panday	**Dr. Santosh K. Gupta**
Date:	**Date:**
Place:	**Place:**

CHEMICAL ENGINEERING DEPARTMENT
CENTRAL LEATHER RESEARCH INSTITUTE
(Council of Scientific & Industrial Research)
Adyar, Chennai-600 020, INDIA

Dr Rames C Panda, MTech & PhD (IITM), MIIChE, MIEAust, AMIChEM
Principal Scientist, Honorary Faculty, Anna University
Chemical Sciences/ Engg Area

THESIS COMPLETION CERTIFICATE

This is to certify that the thesis entitled **"Identification of performance parameters, kinetic modeling and optimization of LPG sweetening unit"** submitted by **Krishnan Jayakumar** to UPES (Full) for the award of the degree of Doctor of Philosophy (Engineering) is a bona fide record of the research work carried out by him under our supervision and guidance. The content of the thesis, in full or parts have not been submitted to any other Institute or University for the award of any other degree or diploma.

Rames Chandra Panda

Dr. Rames C. Panda
Co supervisor

Place: CHENNAI
Date: 12 January 2018

☎ (Off) 24916706(Direct), 24437115, Telex : 041-21014-CLRI IN,
Fax : (044) 24911589 Cable : LESERCH-MADRAS, e-mail : rames.panda@gmail.com ; panda@clri.res.in

ACKNOWLEDGEMENT

Taking this opportunity, I would like to express my sincere and deepest thanks to the distinguished professors and research guides **Dr. Santosh, K Gupta, Dr. Ashoutosh Panday and principal scientist Dr. Rames C. Panda** for their expert guidance, mentorship, encouragement, care and supervision.

I would like to express my sincere gratitude to **Dr. Vijay Parthasarathy, Dr. Gopalakrishnan, Dr. Rajeshwar Mahajan** and **Dr. K. S. Rajmohan** for motivation, support and inspiration.

I would like to express my sincere gratitude to coordinator **Mr. S.S. Farmer** for suggestions and guidance.

I would like to thank **program manager Mrs. Rakhi Ruhal** for prompt assistance and systematic regulatory guidance.

Finally, I would like to thank all the UPES chemical engineering department faculties and CLRI chemical engineering department faculties & UPES, CCE department staff for their cooperation and assistance.

CONTENTS

LIST OF FIGUERS

LIST OF TABLES

APPENDIX

GLOSSARY

LPG	: Liquid Petroleum Gas.
HAZARD	: An event and compound which can cause equipment or personal injury.
Off- spec	: LPG product which is not meeting the product specification.
CAGR	: Compound annual growth rate
NIOSH	: National Institute of Occupational safety and health association
IDLH	: Immediately Dangerous to life or Health
ACGIH	: American Conference of Governmental Industrial Hygienists
TLV	: Threshold limit value
TWA	: Time weighted average
STEL	: Short-term exposure limit
NACE	: National Association of Corrosion Engineers
GDP	: Gross domestic product
SSCC	: Sulfide Stress Corrosion Cracking
HIC	: Hydrogen Induced Corrosion
HE	: Hydrogen Embroilment
OSHA	: Occupational Safety and Health Administration

TSWEET : Process simulation software

AMSIM : Process simulation software

ProTreat : Process simulation software

CO$_2$SIM : Process simulation software

Promax : Process simulation software

CHEMASIM : Process simulation software

CHEMSEP : Process simulation software

Aspen HYSYS: Process simulation software

HETP : Height Equivalent to theoretical plate.

Chapter 1

1.0 Introduction

Liquefied petroleum gas (LPG) is an important and valuable commercial gas, both for its energy as well as its chemical value. LPG (both from wet-gas and from off-gases of the atmospheric distillation unit, ADU) primarily consists of *n*-butane but also contains H_2S and CO_2 as undesirable minority constituents. H_2S is probably the most harmful because it leads to corrosion in mild steel pipelines and process equipment. Gases containing substantial amounts of H_2S are called sour gases, while gases in which only traces of H_2S are present are called sweet gases. The process of removal of H_2S is known as gas sweetening. The presence of CO_2 in LPG reduces the calorific value of the fuel. The most popular process for sour gas sweetening is counter-current mass transfer with amines. Though the kinetics of removal are being established in the laboratory, the technology needs to be studied further, for modeling and scale-up, preferably through simulation, for commercial optimization/exploitations. Accordingly, the present research titled 'Identification of performance parameters, kinetic modeling and optimization of LPG sweetening unit' was planned. This area of research was selected due to its commercial importance considering industrial safety, hazard, equipment integration and product-handling issues. A brief explanation of these are provided below

- Commercial and industrial value
- Environmental limits
- Safety and hazard
- Pipeline and equipment corrosion and

- Handling of off-specification (off-spec) LPG

1.1 Commercial and industrial value

LPG is one of the important petroleum products based on its usage in residential, industrial and commercial sectors, and also in automobiles. LPG is the most preferred fuel because it is non-toxic, clean, ease of material handling and it being cost efficient. Credence Research Inc. reported that the global LPG market was valued at US$ 257.8 billion in 2016 and is expected to reach US$ 339.2 billion by 2024, expanding at a CAGR of 3.5% from 2016 to 2024. The main drivers for the increase in demand are the consumption by the residential sector and an increase in the adoption of LPG as an auto fuel. As per Walt (2017), the global LPG demand will continue to grow and will be mainly driven by Asia and the Middle East.

A market analysis of the global LPG demand study conducted by Media (2016) reveals that the residential usage is 47%, commercial and chemical usage account for 27%, industrial usage is 8% and the rest by others. Recently, there has been a remarkable shift in the LPG usage for automobiles (auto gas). The major advantages of LPG as an auto gas over other conventional fuels are its performance, engine life, fuel economy, cost savings and environmental benefits. The use of LPG as a fuel leads to 75% less carbon monoxide, 85% less hydrocarbon, 40% less oxides of nitrogen and 87% less ozone-forming potential as compared to gasoline (Ramon, 2013).

1.2 Environmental Limits

Burning propane, butane and other LPG products containing H_2S will oxidize it to SO_2, which is harmful to the people affected. It acts directly as an irritant to the mucus membrane and the respiratory track and causes pulmonary edema. Continuous exposure may result in nausea, headaches, delirium and disturbed equilibrium, tremors, convulsions and skin and eye irritation. Emissions from

LPG vehicles used indoors, too, pose a health hazard to workers. The emission is indirectly regulated by all occupational health and safety air quality standards. There are many regulatory authorities in different jurisdictions. Occupational Safety and Health Administration (OSHA) within the Department of Labor sets air quality standards at the federal level in USA. The corresponding regulatory authorities in Canada are located within provincial Ministries of Labor. Most of the air quality standards in North America are based on the guidelines established by the American Conference of Governmental Industrial Hygienists (ACGIH). The threshold limit values (TLV) for pollutants present in LPG exhausts as prescribed by the ACGIH is listed in Table 1.1. The TLVs are time-weighted averages for an 8-hour workday.

Table 1.1 Threshold Limit Values for LPG Exhaust Pollutants

S. No	Substance	TLV (v/v ppm)
1	Carbon Monoxide	25
2	Nitric Oxide	25
3	Nitrogen Dioxide	3
4	Butane	800
5	Sulfur Dioxide	2

1.3 Safety and Hazard

As per IS 4576 (Bureau of Indian Standards, 1999), the limit for the H_2S content in LPG is not more than 5 ppm. H_2S is a flammable and toxic gas and the flammability limit is 4.3-4.6% (43,000-46,000 ppm), which far exceeds the concentrations of concern for personnel protection. H_2S is heavier than air and it will tend to accumulate near the ground when leaked into the atmosphere. As per the National Institute of Occupational Safety and Health Association (NIOSH), the Immediately Dangerous to Life or Health (IDLH) value of H_2S is 100 ppm. At concentrations above the IDLH level, a person's sense of smell is quickly deadened. A bodily response in breathing various concentrations of H_2S is provided in Table 1.2. A broadly recognized authority on the health effects of toxic gases, the American Conference of Governmental Industrial Hygienists (ACGIH), has changed its recommended threshold values of the TLV for airborne H_2S exposure. It recommends a TWA of 1 ppm and a Short Term Exposure Limit (STEL) of 5 ppm. Many companies adopted these limits in their industrial and safety hygiene procedures due to health and legal reasons.

Table 1.2 Physiological responses to various airborne concentrations of H_2S (adapted from ACGIH and NIOSH)

Concentration, ppm	Physiological Response
1000 – 2000	Loss of consciousness and possible death
100 – 1000	Serious respiratory, central nervous and cardiovascular system effects
150 – 200	Fatigue (sense of smell is significantly impaired)
100	Immediately dangerous to life and health (IDLH)
5 – 30	Moderate irritation of the eyes
5 – 10	Relatively minor metabolic changes in exercising individuals during short term exposures
5	Increase in anxiety symptoms
< 5	Metabolic changes observed in exercising individuals
0.032 – 0.02	Begin to smell

As mentioned in Section 1.1, 8 to 11% of LPG is being used globally for industrial applications which include the food processing industry, glass blowing, fast food centers, etc., where the open flame is directly exposed either to the food products or to the industry personnel. Any marginal quality deviation in the H_2S specification in LPG can lead to severe safety and health hazards.

1.4 Pipeline and equipment corrosion

A study conducted by NACE (2002) reported that the total annual estimated direct cost of corrosion in the U.S. is a staggering $276 billion, which is approximately 3.1% of the nation’s Gross Domestic Product (NACE, 2002). That nation’s 163 refineries supplied more than 18 million barrels per day of refined petroleum products in 1996, with a total corrosion-related direct cost of $3.7 billion. Maintenance expenses make up $1.8 billion of this total, vessel expenses are $1.4 billion, and fouling costs were approximately $0.5 billion annually. Hence, it is important to understand that corrosion takes away a considerable percentage of the margin and it is necessary to take mitigating measures to control the corrosion in equipment and pipelines.

1.4.1 H_2S corrosion

H_2S corrosion in equipment and pipelines is a major challenge in upstream and downstream units and in the petrochemical industry. Generally, carbon steel is most susceptible to corrosion even at traces of H_2S present in the stream. H_2S can cause localized corrosion that promotes the sulfide stress corrosion cracking (SSCC), hydrogen induced cracking (HIC) and hydrogen embrittlement (HE). Predominantly, H_2S causes the sulfide stress corrosion cracking in high strength steel, even at low temperatures and low partial pressures. Very small amounts of H_2S (0.005 ppm) can act as a catalyst and enhance the corrosion on pipe surfaces. H_2S corrosion is more dangerous than CO_2 corrosion because the components fail abruptly. The H_2S corrosion mechanism is provided below.

$$H_2S = H^+ + HS^- \qquad (1)$$

$$HS^- = H^+ + S^{2-} \qquad (2)$$

$$Fe^{2+} + S^{2-} = FeS \qquad (3)$$

The presence of H_2S in LPG even at concentrations of 5 ppm, causes changes in the test copper strips and gives green-pink-purple corrosion products, mainly consisting of CuS and Cu_2S. The H_2S present in LPG oxidizes elemental sulfur (Sun and Nesic, 2009). Photographs of H_2S corrosion in carbon steel equipment are provided in Figure 1.1.

Carbonyl sulphide (COS) does not cause corrosion of test copper strips even at concentrations of up to 100 ppm, but in the presence of water, it hydrolyses to H_2S and CO_2, which may accelerate the corrosion processes (Smith and Joosten, 2006).

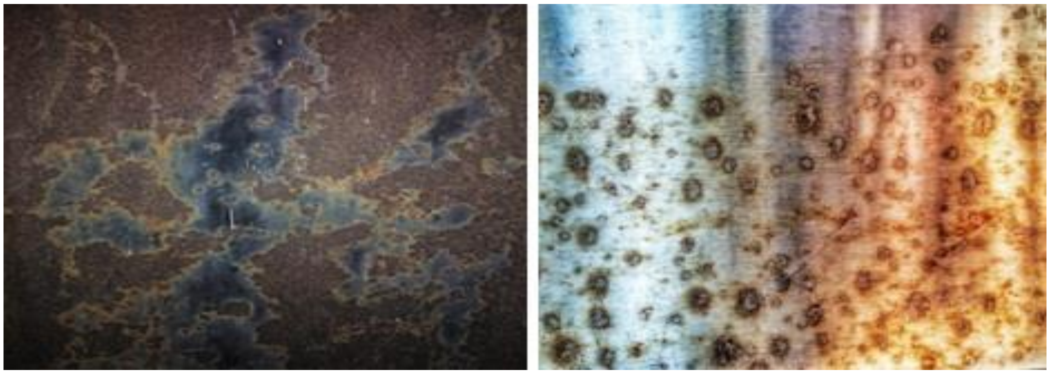

Figure 1.1 Corrosion of oil and gas equipment under the influence of H_2S. (Courtesy: Himipex Oil)

1.4.2 CO_2 corrosion

In LPG pipelines and equipment, in general, internal corrosion begins with CO_2 corrosion. The reaction is of iron from the pipe with aqueous bicarbonate to produce scale (iron carbonate), water and carbon dioxide (Rennie, 2006). Carbon dioxide corrosion is also known as sweet corrosion and it is one of the most important problems in the oil and gas industries. The severity of corrosion depends on several factors such as the concentration of CO_2, temperature, pressure and velocity in the solution (Nordsveen et al., 2003). In CO_2 corrosion of carbon steel, when the concentrations of Fe^{2+} and CO_3^{2-} ions exceed the solubility limit, they can precipitate to form solid ion carbonate according to the reaction

$$Fe^{2+} + CO_3^{2-} = FeCO_3 \qquad (4)$$

The metal anodic dissolution reaction takes place as follows

$$Fe = Fe^{2+} + \ 2e^{-} \qquad (5)$$

The reaction takes place through intermediate reactions involving hydroxyl ions (OH^-) and its individual rate decreases with decreasing pH and a time will come where the cathodic reaction becomes predominant and acts as a rate controlling step on the metal surface:

$$2H^{+} + \ 2e^{-} = H_2 \qquad (6)$$

In the CO_2 medium, the rate of cathodic reaction is mainly affected by the partial pressure of CO_2:

$$Fe^{2+} + \ CO_3^{2-} = FeCO_3 \qquad (7)$$

$$H_2CO_3 + \ 2e^{-} = \ H^{+} + \ HCO_3^{-} \qquad (8)$$

$$2HCO_3^{-} = 2H^{+} + 2CO_3^{2-} \qquad (9)$$

Thus, dissolved CO_2 has the tendency to form weak carbonic acid (H_2CO_3) in the solution which increases the cathodic reaction kinetics by dissociation to bicarbonate and hydrogen ions. A photograph of CO_2 corrosion in carbon steel pipeline is provided in Figure 1.2.

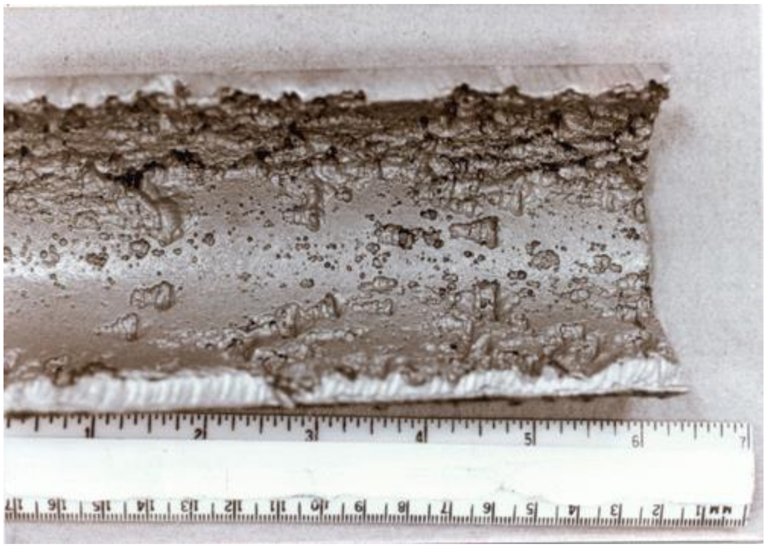

Figure 1.2 Carbon dioxide corrosion of carbon steel (McGuire et al., 2017)

1.5 Handling Off-Spec LPG

Off-spec production for any type of product such as gasoline, jet, diesel, chemicals and LPG is termed as slop. Slop is created when a stream fails the refinery product specifications. Off-spec (slop) production occurs during start-up, shutdown, transportation and flushing (Poe and Mokhatab, 2016). The disadvantage of slop is mainly due to its high cost. Refineries either lose money because the slop production is unrecoverable or it costs a significant amount of money to recover the value. Unlike other products, handling off-spec LPG has limited options for correction by blending, reprocessing and disposal. On some occasions, refineries are forced to adopt non-recovery options such as flaring or use as fuel gas which leads to significant value degradation (Jones and Pujadó, 2006).

When refineries take a liquid product and use it as fuel-gas equivalent, there is significant value degradation. On a barrel to barrel basis, the heat content of the

LPG gas is significantly lower than the value of the liquid fuel. The products downgrade ranges from $15/bbl to $60/bbl, or even more.

Therefore, it is evident that in terms of product value, commercial importance, usage, safety and environment and operational challenges, sour LPG sweetening is an important unit, needing attention in terms of quality consistency and improvement.

From the literature survey it is observed that several publications are available on natural gas, fuel gas, and flue gas sweetening but very few publications are available on LPG sweetening and optimization.

Considering the industrial and commercial value, and considering the significant safety and environmental factors associated with LPG, this research work focusses on the following activities:

- A good literature review of the LPG sweetening process, amine absorption, solvent selection, process and performance parameters, kinetic modeling and optimization was undertaken.
- An industrial LPG absorber was identified, and the data pertaining to the actual operating conditions, the design details, and the feed/product quality details was collected.
- The amine absorption flow sheet was modeled using amine and acid gas package from Aspen HYSYS (Aspen, 2006).
- The performance parameters of the sweetening process were identified.
- The model parameters and output data were validated with actual industrial data.
- The absorber parameters were optimized for maximum product quality.
- The model was used in actual industrial application.

1.6 Research contribution

Though the reaction chemistry is reasonably well established, a good model is required so that scale-up and optimization can be performed. The present study provides a state of art review on the modeling and operational control of the LPG sweetening process. Steady sate and transient profiles of process variables (measured) are obtained using Aspen HYSIS and are validated using plant data. Parametric sensitivity has been carried out to find the effect of parameters, *viz.*, temperature and pressure, on process measurements. Kinetic models along with reaction chemistry are used to find an optimal chemical absorber-reactor design. The outcome of the study has helped in data interpretation, process optimization and control. It is also used to predict the behavior of reacting systems where conditions significantly different from those that have been measured can be studied (with ProMax, Petro-SIM, CHEMCAD, Aspen Plus and Aspen HYSYS. (CuiQing and ShaoMei, 2004; Aylott and van der Merwe, 2008; Hanyak, 2012; Schefflan, 2016)

1.6.1 Process performance and operation

A process simulator is software used for studying the mathematical modeling of the behavior of a chemical process under steady state or dynamic conditions by means of variations of pressures, temperatures and flows. The process simulators are used to predict the behavior of a process, identifying the process behavior at different operating conditions, optimize the process for maximum efficiency, equipment sizing, CAPEX and OPEX.

Process simulation as a discipline uses mathematical models as the basis for analysis, prediction, testing and detection of a process performance. A Model Based Engineering (MBE) approach applies advanced process models with material and energy balance, mass transfer and heat transfer rate equations, equilibrium relationships, summation equations, hydraulic equations and equilibrium equations of the LPG amine process. The model parameters are validated with several experimental laboratory and actual plant operating data.

1.6.2 Advanced process control applications

Steady state and dynamic simulation models are used in advanced process control projects. The first step is to develop a steady state model of the process where APC (Advanced Process Control) is planned. Then, the model is calibrated to reflect the real plant conditions and after adding all dynamic data (volumes, valve sizes, *k* factors, controllers, etc.) and setting up the right pressure-flow relations, it can be simulated in the dynamic mode using the steady-state data for initialization (Deshpande and Ash, 1988). The steady state model can be used to identify new instrumentation needs, to check the feasibility of the inferences and to estimate the potential benefits through process optimization (Bhaskar et al., 2000). It can also be used to detect ill-conditioning of the selected APC variables (Foss et al., 1998). Good dynamic models are able to reproduce all non-linearity and dead times of the process when changing the process conditions or introducing perturbations.

1.6.3 Process design in FEED (Front End Engineering Design)

Process simulation models are used to compare the various process schemes and select the optimum scheme with respect to product quality, energy consumption and equipment size and cost. They provide inputs to engineering disciplines such as mechanical, piping, instrumentation, electrical, pipeline, safety, etc. Simulation models are used to generate heat and material balances for different cases and it gives the inputs to different equipment such as pumps, compressors, chillers, cooling system, utility system, safety, pressure relief, fire network sizing calculations, etc. Simulation models provided input for designing piping, instrumentation, ESD and process control systems related to the process. Amine process simulation models help process designers to decide on absorber and regenerator hydraulics, internal selection and parameters such as type packing, packed bed height, number of trays and type of trays. The models also provide information on piping design data such as dimension, rating and pressure drop. Simulation model provides information on the amine re-boiler, cooler and condenser duty, pressure drop and their dimensions and types. In addition, amine process simulation also provides basic engineering details on the pressure relief system, absorber, regenerator, vessels such as the feed surge drum, KOD, caustic wash and water drums, pump-control systems, interlocks, ESD, etc.

1.7 Outline of the thesis

The thesis is organized into seven chapters:

Chapter 1 provides the introduction of research work and highlights the commercial importance and market value of LPG. A brief information on the factors considered for selecting the research topics such as environmental factors, safety and hazard, corrosion aspects and LPG product handling are discussed. Insights are provided about the research contribution and uses of research model in process and equipment design, advanced process control and engineering design.

In **Chapter 2,** a literature survey on the acid gas process options, absorption methods, kinetic modeling, amine treatment process, process simulation and optimization of flow sheet models in HYSYS are explained in detail.

In **Chapter 3,** the LPG amine absorption processes and the equilibrium and non-equilibrium models are explained. The process simulation model, thermodynamic methods and selection criteria are discussed.

In **Chapter 4,** details of an industrial absorber are provided, the data of which is used for model development and validation. Process description of the refinery configuration, the LPG amine absorption unit process and the process instrumentation and control system are also explained. In addition, absorber parameters, model input parameters and model output parameters are provided.

In **Chapter 5,** the information on the sensitivity analysis of the model and the parameters identified for the analysis and model outputs are provided. The analytical reasoning for the sensitivity of parameters and effect of the model output on the temperature, pressure and concentration is also provided.

In **Chapter 6**, the selection of optimization methods, the optimization schemes available in HYSYS and optimization model output for the various optimization methods is explained.

In **Chapter 7,** the conclusion of the thesis and discussions on the results are provided. Additionally, application of the kinetic model in various sectors such as Front End Engineering Design (FEED), equipment sizing, safety and relief system design, Advanced Process Control (APC) and Model Based Engineering (MBE) are explained.

1.8 Summary

The importance of LPG and the necessity of the sweetening process has been discussed in the current chapter. The problem has been defined to investigate the effects of the operating parameters on the performance of the LPG sweetening process through modeling and to optimize the operating parameters. Environmental restrictions, corrosion problems in equipment and piping are also discussed in the current chapter.

Chapter 2

2.1 Acid gas treating process

The sour gas treating process primarily is the removal of hydrogen sulfide (H_2S), carbon dioxide (CO_2), and organo-sulfides from petroleum products. It is a common process installed in refineries, petrochemical plants, natural gas processing plants, and other industries. Gas treating has been described in several sources, e.g., Kohl and Nielsen (1997), Yu and Astarita (1987) and deCoursey (1974). There are various treatment processes available for H_2S and CO_2 removal and the process selection is categorized such as treatment by chemical solvent, by physical solvents, adsorption processes, membranes separations, and cryogenic methods (Koto, 2014). Recently, many developments have been reported in membrane and direct oxidation methods (Bhide and Stern, 1993, Minier-Matar et al., 2017). In physical and chemical treatment methods, the formulated amines are getting popular (Kohl and Nielsen, 1997; Burr and Lyddon, 2008). Formulated amines have significant advantages over conventional amines due to their low energy requirement, selectivity and stability (Brown and Geosits, 1993). In Figure 2.1, a list of processes is provided based on recent developments (Chapel et al., 1999; Rooney, 2001; Rajani, 2004; Vitse et al., 2011). Process selection depends mostly on the type and quantities of acidic impurities, sweet product quality, Operating conditions, CAPEX and OPEX (Fong et al., 1987; Lokhandwala et al., 1995; Rajani, 2004).

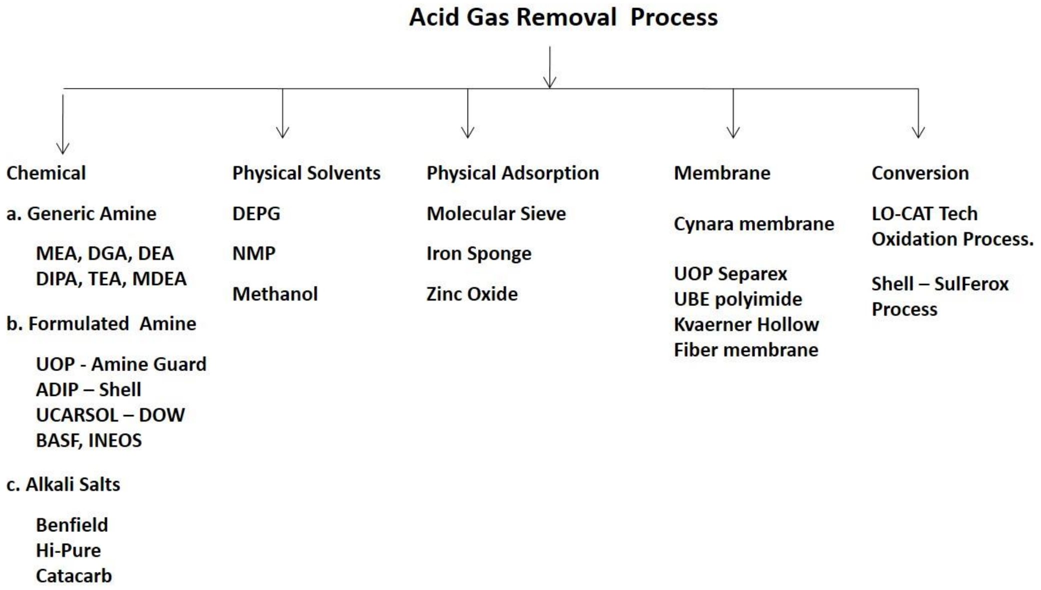

Figure 2.1: Acid gas removal processes with recent developments

A process selection chart for the simultaneous removal of H_2S and CO_2 is provided in Figure 2.2.

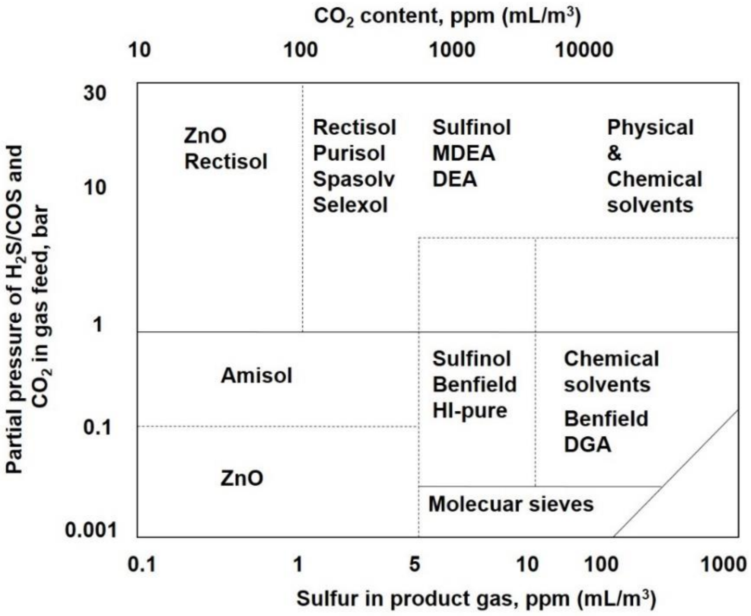

Figure 2.2: Process selection chart for the simultaneous removal of H_2S and CO_2 (Kidnay and Parrish, 2006)

2.2 Absorption

Absorption processes are one of the most important unit operations where acidic LPG is contacted with solvents in which the acidic components are preferentially soluble. Liquid phase absorption processes are divided into the following categories: physical solvents, chemical solvents and hybrid solvents that contain both an amine and a physical solvent. In chemical solvent processes, the absorption of the acid gases is primarily by the use of alkanolamine or alkaline salts of various weak acids such as sodium and potassium salts of carbonate. In physical solvent processes, organic solvents are used and no chemical reaction occurs. Physical solvent methods are used when the partial pressure of the contaminants is more, the treated product specification is reasonable and large gas volumes of feed have to be purified. Unlike chemical solvents, physical solvents are not corrosive and high quality metallurgy is not required. Physical solvents can usually be regenerated from the impurities by reducing the pressure without the addition of heat (Carlsson et al., 2007).

Absorption is usually carried out in a countercurrent tower, where liquid enters at the top and sour feed enters at the bottom. Based on the required surface area for gas-liquid interface, the absorption tower may be fitted with trays, installed with a packed bed, or fitted with sprays or other internals. The solvent selection is based on its solubility, selectivity, volatility, minimum effects on desired product and environment, chemical stability, low cost and availability, non-flammable, non-corrosive, low viscosity and low freezing point. At the operating conditions, high solubility of gases is referred to in terms of the quantity of gas dissolved in a given quantity of solvent. At equilibrium, the partial pressure (fugacity) of the acidic component in the vapor is equal to the fugacity of the same component in the solvent. This defines the equilibrium thermodynamic criterion for the relation of the concentration of a component in the gas and its corresponding concentration in the liquid (Seader et al., 2011). The basic principles for physical absorption are solubility and mass transfer and chemical absorption is based on reaction equilibrium and reaction kinetics.

