NATURAL GAS HYDRATES AND OPTIMIZATION OF COOLING LOAD FOR DEHYDRATION

[1]Waheed Asif, [2]Sana Zahid, [3]Masooma Rustam, [4]Sidra Jabeen, [5]Asim Umer*
Department of Chemical Engineering, University of Engineering & Technology, Lahore, Pakistan
*Department of Chemical Engineering,
Muhammad Nawaz Sharif University of Engineering & Technology, Multan, Pakistan
* asimumer@uet.edu.pk

ABSTRACT: *Drilled natural gas contains fraction of water vapors which can result in line plugging by the hydrate formation. It can also reduce the line capacity due to collection of free water hence can increase the risk of damage to the pipeline and equipments with the corrosive effects of condensed water. Therefore, water vapors must be removed from natural gas up to maximum water limits set by the international standards to prevent damaging effects. In this study natural gas dehydration is investigated by condensation method in which water is separated from the wet natural gas by controlling dew point with the provision of cooling load. A simulation program is developed in HYSYS to determine and optimization of cooling load for water separation. The introduction of pre-cooler before chiller resulted in the 49 % reduction of the cooling load for the dehydration of natural gas.*

Index Terms- Natural gas hydrates, Hydrate structure, Gas dehydration, cooling load optimization

INTRODUCTION:

Natural gas is a mixture of gases, rich in hydrocarbons formed from the buried fossils and plants under high pressure and temperature for thousands of years. Natural gas is available in two phases' hydrates and gas. Both can produce natural gas as a source of energy. Natural gas hydrates reserves are distributed all over the earth about 1.5 x 10^6 m^3 but it still required study for exploring natural gas from the hydrates [1]. Gaseous natural gas is drilled out in gaseous phase contains many impurities particularly water. It is processed to remove all the impurities and used for fuel as the replacement of oil and coal. Condensed water can cause corrosion, erosion or rusting to the equipment, valves, fitting and pipelines. Under favorable conditions, as high pressure and low temperature crystalline compounds formed by the association of water molecules (host) with natural gas (guest) named as natural gas hydrates shown in Figure 1 [8]. Natural gas hydrates causes number of damaging problems for the downstream users including blockage of pipe line. To avoid such problems different studies were carried out to limit water content in natural gas. Standard water quantity in natural gas in the USA and Canada should be less than 7 Lbs/MMCF of wet natural gas which is equivalent to 0.112 grams of water/Sm^3 of wet gas [2]. A typical water specification for gas is 112 mg/Sm^3(7 Lbs/MMSCF of wet natural gas) in the USA while 64 mg/Sm^3 (4 Lbs/MMSCF of wet natural gas) in the Canada and in terms of dew point common specification is -10 ^oC [3]. In Europe the concentration of water is expressed in terms of dew point of water which is -7 ^oC for natural gas at 4 MPa and dew point for hydrocarbons is 0 ^oC at operating pressure. This is equivalent to 0.131 grams of water/Sm^3 of natural gas at 4 MPa. In Nigeria water dew point should be less than 4 ^oC for natural gas at 4 MPa, its means that the natural gas can contain more than twice as much water vapor as in Europe. Further more water quantity in wet natural gas can be calculated by the following equation (1) [4],

$$W_{water} = 593.335*exp(0.05486* t_G)*P_G^{-0.814\ 2} \quad \text{—(1)}$$

W_{water} is in Kilogram of water per 10^6 Sm^3 of natural gas
t_G is temperature of natural gas in ^oC
P_G is pressure of natural gas in MPa.

The range of water in wet natural gas is 4–7 Lbs/MMSCF equivalent to 60-110 mg/m^3 of wet natural gas. Water quantity in wet natural gas depends on its temperature while methane hydrate formation is a function of pressure and specific gravity