High regeneration energy requirement and insensitivity to H_2S and CO_2 partial pressure are the limitations of chemical solvents. On the other hand, physical solvents require low energy and hence are used for the bulk removal of acid gas. Physical solvents are very sensitive to acid gas partial pressure and experience high hydrocarbon slip. Physical solvents like Selexol™ and Rectisol™ can reduce the product CO_2 to about 1 ppm.

2.2.1 Physical Absorption

Physical absorption processes are the type of absorption processes where the solvent interacts physically with the dissolved gas. In this process, the solvent used as an absorbent has such thermodynamic properties that the relative absorption of H_2S and CO_2 is more favored over that for the other components of the gas mixture. Removal of H_2S and CO_2 from the feed gas by the physical solvent absorption is based on the solubility. The partial pressure and the temperature of the feed gas are the two major factors that determine the solubility.

Although there are many physical solvent processes for the removal of H_2S and CO_2 from LPG, not all the processes are capable of removing CO_2 to meet LPG specifications. *Ideal characteristics of a physical solvent are the following:*

- Low solubility of hydrocarbon gas components in the solvent
- Low vapor pressure at operating temperatures to minimize solvent losses
- No degradation under normal operating conditions
- No chemical reaction between the solvent and any component in the feed gas stream
- No corrosion to common metals

2.2.1a Selexol process

The solvent used in the Selexol process is a mixture of dimethyl ethers of polyethylene glycol. The Selexol solvent has high capacity for acid gases, favorable solubility for acid gases *versus* other light gases and high selectivity for H_2S over CO_2. It also has low vapor pressure, which minimizes solvent losses, and is chemically and thermally stable, which eliminates the need for reclaiming or purging. The Selexol process can be configured in a number of ways, depending on the levels of acid gas removal required, from selective H_2S or bulk CO_2 to trace acid-gas removal. For selective H_2S removal, refrigeration is normally not used, but it is necessary when CO_2 removal is also required. Figure 2.3 illustrates the Selexol process for the removal of H_2S and CO_2.

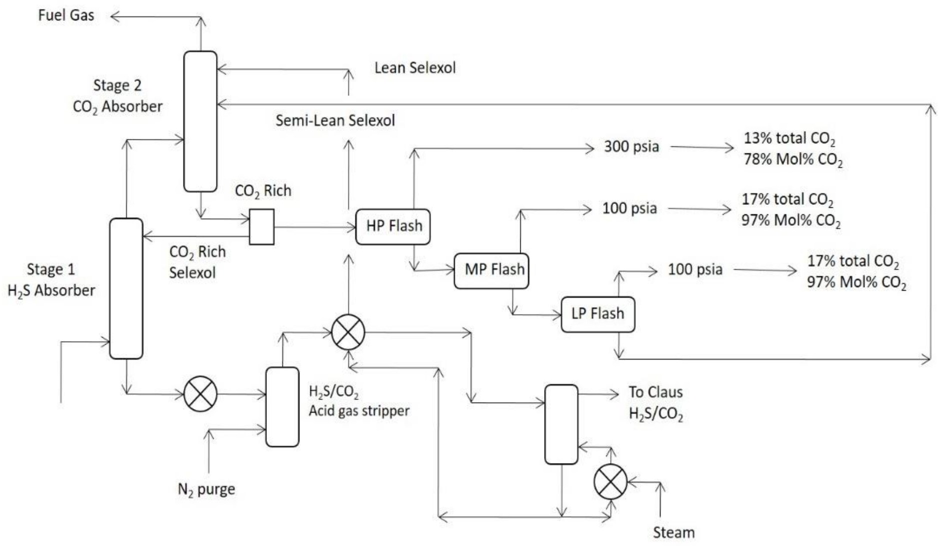

Figure 2.3: Selexol process flow diagram

2.2.1b Rectisol process

The Rectisol process, which uses chilled methanol as a solvent, is distinctive from other physical absorption processes in that it can remove H_2S and CO_2 as well as other gas impurities such as HCN and organic sulfur compounds to very low levels, with H_2S concentrations as low as 0.1 ppm and CO_2 concentrations of just a few ppm. Depending on process requirements, the Rectisol process can be designed in various configurations to achieve (1) deep, non-selective CO_2 and H_2S removal, (2) selective H_2S removal with some degree of CO_2 slippage (3) selective removal and recovery of separate CO_2 and H_2S products, along with the treated product gas stream. Figure 2.4 illustrates the Rectisol process for the removal of H_2S and CO_2.

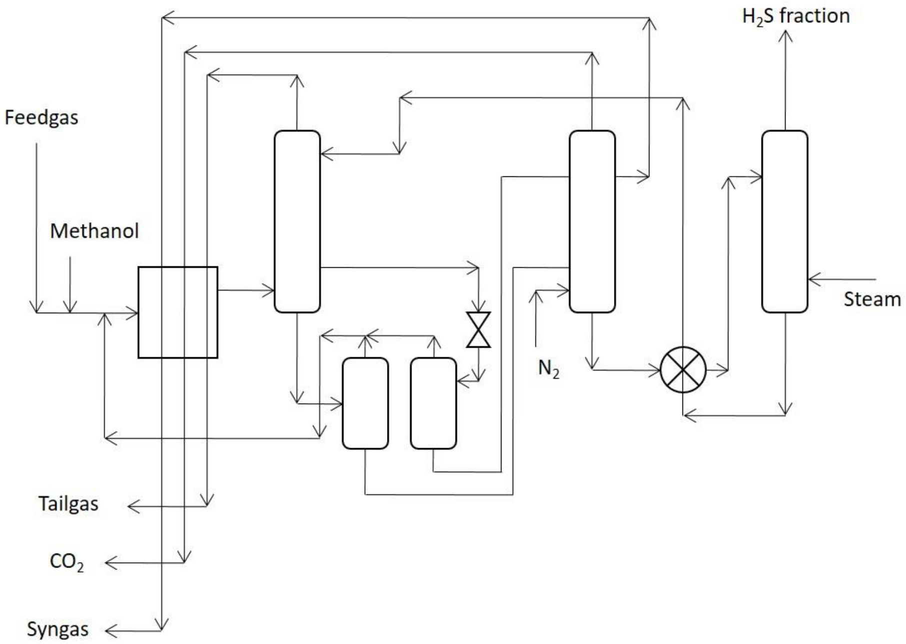

Figure 2.4: Rectisol process flow diagram

2.2.2 Chemical Absorption

In LPG sweetening, chemical absorption processes are widely used to remove acid gases such as H_2S and CO_2 in the gas stream by the action of exothermic reactions of the solvent with the gases. Alkanolamines are most widely used as the chemical solvent for acid gas removal from LPG and other petroleum products. These processes use a solvent, either an alkanolamine or an alkali-salt (hot potassium carbonate processes) in an aqueous solution. The common amine based solvents used for the absorption process are Monoethanolamine (MEA), diethanolamine (DEA), Methyldiethanolamine (MDEA) and Diglycol amine (DGA). These react with the acid gas (CO_2 and H_2S) to form a complex or bond. H_2S and CO_2 are termed as acid gases since they dissociate to form a weak acidic solution when they come into contact with water or an aqueous medium. These amines are weak organic bases.

Alkanolamines have at least one hydroxyl group and one amino group in their chemical structure. The hydroxyl groups increase the water solubility and reduce the vapor pressure of the alkanolamine. The amino group supplies the alkalinity in aqueous solutions, which is necessary for the absorption of acid gases. The absorption capacity and thermodynamic properties of commonly used treating chemicals are provided in Table 2.1.

Table 2.1: Thermodynamic properties of treating chemicals

Properties	MEA	DEA	TEA	DGA	DISPA	Selexol
Molecular Wt.	61.08	105.14	148.19	105.14	133.19	280
Boiling point @ 760 mm Hg, °C	170.5	269	360	221	248.7	270
Freezing point, °C	10.5	28.0	22.4	–12.5	42	–28.9
Pressure, k Pa (abs)	5985	3273	2448	3772	3770	-
Temperature, °C	350	442.1	514.3	402.6	399.2	-
Density @ 20°C, gm/cc	1.0179	1.0919	1.1258	1.0572	0.989 @ 45°C/20°C	-
Weight, kg/m^3						
Relative density 20°C/20°C	1.0179	1.0919 (30/20°C)	1.1258	1.0572	0.989 @ 45°C/20°C	-
Specific heat @ 15.6°C, kJ/(kg · °C)	2.55@ 20°C	2.51	2.93	2.39	2.89 @ 30°C	2.05 @ 5°C
Thermal conductivity, W/(m · °C) @ 20°C	0.256	0.220	–	0.209	-	0.19 @ 25°C
Latent heat of vaporization @ 760 mm Hg, (KJ/kg)	826	670	535	510	430	-
Viscosity, mPa· s	24.1 @ 20°C	350@ 20°C	1013@ 20°C	40@ 16°C	870 @ 30°C	5.8 @ 25°C
Flash point, COC, °C	93	138	185	127	124	151

Hybrid solvent processes, which use a mixture of a chemical and a physical solvent, combine, to a large extent, the advantages of a chemical solvent with those of a physical solvent. Hybrid solvents are more efficient in removing organic sulfur compounds and COS, but have the disadvantage of relatively poor hydrocarbon selectivity, resulting in hydrocarbon losses in the separated acid gases. (Mokhatab et al., 2006)

2.2.3 Mixed and formulated amines

The selectivity of MDEA can be reduced by addition of various amounts of primary or secondary amines (promoters), which enhance CO_2 removal while retaining desirable characteristics of MDEA (Mandal and Bandyopadhyay, 2006). Promoters work by a shuttle mechanism and affect the thermodynamics, but more importantly, they allow the reactivity of the mixture as a whole towards CO_2 to be closely controlled. Finding an optimum concentration of mixed amines (also called blended amines) strongly depends on the H_2S and CO_2 content of the sour gas, operating pressures and gas specifications. After the blend formula is established, normal control schemes will be used to ensure the H_2S specification. However, the CO_2 content in the treated gas will not be controllable except by adjusting the blend composition from time to time (Weiland et al., 2003). Amine mixtures are particularly useful for low-pressure applications because MDEA becomes less capable of CO_2 pickup sufficient enough to meet pipeline specifications. At higher pressures, amine mixtures appear to have little or no advantage over MDEA (Polasek et al., 1992).

Among all amine solvent processes, mixed amines have many advantages due to their ability to meet the most stringent H_2S and CO_2 specifications. Chemical activators are used with methyl diethanolamine (MDEA) to provide cost-effective solutions to remove acid gases as well as the bulk removal of mercaptans and COS from sour gases. The formulated MDEA solvent achieves a high degree of COS removal and retains appreciable selectivity for H_2S over CO_2. The formulated amine process is highly energy efficient due to the elevated acid gas loadings achievable with the solvent. This enables using low circulation rates and reduced energy consumption, as well as reduced equipment size. Additional advantages include very low hydrocarbon slippage, less amine loss due to degradation, less corrosion and low foaming problems. Reclaimer operation is not required, the solvent is nontoxic and biodegradable.

2.2.4 Adsorption

Adsorption processes involve the adsorption of acid gas components by solid adsorbents. The removal processes involve either chemical reaction or ionic bonding of solid particles with the acid gas. Iron oxide, zinc oxide and molecular sieve (zeolite) processes are the most commonly used adsorption media. The attractive forces holding the adsorbate on the adsorbent are weaker than those of chemical bonds, and the adsorbate can generally be desorbed by raising the temperature or reducing the partial pressure of the component in the gas phase. When an adsorbed component reacts chemically with the adsorbent, the process is called chemisorption and desorption is generally not possible. The main advantage of physical adsorption over chemical or physical absorption is its simple and energy-efficient operation and ease of regeneration, which can be achieved with a pressure swing or temperature swing cycle. The most preferred method to regenerate adsorbents is with a hot gas such as N_2 or contaminant-free light hydrocarbon gas.

2.2.4.1 Iron Sponge Process

The sponge iron fixed-bed chemical absorption is the oldest and still the most widely used batch process. This process tends to be highly selective for H_2S and does not normally remove significant quantities of the acid gas. As a result, the hydrogen sulfide stream from the process is usually of high purity. In this process, the inlet gas is fed at the top of the fixed-bed reactor filled with hydrated ferric oxide (Fe_2O_3). The basic reaction is provided below:

$$2Fe_2O_3 + 6H_2S \rightarrow 2Fe_2S + 6H_2O$$

The reaction requires the presence of slightly alkaline water and a temperature below 110 °F. A pH level of the order of 8–10 should be maintained through the injection of caustic soda with the water. The bed is regenerated by controlled oxidation as

$$2Fe_2S + 3O_2 \rightarrow 2Fe_2O_3 + 2S$$

Generally, the iron oxide process is suitable only for small to moderate quantities of hydrogen sulfide (300 ppm) operating at low to moderate pressures (50–500 psig). Removal of large amounts of hydrogen sulfide from gas streams requires a continuous process, such as the Ferrox process or the Stratford process. The Ferrox process is based on the same chemistry as the iron oxide process except that it is fluid and continuous. The Stratford process employs a solution containing vanadium salts and anthraquinone disulfonic acid (Campbell and Maddox, 1974).

2.2.4.2 Zinc Oxide Process

The zinc oxide process is also used for hydrogen sulfide removal from the gas stream. It uses a solid bed of granular zinc oxide to react with hydrogen sulfide as

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

In this process, the exit H_2S concentration can be as low as 1 ppm at a temperature of about 572 °F. The process has been decreasing in use due to the difficulty of disposing zinc sulfide which is considered a heavy metal.

2.2.4.3 Slurry Process

In slurry processes, slurries of iron oxide have been used to selectively absorb hydrogen sulfide. Two different slurry processes are described next.

The Chemsweet process (developed by NATCO) is a zinc oxide based process for the removal of hydrogen sulfide from natural gas. The Chemsweet white powder is a mixture of zinc oxide, zinc acetate and a dispersant to keep the zinc oxide particles in suspension with a ratio of one part in five parts of water. The presence of CO_2 is not important as the pH is low enough to prevent significant absorption of CO_2, even when the ratio of CO_2 to H_2S is high (Manning and Thompson, 1991).

The Sulfa-Check process (marketed by NALCO) selectively removes hydrogen sulfide from natural gas in the presence of carbon dioxide. This process is accomplished in a one-step single-vessel unit using an aqueous solution of sodium nitrite ($NaNO_2$) buffered to stabilize the pH above 8. This process is generally operated at ambient temperature and produces by-product slurry of sulfur and sodium salts.

2.2.5 Membrane Process

Membrane systems consist of semi-permeable elements (polymeric membranes) to separate gases by selective permeation of the gas constituents in contact with the membrane. The gases dissolve in the membrane material and move across the membrane barrier under an imposed partial pressure gradient, which is established by feeding high-pressure gas to one side of the membrane while maintaining the permeate side at much lower pressure. Many different types of membranes have been developed or are under development for industrial separations, but for natural gas separations, the industries generally use cellulose acetate. These membranes are of the solution-diffusion type, in which a thin layer of cellulose acetate is on top of a thicker layer of a porous support material. The membranes are thin so as to maximize mass transfer and thus minimize the surface area and cost, so a support layer is necessary to provide the needed mechanical strength (Lokhandwala et al., 1995).

2.2.6 Cryogenic fractionation

For many years, low-temperature distillation (cryogenic separation) has been a commercial process used to liquefy and purify CO_2 from relatively high purity (>

90%) sources. It involves cooling the gases to a very low temperature so that the CO_2 can be liquefied and separated. This technology requires substantial energy to provide necessary refrigeration. It also needs pretreatment of feed gas to remove components that have a freezing point below the operating temperature to avoid freezing of lines and blockages of process equipment. Cryogenic fractionation seems to have a good prospect for removing CO_2 and H_2S from natural gas because the vapor pressures of the principal components are quite different. However, problems are associated with the separation of CO_2 from methane, CO_2 from ethane and CO_2 from H_2S (GPSA a, b, 2004). A number of techniques are available for solving these problems. CFZ technology, developed at Exxon Mobil Upstream Research Company, is a cryogenic distillation process for the single-step removal of CO_2 and H_2S from natural gas involving the controlled freezing and re-melting of CO_2. It provides the ability to process natural gas more economically without imposing limitations on the amount of CO_2 or H_2S present in the feed gas. Further, the acid gas components are discharged as a high-pressure liquid stream that can be easily pumped for use in enhanced oil recovery operations while yielding a high-quality methane product (Northrop and Valencia, 2009).

Selecting an appropriate gas sweetening process depends on a number of variables. These must be weighed prior to making a process selection. These include the following:

- Sour gas flow rate, composition, pressure and temperature
- Specifications for the sweet gas and the acid gas
- The depth of acid gases and total sulfur removal required, plus the selectivity desired
- Impact of the composition of the concentrated acid gas on the design and costs of the downstream sulfur recovery and tail gas treating processes

- Process complexity and transient behavior (e.g., load-following capability)
- Process flexibility with regard to feedstock changes and potential future tightening of emission limits
- Process train operation, maintenance philosophy
- Capital, operating and royalty costs for the process

Several methods are available for treating LPG. If the quantities of the contaminants are small, a simple caustic wash can be used. For larger quantities, molecular sieves and amine treating systems can be used. While molecular sieves have the advantage of removing water and COS along with H_2S and CO_2, their disadvantages include large capital and operating costs as well as catalyzing the formation of COS when both H_2S and CO_2 are present. The use of amines has become quite popular, especially in plants where amines are also being used to sweeten the sour gas streams in addition to the processing of LPG. In plants with multiple absorbers, a common stripper can be used to regenerate the amine.

2.3 Kinetic Modeling literature

Process models are developed based on a set of equations which predicts the dynamics of a chemical process. Models are used to characterize the behavior of processes and to predict process variables at different operating conditions, to control continuous processes, investigation of process dynamics, optimal process design, for the calculation of optimal processes at given working conditions, etc. It plays an important role in conceptual design, process synthesis, flow sheeting and process integration. Recently, computer aided process modeling capable of performing thermodynamic analysis, material balance, energy balance, optimization and data reconciliation, etc., has become popular.

Modeling of absorbers and strippers follow two general categories (a) equilibrium based approach and (b) rate based approach. The equilibrium approach assumes a theoretical stage in which liquid and gas phases are in equilibrium. This approach is more suitable for non-reactive systems. Chemical reactions are involved in amine absorption, hence rate-based models need to be used. In the rate-based approach, actual rates of multi-component mass and heat transfer as well as chemical reactions are considered.

Models based on the equilibrium assumption provide a simple way for prediction of acid gas partial pressure. They have two major disadvantages:

a. Inefficiency when extrapolated to conditions other than those for which the equilibrium constants were tuned
b. Equilibrium constant gives only an approximation of the species composition.

The following are a few examples of models developed in this group: Deshmukh and Mather (1981), Awan and Saleem (2011) and Danckwerts and McNeil (1967).

The model presented by Kent and Eisenberg (1976) is based on chemical and phase equilibrium, mass balance and Murphree efficiency. The non-idealities, represented by activity coefficients, are lumped into two pseudo-equilibrium constants (for the main reactions of H_2S and CO_2 with MEA or DEA) as a function of temperature. Model parameters are regressed against experimental data. The model showed good predictions of the partial pressures of H_2S and CO_2 for single acid gas systems (H_2S–MEA–H_2O, CO_2–DEA–H_2O) as well as for the mixed systems (CO_2–H_2S–DEA–H_2O, CO_2–H_2S– MEA–H_2O).

Complex models can be divided into activity coefficient or Gibbs energy models and equation of state models. The Gibbs energy/activity coefficient models provide activity coefficients based on expressions for the excess Gibbs energy of the liquid phase. An equation of state is used for the determination of fugacity coefficients of the vapor phase. Deshmukh and Mather (1981) proposed a method based on the Guggenheim theory (Guggenheim and Turgeon, 1955) for the H_2S/CO_2-MEA-H_2O system. In this model, it is assumed that water behaves ideally and all the interaction parameters for water in the model are set to zero.

Even though the model is simple, it shows good results for the CO_2 solubility. It has limitations of describing the phase behavior of the binary MEA-H_2O system. In 1978, Edwards et al. (1978) presented a molecular thermodynamic model for calculating the vapor-liquid equilibrium for dilute solutions of weak electrolytes. They used a Guggenheim-type equation for representation of activity coefficients. Li and Mather (1994) used the Pitzer and Simonson model (1986), which is an extension of the Pitzer model, for modeling the CO_2-MEA-MDEA-H_2O system. Pitzer and Simonson (1986) used the Pitzer model for representing the behavior of the CO_2-MDEA-H_2O and H_2S- MDEA-H_2O systems. Kamps et al. (2003) and Ermatchkov et al. (2006) used the Pitzer model for the MDEA-CO_2-H_2O mixture**.** Arcis et al. (2009) applied the Pitzer model for representing VLE data and the heat of absorption for the MDEA-CO_2-H_2O system.

Under the activity coefficient models, the electrolyte NRTL (non-random two liquid) model, e-NRTL, presented by Chen and Evans (1986) and the extended UNIQUAC model presented by Thomsen and Rasmussen (1999) are most commonly used. The e-NRTL model has been applied for modeling many alkanolamine-acid gas-water systems. A review on the application of models reveals that many researchers (Posey and Rochelle, 1997; Hilliard, 2008) applied the e-NRTL model in their work. Hessen et al. (2009) used the refined e-NRTL model for the CO_2-H_2O-MEA/MDEA system. Hessen et al. (2009) applied the e-NRTL in Aspen PLUS for modeling the VLE, heat capacity and heat of absorption of the CO_2-MDEA-H_2O system. Addicks et al. (2002) applied both the extended UNIQUAC and the e-NRTL methods for VLE calculations for the CO_2-CH_4-MDEA-H_2O system. Faramarzi et al. (2009) used the extended UNIQUAC model for modeling the VLE of the CO2-H2O-MDEA/MEA system.

Equation of state models are the set of thermodynamic equations describing the state of the matter under a given set of physical conditions. The electrolyte equation of state (EoS) model by Fürst and Renon (1993) is well known. It is based on the EoS concept and MSA. Vallee et al. (1999) used the Fürst and

Renon model for the H_2S/CO_2-DEA-H_2O system. Chunxi and Fürst (2000) applied it for CO_2/H_2S-MDEA-H_2O mixtures. Huttenhuis et al. (2008) modified the Solbraa (2002) model for the CO_2-CH_4-MDEA-H_2O system. Derks et al. (2010) used the Fürst and Renon model for the CO_2–PZ–MDEA–H_2O system. Button and Gubbins (1999) applied the SAFT19 model for the CO_2-MEA/DEA-H_2O system. Chapman et al. (1990) developed a model based on the statistical association fluid theory (SAFT). It is based on statistical thermodynamics; the equation of state offers greater predictive capabilities than previous empirical equations. Figure 2.5 provides the pictorial representation of development of models from simple to complex levels flowing from No. 1 to 5. Model 1 is a simple equilibrium model while Model 2 is an equilibrium model with reaction kinetics. Models 3 to 4 are rate based models with increase in complexity from reaction equilibrium to film reactions and electrolytes.

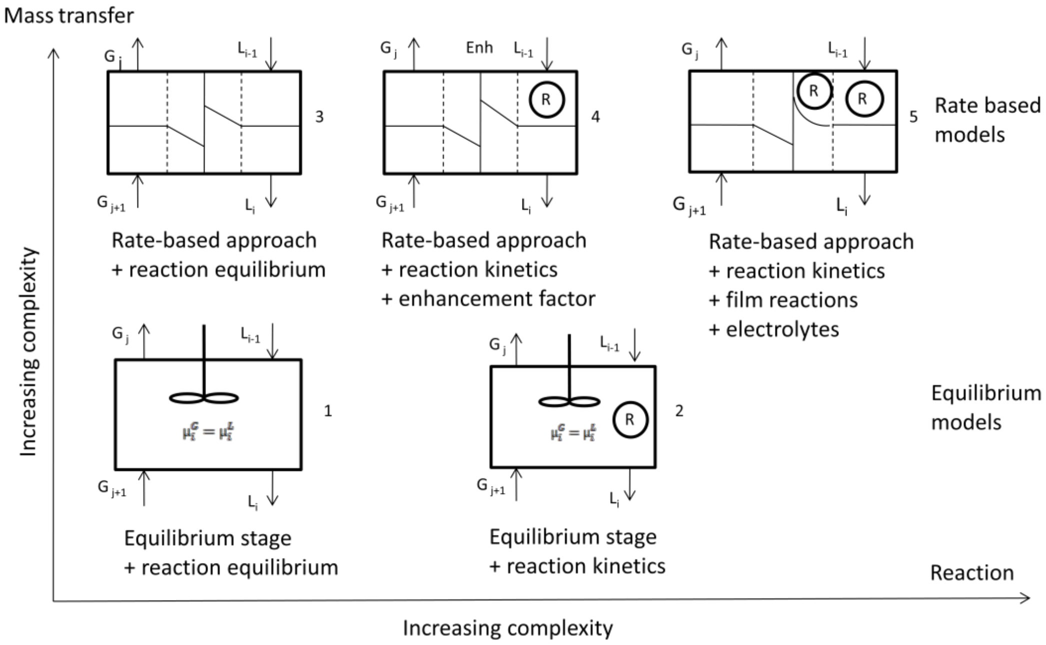

Figure 2.5: Different modeling approaches (Kenig et al., 2001)

2.4 The Amine Treatment Process

Several methods are available commercially to remove the acidic contaminants from LPG. The use of amines is more appropriate for various applications such as recycle gas H_2S absorption in hydro-treating units, fuel gas sweetening, tail gas treating and LPG treating. Centralized amine regeneration regenerates and distributes lean amine to all the facilities. A brief selection method of the amine treating process is provided in Table 2.2.

Table 2.2: Recommended methods of treatment

No.	Inlet Gas Contaminants	Recommended Method of Treatment
1	H_2S > 0.25 g/100SCF and some CO_2	Amine-treat* gas, with small amine side stream sent to a liquid contactor for product treating, as in Figure 2.7
2	$H_2S = 0^+$ - 0.25 g/100 SCF and excessive CO_2	Amine-treat* gas, with small amine side stream sent to liquid contractor for product treating, as in Figure 2.7
3	$H_2S = 0^+$ - 0.25 g/100 SCF and minimal CO_2	Either amine-treat* product gas in liquid contactor or iron-sponge treat product
4	No H_2S and excessive CO_2	Amine-treat* gas only
5	H_2S, CO_2 and COS	Use di-ethanolamine or diglycolamine to amine-treat* both gas and liquid. May require caustic final scrub of the liquids to remove last traces of COS
6	H_2S, CO_2 and some mercaptans (no need for gas sample to undergo the “doctor” test)	Use method indicated above according to H_2S and CO_2 content. Doctor test is a qualitative test for detecting hydrogen sulfide and mercaptan

		sulfur in hydrocarbon liquids
7	H_2S, CO_2 and excessive mercaptans (gas sample to undergo the “doctor” test for sweetness)	Use methods indicated above with di-ethanolamine or di-glycolamine, plus follow with regenerative caustic, Merox, Bender, Perco, or some other process for mercaptan removal or conversion, or treat the product with molecular sieves
	H_2S of 0.25 g/100 SCF is equivalent to approximately 4 ppm V/V	
	‘AMINE-TREAT*’ stands for mono-ethanolamine (MEA), di-ethanolamine (DEA) or di-glycolamine (DGA) process and is shown in Figure 2.6	
	Doctor Test: This is a standard test method for qualitative analysis for active sulfur species in fuels and solvents (Doctor test). In this test, the sample is shaken with a sodium plumbite solution, a small quantity of powdered sulfur added and the mixture shaken again. The presence of mercaptan or hydrogen sulfide or both is indicated by discoloration of the sulfur floating at the oil-water interface or by discoloration of either of the phases. ASTM D 4952 – 02	

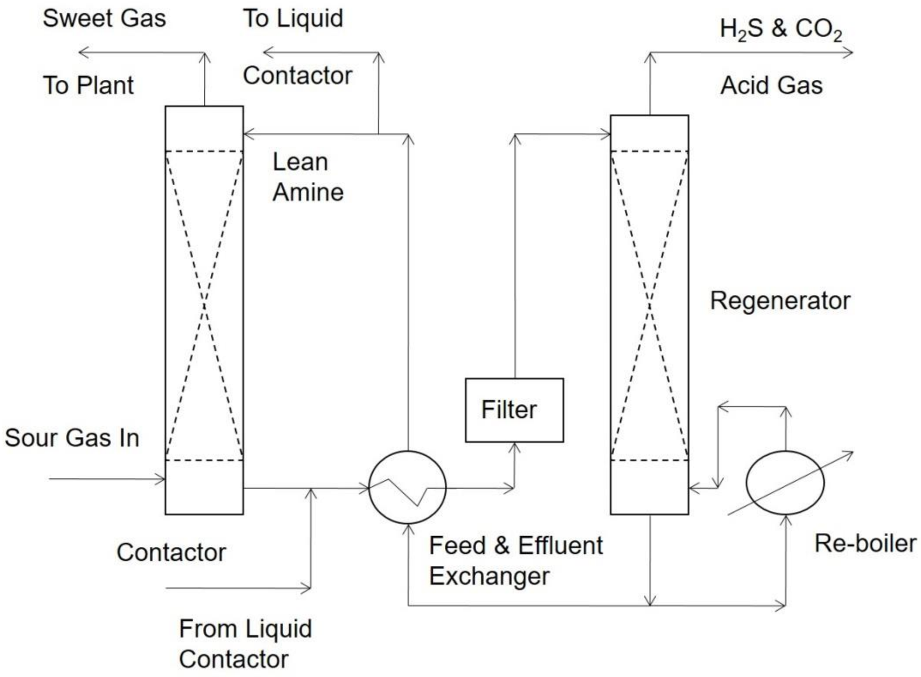

Figure 2.6: Amine-treat system for removal of sulfur and impurities from LPG

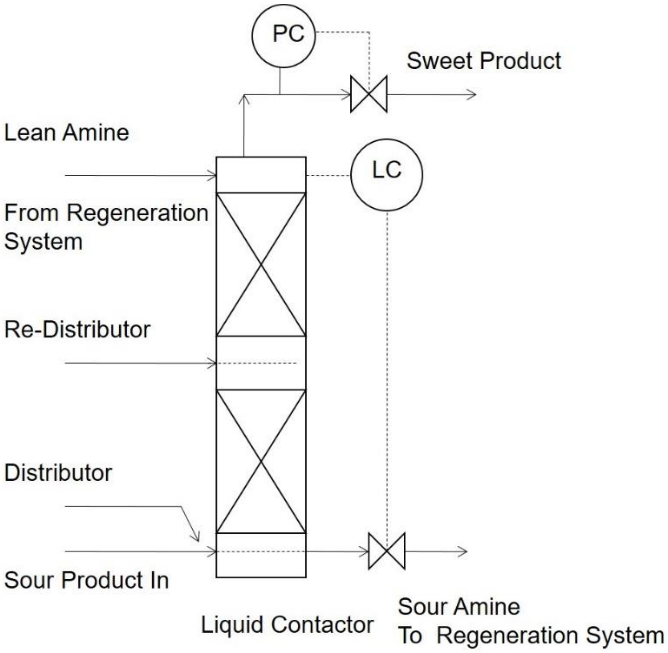

Figure 2.7: Liquid-liquid packed contactor

Generally, refineries adopt a centralized lean amine supply and regeneration facility to treat LPG, fuel gas and for recycle gases in the hydrotreater. For economic reasons, a single treatment process is usually installed. To purify sour LPG, the amine sweetening process is adopted, where sour LPG is treated with alkanolamines in a counter current absorption tower. The sweet LPG is sent for water wash and caustic wash to remove organo-sulfur compounds and entrainments before being routed to storage and certification (Maddox, 1974; Feng et al., 2015).

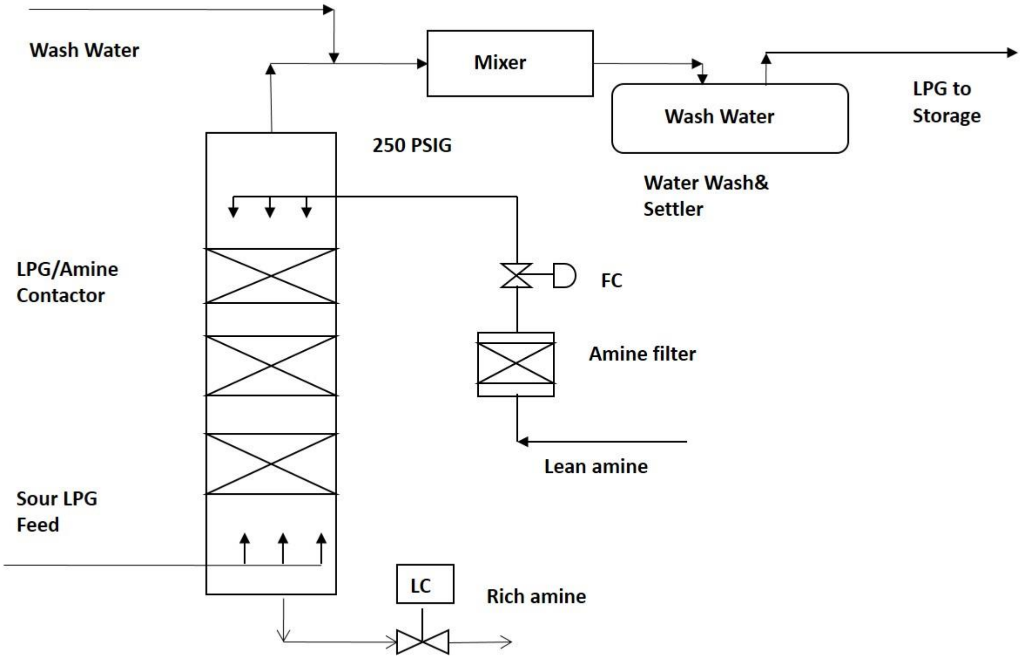

Figure 2.8: LPG sweetening process using alkanolamines

Figure 2.8 is a typical LPG treating system (Kohl and Nielsen, 1997). In this process, sour LPG is pumped to a countercurrent liquid-liquid contactor that contains beds of random packing. The sour LPG enters at the bottom of the column and lean amine is fed to the top of the column at a controlled flow rate through a flow controller. The LPG feed is distributed evenly and formed into droplets by injection into the continuous amine phase at the bottom of the column. The lean amine is distributed across the top of the packing through a flow or level controller, where it joins the continuous amine phase. The density difference between the two phases causes the dispersed LPG to flow upward through the continuous amine phase. The LPG/amine interface is maintained above the top bed and the amine distributor by an interface level controller that controls the rate of discharge of rich amine from the bottom of the contactor. A gravity settler and LPG water wash system are provided. Washing the treated LPG with water improves the recovery of entrained amine and removes dissolved amine from the LPG. A portion of the water-amine stream from the settler is recycled to the LPG stream entering the water wash mixer. Usually the wash-water flow rate is about 25% of the LPG flow. The combined water-LPG stream flows through a static mixer or other mixing device and then to the gravity settler. Depending on the product quality requirement, the LPG from the settler may be further processed in other treating units, such as an extractive Merox unit to remove mercaptans. The operating pressure of the entire LPG treating system is controlled by a pressure controller located downstream of the final LPG treating unit. The treated LPG leaves the contactor and flows to a gravity settler or coalescer where entrained droplets of amine are removed from the LPG. The treated LPG is caustic and water washed to remove mercaptans and sent to storage for certification.

2.5 Solvent selection and operating conditions

The selection of an amine solution depends on process conditions, acid gas partial pressure and purity of the product. The hydroxyl group in the amine increases the water solubility and reduces the vapor pressure of the amine. The amino group supplies the alkalinity in aqueous solutions, which is necessary for absorption of acid gases. Alkanolamines are divided into three categories based on chemical structure: primary, secondary and tertiary amines. Primary amines have a nitrogen atom with two hydrogen atoms attached. The secondary amines have one hydrogen atom attached to a nitrogen atom. In tertiary amines, no hydrogen atoms are attached to nitrogen atoms. The heats of reaction and evaporation decrease from primary to tertiary amines. These enthalpies are directly related to energy needed in amine regeneration. The tertiary amines have higher loading values.

Acid gas loading capability increases from primary to tertiary amines. Each amine has separate ranges of process conditions and parameters. Some typical operating conditions for common amines are summarized in Table 2.3. A comparison between the advantages and disadvantages of different amine solutions is given in Table 2.4.

Table 2.3: Typical operating conditions and data for amines

Amine	MEA	DEA	DGA	MDEA
Amine Strength, wt. %	15 - 20	25 - 35	50 - 70	20 - 50
Loading, mol/mol	0.3 – 0.35	0.3 – 0.35	0.3 – 0.35	Unlimited
H_2S Selectivity	No	Limited condition	No	Most conditions

Table 2.4: Comparison between different solvent solutions

Solution	advantages	disadvantages	Applications
MEA	i. High alkalinity increases the effectiveness for gas absorption ii. High solution capacity allows moderate load/ concentration iii. Solution can easily be reclaimed	i. Formation of irreversible reaction product with sulfur contaminants and loss in solvent ii. Higher corrosion rate iii. High heat of reaction with H_2S and CO_2 iv. Loss is high due to high vapor pressure	Lower loads in sour gas components

DEA	i. Allows relatively higher load than MEA ii. Regenerable compounds iii. Needs lower energy for solvent recovery	i. Low vapor pressure of solvent is suitable for low pressure operation ii. It is difficult to reclaim solvent from contaminated solutions; vacuum iii. Distillation may be needed	Moderate loads in sour gas composition
DGA	i. It can remove H_2S, CO_2,COS, mercaptans ii. Low vapor pressure allows higher concentrations iii. Low circulation rate and steam consumption	i. High heat of solution. High regeneration energy	
DIPA	i. It can remove H_2S, CO_2, COS ii. Non-corrosive iii. Low steam consumption iv. Selective removal yields reduction in sour gas v. Low heat of reaction: low energy needed in regeneration vi. Low corrosion, thermally and chemically stable vii. Sparingly soluble with hydrocarbons	i. Most effective for COS removal ii. Shows selectivity for H_2S over CO_2 iii. Is used for Claus plants iv. High solution capacity v. Proprietary additives can be added to enhance absorption	Allows higher loading

2.6 Operating parameters

Generally, in any amine treatment unit, the primary objective is to sweeten the sour gas that should meet the required purity specifications with respect to H_2S

and CO_2. The secondary objective is to select the amine which optimizes equipment size and minimizes plant operating costs (Kenig et al., 2001). The important factors to consider in the amine selection are:

a. Less amine circulation rate by operating at higher amine acid gas load which could reduce reboiler/condenser size
b. Selective absorption based on specification

Bullin et al. (1981) have recommended design guidelines for the LPG sweetening plants using MEA, DEA and DGA. The guidelines are provided in Table 2.5 while Table 2.6 summarizes the general operating guidelines of amine treatment units.

Table 2.5: Operating conditions for LPG sweetening with amines

	Wt. % Amine	Max. Loading (mol/mol)
MEA	5 – 20	0.3 – 0.4
DEA	25 – 35	0.35 – 0.65
DGA	50 – 70	0.45 – 0.65

Table 2.6: Approximate guidelines of amine treatment

Items	**MEA**	**DEA**	**DGA**	**MDEA**
Acid gas pickup, SCF/gal @ 100^{o}F	3.1-4.3	6.7-7.5	4.7-7.3	3.0-7.5
Acid gas pickup, mole/mole amine	0.33-0.40	0.2-0.8	0.25-0.38	0.2-0.8
Lean solution residual acid gas, mole/mole amine	0.12	0.01	0.06	0.005-0.01
Rich solution acid gas loading, mole/mole amine	0.45-0.52	0.21-0.81	0.35-0.44	0.20-0.81
Max solution conc., % wt.	25	40	60	65
Approximate reboiler heat duty, BTU/gal lean solution	1000-1200	840-1000	1100-1300	800-900

Reboiler temperature, ^{o}F	225-260	230-260	250-270	230-270
Heat of reaction, BTU/lb. H_2S BTU/lb. CO_2	610-825	555-730	674-850	530-630
Utility demand, LP steam (lb./gal)	0.8-1.5	0.7-1.1	1.5	1.0
Solvent loss, lb./mm SCF of sweet gas	2-4	1-2	2-4	1-2
Circulation rate, gpm	1900-2000	1500-1580	1680-1780	1420-1500

Commonly used ethanol amines including MEA, DEA, DGA, MDEA and MDEA based solvents usually perform satisfactorily for liquid treating (Kohl and Nielsen, 1997). The contact time required for the two liquid phases is relatively long, generally up to 30 min, when the phase separation step is included in the process. This provides adequate time for the slow reaction between CO_2 and the amines. For selective absorption, an amine such as MDEA, is best known for its ability to preferentially absorb H_2S and is used in (Fong et al., 1987) in tail gas clean-up units since it is desirable to slip as much CO_2 as possible while absorbing the maximum amount of H_2S to be recycled back to the Claus unit in sulfur recovery. Mixed amines are typically mixtures of MDEA and DEA or MEA which enhance CO_2 removal while retaining desirable characteristics of MDEA such as reduced corrosion problems and low heats of reaction.

In CAPEX and OPEX review (Astarita et al., 1983), 50 to 70% of the initial investment for an amine sweetening unit is directly associated with the magnitude of the solvent circulation rate. Another 10 to 20% of the initial investment is dependent on the regeneration energy requirement and about 70% of operating costs, excluding labor, results from regeneration.

Since selection of the proper amine greatly reduces both the regeneration energy requirement and solution circulation rate, the choice of the amine or combination of amines best suited to the conditions can have a dramatic impact on the overall costs associated with a sweetening unit.

2.7 Absorption models with process simulation

Computer aided process simulators are widely used in process design, process analysis and optimization. The simulators comprise of physical and thermodynamic property data banks for components. The simulators also have in-built models of unit operations, columns, reactors, etc. They are used to perform process calculations for conceptual design, detailed process calculation, mass and energy balances, flow sheeting, dynamic analysis and cost optimization. Aspen PLUS, BATCH PLUS, HYSIS (Aspen, 2006), PRO/II, CHEMCAD, UNISIM and PROMAX are some typical commercial simulators in use. Several research publications have reported simulation results on amine absorption using HYSYS. Acid gas cleaning is an in-built functionality of Aspen HYSYS. The ‘Acid Gas’ package in Aspen HYSYS provides information using the e-NRTL model and the Peng-Robinson (1976) equation of state.

2.7.1 Process simulation options

The amine absorption model for CO_2 absorption using MEA with Aspen HYSYS and Aspen PLUS were studied by ErikØi (2012). The model was developed with specified Murphee efficiencies and a rate-based approach. The study found that the differences between the properties as predicted by Aspen HYSYS and Aspen PLUS using the equilibrium models of Kent-Eisenberg, Li-Mather and e-NRTL were small. There were some differences in the removal efficiency and the temperature profiles between the results based on Murphree efficiencies and results with rate-based simulations. The calculations predicted that all the model results are roughly the same when the objective was to calculate the efficiency of CO_2 removal with respect to the circulation rate, number of column stages and temperature. Similarly, a rate-based model for CO_2 absorption studied by ErikØi (2012) and Vitse et al. (2011) showed the superiority of the rate-based models over the traditional equilibrium-stage models for the recently available pilot plant data from the University of Texas at Austin (Zhang and Chen, 2013) for CO_2 capture with aqueous mono ethanolamine.

Erfani et al. (2015) used Aspen HYSYS (Version 7.3) and Aspen PLUS (Version 7.3) for simulation of a CO_2 removal unit. In Aspen HYSYS simulations, the Kent-Eisenberg and Li-Mather models were used. Nuchitprasittichai and Cremaschi (2013) used Aspen HYSYS to analyze the impact of different amine absorbents and their concentrations on the absorber and stripper column heights and the operating conditions of CO_2 recovery plant for post combustion of CO_2 removal.

ErikØi (2012) modeled the combination of a gas power plant along with MEA (mono ethanol amine)-based CO_2 removal process using the Aspen HYSYS process simulator. ErikØi also used the Amines Property Package and the Peng Robinson model, both being in-built subroutines in Aspen HYSYS. The adiabatic efficiencies in compressors, gas turbines and steam turbines have been fitted to achieve a total thermal efficiency in the natural gas based power plant. The acid gas removal along with energy consumption for the process was calculated with respect to the amine circulation rate, absorption temperature, packed bed height and steam enthalpy. The amine absorption model developed in Aspen HYSYS was found to be useful to understand the sensitivity of changing amine circulation rate, packed bed height, operating temperature and the bottom reboiler temperature.

Theoretical investigation of simultaneous absorption of CO_2 and H_2S into aqueous solutions of MDEA and DEA was carried out by Zare and Mirzaei (2009). Thermodynamic packages like, e-NRTL, Amines (experimental) equation of states and amine package were used. The sensitivity of temperature, operating pressure, amine circulation rate, amine concentration and efficiency of packed bed (Murphree efficiency) on the rate of absorption were studied. The research highlights that when the flow of lean amine and its concentration are increased, an increase in the absorption of CO_2 and H_2S was observed. When the temperature of the inlet amine was increased in the absorber, CO_2 and H_2S lifted to upper stages of the absorber resulting in a decrease in the absorption of acid gases. This study revealed that the sweet gas concentration is greatly influenced by the packing height. In conclusion, when lean amine concentration and flow increased, CO_2 and H_2S absorption efficiency increased and when lean amine temperature increased, the CO_2 and H_2S slippage to upper stages of absorber increased and absorption of acid gases decreased. The CO_2 and H_2S concentration in sweet gas (clean gas) increases with the CO_2 percentage in the clean gas which is greatly influenced by the packed bed height, but the effect of packing height on H_2S removal was observed to be less significant.

Kim and Kim (2004) simulated the solvent absorption process and optimized the condition for minimum energy required in desorption. Qeshta et al. (2015) simulated the LPG sweetening process using MDEA in HYSYS and conducted a sensitivity analysis. The optimum operating parameters were identified and the model output predicted the H_2S content in the product LPG within the limit of 0 to 10 ppm.

2.8 Optimization

Aspen HYSYS® also has an in-built multi-variable steady state optimization program, Aspen HYSYS Optimizer (2006). Once the process flow sheet has been built and converged solutions have been obtained, the optimizer tool can be used to find the operating conditions to minimize or maximize an objective function. The spreadsheet option in the optimizer can be used to define the objective function as well as expressions for any constraint. HYSYS has a number of in-built algorithms like the Fletcher Reeves, Quasi-Newton, Box, SQP, and mixed optimization.

The Fletcher Reeves (1964) optimization method is based on the Fletcher Reeves conjugate gradient scheme. It is efficient for general minimization with no constraints (Gupta, 2015). The Quasi-Newton method is similar to the Fletcher and Reeves method. It calculates the new search direction from approximations of the inverse of the Hessian matrix. The Box method is based on the "complex" method of Box (1965), the downhill simplex algorithm of Weise (2009) and the

Box algorithm as given by Kuester and Mize (1973). The Box method is a sequential search technique which solves problems with non-linear objective functions with inequality constraints (no derivatives are required). It handles inequality constraints but not equality constraints. The Sequential Quadratic Programming (SQP) method handles inequality and equality constraints. SQP is considered to be the most efficient method for minimization with general linear and nonlinear constraints, provided a reasonable initial point is used and the number of primary variables is small. The implemented procedure is based entirely on the Harwell subroutines, VF13 and VE17. The program follows closely the algorithm of Powell (1978). It minimizes a quadratic approximation of the Lagrangian function subject to linear approximations of the constraints. The second derivative matrix of the function is estimated automatically. A line search procedure utilizing the “watchdog” technique (Chamberlain et al., 1982) is used to force convergence. The mixed method attempts to take advantage of the global convergence characteristics of the Box method and the efficiency of the SQP method. After convergence, the SQP method is then used to locate the final solution using the desired tolerance.

It is observed from the study that only a few studies have been reported on the modeling, simulation and optimization of the acid gas treatment of LPG (Feng et al., 2015; Tse and Santos, 1993; Qeshta et al., 2015; Nuchitprasittichai and Cremaschi, 2013). Moreover, considering its market value and its commercial importance there is ample scope available for further studies. Industries are continuously making efforts to minimize the operating cost and improve efficiency by optimization. Therefore, there is a definite requirement to further study the LPG sweetening process, develop a model, identify the performance parameters and optimize for performance improvement. The research outcome could help industries to operate the system with maximum efficiency and also, the developed models can be used for online supervisory control applications.

2.9 Summary

Industries adopt various technologies for acid gas treating. Selection of technology depends on many factors such as feed composition, expected product quality, operating conditions, configuration, CAPEX and OPEX. For treatment of sour LPG, the amine absorption process is one of the best processes for refineries due to proven technology, product quality, operational flexibility and a centralized amine treatment unit that reduce CAPEX and OPEX.

Chapter 3

3.1 Alkanolamine models

A kinetic model should be able to predict vapor liquid equilibrium, reaction kinetics and hydrodynamics of the process. It should also be able to incorporate the effects of reactions on the mass transfer and the thermal properties such as heat of reaction, heat transfer between phases and latent heat of evaporation or condensation. The literature survey reveals that LPG amine absorption models are broadly divided into two categories: (1) equilibrium models and (2) rate based models. Information is collected on available commercial, industrial and academic models. Academic models are listed in Table 3.1 and commercial and industrial models are listed in Table 3.2.

Table 3.1: List of academic models

Model	**Flow sheet options**	**Validation**	**Thermodynamics**	
			Gas	Liquid
Cornelissen (1980)	Tray absorber	Experiments based on a 0.11 m dia. column	H_2S-Amine equilibrium by experiment	Not applicable
Yu and Astarita (1987)	Packed absorber	none	Semi empirical fit to data from Jou et al. (1982)	Not applicable

Kelly et al. (1984)	Packed absorber	Experiment based on 0.053 m dia. column	Edwards (1974)	Redlick and Kwong (1949) modified by Cheuh and Prausnitz (1967)
van Swaaij and Versteeg (1992)	Absorber/ Stripper, SRU, Shell Claus off-gas	None	Blauwhoff and van Swaaij (1980)	Reversible reactions are considered. Rate constants from Danckwerts and Sharma (1966)

Table 3.2: List of commercial and industrial alkanolamine models

Model	**Type of Amine**	**Thermodynamics**	
		Liquid	**Gas**
Bullin et al. (1981) (TSWEET)	MEA, DEA, DGA, MDEA, Mixed amines	Modified Kent Eisenberg (1976) model	Soave-Redlich-Kwong (Soave, 1972)
Tomcej and Otto (1989) (AMSIM)	MEA, DEA, MDEA	Modified Kent Eisenberg (1976) model, Chakma and Meisen (1990)	Not available
Weiland et al. (1985) (GAS PLANT)	MEA, DEA, DGA, MDEA, Mixed amines	Chakravarty (1985) added to Deshmukh and Mather (1981)	Peng-Robinson (1976)
Dow Chemical Co.	MEA, DEA, DGA, MDEA, Mixed amines	Chakravarty et al. (1985) added to Deshmukh and Mather (1981). Separate model for low loading	Peng-Robinson (1976)

The basic rate approach for non-reactive systems was developed by Krishnamurthy and Taylor (1985). Cornelissen et al. (1980) modified the

approach to include CO and H_2S absorption in alkanolamine. Weiland et al. (1985) developed models for regeneration. Sardar et al. (1985) made further improvements and compared the model output with data. Campbell and Weiland (1989) used the rate-based model for amine blends.
Tomcej and Otto (1989) extended the Krishnamurthy and Taylor (1985) method by the addition of an unsteady-state, finite difference mass transfer model to define the concentration profiles of absorbing and reacting species in the liquid and further improvement was done which provides a more accurate representation of the concentration gradients in the liquid phase as it flows *across* a tray.

The models developed by Bullin and Polasek (1982), Tomcej and Otto (1989) and Weiland et al. (1985) are commercially known as TSWEET, AMSIM and GASPLANT/GASPLANT PLUS. Due to their commercial use, these models have been extensively verified against pilot plant data. The program, AMSIM, developed by Tomcej and Otto (1989) used a stage efficiency approach to perform non-equilibrium modeling but the model assumes thermal equilibrium on each stage. This model is not applicable for mixed amines. GASPLANT PLUS was the first amine simulator used for single and mixed amines with flexible flow sheet options. Bullin et al. (1990) used rigorous tray by tray calculations using the Ishii and Otto (1973) and Holmes et al. (1984) models.

In the model of Tomcej and Otto (1989) for mass transfer calculations, the enhancement factor uses a pseudo first-order expression and the mass transfer involves bubble cap trays (Sharma et al., 1969). The model is solved by rigorous tray by tray calculations using the revised versions of the Tomcej and Otto (1989) and Tomcej et. al. (1987).

In the Weiland et al. (1985) model for mass transfer calculations, the enhancement factor is based on Welleck et al. (1978) and the packing mass transfer coefficients are based on Onda et al. (1968) and Welleck et al. (1978). The numerical approach is based on the simultaneous solution of equations using the Newton-Raphson technique as suggested by Chakravarty et al. (1985) and Weiland et al. (1985)**.**

In the Dow chemical company model, the mass transfer coefficients are calculated based on the AIChE (1958) and Scheffe (1984) correlations, and is numerically solved by the Newton-Raphson method as suggested by Katti and Wolcott (1987).

3.1.1 Pro Treat^{TM}

Pro Treat^{TM} is a commercial rate based process simulator specific to absorption processes developed by the Optimized Gas Treating Inc. It uses a rate based calculation that includes column modeling and several packing materials (Cousins et al., 2011). All the packing materials used in these pilot studies could be simulated. It is based on two thermodynamic packages using the Kent-Eisenberg or a Lee-Mather approach for the amine and amine blends.

3.1.2 CO_2SIM:

CO_2SIM is a software package developed by NTNU and SINTEF. The simulator is for absorption processes and follows a rate based approach (Tobiesen et. al., 2012). It is limited to a fewer number of packing materials and for this study the Flexi Pack 700 had to be substituted with another packing with a constant active interfacial area. For the IMTP 50 packing, the correlations developed in CASTOR Project (Dugas et al., 2009) are used.

3.1.3 Pro Max:

Pro Max is a commercial process simulator developed by Bryan Research & Engineering. The software has the capability to design and optimize chemical and refining processes. It is combined with Microsoft Visio® for user friendly interface (Burr and Lyddon, 2008). The software is updated with more than 50 thermodynamic packages (e.g., Electrolytic-ELR and NRTL).

3.1.4 CHEMASIM:

A process model of the CO_2 absorption in MEA solution is implemented in a simulator, CHEMASIM. CHEMASIM is a powerful tool for steady-state simulations of chemical processes and was developed by BASF SE. CHEMASIM contains a non-equilibrium absorber and desorber model based on the rigorous calculation of heat and mass transfer between gas and liquid phases taking into account the complete chemical reaction system. (Luo et al., 2009).

3.1.5 CHEMSEP

ChemSep was started in 1988 at the University of Technology, Delft in the Netherlands by Haket, Kooijman and Taylor (Kooijman and Taylor, 2006). ChemSep was designed with flexibility such as menu-driven, user-friendly interface with an integrated help system and an autopilot mode that allows the user through the data input phase. In 1991, the non-equilibrium model was added. In 2005, ChemSep became Cape-Open compliant and thus programmable inside flow-sheeting tools such as Aspen Plus (Aspentech), PRO/II (SimSci/Escor) and COCO (Amsterchem) (Burr and Lyddon, 2008).

3.1.6 Aspen HYSYS (ASPEN Tech)

AspenTech bought the program HYSYS from Hypro-Tech in 2002 and in 2006 the program name was changed to Aspen HYSYS. One of the advantages of using a process simulation program for calculations is that the available thermodynamic properties can be used. The older version of Aspen HYSYS had an Amines Property Package. Within the Amines Property Package, one of the two models, Kent-Eisenberg or Li-Mather, could be selected. A later version uses the acid gas package. The column models in Aspen PLUS are equilibrium based and can be specified with Murphree efficiencies on each stage. Aspen PLUS has an Electrolyte-NRTL (Non-Random-Two-Liquid) equilibrium model which is based on the model of Austgen et al. (1989).

3.1.6.1 Comparison between equilibrium and rate based models

The equilibrium models assume vapor-liquid equilibrium at each stage. The departure from equilibrium is accounted for by tray efficiency (tray columns) or the height equivalent of a theoretical plate (HETP, for packed columns). The rate based models assume that the vapor-liquid equilibrium occurs only at the interface and use the Maxwell-Stefan equation to describe the mass transfer between the vapor phase and the liquid phase. Lee and Dudukovic (1998) compared an equilibrium model with a rate-based model for a tray reactive distillation column and concluded that the rate-based model is preferred because the Murphree tray efficiency is difficult to predict. However, no experimental data was available to support their conclusion that rate based models should be preferred. Burr and Lyddon (2008) also compared an equilibrium model with a rate based model for reactive distillation and found that there are multiplicities in both the equilibrium model and the rate based model but that the “window” within which steady-state multiplicity is observed is much narrower with the rate based model.

3.1.6.1a Murphree efficiency

The principle of the definition of Murphree efficiency based on the gas phase mole fraction (y) for a tray column is shown in Figure 3.1. For a packed column, a tray in Figure 3.1 can represent a packing height section.

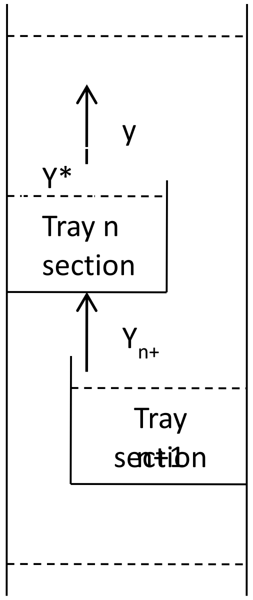

Figure 3.1: Illustration of Murphree efficiency, $E_M = (y-y_{n+1})/(y^*- y_{n+1})$, where y* is in equilibrium with the liquid on stage n

Using Murphree efficiency, E_M, is a simple way to make a more realistic description of the concentration and temperature profiles as a function of column height compared to only using ideal equilibrium stages. When specifying the Murphree efficiency in process simulation programs, it is assumed that the gas and liquid temperatures are equal at each stage. A Murphree efficiency, say for example 0.25, can be specified for every stage which is equivalent to an order of magnitude 1 to 2 m of packing height.

The equilibrium acid gas solubility and kinetic parameters for the aqueous alkanolamine solution in contact with H_2S and CO_2 are incorporated in the property package. The property package is fitted to experimental data. Equilibrium solubility limitations of amine property package are provided in Table 3.3.

Table 3.3: Equilibrium solubility limitations of the amine property package

Alkanolamine	Alkanolamine Concentrations (wt. %)	Acid Gas Partial Pressure (psia)	Temperature (°F)
MEA	0 – 30	0.00001 – 300	77 – 260
DEA	0 – 50	0.00001 – 300	77 – 260
TEA	0 – 50	0.00001 – 300	77 – 260
MDEA	0 – 50	0.00001 – 300	77 – 260
DGA	50 – 70	0.00001 – 300	77 – 260
DIPA	0 – 40	0.00001 – 300	77 – 260

3.1.6.2 Stage efficiency

The stage efficiency as defined under the Amines property package option is given by

$$\eta = \frac{(V_j + SV_j)Y_j - V_{j+1}Y_{ij+1}}{(V_j + SV_j)K_{ij}X_{ij} - V_{j+1}Y_{ij+1}}$$

where

η = *Stage efficiency*

i = *Component number*

j = *Stage number*

K = *Equilibrium ratio*

V = *Molar flow rate of vapor*

X = *Mole fraction in liquid phase*

Y = *Mole fraction in vapor phase*

The stage efficiency is a function of the kinetic rate constants for the reactions between each acid gas and the amine, the physicochemical properties of the amine solution, the pressure, temperature and the mechanical tray design variables such as tray diameter, weir height and weir length.

For vapor liquid equilibrium, the vapor phase is calculated using the Peng-Robinson (1976) method and the liquid phase is calculated using modified Kent-Eisenberg (1976) calculation. For single amine-H_2S-CO_2-H_2O system, the following reactions are considered:

$$Amine^+ <=> Amine + H^+$$

$$H_2S <=> HS^+ + H^+$$

$$CO_2 + H_2O <=> HCO_3^- + H^+$$

$$H_2O <=> OH^- + H^+$$

$$HCO_3^- <=> CO_3^- + H^+$$

$$HS^- <=> S^- + H^+$$

The equilibrium constant, K, is expressed by

$$K = \pi_i (x_i y_i)^{\beta i}$$

The equilibrium constant is expressed as a function of temperature as

$$lnK = C_1 + \frac{C_2}{T} + C_3 lnT + C_4 T$$

3.1.6.3 Rate based modeling

Rate based distillation calculations directly account for the mass and heat transfer rate phenomena and multi component interactions are considered. The mathematical model for the rate based calculation consists of material balance, energy balance, mass transfer, energy transfer and phase equilibrium equations. The Equilibrium model assumes that phase and thermal equilibria are achieved between the liquid and vapor streams leaving a stage. The Rate based model assumes that phase and thermal equilibria are achieved in the V-L interface while there are transfer resistances in the vapor and liquid films. The Equilibrium model uses an apparent composition approach which assumes that the liquid phase is in chemical (molecular and ionic) equilibrium. The Rate based model uses a true composition approach and accounts for equilibrium reactions and rate limiting kinetic reactions directly. The main features of rate based modeling are listed below:

i. The resistance to mass and heat transfer is concentrated in two thin films (two-film theory)

ii. Phase and thermal equilibria are achieved only at the interfaces between the liquid and vapor films

iii. The interface area and mass transfer coefficients are computed from column correlations that account for column type/geometry, operating conditions, and fluid properties. The heat transfer coefficient is computed using the Chilton-Colburn analogy from mass transfer coefficients

iv. The resistance films may be further divided/discretized into film regions to account for highly nonlinear profiles when fast reactions are present. This is often the case for acid-gas columns

v. The multi component Maxwell-Stefan relation is used to relate the driving force (composition differences and electrical potential difference) and diffusion fluxes for each film region

vi. Fourier’s law is used to relate the temperature difference to the energy flux for each film region

vii. The change of mass transfer fluxes due to reactions in the film regions are accounted for

viii. Separate material and energy balances are performed on liquid and vapor phases

The model is based on a stage (section of packing) as shown in the Figure 3.2.

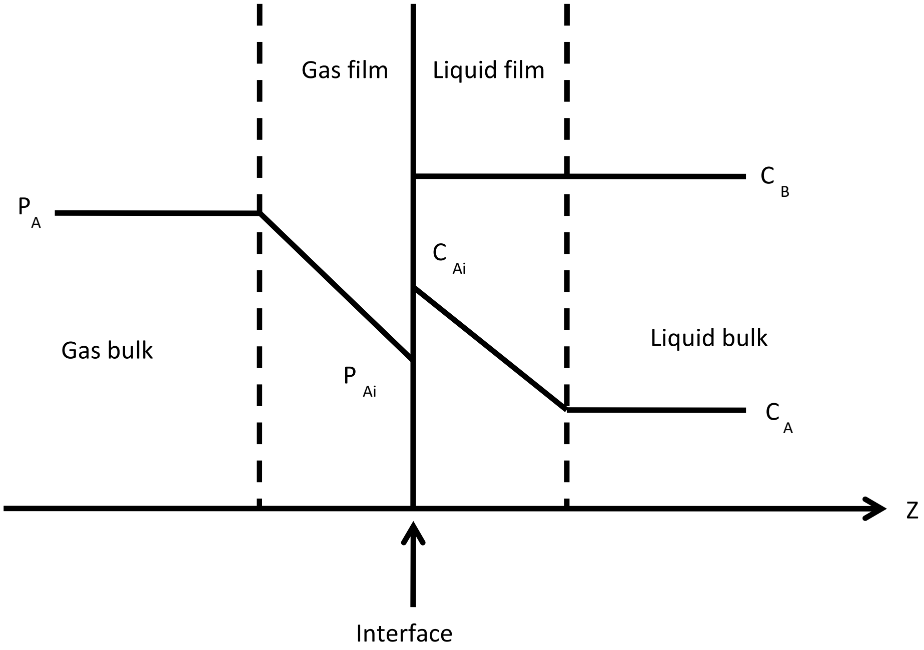

Figure 3.2: Two film theory at the gas/liquid interface

The Aspen rate based distillation uses a rigorous multi-component mass transfer theory (Krishna and Standart, 1976) with the binary mass transfer coefficients to evaluate multi component mass transfer coefficients and component mass transfer rates between vapor and liquid phases. The Chilton and Colburn method is normally used for heat transfer coefficients. The Hanley-Chen (2012) correlation predicts mass transfer coefficients and interfacial area for Pall rings. The mathematical model is based on a stage (section of packing) as shown in the diagram in Figure 3.3. In the equations and variables, subscript, j, refers to the stage number. Stages are numbered from the top down.

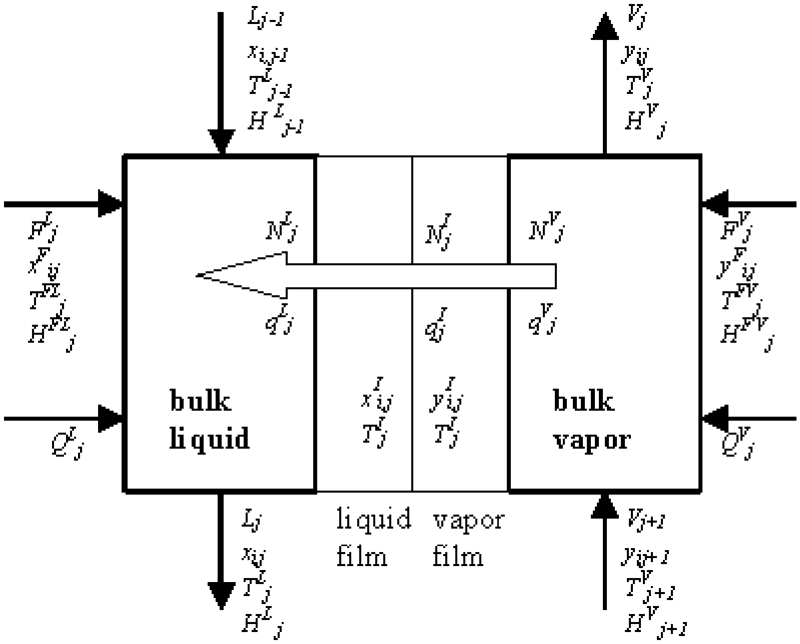

Figure 3.3: Mathematical representation of a stage

Material balance for bulk liquid

$$\boldsymbol{F_j^L\, x_y^F + L_{j-1}x_{ij-1} + N_{ij}^L + r_{ij}^L - L_j x_y = 0}$$

Material balance for bulk vapor

$$\boldsymbol{F_j^V y_{ij}^F + V_{j+1 y_{ij+1}} - N_{ij}^V + r_{ij}^V - V_{j\, y_{ij}} = 0}$$

Material balance for liquid film

$$\boldsymbol{N_{ij}^I + r_{ij}^{fL} - N_{ij}^L = 0}$$

Material balance for vapor film

$$\boldsymbol{N_{ij}^V + r_{ij}^{fV} - N_{ij}^I = 0}$$

Energy balance for bulk liquid

$$F_j^L H_j^{FL} + L_{j-1} H_{j-1}^L + Q_j^L + q_j^L - L_j H_j^L = 0$$

Energy balance for bulk vapor

$$F_j^V H_j^{FV} + V_{j+1} H_{j+1}^V + Q_j^V - q_j^V - V_j H_j^V = 0$$

Energy balance for liquid film

$$q_j^I - q_j^L = 0$$

Energy balance for vapor film

$$q_j^V - q_j^I = 0$$

Phase equilibrium at the interface

$$y_{ij}^I - K_{ij} x_{ij}^I = 0$$

Here:

F	Feed molar flow rate [kmol/s]
x	Bulk liquid mole fraction
y	Bulk vapor mole fraction

Superscripts:

F	Feed
f	Film
L	Liquid
V	Vapor
I	Interface

Subscripts

q	*Heat transfer rate*
r	*Reaction rate*
i	*Component*
j	*Stage*

k	*Component*
n	*Last component*
V	*Vapor*
a	*Interfacial unit area*
ai	*Interfacial area for mass transfer*
F	Feed molar flow rate
H	Enthalpy
Z	Average flow path length
N	Mass transfer rate
V	Vapor molar flow rate
T	Temperature

3.1.6.3 Onda et al. (1968) correlation to calculate mass transfer coefficients

$$K_{i,k}^{L} = 0.0051(Re_L')^{0.667} Sc_{L,i,k}^{-0.5} (a_p d_p)^{0.4} \left[\frac{\mu^L g}{\rho_t^L}\right]^{0.333}$$

$$k_{i,k}^{L} = \begin{cases} 2.00 Re_V^{0.7} Sc_{V,i,k}^{0.333} a_p\, D_{i,k}^{V} (a_p d_p)^{-2} & for\ d_p < 0.015\, m \\ 5.23 Re_V^{0.7} Sc_{V,i,k}^{0.333} a_p\, D_{i,k}^{V} (a_p d_p)^{-2} & for\ d_p > 0.015\, m \end{cases}$$

$$a^I = a_w A_t h_p$$

$$a_w = a_p[1 - exp(-1.45(\tfrac{\sigma_c}{\sigma})^{0.75} Re^{0.75} Fr_L^{-0.05} We_L^{0.2})]$$

Variable	Description	Units	Method
$k_{i,k}^{L}$	Binary mass transfer coefficient for liquid	m/s	$0.0051(Re_L')^{0.667} Sc_{L,i,k}^{-0.5} (a_p d)_p^{\ 0.4} \left[\frac{\mu^L g}{\rho_t^L}\right]^{0.333}$
$k_{i,k}^{L}$	Binary mass transfer coefficient for	m/s	$2.00 Re_V^{0.7} Sc_{V,i,k}^{0.333} a_p\, D_{i,k}^{V} (a_p d_p)^{-2}$

	vapor		
a^I	Total interfacial area for mass transfer	m^2	$a_w A_t h_p$
a_w	Wetted surface area per unit volume of the column	m^2	$a_p[1 - exp(-1.45(\frac{\sigma_c}{\sigma})^{0.75} Re^{0.75} Fr_L^{-0.05} We_L^{0.2})]$
F_{rI}	Froude number for the liquid		$\frac{a_p (u_s^L)^2}{g}$
Re_L, Re_V	Reynolds number for liquid, vapor		$\frac{\rho_t^L u_s^L}{\mu^L a_p}, \frac{\rho_t^V u_s^V}{\mu^V a_p}$
A_t	Cross sectional area of column	m^2	-
$a_{p.}$	Specific area of packing	m^2	-

In the Aspen rate-based distillation, the full set of equations is solved using Newton's method, using the solution from the equilibrium-based model as the initial guess.

3.2 Summary

From the above review, it is understood that there are different methods adopted for modeling of the LPG amine absorption process. The methods used in various simulators have been analyzed. A systematic comparison between the HYSYS amine package and the acid gas package has been carried out and the significance of model selection is provided. From the state of art review of the literature, it is concluded that the acid gas package is most suitable for the LPG amine absorption process.

Chapter 4

4.1 Refinery configuration

The model was made for the industrial LPG amine absorber in a refinery having crude, condensate and RFCC complex. The typical refinery configuration is provided in Figure 4.1.

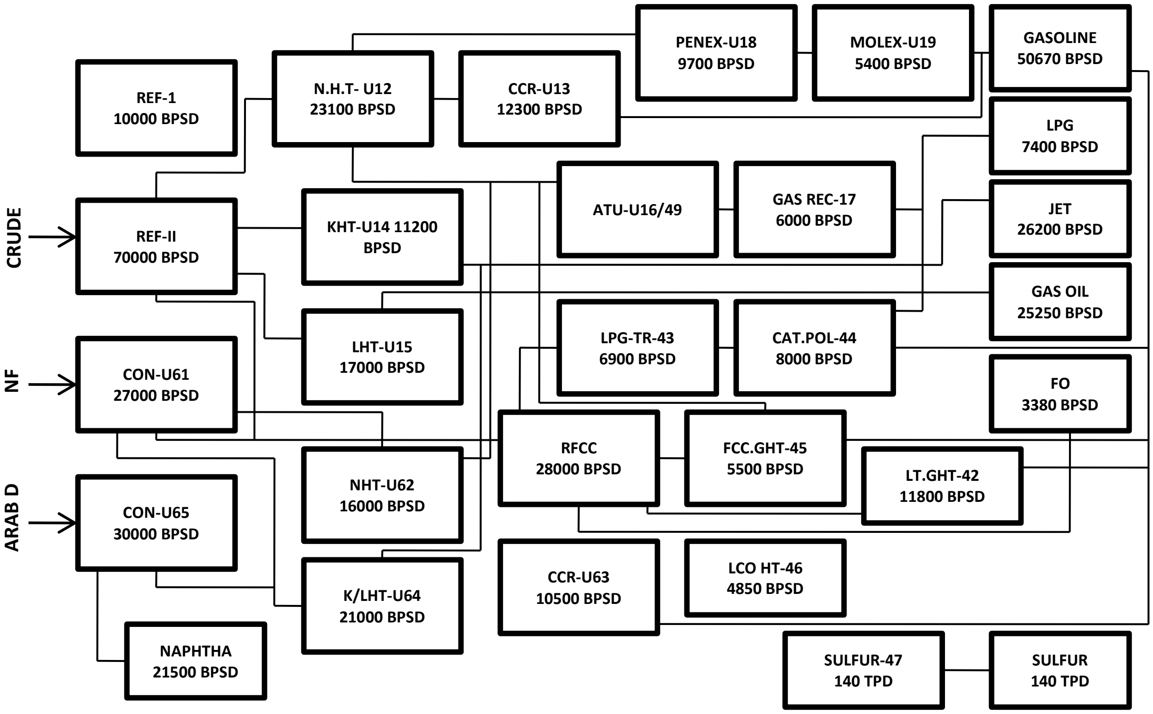

Figure 4.1: Overall refinery configuration

The overall refinery configuration is divided into three sections – the crude section, condensate section and the RFCC complex. In addition to the above common facilities such as gas processing, sulfur complex, treating units, oil movement and utility units are also present. The refining capacity of the crude section is 80,000 BPSD and of the condensate complex is 57,000 BPSD.

The crude section consists of crude distillation, platforming, hydrotreating, penex and molex units. The condensate section consists of condensate distillation, CCR and hydrotreating units. The RFCC complex consists of RFCC, hydrotreating units and catalytic polymerization units. LPG, gasoline, gas oil, naphtha, JET, FO and sulfur are the major products produced.

4.2 Process description of the LPG amine absorber

The process flow diagram for a typical LPG amine treatment process is shown in Figure 4.2. The sour LPG streams from a naphtha hydrotreater, debutanizer overhead liquid and the LPG recovery section in the gasoline hydrotreater in the FCC unit and naphtha hydrotreater in the crude unit are *mixed* and fed at the bottom of the packed bed absorber. The MEA solvent is used to extract CO_2 and H_2S. Pure MEA is not recommended due to its high corrosiveness in presence of acid gas and the cost. A solution of MEA in water is used as solvent, instead. The solvent, i.e., MEA-water mixture, is passed through a cooler and fed at the top of the absorber. The flow rate of the lean amine-water mixture coming down the absorber is controlled using a flow controller. The treated LPG, i.e., the sweet LPG, exits from the top of the absorber. The MEA carried-over at the top is recovered from the sweet gas through an amine separator drum. The product LPG is treated in a caustic wash drum to remove residual sulfur compounds. After this, the sweet LPG is water-washed to remove carried-over caustic and then filtered in an LPG coalescing unit. The treated LPG is stored in LPG spheres and dispatched for marketing.

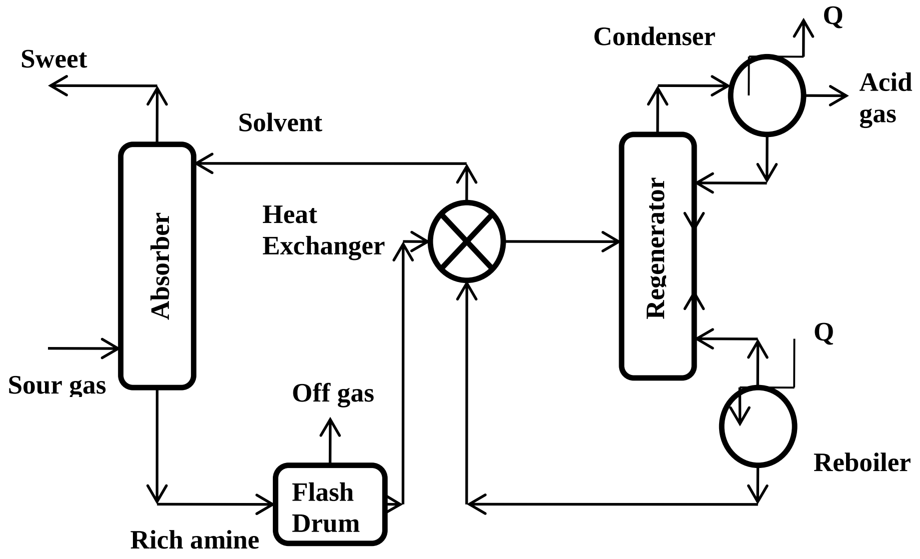

Figure 4.2: Flow sheet for a typical LPG sweetening process

The quality of the sweet LPG is tested for sulfur using a copper strip corrosion test, Doctor Test (ASTM D 4952-02). It involves immersion of a polished copper strip in the LPG stream at 37.8 ºC for 1 hour, and then comparison of its appearance with a set of commercial standards prepared as per ASTM procedure. The lean amine concentration (wt. %) is analyzed as per the UOP 825-02 test method and the H_2S concentration (ppm) analyzed as per the UOP 827-81 (2002) standard.

4.2.1 Process monitoring and control system

The temperature and pressure of the sour LPG is monitored and recorded through respective field indicators and transmitters and the flow is controlled through an FICV flow controller. The absorber level is controlled through a level indicator and controller (LIC) and the LIC is cascaded to the flow controller of the rich amine. By this, the solvent level in the packed bed is maintained by the rich amine flow. The rich amine temperature and pressure are monitored and recorded. The pressure drop across the column is recorded through a differential pressure indicator. The column pressure is maintained through a pressure indicator and controller (PIC) installed at the treated LPG line going to the storage. The treated

LPG temperature and flow are recorded through respective transmitters. Separate level indicators and transmitters are installed at the separator, caustic and water wash drum. The lean amine make-up to the column is monitored and recorded through a flow indicator and controller (FIC). The lean amine temperature and pressure are monitored and recorded through transmitters. Process alarms are provided for the column level, feed temperature, column pressure and pressure drop. Level alarms are provided for the separator drum, the caustic and the water wash drums.

All the indicators, transmitters and controllers are configured in a DCS (distributed control system). The history of the DCS process parameters are collected in the refinery information system and used for operation analysis, optimization, trouble shooting, reliability analysis and condition monitoring.

4.3 Plant data collection

4.3.1 The composition of the sour LPG is analyzed regularly and the details of the analysis are given in Table 4.1.

Table 4.1: Sour LPG composition (vol. %)

Parameter	**Sample-1**	**Sample-2**	**Sample-3**	**Sample-4**	**Sample-5**	**Sample-6**
H_2S	0.78	1.16	1.07	0.67	2.14	1.02
C_1	0.58	0.46	0.44	0.35	4.05	0.33
C_2	7.68	7.17	6.78	8.25	20.39	7.77
C_3	26.66	25.66	25.61	34.11	34.99	37.39
IC_4	13.39	15.39	15.69	20.46	18.82	28.61
NC_4	50.46	49.04	49.38	33.1	17.88	20.67
IC_5	0.45	0.92	0.86	2.53	1.33	3.54
NC_5	< 0.1	0.2	0.17	0.53	0.4	0.67
T. Olefins	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1

Parameter	**Sample-7**	**Sample-8**	**Sample-9**	**Sample-10**	**Sample-11**	**Sample-12**
H_2S	0.43	1.13	1.34	1.58	1.96	0.66
C_1	0.44	0.53	0.77	0.42	0.4	1.22
C_2	5.67	4.12	5.16	8.13	6.83	9.42
C_3	31.45	19.12	20.81	35.06	28.77	42.6
IC_4	25.63	16.59	11.8	25.22	22.14	21.32
NC_4	31.8	54.35	58.23	28.34	38.21	23.36
IC_5	4.02	3.5	1.6	0.95	1.39	1.11
NC_5	0.56	0.66	0.29	0.29	0.3	0.31
T. Olefins	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10

4.3.2 H_2S and copper corrosion tests on the sweet LPG

The H_2S and copper corrosion tests are conducted on the sweet LPG and the details of the analysis are tabulated in Table 4.2. The absorber process parameters used for model development in the current study are provided in Table 4.3.

Table 4.2: Sweet LPG analysis (Industrial Values)

Parameter	**Sample-1**	**Sample-2**	**Sample-3**	**Sample-4**	**Sample-5**	**Sample-6**
H_2S (ppm)	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Doctor Test	IA*	IA	IA	IA	IA	IA
Parameter	**Sample-7**	**Sample-8**	**Sample-9**	**Sample-10**	**Sample-11**	**Sample-12**
H_2S (ppm)	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Doctor Test	IA	IA	IA	IA	IA	IA

1A: ASTM D 130 corrosion color match scale.

The process parameters of the LPG absorber are given in Table 4.3.

Table 4.3: Absorber process parameters (daily average)

Parameter	**Sample-1**	**Sample-2**	**Sample-3**	**Sample-4**	**Sample-5**	**Sample-6**
Sour LPG flow, m^3/h	7.89	6.801	3.643	3.511	2.301	2.248
Lean amine flow, m^3/h	6.927	6.366	5.794	6.226	6.905	7.251
Sour LPG Temperature, °C	26.650	27.691	25.602	31.632	38.080	37.056
Treated LPG Temperature, °C	40.201	41.786	39.054	42.778	43.450	43.019
Lean amine Temp., °C	43.811	45.985	44.389	45.533	45.224	46.154
Absorber pressure, bar g	17.398	17.312	17.087	17.131	17.218	17.094
Lean amine concentration, wt. %	16	15.4	15.8	17.0	14.9	14.63
Lean amine H_2S, ppm	1309	1183	1325	1281	1125	1348
Rich amine conc.[*1]	15.3	14.9	15	16.6	14.6	14.07
Rich amine loading[*1]	0.26	0.24	0.28	0.21	0.23	0.27

Parameter	**Sample-7**	**Sample-8**	**Sample-9**	**Sample-10**	**Sample-11**	**Sample-12**
Sour LPG flow, m^3/h	2.767	3.776	NA	NA	3.723	3.534
Lean amine, flow, m^3/h	7.30	7.40	7.25	6.54	6.177	6.315
Sour LPG Temp., °C	23.27	35.69	38.583	37.694	34.983	31.285
Treated LPG Temp., °C	40.84	45.193	43.708	43.160	41.834	40.465
Lean amine Temp., °C	46.547	46.091	44.105	43.827	42.970	43.289
Absorber pressure, bar g	17.127	17.208	17.266	17.0	17.119	17.106
Lean amine conc., wt. %	15.7	16.5	16.4	15.4	16.65	15.96
Lean amine H_2S, ppm	964	1074	1976	1460	1134	1132
Rich amine conc.^{*1}	15.2	15.4	15.3	14.7	16.9	15.07
Rich amine loading^{*1}	0.26	0.28	0.23	0.24	0.19	0.26

^{*1} Common stream from all absorbers

4.4 Development of the simulation model

A steady state flow sheet model is developed in HYSYS. The stream properties are provided in Table 4.4 and the snapshot of the flow sheet of the unit simulated is provided in Figure 4.3.

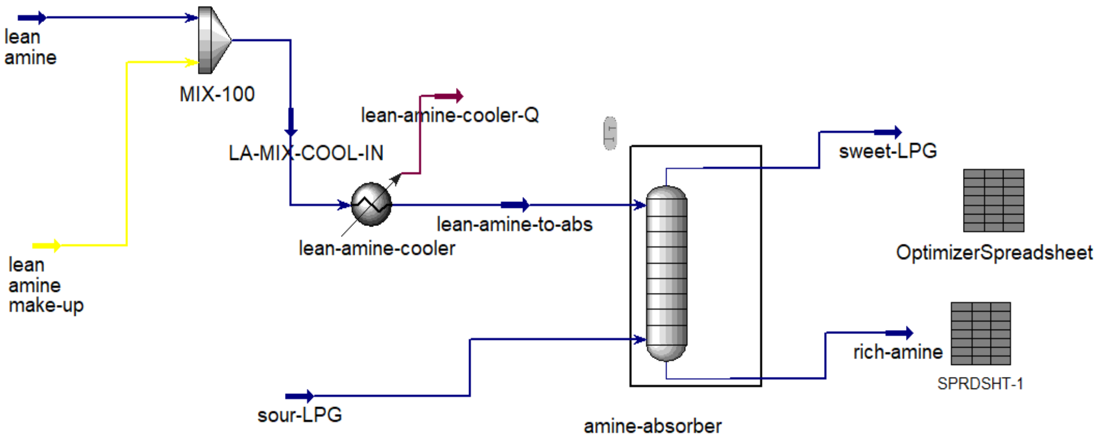

Figure 4.3: Snapshot of the flow sheet model

Table 4.4 Properties of the feed and product streams

	Stream	**Notation**	**Notation**	**Units**
1	Lean amine	Flow	L_1	kmol/hr
2		Pressure	P_1	bar g
3		Temperature	T_{L1}	° C
4		Concentration	$X_{A,1}$	wt. %
5		H_2S loading	$C_{A,L1}$	mol/mol
6		CO_2 loading	$C_{B,L2}$	mol/mol
7	Rich amine	Flow	L_2	kmol/hr
8		Pressure	P_2	bar g
9		Temperature	T_{L2}	°C

10		Concentration	$X_{A,2}$	wt. %
11		H_2S loading	$C_{A,L2}$	mol/mol
12		CO_2 loading	$C_{B,L2}$	mol/mol
13	Sweet LPG	Flow	G_1	kmol/hr
14		Pressure	P_1	bar g
15		Temperature	T_{G1}	°C
16		H_2S content	Y_{A1}	kmol/hr
17		CO_2 content	Y_{B1}	kmol/hr
18	Sour LPG	Flow	G_2	kmol/hr
19		Pressure	P_2	bar g
20		Temperature	T_{G2}	°C
21		H_2S content	Y_{A2}	kmol/hr
22		CO_2 content	Y_{B2}	kmol/hr

The block diagram and the information of the typical input [on a particular (Reference) day] and results from Aspen HYSIS^{TM} for the output streams are shown in Figure 4.4. The amine absorber (AA) is a packed column of height, Z_{max}, filled with metal Pall rings of an appropriate size (these details are not revealed for proprietary reasons, as the data has been obtained from an industrial absorber). The lean amine stream enters at the top, labeled as point 2, and exits at the bottom of the column, labeled as point 1. The sour LPG enters at the bottom of the column and exits at the top. The properties and compositions of the input and output streams are shown in Tables 4.5 and 4.6.

Table 4.5: Input stream properties and compositions on a particular day (Reference)

Lean Amine			
Parameters	**Value**	**Parameters**	**Value**
Temperature, T_{L2}	45 °C	Mavg, Lean-	19.8604
Pressure, P_2	18.165 bar abs	MEA, W_2	13.1 wt. %
Volumetric flow	6.726 m^3/h	H2O, ~ (1- W_2)	86.78 wt. %
Molar flow, L_2	338.69 kmol/h		
H_2S molar flow, X_A,L_2	0.2355 kmol/h		
H_2S, ppm (wt. / wt.)	1193		
Sour LPG			
Parameters	**Value**	**Parameters**	**Value**
Temperature, T_{G1}	29.6 °C	M_{avg}, Sour-LPG	51.77 kg/kmol
Pressure, P_1	18.565 bar abs	Methane	0.22 vol. %
Volumetric flow	3.86 m^3/h	Ethane	6.7 vol. %
Molar flow, G_1	40.389 kmol/h	Propane	35.73 vol. %
H_2S molar flow, Y_A,G_1	0.25 kmol/h	*n*-butane	23.46 vol. %
H_2S (vol. /vol.)	0.62 vol. %	*i*-butane	27.67 vol. %
H_2S, ppm	6200	*n*-pentane	1.2 vol. %
		i-pentane	4.4 vol. %
		Propene	0.1 vol. %

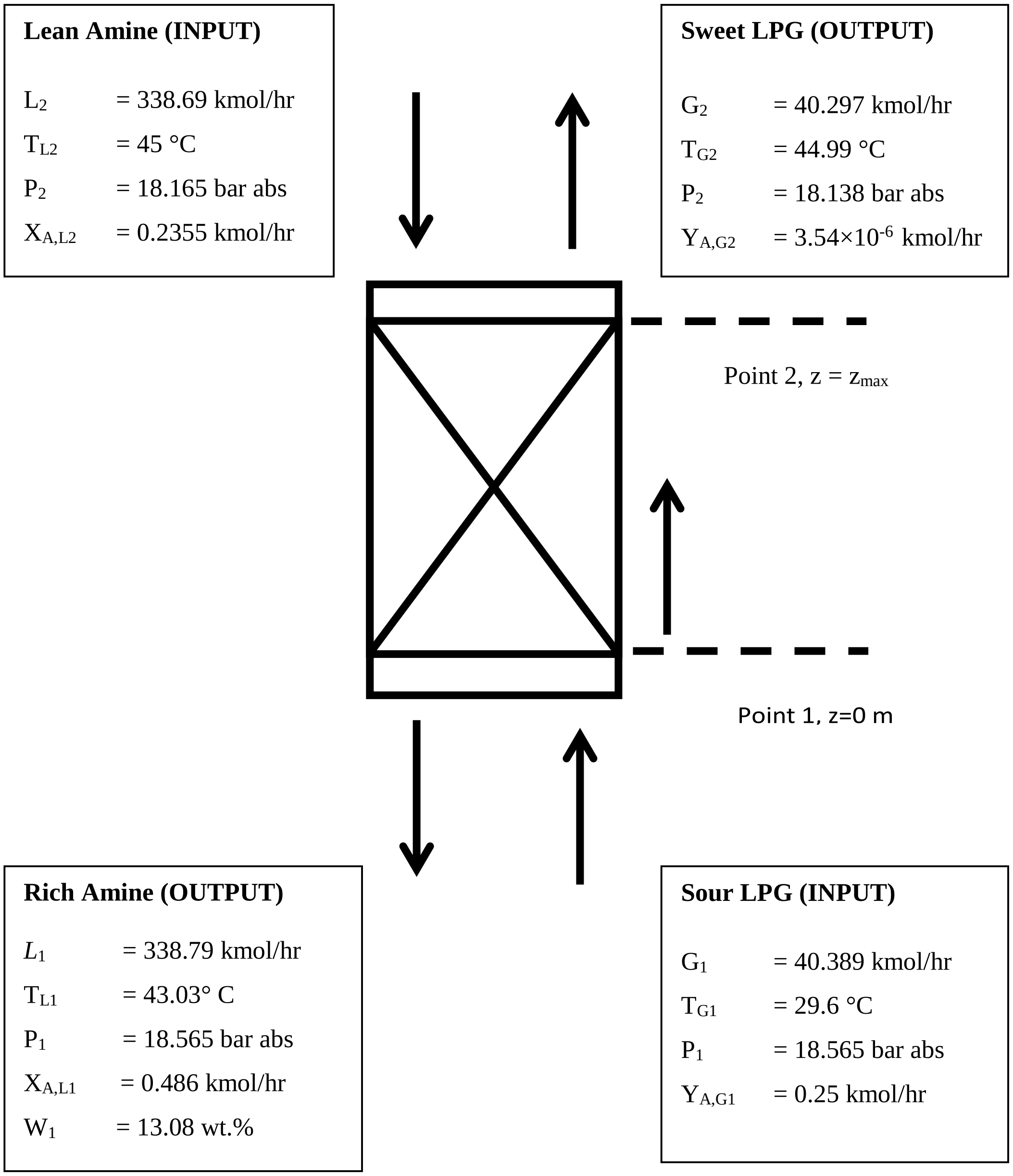

Figure 4.4: Typical (Reference) input on a particular day, and results of the output streams from Aspen HYSIS™

Table 4.6: Properties and compositions of the output streams (Reference)

Rich Amine			
Parameters	**Value from Aspen HYSIS™**	**Parameters**	**Value from Aspen HYSIS™**
Temperature, T_{L1}	43.03 °C	M_{avg},	19.8756 g/gmol
Pressure, P_1	18.565 bar abs	MEA, W_1	13.08 wt. %
Volumetric flow	6.692 m^3/h	H_2O, ~ (1- W_1)	86.63 wt. %
Molar flow, L_1	338.79 kmol/h		
H_2S molar flow, $X_{A,L1}$	0.486 kmol/h		
H_2S, ppm (wt./wt.)	2458.3		
Sweet LPG			
Parameters	**Value from Aspen HYSIS™**	**Parameters**	**Value from Aspen HYSIS™**
Temperature,@ T_{G2}	44.99 °C	M_{avg}, Sour-LPG	51.77g/gmol
Pressure,@ P_2	18.138 bar abs	Methane	0.22 vol. %
Volumetric flow	3.848 m^3/ h	Ethane	6.7 vol. %
Molar flow, G_2	40.297 kmol/h	Propane	35.63 vol. %
H_2S molar flow, $Y_{A,G2}$	3.54×10^{-6} kmol/h	*n*-butane	23.51 vol. %
H_2S	8.81×10^{-8} vol. %	*i*-butane	27.72 vol. %
H_2S, @ ppm (vol./vol.)	0.0881	*n*-pentane	1.2 vol. %
MEA	2.26×10^{-4} kmol/h	*i*-pentane	4.4 vol. %
		Propene	0.09 vol. %

The pressure of 18.165 bar and the temperature of 43 °C is observed industrial values. The industrial H_2S is < 0.3 ppm while the value from ASPEN (0.0881 ppm) is below the detection limit.

4.5 Profiles along the Absorber Column from Aspen HYSIS

The model (Aspen HYSIS^{TM})-generated profiles of some important parameters along the length, Z, of the column are provided here, to gain a deeper understanding of the amine absorption process. The temperatures of the liquid and vapor phases along the column height, i.e., T_{Liquid} (Z) and T_{Vapor} (Z), are plotted in Figure 4.5 (in a normalized manner).

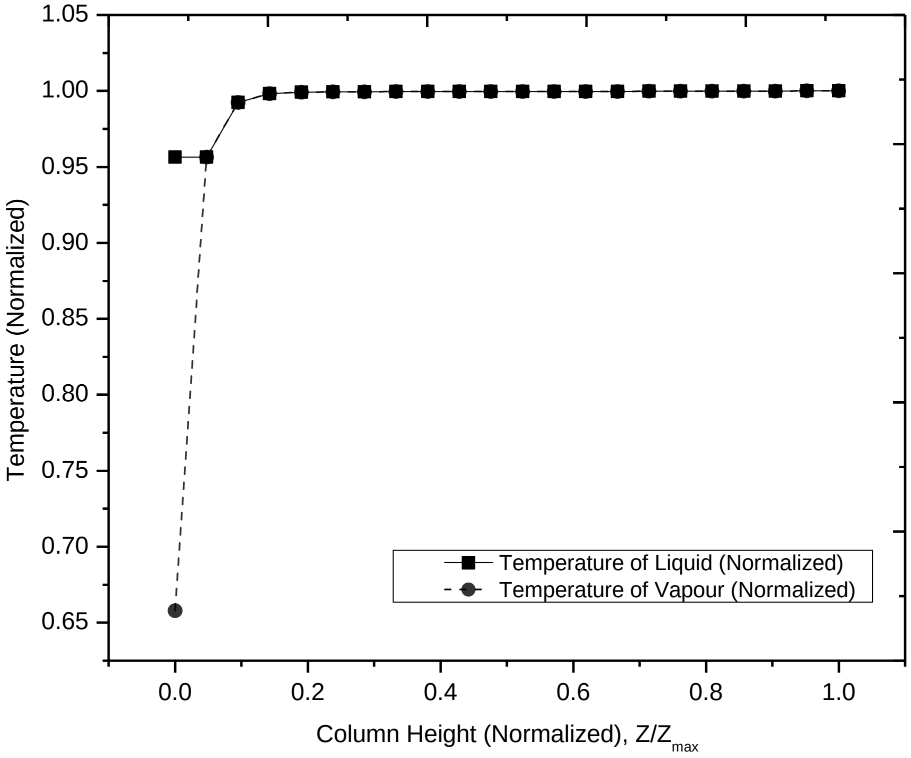

Figure 4.5: Normalized temperature profile of the liquid and vapor along the column.

The Aspen HYSIS™ simulation shows that the liquid temperature decreases slowly from the top of the column as the liquid flows down. There is a sudden jump in the temperature of the gas as it enters, from its inlet value of 29.6 °C to a value of 44.95 °C in the first two trays, indicating a fast reactive absorption associated with exothermic release of heat. As the gas keeps on picking up more and more H_2S, its temperature continues to increase, although more moderately. The decrease in temperature at the bottom of the tower is due to the entry of the colder gas at the bottom that contacts the warm liquid there.

The (normalized) pressure variation along the column is shown in Figure 4.6. It shows a gradual decrease along the column length.

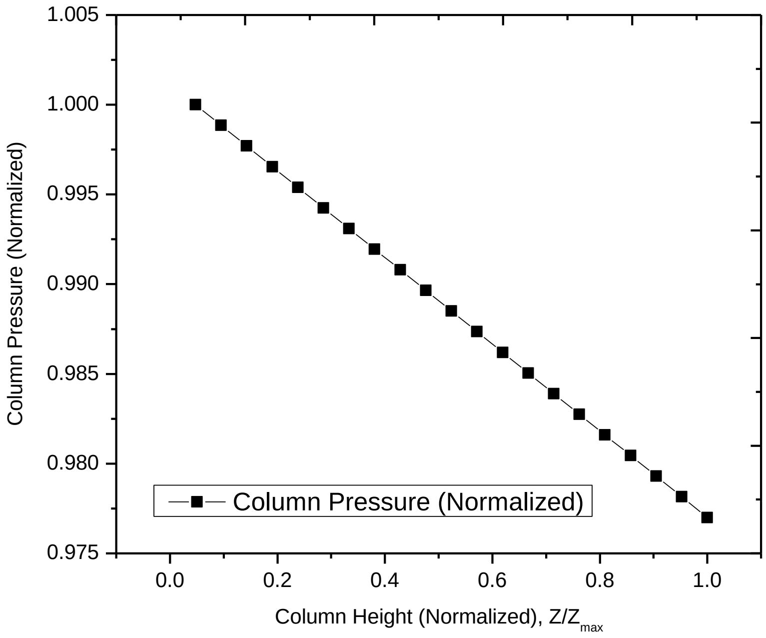

Figure 4.6: The (normalized) pressure profile along the column

The molar flow rates of H_2S in the vapor and liquid phases are shown in Figure 4.7. The mole fraction of H_2S in the LPG decreases with increasing Z, while that in the amine solution increases as the liquid goes down (decreasing Z). The H_2S concentration in the MEA solution shows a sudden increase near the bottom of the absorber, revealing almost instantaneous reaction with the solvent. However, in the gas phase, its concentration declines slowly with increase in the axial location of the absorber. The plots show that the bottom location of the absorber is very sensitive and suggests that sensors need to be located there. The liquid and vapor stream conditions at different values of z (from Aspen HYSIS) are provided in Table 4.7.

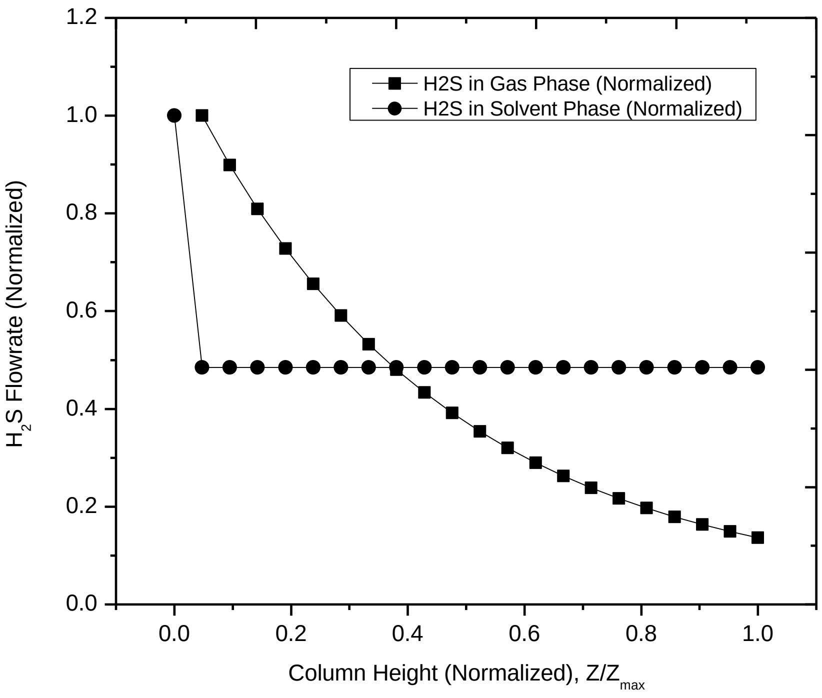

Figure 4.7: Normalized profiles of the molar flow rates of H_2S in the liquid [$X_{A,L}(Z)$] and vapor [$Y_{A,G}(Z)$] phases along the column

Table 4.7: Liquid and vapor stream conditions at different values of Z (from Aspen HYSIS) on the Reference day

Component	**Location, Z = 10.5 m LIQUID**	**Location, Z = 10.5 m VAPOR**	**Location, Z = 8.0 m LIQUID**	**Location, Z= 8.0 m VAPOR**	**Location, Z= 6.0 m LIQUID**	**Location, Z = 6.0 m VAPOR**
L,G, kmol/hr	338.69729	40.29709	338.7474	40.3474	338.7467	40.3466
T °C	45	45	44.987		44.981	
P, bar-abs	18.165	18.165	18.265		18.345	
H_2S (c_A), kmol H_2S/hr	0.23550	3.54E-06	0.23550	5.61E-06	0.235511	8.30E-06
CO_2 (c_B), kmol CO_2/hr	0.0000	0.0000	0.0000	0.0000	2.66E-04	8.88E-02
Methane	0.0000	8.85E-02	2.65E-04	8.88E-02	8.70E-03	2.705662
Ethane	0.0000	2.696975	8.66E-03	2.705623	3.87E-02	14.38899

Propane	0.0000	14.35037	3.85E-02	14.38882	1.29E-03	9.475373
n-butane	0.0000	9.474085	1.28E-03	9.475368	1.52E-03	11.17577
i-butane	0.0000	11.1742	1.51E-03	11.17577	3.45E-04	1.777138
n-pentane	0.0000	1.776793	3.44E-04	1.777136	9.42E-05	0.484674
i-pentane	0.0000	0.484579	9.38E-05	0.484673	6.23E-04	4.04E-02
Propene	0.0000	3.97E-02	6.21E-04	4.04E-02	0.00000	0.00000
Hydrogen	0.0000	0.00000	0.00000	0.00000	324.0335	0.2096
H_2O	324.0355	0.211490	324.0344	0.210562	14.42627	2.23E-04
MEA	14.426	2.25E-04	14.42627	2.24E-04		

Table 4.7: Liquid and vapor stream conditions at different values of Z (from Aspen HYSIS) on the Reference day …..continued

Component	**Location, Z = 4.0 m LIQUID**	**Location, Z = 4.0 m VAPOR**	**Location, Z = 2.0 m LIQUID**	**Location, Z = 2.0 m VAPOR**	**Location, Z = 0.0 m LIQUID**	**Location, Z = 0.0 m VAPOR**
L,G , kmol/hr	338.7461	40.3460	338.744	40.3453	338.7896	40.38943
T, °C	44.978		44.959		43.03	29.6
P, bar-abs	18.425		18.505		18.565	
H_2S (c_A)	0.235516	1.25E-05	0.23552	1.89E-5	0.485916	0.250414
Methane	2.67E04	8.88E-02	2.68E-04	8.89e-2	2.74E-04	8.89E-02
Ethane	8.74E-03	2.705701	8.78E-03	2.70574	9.11E-03	2.70609
Propane	3.89E-02	14.38916	3.90E-02	14.3893	4.03E-02	14.3907
n-butane	1.29E-03	9.475379	1.30E-03	9.47538	1.27E-03	9.47536
i-butane	1.53E-03	11.17578	1.53E-03	11.1757	1.50E-03	11.1757
n-pentane	3.47E-04	1.777139	3.48E-04	1.77714	3.41E-04	1.77713
i-pentane	9.46E-05	0.484674	9.50E-05	0.48467	9.32E-05	0.48467
Propene	6.26E-04	4.04E-02	6.29E-04	4.03E-2	6.50E-04	4.04E-02
Hydrogen	0.00000	0.00000	0.0000	0.000	0.00000	0.0000
H_2O	324.0326	0.208871	324.0311	0.2077	323.8240	0.0000
MEA (x_A)	14.4262	2.22E-04	14.4262	2.21E-4	14.42605	0.0000

The flow rates of MEA in the vapor are shown in Figure 4.8 and of MEA in the liquid is provided in Figure 4.9.

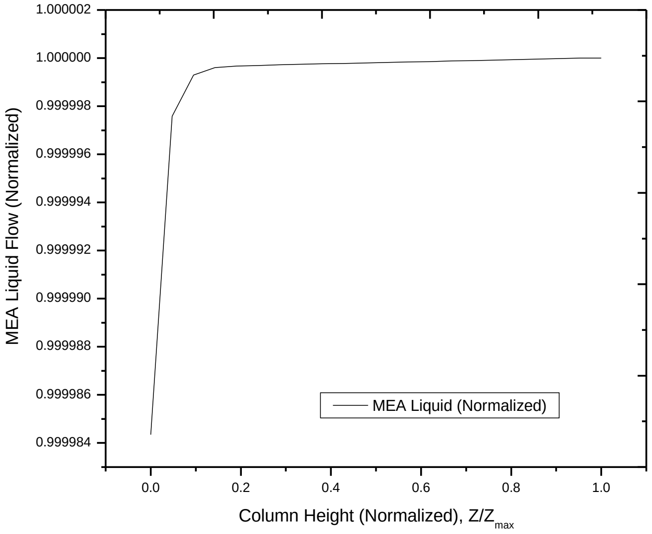

Figure 4.8: Flow rate of MEA in the liquid

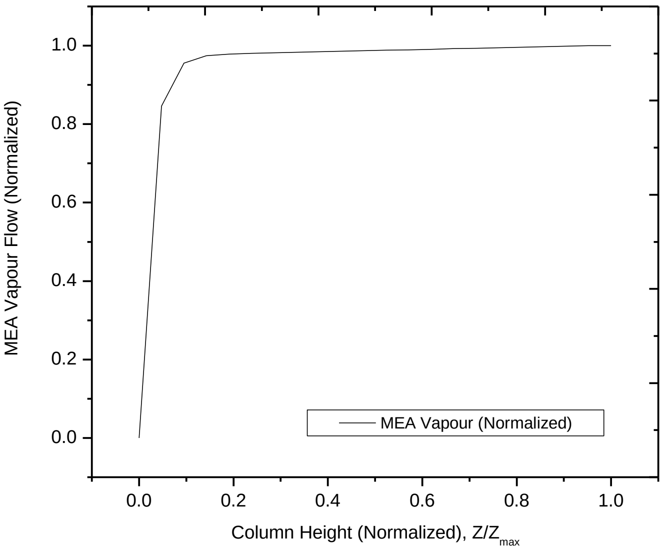

Figure 4.9: Flow rate of MEA in the vapor

The flow rates of hydrocarbon contents in the vapor and liquid streams are provided in Figures 4.10-4.23.

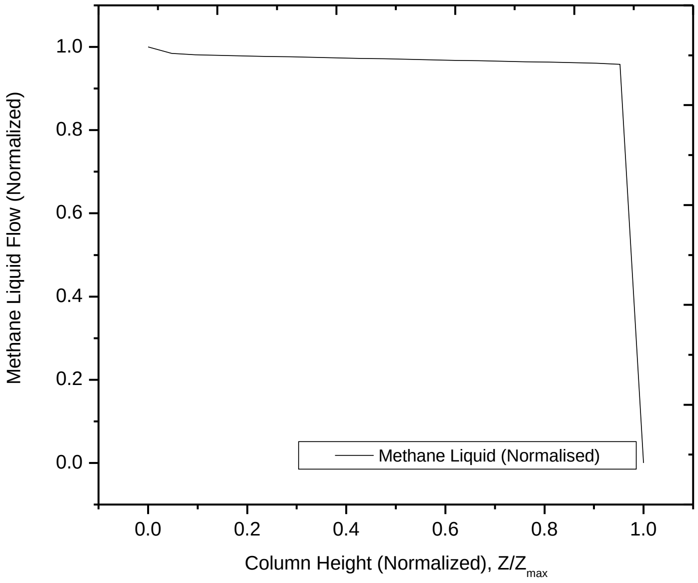

Figure 4.10: Flow rate of methane in the liquid

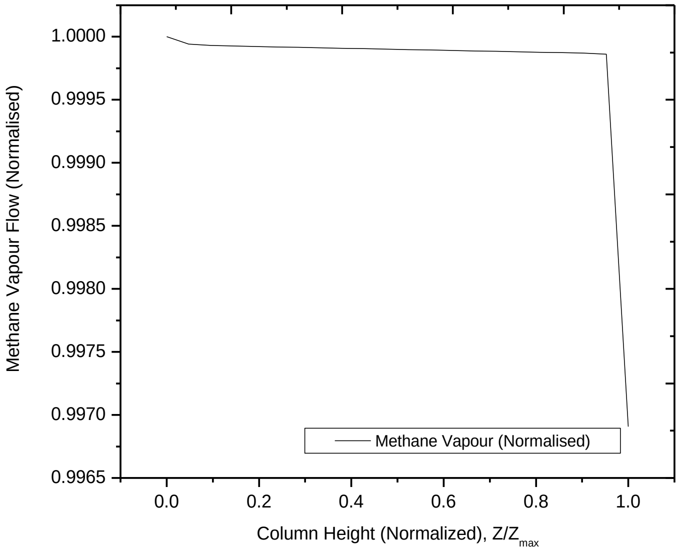

Figure 4.11: Flow rate of methane in the vapor

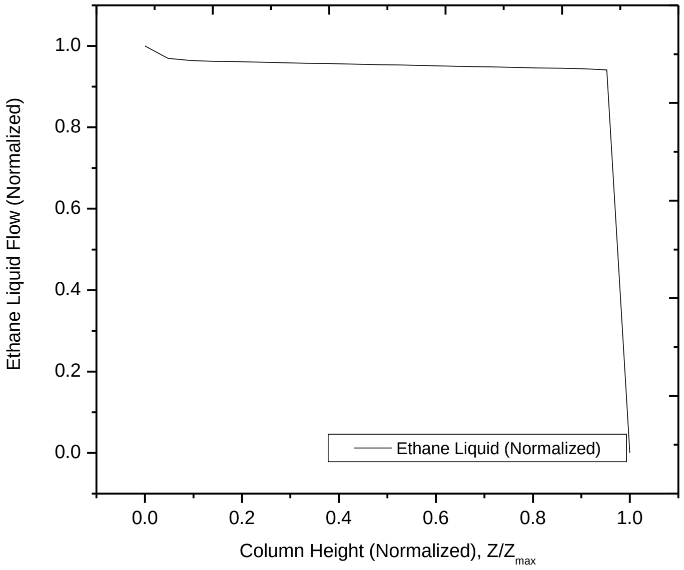

Figure 4.12: Flow rate of ethane in the liquid

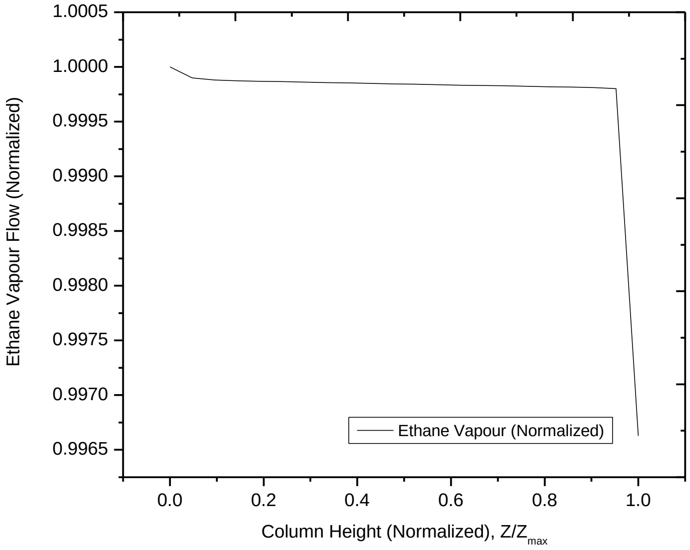

Figure 4.13: Flow rate of ethane in the vapor

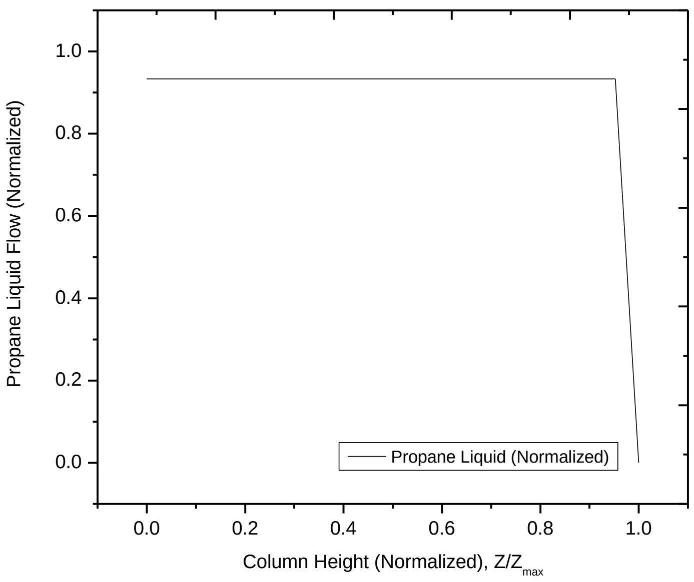

Figure 4.14: Flow rate of propane in the liquid

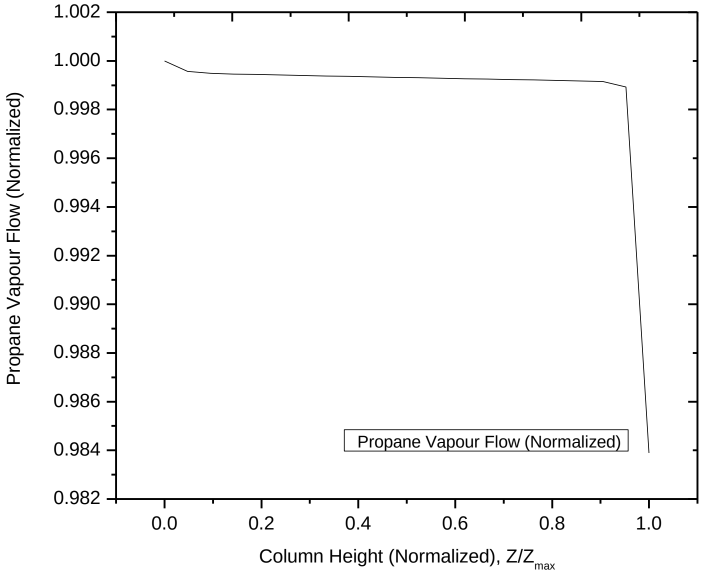

Figure 4.15: Flow rate of propane in the vapor

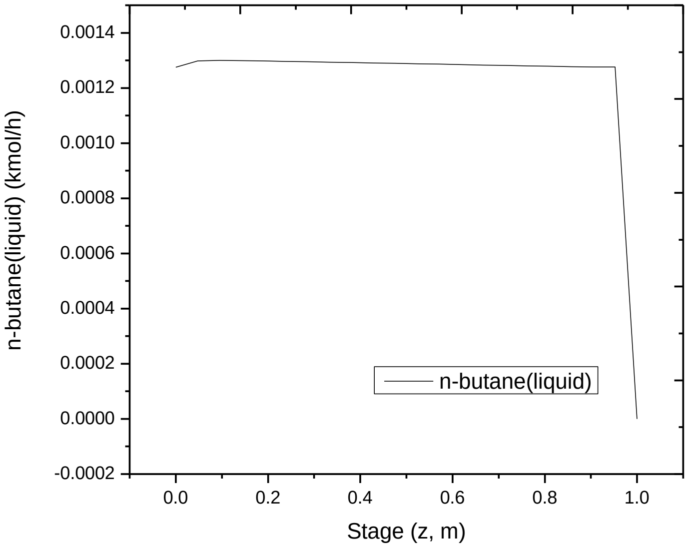

Figure 4.16: Flow rate of n-butane in the liquid

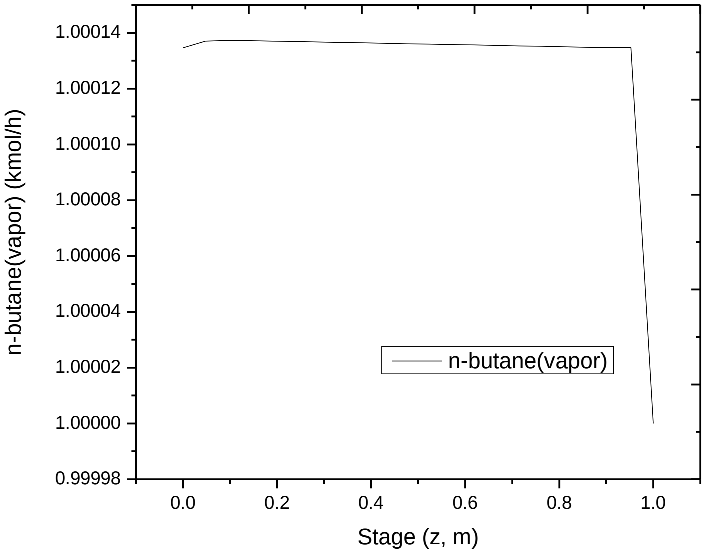

Figure 4.17: Flow rate of n-butane in the vapor

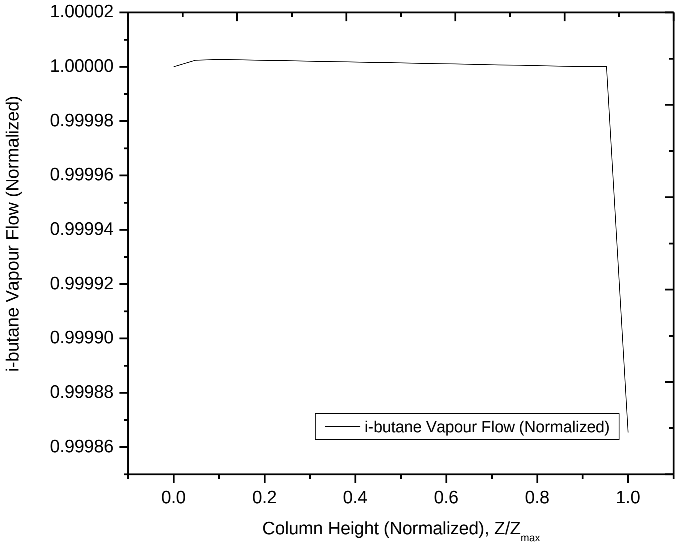

Figure 4.18: Flow rate of i-butane in the vapor

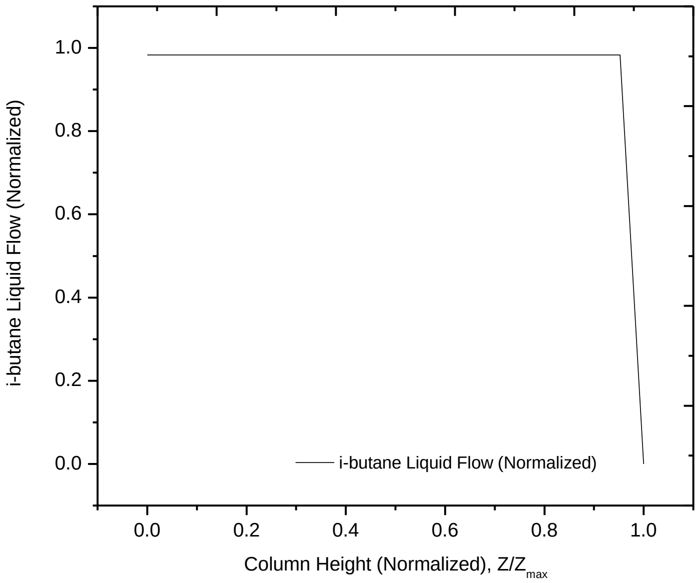

Figure 4.19: Flow rate of i-butane in the liquid

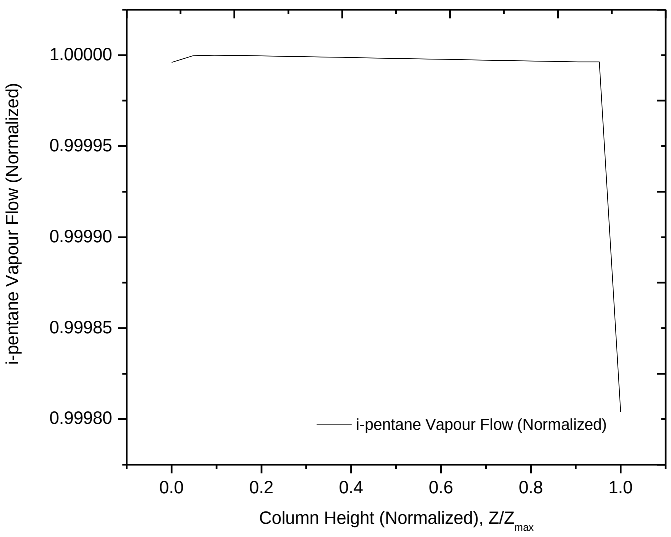

Figure 4.20: Flow rate of i-pentane in the vapor

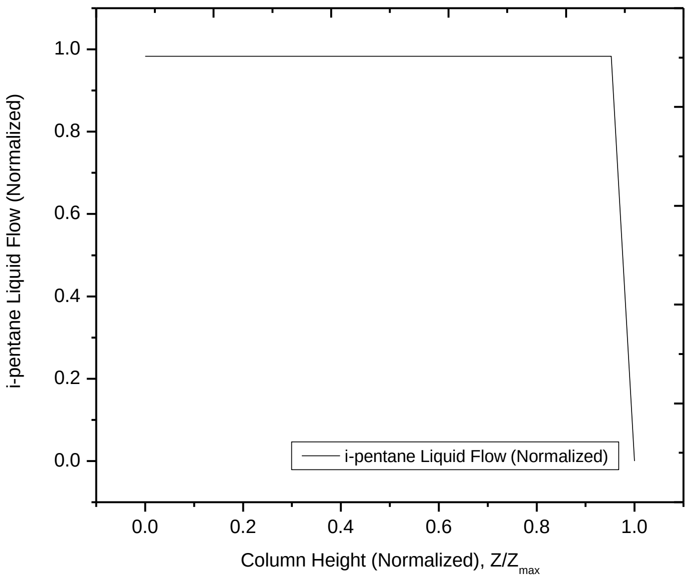

Figure 4.21: Flow rate of i-pentane in the liquid

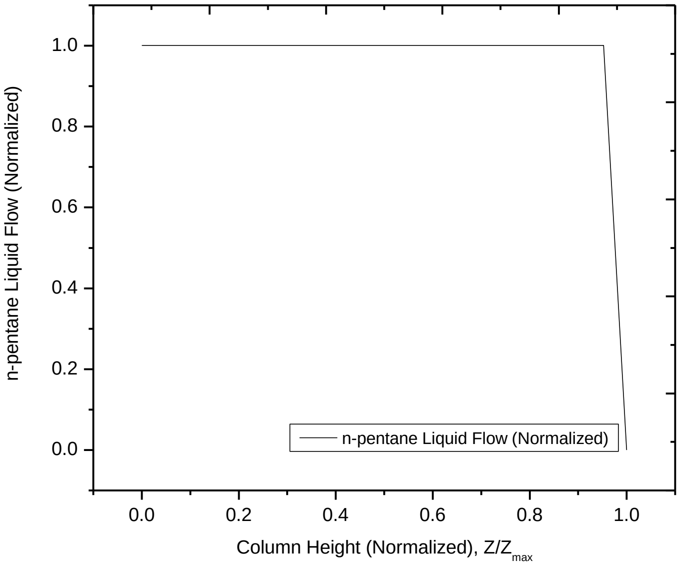

Figure 4.22: Flow rate of n-pentane in the liquid

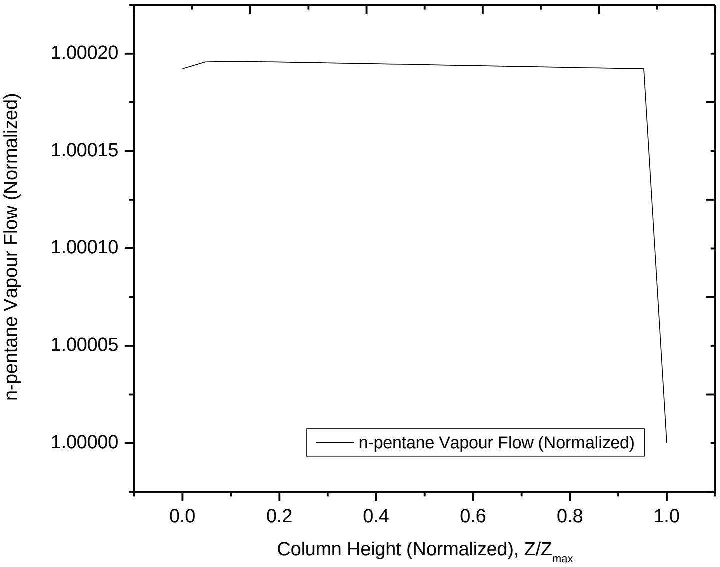

Figure 4.23: Flow rate of n-pentane in the vapor

4.6 Summary

In summary, the complexity of the refinery processes has been studied. The sources of sour LPG generation and LPG amine absorption process and operating conditions are explained. The actual operating and design data of the industrial LPG absorber are provided. The industrial and model output data, stream parameters, profiles of components across the bed are worked out. The sensitivity analysis of the model with key parameters has been done and model outputs are obtained in the next chapter.

Chapter 5

5.1 Sensitivity Analysis Using Aspen HYSIS

Some of the important operating conditions and their ranges are identified based on existing studies (Holmes et al., 1984; Zare and Mirazei, 2009) and actual industrial observations. This is done to study their influence on the operation of the absorber and, thus, pave the way for optimization studies. It is found that the lean amine temperature, column pressure, flow rate of the solvent, H_2O, H_2S and MEA compositions are the main operating conditions that affect the quality of the product. The usual range of H_2S is from 3.5 ppm for pipeline use to higher values for combustion purposes. The usual range of CO_2 is from 2% for pipeline use to lower values of about 100 ppm for LPG separation/purification systems.

5.2 Effect of solvent temperature on product quality

The column temperature plays an important role in controlling the absorption of CO_2. As the reaction of MEA with H_2S and CO_2 (in LPG) is kinetically controlled, an increase in the column temperature favors the reaction rate. However, the solubility of H_2S in the solvent (i.e., in the MEA-water mixture) above 45°C decreases, which finally decreases the absorption of H_2S, thereby over-riding the effect of high reaction rates. Figure 5.1 provides the effect of the solvent temperature on the H_2S content of the sweet LPG (temperature of the solvent is varied from 42°C to 47 °C; Reference value: 45 °C).

The model output at different solvent temperatures is provided in Table 5.1.

Table 5.1: Model outputs at different solvent temperatures

	Temperature of the lean amine stream, °C	Flow rate of H_2S in the sweet LPG stream, kmol/hr
MEA composition (at the top) = 13.1 wt. %	42	2.83×10^{-06}
	43	3.05×10^{-06}
	44	3.29×10^{-06}
	45 (Reference)	3.54×10^{-06}
	46	3.83×10^{-06}
	46	4.13×10^{-06}

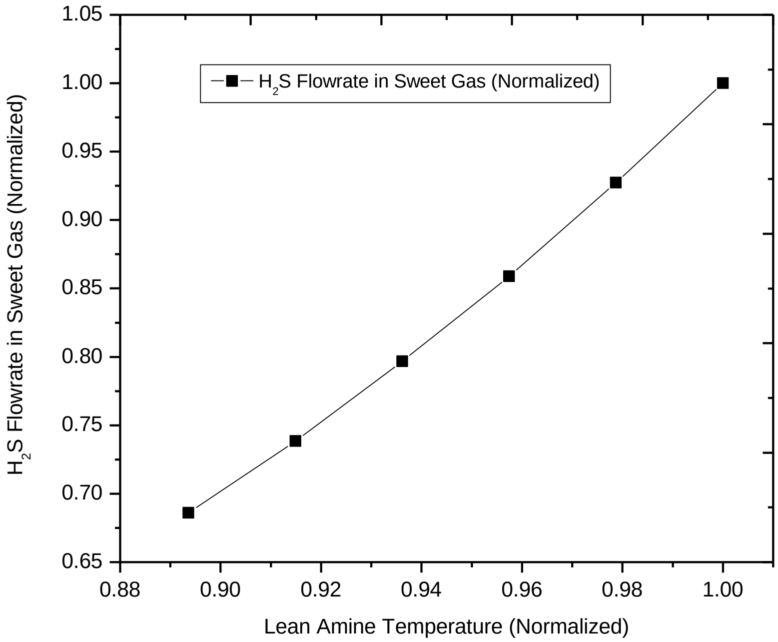

Figure 5.1: Effect of the temperature of the lean amine stream on the outlet value of H_2S

5.3 Effect of absorber pressure on the product quality

The absorber pressure is another important parameter and in the industrial absorber, it is controlled through the pressure of the sweet LPG stream, by a pressure controller situated at the top of the unit. The results of the simulation are shown in Table 5.2. The absorber pressure is varied from 18 bar abs. to 19 bar abs. The increase in the absorber pressure results in lower concentrations of H_2S in the sweet LPG stream and better absorption of H_2S in the rich amine stream. This may be attributed to a shift in the VLE. (Kim and Kim, 2004)

Table 5.2: Effect of the absorber pressure on the flow rate of H_2S

	Pressure at the top, bar abs	Flow rate of H_2S in the sweet LPG, kmol/hr
T (at the top) = 45 ˚C MEA concentration (at the top) = 13.1 wt. %	18.00	3.62×10^{-06}
	18.165 (Reference)	3.54×10^{-06}
	18.33	3.46×10^{-06}
	18.49	3.38×10^{-06}
	18.66	3.30×10^{-06}
	18.82	3.22×10^{-06}
	18.99	3.14×10^{-06}

Increasing the absorber pressure decreases the ratio of the acid gas partial pressure to the total pressure in the absorber overhead which results in lower acid gas concentrations in the overhead product, thus improving the acid gas removal by the amine solution. The absorber should be designed to operate at the highest practical pressure, within the constraints imposed by the needs of the upstream and downstream units. The model output at different absorber pressures is shown in Figure 5.2.

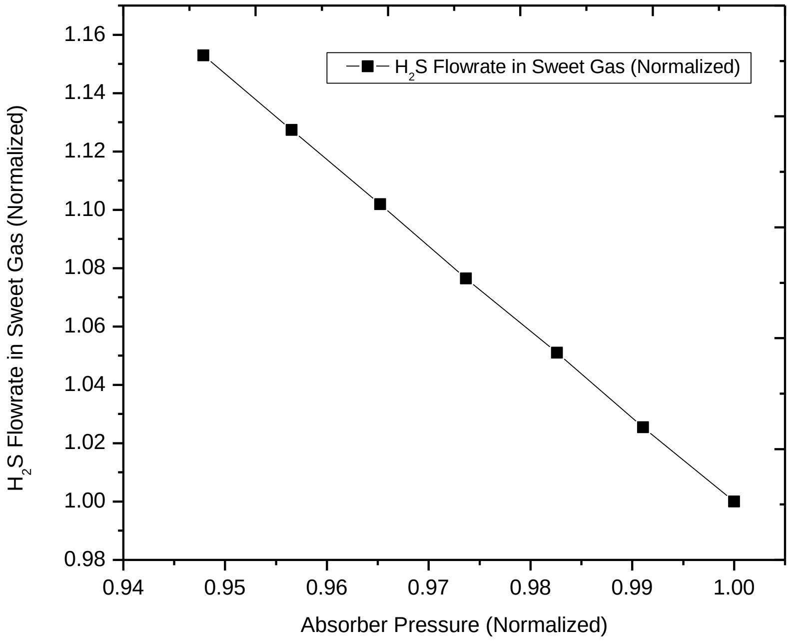

Figure 5.2: Effect of the absorber pressure on the value of H_2S in the product

5.4 Effect of solvent concentration on product quality

The lean amine concentration is of significant importance due to its impact on the quality of the sweet LPG and the associated corrosion. Lower concentrations of the lean amine can lead to corrosion. High amine loading also leads to corrosion. Very high amine concentrations also lead to high operating costs. Table 5.3 and Figure 5.3 show the effect of increasing MEA concentrations (at the top) as it is varied from 13 to 17 wt. %. The effect, as expected, is that with increasing concentration of the lean amine, the H_2S content decreases in the sweet LPG stream, while it increases in the rich amine stream.

Table 5.3: Effect of increasing MEA concentrations on LPG product quality

T (at the top) = 45 °C P_2 (at the top) = 18.165 bar abs	Concentration of lean amine, wt. %	Flow rate of H_2S in the sweet LPG, kmol/hr
	13.1 (Reference)	3.54×10^{-06}
	13.9	2.41×10^{-06}
	14.6	1.70×10^{-06}
	15.4	1.24×10^{-06}
	16.2	9.25×10^{-07}
	16.9	7.05×10^{-07}
	17.58	5.48×10^{-07}

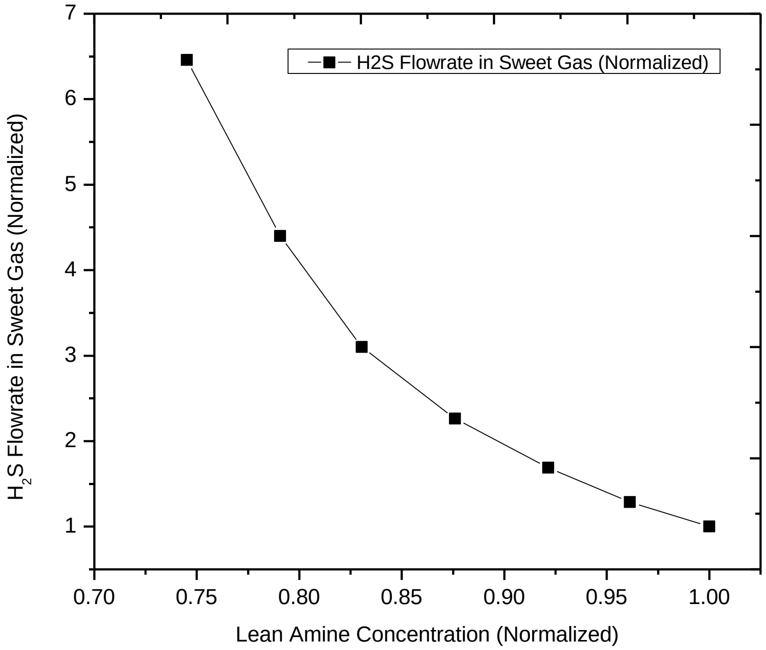

Figure 5.3: Effect of the normalized lean amine concentration on the (normalized) flow rate of H_2S in the sweet LPG

The effects of these three operating parameters on the H_2S content of the sweet LPG are summarized qualitatively in Table 5.4.

Table 5.4: Effect (qualitative) of operating parameters on the concentration of H_2S in the sweet LPG

Parameter	Minimum	Maximum	Effect on the H_2S content in the sweet LPG stream (with increasing values of the parameter)
Temperature of the lean amine	42 °C	47 °C	Increases (undesirable)
Pressure at the top, P_2	18 bar abs	19 bar abs.	Decreases (desirable)
Concentration of the lean amine	13.1 wt. %	17.58 wt. %	Decreases (desirable)

5.5 Summary

In summary, the sensitivity of the model has been checked against various process parameters. The key parameters which significantly affect the product quality are the lean amine temperature, lean amine concentration and the absorber pressure. The minimum and maximum ranges of the parameters are found and fixed, based on the industrial condition. The results of the sensitivity analysis are summarized.

Chapter 6

6.1 Optimization

Optimization provides the operations engineers the basic tools to perform ongoing process improvement studies. Optimization studies gives improved plant performance, efficient plant operation and, finally, to increased profitability. Typically, optimization studies involve an economic analysis of a profit function and operating constraints.

Aspen HYSYS contains a multi-variable Steady State Optimizer. Once the flow sheet model has been built and a converged solution has been obtained for the model, the optimizer can be utilized to find the operating conditions which minimize or maximize an objective function. The Optimizer has the spreadsheet option for defining the objective functions as well as any constraint expressions. A short terminology follows:

Primary Variables: These are flow sheet variables whose values are manipulated in order to minimize (or maximize) the objective function. The upper and lower bounds for the primary variables are used to set the search range. They are referred to as decision variables in evolutionary optimizing techniques.

Objective Function: This is the function which is to be minimized (or maximized). The function has to be defined within the spreadsheet. This allows flexibility in defining the function.

Constraint Functions: Inequality and equality constraint functions are also defined in the spreadsheet. While solving the objective function the optimizer is expected to meet any constraints that are defined.

6.2 Optimization schemes

The Optimizer manipulates the values of a set of primary variables in order to minimize (or maximize) a defined objective function, constructed from the several process variables (Press et al., 1989). For example

$\min f(x_1, x_2, x_3, \ldots, x_n)$

where: $x_1, x_2, \ldots, x_n$ *are process variables*

Each primary variable, $\boldsymbol{x}$, will be selected for optimality within specified bounds (ranges):

$$x_{i,\ LowerBound} < x_i < x_{i,\ UpperBound} \quad with\ i = 1, \ldots., n$$

x_i *is a process variable used to define the Objective Function to be optimized.*

Five types of optimization in-built schemes are available in Aspen HYSYS:

Box Type: This method is a sequential search technique which solves problems with non-linear objective functions, subject to non-linear inequality constraints. No derivatives are required. It handles inequality constraints but not equality constraints. This method is not very efficient in terms of the required number of function evaluations. It generally requires a large number of iterations to converge to the solution. (Box, 1965)

SQP Method: The Sequential Quadratic Programming (SQP) method handles inequality and equality constraints. SQP is considered to be the most efficient method for minimization with general linear and non-linear constraints, provided a reasonable initial point is used and the number of primary variables is small. The implemented procedure is based entirely on the Harwell subroutines, VF13 and VE17 (Press et al., 1989). The program follows closely the algorithm of Powell. It minimizes a quadratic approximation of the Lagrangian function subject to linear approximations of the constraints. The second derivative matrix of the Lagrangian function is estimated automatically. A line search procedure utilizing the "watchdog" technique (Chamberlain et al., 1982) is used to force convergence.

Mixed Method: The mixed method handles inequality constraints only. It is a combination of the Box and the SQP methods. It starts the minimization with the Box method using a very loose convergence tolerance. After convergence, the SQP method is used to locate the final solution.

Fletcher Reeves Method: The procedure implemented is the Polak-Ribiere modification of the Fletcher-Reeves conjugate gradient scheme. The approach closely follows that described by (Press et al., 1989), with modifications to allow for lower and upper bounds on the variables. This method is efficient for general minimization involving no constraints.

Quasi-Newton Method: The Quasi-Newton method of Broyden-Fletcher-Goldfarb-Shanno (BFGS) is also described by Press et al. (1989) In terms of applicability and limitations, this method is similar to the Fletcher-Reeves method.

A summary of the different optimization schemes is provided in Table 6.1.

Table 6.1: Optimization schemes

Method	Unconstrained problems	Constrained problems: Equality	Constrained problems: Inequality	Calculates derivatives
Box	x	x	√	√
SQP	x	√	√	x
Mixed	x	x	√	x
Fletcher-	x	x	x	x

Reeves				
Quasi-Newton	x	x	x	x

6.3 Single objective optimization (SOO) of the industrial absorber

The model of the industrial LPG sweetening absorber, developed and validated as described in earlier chapters, is used. Optimization was done using the SQP method, which can handle inequality and equality constraints. This technique approximates the actual, non-linear objective function around a starting point (solution) using a quadratic approximation of the objective function. In addition, the non-linear constraints are linearized. A line-search procedure utilizing the 'watchdog' technique is used to attain convergence using a Lagrangian function.

The SOO problem solved here in terms of three (most important) operating (decision) variables is given by

Min f (W_2, T_{L2}, P_2) ≡ flow rate of H_2S in the sweet amine ≡ $Y_{A,G2}$

subject to (s.t.):

$13.1 \geq W_2 \geq 17.58$ wt. %
$42 \geq T_{L2} \geq 47$ °C
$18 \geq P_2 \geq 19$ bar abs.
with initial guesses (to SQP) given as

$W_2 = 13.1$ wt. %
$T_{L2} = 42$ °C, and
$P_2 = 18$ bar abs

The optimal solutions obtained from Aspen HYSIS^{TM} are
$W_2 = 17.57$ wt. %
$T_{L2} = 42$ °C, and
$P_2 = 19$ bar abs

The optimal value of the objective function, $Y_{A, G2}$, comes out as 3.636 × 10^{-7} kmol/hr.

The computational parameters used in Aspen HYSIS™ are
Tolerance: 10^{-5}
Maximum number of iterations: 100
Maximum change per iteration: 0.5
Maximum function evaluations = 500
Shift-A = 10^{-4}
Shift-B = 10^{-4}

This solution matched quite well the results using the *simulation mode* of optimization, see Appendix 1 (i.e., running the simulation over several values of the decision variables, one by one):

W_2 = 17.58 wt. %
T_{L2} = 42 °C
P_2 = 19 bar abs
with
$Y_{A,G2}$ = 3.634 × 10^{-7} kmol/hr

The optimal values of $Y_{A,G2}$ of the same SOO problem using other optimization algorithms (e.g., Fletcher Reeves, Quasi Newton, Box Complex, Mixed in Aspen HYSIS™) are provided in Table 6.2.

Table 6.2: Optimum values of the product H_2S using different optimization algorithms (single objective optimization, SOO)

Method	Optimum Value
Fletcher Reeves	3.6871 × 10^{-7} kmol/hr
Quasi Newton	3.6870 × 10^{-7} kmol/hr
Box complex	3.6206 × 10^{-7} kmol/hr
Mixed	3.6207 ×10^{-7} kmol/hr

SQP	3.6360×10^{-7} kmol/hr

6.4 Summary

Optimization and improvement of the performance are integral parts of any process. Industries continually make efforts for modification to improve profitability. In line with this, optimization of the model has been done and optimum operating conditions for the best product quality have been found. This can be utilized for any advanced process monitoring, supervisory controls and in process equipment design. Thus, modeling will provide help for scaling-up the capacity while optimization will help in running the plant with optimum inventory and utility.

Chapter 7

7.1 Importance of LPG amine absorption process

LPG is an important industrial product in terms of market value, commercial and residential usage. The demand is increasing day by day as it is increasingly being used as an auto gas. In addition, LPG treating is an important process due to the toxic and corrosive nature of the H_2S and CO_2 impurities in sour LPG. The detailed corrosion effects on piping, industrial equipment, storage and handling have been described in Chapter 1. The environmental, safety and hazard significance have been explained in detail.

7.2 LPG amine absorption modeling literature

A systematic survey has been conducted on the LPG treating process, amine absorption process, process selection methods, amine treating process, operating conditions, modeling method, model selection, process simulation and optimization. A detailed literature review has been provided in Chapter 2. From the literature survey it is concluded that industries adopt various technologies for acid gas treating and technology selection depends on many factors such as feed composition, expected product quality, operating conditions, configuration, CAPEX and OPEX. For treatment of sour LPG, the amine absorption process is one of the best processes for refineries due to product quality, proven technology, operational flexibility and a centralized amine treatment unit reduces CAPEX and OPEX.

7.3 Amine absorption model

In this chapter, various acid gas absorption modeling methods were discussed and the suitability of the models for various operating and processes were reviewed. Also, calculation methods used in various simulators were analyzed. A systematic comparison between the Aspen HYSYS amine package and acid gas package was studied and the significance of model selection was provided. From the literature it was concluded that the acid gas package was the most suitable for the LPG amine absorption process.

7.4 LPG amine absorption process and simulation model

The complexity of the refinery configuration was explained. The sources of sour LPG generation and LPG amine absorption process and operating conditions were explained. The actual operating and design data of the industrial LPG absorber were provided. The industrial and model output data, stream parameters and components profiles across the bed were provided. A sensitivity analysis of the model with respect to the key parameters was done and model outputs were provided in the next chapter.

7.5 Model validation and sensitivity analysis

The model output was compared with actual industrial data. Model stream quality was compared with industrial laboratory data. The sensitivity of the model was checked with various process parameters. The key parameters which significantly affect the product quality were found to be the lean amine temperature, lean amine concentration and the absorber pressure. The minimum and maximum range of the parameters was fixed based on industrial conditions. The results on the sensitivity analysis were summarized.

7.6 Optimization of LPG amine absorption process

The converged, steady state flow sheet model was used for optimization. The optimization was carried out using the in-built applications in Aspen HYSYS as well as the case study (simulation mode) method was used. Optimization was done with an objective of minimum impurities in the LPG product. The optimizer results obtained using various optimization tools were discussed.

7.7 Applications of research (steady state flow sheet models and optimization)

Competence: Steady-state simulation models provide powerful insights into the plant behavior that can be used to enhance designs, safety and operations of process facilities while minimizing capital and operating costs.

Process design: It is a powerful tool that helps engineers to create optimal process designs based on critical business objectives.

Environmental compliance: It ensures that process designs meet all environment regulations in a variety of extreme operating cases.

Product quality: Simulation ensures that the process design will produce the desired product quality for a variety of feed-stocks.

Operation analysis: Flow sheet models help to evaluate the root cause of process problems to help ensure that corrective actions will be effective.

Design review: Provide engineers with a safe, cost-effective way to test proposed solutions before implementing them, thus minimizing the risk of rework.

Performance and optimization: Steady-state simulation can be used to monitor plant performance to track performance degradation and suggest corrective action and maximize the profitability of plant performance by optimizing the performance on a real-time basis in an advisory or closed-loop manner.

Data reconciliation and process optimization: Ensure that the model accurately matches current plant performance by reconciling column efficiencies, heat exchanger fouling or reactor catalyst activity to current process data.

Appendix 1

Appendix 1.1 Optimization study Case 1 temperature variation

Temperature Variation	13.1 wt. %, 18.165 bar-abs., 42 ^oC to 47 ^oC					
State	State 1	State 2	State 3	State 4	State 5	State 6
lean-amine-abs Temperature, ^oC	42	43	44	45	46	47
sweet-LPG-Master Comp. Molar Flow (H_2S)	2.83E-06	3.05E-06	3.29E-06	3.55E-06	3.83E-06	4.13E-06

Appendix 1.2 Optimization study Case 2 pressure variation

Pressure Variation	13.1 wt. %, 45 ^oC, 18 bar abs. to 19 bar abs.					
State	State 1	State 2	State 3	State 4	State 5	State 6
Stage Pressure (1__LPG-ABS)	18	18.2	18.4	18.6	18.8	19
sweet-LPG-Master Comp. Molar Flow (H_2S)	3.22E-06	3.23E-06	3.20E-06	3.17E-06	3.13E-06	3.10E-06

Appendix 1.3 Optimization study Case 3 concentration variation

Concentration Variation	45 ^oC, 18.165 bar abs., 13.1 wt. % to 17.588 wt. %						
State	State 1	State 2	State 3	State 4	State 5	State 6	State 7
lean amine make-up - Molar Flow	0	1	2	3	4	5	6
sweet-LPG - Master Comp Molar Flow (H_2S)	3.54E-06	2.41E-06	1.70E-06	1.24E-06	9.26E-07	7.06E-07	5.48E-07
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.1309829	0.138803	0.14648398	0.154029	0.16144175	0.16872574	0.17588428

Appendix 1.4 Optimization study Case 4 lean amine temperature and concentration variation

State	State 1	State 2	State 3	State 4	State 5	State 6	
lean-amine-abs-Temperature, ^{o}C	42	42	42	42	42	42	
lean amine make-up -Molar Flow	0	1	2	3	4	5	
sweet-LPG-Master Comp Molar Flow (H_2S)	2.83E-06	1.90E-06	1.33E-06	9.62E-07	7.13E-07	5.40E-07	
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.1309829	0.138803	0.14648398	0.154029	0.16144175	0.16872574	
State	State 7	State 8	State 9	State 10	State 11	State 12	State 13
lean amine make-up-Molar Flow	1	1	1	1	1	1	2
Stage Pressure (1__LPG-ABS)	18	18.2	18.4	18.6	18.8	19	18
sweet-LPG-Master Comp Molar Flow (H_2S)	2.21E-06	2.20E-06	2.18E-06	2.16E-06	2.13E-06	2.11E-06	1.55E-06
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.138803	0.138803	0.138803	0.138803	0.138803	0.138803	0.146484
State	State 14	State 15	State 16	State 17	State 18	State 19	State 20
lean amine make-up-Molar Flow	2	2	2	2	2	3	3
Stage Pressure (1__LPG-ABS)	18.2	18.4	18.6	18.8	19	18	18.2
sweet-LPG-Master Comp. Molar Flow (H_2S)	1.55E-06	1.54E-06	1.52E-06	1.50E-06	1.49E-06	1.13E-06	1.13E-06
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.146484	0.146484	0.146484	0.146484	0.146484	0.154029	0.154029

Appendix 1.4 (continued) Optimization study Case 4 lean amine temperature and concentration variation

State	State 21	State 22	State 23	State 24	State 25	State 26	State 27
lean amine make-up-Molar Flow	3	3	3	3	4	4	4
Stage Pressure (1__LPG-ABS)	18.4	18.6	18.8	19	18	18.2	18.4
sweet-LPG-Master Comp. Molar Flow (H_2S)	1.12E-06	1.11E-06	1.10E-06	1.09E-06	8.44E-07	8.44E-07	8.37E-07
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.154029	0.154029	0.154029	0.154029	0.161442	0.161442	0.161442

State	State 28	State 29	State 30	State 31	State 32	State 33	State 34
lean amine make-up-Molar Flow	4	4	4	5	5	5	5
Stage Pressure (1__LPG-ABS)	18.6	18.8	19	18	18.2	18.4	18.6
sweet-LPG-Master Comp. Molar Flow (H_2S)	8.28E-07	8.19E-07	8.10E-07	6.44E-07	6.44E-07	6.39E-07	6.32E-07
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.161442	0.161442	0.161442	0.168726	0.168726	0.168726	0.168726

State	State 35	State 36	State 37	State 38	State 39	State 40	State 41	State 42
lean amine make-up-Molar Flow	46	47	47	47	47	47	47	47
Stage Pressure (1__LPG-ABS)	6	0	1	2	3	4	5	6
sweet-LPG-Master Comp. Molar Flow (H_2S)	6.01E-07	4.13E-06	2.83E-06	2.01E-06	1.47E-06	1.10E-06	8.46E-07	6.60E-07
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.175884	0.130983	0.138803	0.146484	0.154029	0.161442	0.168726	0.175884

Appendix 1.5 Optimization study Case 5 lean amine concentration and absorber pressure variation

State	State 1	State 2	State 3	State 4	State 5	State 6	State 7	State 8
lean amine make-up-Molar Flow	0	0	0	0	0	0	1	1
Stage Pressure (1__LPG-ABS)	18	18.2	18.4	18.6	18.8	19	18	18.2
sweet-LPG-Master Comp. Molar Flow (H_2S)	3.23E-06	3.23E-06	3.20E-06	3.17E-06	3.14E-06	3.10E-06	2.21E-06	2.20E-06
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.130983	0.130983	0.130983	0.130983	0.130983	0.130983	0.138803	0.138803
State	State 9	State 10	State 11	State 12	State 13	State 14	State 15	State 16
lean amine make-up-Molar Flow	1	1	1	1	2	2	2	2
Stage Pressure (1__LPG-ABS)	18.4	18.6	18.8	19	18	18.2	18.4	18.6
sweet-LPG-Master Comp. Molar Flow (H_2S)	2.18E-06	2.16E-06	2.13E-06	2.11E-06	1.55E-06	1.55E-06	1.54E-06	1.52E-06
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.138803	0.138803	0.138803	0.138803	0.146484	0.146484	0.146484	0.146484
State	State 17	State 18	State 19	State 20	State 21	State 22	State 23	State 24
lean amine make-up Molar Flow	2	2	3	3	3	3	3	3
Stage Pressure (1__LPG-ABS)	18.8	19	18	18.2	18.4	18.6	18.8	19
sweet-LPG-Master Comp. Molar Flow (H_2S)	1.50E-06	1.49E-06	1.13E-06	1.13E-06	1.12E-06	1.11E-06	1.10E-06	1.09E-06
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.146484	0.146484	0.154029	0.154029	0.154029	0.154029	0.154029	0.154029
State	State 25	State 26	State 28	State 29	State 30	State 31	State 32	State 33
lean amine make-up-Molar Flow	4	4	4	4	4	5	5	5
Stage Pressure (1__LPG-ABS)	18	18.2	18.6	18.8	19	18	18.2	18.4
sweet-LPG-Master Comp. Molar Flow (H_2S)	8.44E-07	8.44E-07	8.28E-07	8.19E-07	8.10E-07	6.44E-07	6.44E-07	6.39E-07
lean-amine-to-abs-Comp Mass Frac. (MEAmine)	0.161442	0.161442	0.161442	0.161442	0.161442	0.168726	0.168726	0.168726

Appendix 1.5 (continued) Optimization study Case 5 lean amine concentration and absorber pressure variation

State	State 34	State 35	State 36	State 37	State 38	State 39	State 40	State 41	State 42
lean amine make-up-Molar Flow	5	5	5	6	6	6	6	6	6
Stage Pressure (1__LPG-ABS)	18.6	18.8	19	18	18.2	18.4	18.6	18.8	19
sweet-LPG-Master Comp. Molar Flow (H_2S)	6.32E-07	6.25E-07	6.19E-07	5.00E-07	5.00E-07	4.95E-07	4.90E-07	4.85E-07	4.80E-07
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.168726	0.168726	0.168726	0.175884	0.175884	0.175884	0.175884	0.175884	0.175884

Appendix 1.6 Optimization study Case 6 absorber pressure and lean amine temperature variation

State	State 1	State 2	State 3	State 4	State 5	State 6	State 7	State 8
lean amine make-up-Molar Flow	18	18	18	18	18	18	18.2	18.2
Stage Pressure (1__LPG-ABS)	42	43	44	45	46	47	42	43
sweet-LPG - Master Comp Molar Flow (H_2S)	2.60E-06	2.80E-06	3.03E-06	3.26E-06	3.53E-06	3.81E-06	2.57E-06	2.77E-06
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.130983	0.130983	0.130983	0.130983	0.130983	0.130983	0.130983	0.130983
State	State 9	State 10	State 11	State 12	State 13	State 14	State 15	State 16
lean amine make-up-Molar Flow	18.2	18.2	18.2	18.2	18.4	18.4	18.4	18.4
Stage Pressure (1__LPG-ABS)	44	45	46	47	42	43	44	45
sweet-LPG-Master Comp. Molar Flow (H_2S)	2.99E-06	3.23E-06	3.49E-06	3.76E-06	2.54E-06	2.74E-06	2.96E-06	3.19E-06
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.130983	0.130983	0.130983	0.130983	0.130983	0.130983	0.130983	0.130983
State	State 17	State 18	State 19	State 20	State 21	State 22	State 23	State 24
lean amine make-up-Molar Flow	18.4	18.4	18.6	18.6	18.6	18.6	18.6	18.6
Stage Pressure (1__LPG-ABS)	46	47	42	43	44	45	46	47
sweet-LPG-Master Comp. Molar Flow (H_2S)	3.45E-06	3.72E-06	2.52E-06	2.71E-06	2.93E-06	3.16E-06	3.41E-06	3.68E-06
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.130983	0.130983	0.130983	0.130983	0.130983	0.130983	0.130983	0.130983

Appendix 1.6 (continued) Optimization study Case 6 absorber pressure and lean amine temperature variation

lean amine make-up Molar Flow	18.8	18.8	18.8	18.8	18.8	18.8	19	19
Stage Pressure (1__LPG-ABS)	42	43	44	45	46	47	42	43
sweet-LPG-Master Comp. Molar Flow (H_2S)	2.49E-06	2.68E-06	2.90E-06	3.13E-06	3.38E-06	3.64E-06	2.46E-06	2.65E-06
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.130983	0.130983	0.130983	0.130983	0.130983	0.130983	0.130983	0.130983
State								
lean amine make-up-Molar Flow	19	19	19	19				
Stage Pressure (1__LPG-ABS)	44	45	46	47				
sweet-LPG-Master Comp. Molar Flow (H_2S)	2.87E-06	3.09E-06	3.34E-06	3.61E-06				
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.130983	0.130983	0.130983	0.130983				

Appendix 1.7 Optimization study Case 7 lean amine temperature, absorber pressure and lean amine concentration variation

State	State 1	State 2	State 3	State 4	State 5	State 6	State 7	State 8
Stage Pressure (1__LPG-ABS)	18	18	18	18	18	18	18	18
lean-amine-to-abs-Temperature	42	42	42	42	42	42	42	43
lean amine make-up-Molar Flow	0	1	2	3	4	5	6	0
sweet-LPG-Master Comp Molar Flow (H_2S)	2.60E-06	1.75E-06	1.23E-06	8.85E-07	6.56E-07	4.98E-07	3.84E-07	2.80E-06
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.130983	0.138803	0.146484	0.154029	0.161442	0.168726	0.175884	0.130983
State	State 9	State 10	State 11	State 12	State 13	State 14	State 15	State 16
Stage Pressure (1__LPG-ABS)	18	18	18	18	18	18	18	18
lean-amine-to-abs-Temperature	43	43	43	43	43	43	44	44
lean amine make-up-Molar Flow	1	2	3	4	5	6	0	1
sweet-LPG-Master Comp. Molar Flow (H_2S)	1.89E-06	1.33E-06	9.63E-07	7.16E-07	5.44E-07	4.20E-07	3.03E-06	2.05E-06
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.138803	0.146484	0.154029	0.161442	0.168726	0.175884	0.130983	0.138803
State	State 17	State 18	State 19	State 20	State 21	State 22	State 23	State 24
Stage Pressure (1__LPG-ABS)	18	18	18	18	18	18	18	18
lean-amine-to-abs-Temperature	44	44	44	44	44	45	45	45
lean amine make-up-Molar. Flow	2	3	4	5	6	0	1	2
sweet-LPG-Master Comp. Molar Flow (H_2S)	1.44E-06	1.05E-06	7.82E-07	5.95E-07	4.61E-07	3.26E-06	2.22E-06	1.57E-06
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.146484	0.154029	0.161442	0.168726	0.175884	0.130983	0.138803	0.146484

Appendix 1.7 (continued) Optimization study Case 7 Lean amine temperature, absorber pressure and lean amine concentration variation

State	State 25	State 26	State 27	State 28	State 29	State 30	State 31	State 32
Stage Pressure (1__LPG-ABS)	18	18	18	18	18	18	18	18
lean-amine-to-abs-Temperature	45	45	45	45	46	46	46	46
lean amine make-up-Molar Flow	3	4	5	6	0	1	2	3
sweet-LPG-Master Comp. Molar Flow (H_2S)	1.14E-06	8.54E-07	6.51E-07	5.06E-07	3.53E-06	2.41E-06	1.71E-06	1.24E-06
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.154029	0.161442	0.168726	0.175884	0.130983	0.138803	0.146484	0.154029
State	State 33	State 34	State 35	State 36	State 37	State 38	State 39	State 40
Stage Pressure (1__LPG-ABS)	18	18	18	18	18	18	18	18
lean-amine-to-abs-Temperature	46	46	46	47	47	47	47	47
lean amine make-up-Molar Flow	4	5	6	0	1	2	3	4
sweet-LPG-Master Comp Molar Flow (H_2S)	9.33E-07	7.13E-07	5.55E-07	3.81E-06	2.61E-06	1.85E-06	1.36E-06	1.02E-06
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.161442	0.168726	0.175884	0.130983	0.138803	0.146484	0.154029	0.161442
State	State 41	State 42	State 43	State 44	State 45	State 46	State 47	State 48
Stage Pressure (1__LPG-ABS)	18	18	18.2	18.2	18.2	18.2	18.2	18.2
lean-amine-to-abs-Temperature	47	47	42	42	42	42	42	42
lean amine make-up-Molar Flow	5	6	0	1	2	3	4	5
sweet-LPG-Master Comp Molar Flow (H_2S)	7.81E-07	6.10E-07	2.57E-06	1.73E-06	1.21E-06	8.75E-07	6.49E-07	4.92E-07
lean-amine-to-abs-Master Comp. Mass Frac. (MEAmine)	0.168726	0.175884	0.130983	0.138803	0.146484	0.154029	0.161442	0.168726

Appendix 1.7 (continued) Optimization study Case 7 lean amine temperature, absorber pressure and lean amine concentration variation

State	State 49	State 50	State 51	State 52	State 53	State 54	State 55	State 56
Stage Pressure (1__LPG-ABS)	18.2	18.2	18.2	18.2	18.2	18.2	18.2	18.2
lean-amine-to-abs - Temperature	42	43	43	43	43	43	43	43
lean amine make-up - Molar Flow	6	0	1	2	3	4	5	6
sweet-LPG - Master Comp Molar Flow (H_2S)	3.80E-07	2.77E-06	1.87E-06	1.32E-06	9.53E-07	7.08E-07	5.38E-07	4.16E-07
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.175884	0.130983	0.138803	0.146484	0.154029	0.161442	0.168726	0.175884
State	State 57	State 58	State 59	State 60	State 61	State 62	State 63	State 64
Stage Pressure (1__LPG-ABS)	18.2	18.2	18.2	18.2	18.2	18.2	18.2	18.2
lean-amine-to-abs - Temperature	44	44	44	44	44	44	44	45
lean amine make-up - Molar Flow	0	1	2	3	4	5	6	0
sweet-LPG - Master Comp Molar Flow (H_2S)	2.99E-06	2.03E-06	1.43E-06	1.04E-06	7.73E-07	5.88E-07	4.56E-07	3.23E-06
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.130983	0.138803	0.146484	0.154029	0.161442	0.168726	0.175884	0.130983
State	State 65	State 66	State 67	State 68	State 69	State 70	State 71	State 72
Stage Pressure (1__LPG-ABS)	18.2	18.2	18.2	18.2	18.2	18.2	18.2	18.2
lean-amine-to-abs - Temperature	45	45	45	45	45	45	46	46
lean amine make-up - Molar Flow	1	2	3	4	5	6	0	1
sweet-LPG - Master Comp Molar Flow (H_2S)	2.20E-06	1.55E-06	1.13E-06	8.45E-07	6.44E-07	5.00E-07	3.49E-06	2.38E-06
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.138803	0.146484	0.154029	0.161442	0.168726	0.175884	0.130983	0.138803

Appendix 1.7 (continued) Optimization study Case 7 lean amine temperature, absorber pressure and lean amine concentration variation

State	State 73	State 74	State 75	State 76	State 77	State 78	State 79	State 80
Stage Pressure (1__LPG-ABS)	18.2	18.2	18.2	18.2	18.2	18.2	18.2	18.2
lean-amine-to-abs - Temperature	46	46	46	46	46	47	47	47
lean amine make-up - Molar Flow	2	3	4	5	6	0	1	2
sweet-LPG - Master Comp Molar Flow (H_2S)	1.69E-06	1.23E-06	9.23E-07	7.05E-07	5.49E-07	3.76E-06	2.58E-06	1.83E-06
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.146484	0.154029	0.161442	0.168726	0.175884	0.130983	0.138803	0.146484
State	State 81	State 82	State 83	State 84	State 85	State 86	State 87	State 88
Stage Pressure (1__LPG-ABS)	18.2	18.2	18.2	18.2	18.4	18.4	18.4	18.4
lean-amine-to-abs - Temperature	47	47	47	47	42	42	42	42
lean amine make-up - Molar Flow	3	4	5	6	0	1	2	3
sweet-LPG - Master Comp Molar Flow (H_2S)	1.34E-06	1.01E-06	7.73E-07	6.03E-07	2.54E-06	1.71E-06	1.20E-06	8.66E-07
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.154029	0.161442	0.168726	0.175884	0.130983	0.138803	0.146484	0.154029
State	State 89	State 90	State 91	State 92	State 93	State 94	State 95	State 96
Stage Pressure (1__LPG-ABS)	18.4	18.4	18.4	18.4	18.4	18.4	18.4	18.4
lean-amine-to-abs - Temperature	42	42	42	43	43	43	43	43
lean amine make-up - Molar Flow	4	5	6	0	1	2	3	4
sweet-LPG - Master Comp Molar Flow (H_2S)	6.42E-07	4.87E-07	3.75E-07	2.74E-06	1.85E-06	1.30E-06	9.42E-07	7.01E-07
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.161442	0.168726	0.175884	0.130983	0.138803	0.146484	0.154029	0.161442

Appendix 1.7 (continued) Optimization study Case 7 lean amine temperature, absorber pressure and lean amine concentration variation

State	State 97	State 98	State 99	State 100	State 101	State 102	State 103	State 104
Stage Pressure (1__LPG-ABS)	18.4	18.4	18.4	18.4	18.4	18.4	18.4	18.4
lean-amine-to-abs - Temperature	43	43	44	44	44	44	44	44
lean amine make-up - Molar Flow	5	6	0	1	2	3	4	5
sweet-LPG - Master Comp Molar Flow (H_2S)	5.32E-07	4.11E-07	2.96E-06	2.01E-06	1.41E-06	1.03E-06	7.65E-07	5.82E-07
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.168726	0.175884	0.130983	0.138803	0.146484	0.154029	0.161442	0.168726
State	State 105	State 106	State 107	State 108	State 109	State 110	State 111	State 112
Stage Pressure (1__LPG-ABS)	18.4	18.4	18.4	18.4	18.4	18.4	18.4	18.4
lean-amine-to-abs - Temperature	44	45	45	45	45	45	45	45
lean amine make-up - Molar Flow	6	0	1	2	3	4	5	6
sweet-LPG - Master Comp Molar Flow (H_2S)	4.51E-07	3.19E-06	2.17E-06	1.54E-06	1.12E-06	8.36E-07	6.37E-07	4.95E-07
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.175884	0.130983	0.138803	0.146484	0.154029	0.161442	0.168726	0.175884
State	State 113	State 114	State 115	State 116	State 117	State 118	State 119	State 120
Stage Pressure (1__LPG-ABS)	18.4	18.4	18.4	18.4	18.4	18.4	18.4	18.4
lean-amine-to-abs - Temperature	46	46	46	46	46	46	46	47
lean amine make-up - Molar Flow	0	1	2	3	4	5	6	0
sweet-LPG - Master Comp Molar Flow (H_2S)	3.45E-06	2.35E-06	1.67E-06	1.22E-06	9.13E-07	6.98E-07	5.43E-07	3.72E-06
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.130983	0.138803	0.146484	0.154029	0.161442	0.168726	0.175884	0.130983

Appendix 1.7 (continued) Optimization study Case 7 lean amine temperature, absorber pressure and lean amine concentration variation

State	State 121	State 122	State 123	State 124	State 125	State 126	State 127	State 128
Stage Pressure (1__LPG-ABS)	18.4	18.4	18.4	18.4	18.4	18.4	18.6	18.6
lean-amine-to-abs - Temperature	47	47	47	47	47	47	42	42
lean amine make-up - Molar Flow	1	2	3	4	5	6	0	1
sweet-LPG - Master Comp Molar Flow (H_2S)	2.55E-06	1.81E-06	1.33E-06	9.98E-07	7.65E-07	5.97E-07	2.52E-06	1.69E-06
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.138803	0.146484	0.154029	0.161442	0.168726	0.175884	0.130983	0.138803
State	State 129	State 130	State 131	State 132	State 133	State 134	State 135	State 136
Stage Pressure (1__LPG-ABS)	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6
lean-amine-to-abs - Temperature	42	42	42	42	42	43	43	43
lean amine make-up - Molar Flow	2	3	4	5	6	0	1	2
sweet-LPG - Master Comp Molar Flow (H_2S)	1.19E-06	8.56E-07	6.35E-07	4.81E-07	3.71E-07	2.71E-06	1.83E-06	1.29E-06
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.146484	0.154029	0.161442	0.168726	0.175884	0.130983	0.138803	0.146484
State	State 137	State 138	State 139	State 140	State 141	State 142	State 143	State 144
Stage Pressure (1__LPG-ABS)	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6
lean-amine-to-abs - Temperature	43	43	43	43	44	44	44	44
lean amine make-up - Molar Flow	3	4	5	6	0	1	2	3
sweet-LPG - Master Comp Molar Flow (H_2S)	9.32E-07	6.93E-07	5.26E-07	4.07E-07	2.93E-06	1.98E-06	1.40E-06	1.01E-06
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.154029	0.161442	0.168726	0.175884	0.130983	0.138803	0.146484	0.154029

Appendix 1.7 (continued) Optimization study Case 7 Lean amine temperature, absorber pressure and lean amine concentration variation

State	State 145	State 146	State 147	State 148	State 149	State 150	State 151	State 152
Stage Pressure (1__LPG-ABS)	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6
lean-amine-to-abs - Temperature	44	44	44	45	45	45	45	45
lean amine make-up - Molar Flow	4	5	6	0	1	2	3	4
sweet-LPG - Master Comp Molar Flow (H_2S)	7.57E-07	5.76E-07	4.46E-07	3.16E-06	2.15E-06	1.52E-06	1.11E-06	8.27E-07
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.161442	0.168726	0.175884	0.130983	0.138803	0.146484	0.154029	0.161442
State	State 153	State 154	State 155	State 156	State 157	State 158	State 159	State 160
Stage Pressure (1__LPG-ABS)	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6
lean-amine-to-abs - Temperature	45	45	46	46	46	46	46	46
lean amine make-up - Molar Flow	5	6	0	1	2	3	4	5
sweet-LPG - Master Comp Molar Flow (H_2S)	6.30E-07	4.90E-07	3.41E-06	2.33E-06	1.65E-06	1.21E-06	9.04E-07	6.91E-07
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.168726	0.175884	0.130983	0.138803	0.146484	0.154029	0.161442	0.168726
State	State 161	State 162	State 163	State 164	State 165	State 166	State 167	State 168
Stage Pressure (1__LPG-ABS)	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6
lean-amine-to-abs - Temperature	46	47	47	47	47	47	47	47
lean amine make-up - Molar Flow	6	0	1	2	3	4	5	6
sweet-LPG - Master Comp Molar Flow (H_2S)	5.38E-07	3.68E-06	2.52E-06	1.80E-06	1.31E-06	9.88E-07	7.57E-07	5.91E-07
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.175884	0.130983	0.138803	0.146484	0.154029	0.161442	0.168726	0.175884

Appendix 1.7 (continued) Optimization study Case 7 lean amine temperature, absorber pressure and lean amine concentration variation

State	State 169	State 170	State 171	State 172	State 173	State 174	State 175	State 176
Stage Pressure (1__LPG-ABS)	18.8	18.8	18.8	18.8	18.8	18.8	18.8	18.8
lean-amine-to-abs - Temperature	42	42	42	42	42	42	42	43
lean amine make-up - Molar Flow	0	1	2	3	4	5	6	0
sweet-LPG - Master Comp Molar Flow (H_2S)	2.49E-06	1.67E-06	1.17E-06	8.47E-07	6.29E-07	4.76E-07	3.67E-07	2.68E-06
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.130983	0.138803	0.146484	0.154029	0.161442	0.168726	0.175884	0.130983
State	State 177	State 178	State 179	State 180	State 181	State 182	State 183	State 184
Stage Pressure (1__LPG-ABS)	18.8	18.8	18.8	18.8	18.8	18.8	18.8	18.8
lean-amine-to-abs - Temperature	43	43	43	43	43	43	44	44
lean amine make-up - Molar Flow	1	2	3	4	5	6	0	1
sweet-LPG - Master Comp Molar Flow (H_2S)	1.81E-06	1.27E-06	9.22E-07	6.86E-07	5.21E-07	4.03E-07	2.90E-06	1.96E-06
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.138803	0.146484	0.154029	0.161442	0.168726	0.175884	0.130983	0.138803
State	State 185	State 186	State 187	State 188	State 189	State 190	State 191	State 192
Stage Pressure (1__LPG-ABS)	18.8	18.8	18.8	18.8	18.8	18.8	18.8	18.8
lean-amine-to-abs - Temperature	44	44	44	44	44	45	45	45
lean amine make-up - Molar Flow	2	3	4	5	6	0	1	2
sweet-LPG - Master Comp Molar Flow (H_2S)	1.38E-06	1.00E-06	7.49E-07	5.70E-07	4.42E-07	3.12E-06	2.13E-06	1.50E-06
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.146484	0.154029	0.161442	0.168726	0.175884	0.130983	0.138803	0.146484

Appendix 1.7 (continued) Optimization study Case 7 lean amine temperature, absorber pressure and lean amine concentration variation

State	State 193	State 194	State 195	State 196	State 197	State 198	State 199	State 200
Stage Pressure (1__LPG-ABS)	18.8	18.8	18.8	18.8	18.8	18.8	18.8	18.8
lean-amine-to-abs - Temperature	45	45	45	45	46	46	46	46
lean amine make-up - Molar Flow	3	4	5	6	0	1	2	3
sweet-LPG - Master Comp Molar Flow (H_2S)	1.09E-06	8.18E-07	6.24E-07	4.84E-07	3.38E-06	2.30E-06	1.63E-06	1.19E-06
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.154029	0.161442	0.168726	0.175884	0.130983	0.138803	0.146484	0.154029
State	State 201	State 202	State 203	State 204	State 205	State 206	State 207	State 208
Stage Pressure (1__LPG-ABS)	18.8	18.8	18.8	18.8	18.8	18.8	18.8	18.8
lean-amine-to-abs - Temperature	46	46	46	47	47	47	47	47
lean amine make-up - Molar Flow	4	5	6	0	1	2	3	4
sweet-LPG - Master Comp Molar Flow (H_2S)	8.94E-07	6.83E-07	5.32E-07	3.64E-06	2.50E-06	1.78E-06	1.30E-06	9.78E-07
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.161442	0.168726	0.175884	0.130983	0.138803	0.146484	0.154029	0.161442
State	State 209	State 210	State 211	State 212	State 213	State 214	State 215	State 216
Stage Pressure (1__LPG-ABS)	18.8	18.8	19	19	19	19	19	19
lean-amine-to-abs - Temperature	47	47	42	42	42	42	42	42
lean amine make-up - Molar Flow	5	6	0	1	2	3	4	5
sweet-LPG - Master Comp Molar Flow (H_2S)	7.49E-07	5.84E-07	2.46E-06	1.66E-06	1.16E-06	8.38E-07	6.22E-07	4.71E-07
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.168726	0.175884	0.130983	0.138803	0.146484	0.154029	0.161442	0.168726

Appendix 1.7 (continued) Optimization study Case 7 lean amine temperature, absorber pressure and lean amine concentration variation

State	State 217	State 218	State 219	State 220	State 221	State 222	State 223	State 224
Stage Pressure (1__LPG-ABS)	19	19	19	19	19	19	19	19
lean-amine-to-abs - Temperature	42	43	43	43	43	43	43	43
lean amine make-up - Molar Flow	6	0	1	2	3	4	5	6
sweet-LPG - Master Comp Molar Flow (H_2S)	3.63E-07	2.65E-06	1.79E-06	1.26E-06	9.12E-07	6.78E-07	5.15E-07	3.98E-07
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.175884	0.130983	0.138803	0.146484	0.154029	0.161442	0.168726	0.175884
State	State 225	State 226	State 227	State 228	State 229	State 230	State 231	State 232
Stage Pressure (1__LPG-ABS)	19	19	19	19	19	19	19	19
lean-amine-to-abs - Temperature	44	44	44	44	44	44	44	45
lean amine make-up - Molar Flow	0	1	2	3	4	5	6	0
sweet-LPG - Master Comp Molar Flow (H_2S)	2.87E-06	1.94E-06	1.37E-06	9.93E-07	7.41E-07	5.64E-07	4.37E-07	3.09E-06
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.130983	0.138803	0.146484	0.154029	0.161442	0.168726	0.175884	0.130983
State	State 233	State 234	State 235	State 236	State 237	State 238	State 239	State 240
Stage Pressure (1__LPG-ABS)	19	19	19	19	19	19	19	19
lean-amine-to-abs - Temperature	45	45	45	45	45	45	46	46
lean amine make-up - Molar Flow	1	2	3	4	5	6	0	1
sweet-LPG - Master Comp Molar Flow (H_2S)	2.10E-06	1.49E-06	1.08E-06	8.09E-07	6.17E-07	4.79E-07	3.34E-06	2.28E-06
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.138803	0.146484	0.154029	0.161442	0.168726	0.175884	0.130983	0.138803

Appendix 1.7 (continued) Optimization study Case 7 lean amine temperature, absorber pressure and lean amine concentration variation

State	State 241	State 242	State 243	State 244	State 245	State 246	State 247	State 248
Stage Pressure (1__LPG-ABS)	19	19	19	19	19	19	19	19
lean-amine-to-abs - Temperature	46	46	46	46	46	47	47	47
lean amine make-up - Molar Flow	2	3	4	5	6	0	1	2
sweet-LPG - Master Comp Molar Flow (H_2S)	1.62E-06	1.18E-06	8.85E-07	6.76E-07	5.26E-07	3.60E-06	2.47E-06	1.76E-06
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.146484	0.154029	0.161442	0.168726	0.175884	0.130983	0.138803	0.146484

State	State 249	State 250	State 251	State 252
Stage Pressure (1__LPG-ABS)	19	19	19	19
lean-amine-to-abs - Temperature	47	47	47	47
lean amine make-up - Molar Flow	3	4	5	6
sweet-LPG - Master Comp Molar Flow (H_2S)	1.29E-06	9.67E-07	7.41E-07	5.78E-07
lean-amine-to-abs - Master Comp Mass Frac (MEAmine)	0.154029	0.161442	0.168726	0.175884

Appendix-**2**

Research publications by the author

1. K. Jayakumar, R. C. Panda, A. Panday and S. K. Gupta, **"Simulation and optimization of an LPG absorber in an *industrial* amine treating unit (ATU)",** International Journal of Chemical Engineering Research. ISSN 0975-6442 Volume 9, Number 1 (2017), pp. 69-87.

2. K. Jayakumar, R. C. Panda and A. Panday, "**A Review: State-of-the-Art LPG Sweetening Process",** International Journal of Chemical Engineering Research. ISSN 0975-6442 Volume 9, Number 2 (2017), pp. 175-206.

References

Addicks, J., G.A. Owren, A.O. Fredheim, and K. Tangvik. 2002. "Solubility of Carbon Dioxide and Methane in Aqueous Methyldiethanolamine Solutions." *Journal of Chemical & Engineering Data* 47(4):855-860.

Arcis, H., L. Rodier, K. Ballerat-Busserolles, and J.Y. Coxam. 2009. "Modeling of (Vapor + Liquid) Equilibrium and Enthalpy of Solution of Carbon Dioxide (CO_2) in Aqueous Methyldiethanolamine (MDEA) Solutions." *The Journal of Chemical Thermodynamics* 41(6): 783–789.

American Institute of Chemical Engineers. 1958. "Bubble-tray Design Manual-Prediction of Fractionation Efficiency." *Distillation Subcommittee of the Research Committee,* American Institute of Chemical Engineers.

ASPEN. 2006. "Aspen HYSYS Customization Guide." *Aspen Technology Inc.*, 20 Crosby Dr., Bedford, MA, USA.

Astarita, G., D.W. Savage, and A. Bisio. 1983. *Gas Treating with Chemical Solvents*. Wiley, New York.

ASTM D 4952 02, "Qualitative Analysis for Active Sulfur Species in Fuels and Solvents (Doctor Test)," www.astm.org.

Austgen, D.M., G.T. Rochelle, X. Peng, and C.C. Chen. 1989. "Model of Vapor-Liquid Equilibria for Aqueous Acid Gas-Alkanolamine Systems Using the Electrolyte-NRTL Equation." *Industrial and Engineering Chemistry Research* 28: 1060–1073.

Awan, J.A., and M. Saleem. 2011. "An Overview of the Thermodynamic Models for Acid Gases in Electrolyte Solutions." *Journal of Faculty of Engineering and Technology* 18(1): 13-29.

Aylott, M., and B. van der Merwe. 2008. "Petro-SIM Simulator and Cape-Open: Experiences and Successes*." 5th Cape-Open US Conference*, *AIChE Annual Meeting*, Proceedings, 476a, Philadelphia, PA, USA.

Bhaskar, V., S.K. Gupta and A.K. Ray. 2000. "Applications of Multi Objective Optimization in Chemical Engineering." *Reviews in Chemical Engineering* 16(1): 1-54.

Bhide, B.D., and S.A. Stern. 1993. "Membrane Processes for the Removal of Acid Gases from Natural Gas. II. Effects of Operating Conditions, Economic Parameters and Membrane Properties." *Journal of Membrane Science* 81(3): 239–252.

Blauwhoff, P.M., and W.P.M. van Swaaij. *1980*. "Gas-Liquid Equilibria Between H_2S, CO_2 and Aqueous Amine Solutions." *2nd International Conference on Phase Equilibria and Fluid Properties in the Chemical Industry*, EFCE Publication, Berlin: (Part I) 78.

Box, M.J. 1965. "A New Method of Constrained Optimization and a Comparison with Other Methods." *The Computer Journal* 8(1): 42–52.

Brown, C.R., and R. Geosits. 1993. "Efficient Low Temperature Solvent Removal of Acid Gases." *United States Patent****, Patent Number:*** *5220782*, Bechtel Group, Inc.

Bullin, J.A., J.C. Polasek, *and* J.W. Holmes. 1981. "Optimization of New and Existing Amine Gas Sweetening Plants by Computer Simulation," *Proceedings* of *60th GPA Annual Convention,* Gas Processors Association, Oklahoma, OK, USA *142-148*.

Bullin, J.A., J.C. Polasek, and S.T. Donnelly. 1990. "The Use of MDEA and Mixtures of Amines for Bulk CO_2 Removal," *Proceedings of 69th Gas Processors Association Convention,* Tulsa, OK, USA: 135–139.

Bullin, J. A., and J.C. Polasek. 1982. "*Selective Absorption with Amines*," *Proceedings of the 61st Annual GPA Convention*, Dallas, TX, USA, Gas Processors Association, Oklahoma, OK, USA: *86*–90.

Bureau of Indian Standards. 1999. "Indian Standard Liquified Petroleum Gases Specification." *IS 4576: 1999 (Reaffirmed 2009),* Manak Bhavan, Bahadur Shah Zafar Marg, New Delhi, India.

Burr, B., and L. Lyddon. 2008. “A Comparison of Physical Solvents for Acid Gas Removal.” *87th Annual Gas Processors Association Convention,* Grapevine, TX, USA, 2–5.

Button, J.K., and K.E. Gubbins. 1999. “SAFT Prediction of Vapour-Liquid Equilibria of Mixtures Containing Carbon Dioxide and Aqueous Monoethanolamine or Diethanolamine.” *Fluid Phase Equilibria* 158: 175–181.

Campbell, J.M., and R.N. Maddox. 1974. “Gas Conditioning and Processing.” *Campbell Petroleum Series*, 3rd Ed., Campbell Publishing Co., Norman, OK, USA.

Campbell, S.W., and R.H. Weiland. 1989. “Modeling CO_2 Removal by Amine Blends.” *American Institute of Chemical Engineers Spring National Meeting*. Houston, TX, USA.

Carlsson, A.F., T. Last, and C.J. Smit. 2007. “Design and Operation of Sour Gas Treating Plants for H_2S, CO_2, COS and Mercaptans”. 86th GPA Annual Conference, Gas Processors Association, San Antonio, TX, USA.

Chakma, A., and A. Meisen. 1990. “Improved Kent-Eisenberg Model for Predicting CO_2 Solubilities in Aqueous Diethanolamine (DEA) Solutions.” *Gas Separation and Purification* 4(1): 37–40.

Chakravarty, T., U.K. Phukan, and R.H. Weiland. 1985. “Reaction of Acid Gases with Mixtures of Amines.” *Chemical Engineering Progress* 4: 32–36.

Chamberlain, R.M., M.J.D. Powell, C. Lemarechal, and H.C. Pedersen. 1982. “The Watchdog Technique for Forcing Convergence in Algorithms for Constrained Optimization.” in *Algorithms for Constrained Minimization of Smooth Nonlinear*

Functions: Buckley, A.G., and J.L. Goffin, Eds., pp. 1–17, Mathematical Programming Studies, Vol. 16, MATHPROGRAMM, Springer, Berlin, Germany.

Chapel, D.G., C.L. Mariz, and J. Ernest. 1999. “Recovery of CO_2 from Flue Gases: Commercial Trends.” in *Annual Meeting of the Canadian Society of Chemical Engineering*, Saskatoon, Saskatchewan, Canada.

Chapman, W.G., K.E. Gubbins, G. Jackson, and M. Radosz. 1990. “New Reference Equation of State for Associating Liquids.” *Industrial & Engineering Chemistry Research* 29(8): 1709–1721.

Chen, C.-C., and L.B. Evans. 1986. “A Local Composition Model for the Excess Gibbs Energy of Aqueous Electrolyte Systems.” *American Institute of Chemical Engineers Journal* 32(3): 444–454.

Chueh, P. L., and J. M. Prausnitz. 1967. “Vapor-Liquid Equilibria at High Pressures: Calculation of Partial Molar Volumes in .Nonpolar Liquid Mixtures.” *American Institute of Chemical Engineers Journal* 13(6): 1099–1113.

Chunxi, L., and W. Fürst. 2000. “Representation of CO_2 and H_2S Solubility in Aqueous MDEA Solutions Using an Electrolyte Equation of State.” *Chemical Engineering Science* 55(15): 2975–2988.

Cornelissen, R., A.A.C.M. Beenackers, F.P.H. van Beckum, and W.P.M. van Swaaij. 1980. “Numerical Calculation of Simultaneous Mass Transfer of Two Gases Accompanied by Complex Reversible Reactions.” *Chemical Engineering Science* 35(5): 1245–60.

Cousins, A., L.T. Wardhaugh, and P.H.M. Feron. 2011. "*Preliminary Analysis of Process Flow Sheet Modifications* for E*nergy Efficient* CO_2 *Capture* from F*lue Gases Using Chemical Absorption*." *Chemical Engineering Research and Design, 89*(*8A*): 1237–1251.

CuiQing, G.M.L., and R. ShaoMei. 2004. "ChemCAD Software and Application in Chemical Engineering Course Design." *Computers and Applied Chemistry* 5: 028.

Danckwerts, P.V., and K.M. McNeil. 1967. “The Effects of Catalysis on Rates of Absorption of CO_2 into Aqueous Amine Potash Solutions.” *Chemical Engineering Science* 22(7): 925–930.

Danckwerts, P.V., and M.M. Sharma. 1966 "Absorption of Carbon Dioxide into Solutions of Alkalis and Amines." *The Chemical Engineer*: 244–280.

DeCoursey, W. 1974. "Absorption with Chemical Reaction: Development of a New Relation for the Danckwerts Model." *Chemical Engineering Science* 29(9): 1867-1872.

Derks, P.W.J., J.A. Hogendoorn, and G.F. Versteeg. 2010. “Experimental and Theoretical Study of the Solubility of Carbon Dioxide in Aqueous Blends of Piperazine and N-Methyldiethanolamine.” *Journal of Chemical Thermodynamics* 42(1): 151–163.

Deshmukh, R.D, and A.E. Mather. 1981. “A Mathematical Model for Equilibrium Solubility of Hydrogen Sulfide and Carbon Dioxide in Aqueous Alkanolamine Solutions.” *Chemical Engineering Science* 36(2): 355–362.

Deshpande, P.B., *and* R.H. Ash. *1988*. *“Computer* Process Control with Advanced Control Applications.” *2nd Ed., Instrument Society of America*, Research Triangle Park, NC, USA.

Dugas, R., P. Alix., E. Lemaire., P. Broutin., and G. Rochelle. 2009. "Absorber Model for CO_2 Capture by Monoethanolamine - Application to CASTOR Pilot Results." *Energy Procedia* 1: 103–107.

Edwards, T.J. 1974. "Thermodynamics of Aqueous Solutions Containing One or More Volatile Weak Electrolytes." Master's Thesis, University of California, Berkeley CA, USA.

Edwards, T.J., G. Maurer, J. Newman, and J.M. Prausnitz. 1978. “Vapor-liquid Equilibria in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes.” *American Institute of Chemical Engineers Journal* 24(6): 966–976.

Erfani, A., S. Boroojerdi, and A. Dehghani. 2015. “Simulation of an Operational Amine Based CO_2 Removal Plant as an Example of CO_2 Capture at Coal-Fired Power Plants.” *Petroleum and Coal* 57(1): 85–92.

ErikØi, L. 2012. “Comparison of Aspen HYSYS and Aspen Plus Simulation of CO_2 Absorption into MEA from Atmospheric Gas.” *Energy Procedia* 23: 360–369.

Ermatchkov, V., Á.P-S. Kamps, and G. Maurer. 2006. “Solubility of Carbon Dioxide in Aqueous Solutions of N-Methyldiethanolamine in the Low Gas Loading Region.” *Industrial and Engineering Chemistry Research* 45(17): 6081–6091.

Faramarzi, L., G.M. Kontogeorgis, K. Thomsen, and E.H. Stenby. 2009. “Extended UNIQUAC Model for Thermodynamic Modeling of CO_2 Absorption in Aqueous Alkanolamine Solutions.” *Fluid Phase Equilibria* 282(2): 121–132.

Feng, Z., S. Benxian, S. Hui, L. Jichang, and S. Jianfeng. 2015. "Simultaneous Removal of H_2S and Organosulfur Compounds from Liqueifed Petroleum Gas Using Formulated Solvents: Solubility Parameter Investigation and Industrial Test." *China Petroleum Processing and Petrochemical Technology* 17(1): 75-81.

Fletcher, R., and C.M. Reeves, 1964. “Function Minimization by Conjugate Gradients.” *The Computer Journal* 7: 149-154.

Fong, H.L., D.S. Kushner, and R.T. Scott. 1987. “Gas Desulfurization Using Sulferox.” *Proceedings of Laurence Reid Gas Conditioning Conference,* University of Oklahoma, Norman OK, USA: 2–4.

Foss, B.A., B. Lohmann, and W. Marquardt. 1998. "A Field Study of the Industrial Modeling Process." *Journal of Process Control* 8(5-6): 325-338.

Fürst, W., and H. Renon. 1993. “Representation of Excess Properties of Electrolyte

Solutions Using a New Equation of State." *American Institute of Chemical Engineers Journal* 39(2): 335–343.

Gas Processors and Suppliers Association. 2004a. "Engineering Data Book." 12th Edition, Section 8, Fired Equipment, GPSA, Tulsa, OK, USA: 8-7.

Gas Processors and Suppliers Association. 2004b. "*Engineering Data Book*." 12th Edition, Section 21, Hydrocarbon Treating, GPSA, Tulsa, OK, USA: 611-644.

Guggenheim, E.A., and J.C. Turgeon. 1955. "Specific Interaction of Ions." *Transactions of the Faraday Society* 51: 747–761.

Gupta, S.K. 2015. "Numerical Methods for Engineers." 3rd Edition. New Age International Publishers, New Delhi, India.

Hanley, B., and C.C. Chen. 2012. "*New Mass* T*ransfer Correlations for Packed Towers,*" *American Institute of Chemical Engineers Journal 58(7): 132-152.*

Hanyak, M.E. 2012. "Chemical Process Simulation and the Aspen HYSYS Software." *Department of Chemical Engineering, Bucknell University*, Lewisburg, PA, USA.

Hessen, E.T., T.H.-Warberg, and H.F. Svendsen. 2009. "Thermodynamic Models for CO_2-H_2O-Alkanolamine Systems, a Discussion." *Energy Procedia* 1(1): 971–978.

Hilliard, M.D. 2008. "A Predictive Thermodynamic Model for an Aqueous Blend of Potassium Carbonate, Piperazine, and Monoethanolamine for Carbon Dioxide Capture from Flue Gas." *Doctoral Thesis at* the Norwegian University of Science and Technology, Trondheim, Norway.

Holmes, J.W., M.L. Spears *and* J.A. Bullin. 1984. "Sweetening LPGs with Amines." *Chemical Engineering Progress*: 80(5), 47–50.

Huttenhuis, P.J.G., N.J. Agrawal, E. Solbraa, and G.F. Versteeg. 2008. "The Solubility of Carbon Dioxide in Aqueous N-Methyldiethanolamine Solutions." *Fluid Phase Equilibria* 264(1–2): 99–112.

Ishii, Y., and F.D. *Otto*. 1973. "A *General Algorithm* for *Multistage Multicomponent Separation*. *Calculations*." *Canadian Journal* of *Chemical Engineering 51*: *601–606.*

Jones, D.S. and P.P. Pujadó. 2006. “Handbook of Petroleum Processing.” Springer Science and Business Media, Berlin, Germany.

Jou, F.-Y., A.E. Mather, and F.D. Otto. 1982. “Solubility of H_2S and CO_2 in Aqueous Methyldiethanolamine Solutions.” *Industrial and Engineering Chemistry, Process Design and Development* 21: 539–544.

Kamps, Á.P.-S., J. Xia, and G. Maurer. 2003. “Solubility of CO_2 in (H_2O + Piperazine) and in (H_2O + MDEA + Piperazine).” *American Institute of Chemical Engineers Journal* 49(10): 2662–2670.

Katti, S.S., *and* R.A. Wolcott. 1987. “Fundamental Aspects of Gas Treating with Formulated Amine Mixtures.” *American Institute of Chemical Engineers Meeting,* Minneapolis, MN, USA.

Kenig, E.Y., R. Schneider, and A. Górak. 2001. “Reactive Absorption: Optimal Process Design *via* Optimal Modelling.” *Chemical Engineering Science* 56(2): 343–350.

Kent, R.L., and B. Eisenberg. 1976. “Better Data for Amine Treating.” *Hydrocarbon Processing* 55(2): 87-90.

Kidnay, A.J., and W.R. Parrish. 2006. “Fundamentals of Natural Gas Processing.” CRC Press, Boca Raton, FL, USA 418.

Kim, S., and H.-T. Kim. 2004. “Aspen Simulation of CO_2 Absorption System with Various Amine Solution.” *Preprint, American Chemical Society, Division of Fuel Chemistry* 49: 251–252.

Kohl, A.L., and R. Nielsen. 1997. “*Gas Purification”*. Gulf Professional Publishing, Houston, TX, USA.

Kooijman, H.A., and R. Taylor. *2006. "The ChemSep Book*." 2^{nd} Edition, Amsterdam, Netherlands.

Koto, J. 2014. “Absorption Acid Gas Removal in Liquefied Natural Gas Process.” *Journal of Ocean, Mechanical and Aerospace Science and Engineering*, 7: 24-28.

Krishna, R., and G.L. Standart. 1976. "A Multicomponent Film Model Incorporating a General Matrix Method of Solution to the Maxwell-Stefan Equations. *American Institute of Chemical Engineers Journal*, 22(2), 383–389.

Krishnamurthy, R., and R. Taylor. 1985. "A Nonequilibrium Stage Model of Multicomponent Separation Processes. Part I: Model Description and Method of Solution." *American Institute of Chemical Engineers Journal* 31(3): 449–456.

Kuester, J.L. and J.H. Mize. 1973. “Optimization Techniques with Fortran.” McGraw-Hill, New York.

Lee, J.-H., and M.P. Dudukovic. (1998). A Comparison of the Equilibrium and Nonequilibrium Models for a Multicomponent Reactive Distillation Column. *Computers and Chemical Engineering*, 23(1), 159–172.

Li, Y.-G., and A.E. Mather. 1994. “Correlation and Prediction of the Solubility of Carbon Dioxide in a Mixed Alkanolamine Solution.” *Industrial and Engineering Chemistry Research* 33(8): 2006–2015.

Lokhandwala, K.A., R.W. Baker, and K.D. Amo. 1995. “Sour Gas Treatment Process.” *United States Patent****, Patent Number:*** 5407467.

Luo, X., J.N. Knudsen., D.D. Montigny, D. Sanpasertparnich, T. Idem, R. Gelowitz, D. Notz, R. Hoch, S. Hasse., and E. Lemaire. 2009. “Comparison and Validation of Simulation Codes against Sixteen Sets of Data from Four Different Pilot Plants.” *Energy Procedia* 1(1): 1249–56.

Mandal, B., and S.S. Bandyopadhyay. 2006. “Simultaneous Absorption of CO_2 and H_2S into Aqueous Blends of N-Methyldiethanolamine and Diethanolamine.” *Environmental Science and Technology* 40(19): 6076–6084.

McGuire, P.L., R. Okuno, L.G. Thomas, and L.W. Lake. 2017. “Ethane-Based Enhanced Oil Recovery: An Innovative and Profitable Enhanced-Oil-Recovery Opportunity for a Low-Price Environment.” *SPE Reservoir Evaluation and Engineering* 20(1): 42–58.

Media, A. 2016. "Statistical Review of Global LPG." *Argus Media Group,* Argus House, London, UK.

Minear-Matar, J., A. Janson, A. Hussain, and S. Adham. 2017. “Application of Membrane Contactors to Remove Hydrogen Sulfide from Sour Water.” *Journal of Membrane Science* 541: 378-385.

Mokhatab, S., A.P. William, and J.G. Speight. 2006. “*Handbook of Natural Gas Transmission and Processing*”. Gulf Professional Publishing, Houston, TX, USA.

NACE. 2002. "Corrosion Costs and Preventive Strategies." NACE International, Houston, TX, USA.

Nordsveen, M., S. Nesic, R. Nyborg and A. Stangeland. 2003. "A Mechanistic Model for Carbon Dioxide Corrosion of Mild Steel in the Presence of Protective Iron Carbonate Films—Part 1: Theory and Verification." *Corrosion* 59: 443–456.

Northrop, P.S., and J.A. Valencia. 2009. “The CFZ^{TM} Process: A Cryogenic Method for Handling High CO_2 and H_2S Gas Reserves and Facilitating Geosequestration of CO_2 and Acid Gases.” *Energy Procedia* 1(1): 171–177.

Nuchitprasittichai, A., and S. Cremaschi. 2013. “Optimization of CO_2 Capture Process with Aqueous Amines: A Comparison of Two Simulation-Optimization Approaches.” *Industrial and Engineering Chemistry Research* 52(30): 10236–10243.

Onda, *K.,* H. Takeuchi and Y. Okumoto. *1968.* *"*Mass Transfer Coefficients between Gas and Liquid Phases in Packed Columns.*" Journal of Chemical Engineering of Japan 1:* 56–62.

Peng, D.-Y. and D.B. Robinson. 1976. "A New Two-Constant Equation of State." *Industrial and Engineering Chemistry, Fundamentals* 15(1): 59-64.

Pitzer, K.S., and J.M. Simonson. 1986. "Thermodynamics of Multicomponent, Miscible, Ionic Systems: Theory and Equations." *The Journal of Physical Chemistry* 90(13): 3005–3009.

Poe, W.A., and S. Mokhatab. *2016*. "Modeling, Control and Optimization of Natural Gas Processing Plants*."* 1st Edition, Gulf Professional Publishing, Houston, TX, USA.

Polasek, J.C., G.a.I.-Silva and J.A. Bullin. 1992. "Using Mixed Amine Solutions for Gas Sweetening." *Proceedings of the 71st GPA Annual Convention, Gas Processors Association*, Tulsa, OK: 58-63.

Posey, M.L., and G.T. Rochelle. 1997. "A Thermodynamic Model of Methyldiethanolamine (CO_2−H_2S–Water)." *Industrial and Engineering Chemistry Research*: 36(9): 3944–3953.

Powell, M.J.D. 1978. "A Fast Algorithm for Nonlinearly Constrained Optimization Calculations, "*Numerical Analysis*", Lecture Notes in Mathematics, G.A. Watson, Ed., Springer, Berlin, Germany, 630.

Press, W.H., B.P. Flannery, S.A. Teukolsky, and W.T. Vetterling. 1989. "*Numerical Recipes*." Cambridge University Press, Cambridge, UK.

Qeshta, H.J., S. Abuyahya, P. Pal, and F. Banat. 2015. "Sweetening Liquefied Petroleum Gas (LPG): Parametric Sensitivity Analysis Using Aspen HYSYS." *Journal of Natural Gas Science and Engineering* 26: 1011–1017.

Rajani, J.B. 2004. *"*Treating Technologies of Shell Global Solutions for Natural Gas and

Refinery Gas Streams.” *12th Oil and Gas Petrochemical Congress in Tehran, Research Institute of Petroleum*, Iran.

Ramón, L.S. 2013. “Auto Gas in Europe, the Sustainable Alternative, an LPG Industry Roadmap.” *European LPG Association (AEGPL)*, Brussels, Belgium.

Redlich, *O., and* J.N.S Kwong. 1949. *"*On the Thermodynamics of Solutions. V. An Equation of State Fugacities of Gaseous Solutions.” *Chemical Reviews* 44: 233–244.

Rennie, S. 2006. “Corrosion and Materials Selection for Amine Service”, *Materials Forum* 30:126–130.

Rooney, P.C. 2001. “Composition and Process for Removal of Acid Gases.” *United States Patent, Patent Number: 6,165,432, Dow Chemical Company*, Midland, MI, USA.

Sardar, H., and R.H. Weiland. 1984. “A Nonequilibrium Stage Approach for the Design and Simulation of Gas Treating Units.” *American Institute of Chemical Engineers Annual Meeting*, San Francisco, CA, USA.

Sardar, H., M.S. Sivasubramanian., and R.H. Weiland. 1985. "*Simulation of Commercial Amine Treating* Units." *35th Proceedings of the Gas Conditioning Conference*, *University of Oklahoma, Norman*, OK, USA.

Scheffe, R.D. 1984. “Mass Transfer Characteristics of Valve Trays.” Ph.D. Thesis, Clarkson University, Potsdam, NY, USA.

Schefflan, R. 2016. “Teach Yourself the Basics of Aspen Plus.” Wiley, Hoboken, NJ, USA.

Seader, J.D., E.J. Henley and D.K. Roper. 2011. "Separation Process Principles." *3rd Edition.*, Wiley, Hoboken, NJ, USA.

Sharma, M.M., R.A. Mashelkar, and V.D. Mehta. 1969. "Mass Transfer in Plate Columns." *British Chemical Engineering* 14: 70–76.

Smith, S.N., and M.W. Joosten. 2006. “Corrosion of Carbon Steel by H_2S in CO_2 Containing Oilfield Environments.” *Nace - International Corrosion Conference Series* (6115): 1–26.

Soave, G. 1972. "Equilibrium Constants from a Modified Redlich-Kwong Equation of State." *Chemical Engineering Science*, 27: 1197–1203.

Solbraa, E. 2002. *“*Equilibrium and Non-equilibrium Thermodynamics of Natural Gas Processing*." Ph.D. Thesis, Norwegian University* of *Science and Technology*, Trondheim, Norway.

Sun, W., and S. Nesic. 2009. "A Mechanistic Model of Uniform Hydrogen Sulfide/Carbon Dioxide Corrosion of Mild Steel." *Corrosion* **65**(5): 291-307.

Thomsen, K., and P. Rasmussen. 1999. “Modeling of Vapor-Liquid-Solid Equilibrium in Gas-Aqueous Electrolyte Systems.” *Chemical Engineering Science* 54(12): 1787-1802.

Tobiesen, F.A., M. Hillestad, H. Kvamsdal, and A. Chikukwa. 2012. “A General Column Model in CO_2SIM for Transient Modelling of CO_2 Absorption Processes.” *Energy Procedia* 23(1876): 129–139.

Tomcej, A.R., and F.D. Otto. 1989. “Absorption of CO_2 and N_2O into Aqueous Solutions of Methyldiethanolamine.” *American Institute of Chemical Engineers Journal* 35(5): 861–864.

Tomcej R.A., F.D. Otto, H.A. Rangwala, and B.R. Marrel. 1987. “Tray Design for Selective Absorption Gas.” in *Gas Conditioning Conference*. Norman, OK, USA.

Tse, J., and J. Santos. 1993. *“*The Evaluation and Design of LPG Treaters.” *Laurance Reid Gas Conditioning Conference Proceedings*, *43rd Annual Conference*, University of Oklahoma, Norman, *OK, USA.*

UOP 825-81, Monoethanolamine in Solutions by Color Indicator Titration, ASTM International, West Conshohocken, PA, USA, 2002, www.astm.org.

Vallée, G., P. Mougin, S. Jullian, and W. Fürst. 1999. "Representation of CO_2 and H_2S absorption by Aqueous Solutions of Diethanolamine Using an Electrolyte Equation of State." *Industrial* and *Engineering Chemistry Research 38*(*9): 3473*-3480.

van Swaaij, W.P.M., and G.F. Versteeg. 1992. "Mass Transfer Accompanied with Complex Reversible Chemical Reactions in Gas-liquid Systems: An Overview." *Chemical Engineering Science* 47(13–14): 3181–3195.

Vitse, F., B. Baburao., R. Dugas., L. Czarnecki L., and C. Schubert. 2011. "Technology and Pilot Plant Results of the Advanced Amine Process." *Energy Procedia* 4: 5527–5533.

Walt, H., 2017. "Finding Global End Use Markets for the Growing LPG Supply." IHS Markit, London, UK.

Weiland, R.H., M. Sivasubramanian, and J.C. Dingman. 2003. "Effective Amine Technology: Controlling Selectivity, Increasing Slip, and Reducing Sulfur." 53rd Annual Laurance Reid Gas Conditioning Conference, Norman, OK, USA 24:79-97.

Weiland, R.H., H. Sardar and M.S. Sivasubramanian. 1985. "Simulation of Commercial Amine Treating Units." *Proceedings of the 35th Annual Lawrence Reid Gas Conditioning Conference*. University of Oklahoma, Norman, OK, USA.

Weise, T.G. 2009. *"Optimization Algorithms--Theory and Application."* 2nd Edition, University of Kassel, Distributed Systems Group, self published.

Wellek, W.R., J.R.H. Brunson, and F. Law. 1978. "Enhancement Factors for Gas-Absorption with Second-Order Irreversible Chemical Reaction." *The Canadian Journal of Chemical Engineering* 56(2): 181–186.

Yu, W.C., and G. Astarita. 1987. "Selective Absorption of Hydrogen Sulphide in Tertiary Amine Solutions." *Chemical Engineering Science* 42(3): 419-424.

Zare, A.H., and H.S. Mirazei. 2009. “Removal of CO_2 and H_2S using Aqueous Alkanolamine Solutions.” *World Academy of Science, Engineering and Technology* 49: 1-2.

Zhang, Y., and C.C. Chen. 2013. “Modeling CO_2 Absorption and Desorption by Aqueous Monoethanolamine Solution with Aspen Rate Based Model.” *Energy Procedia* 37: 1584-96.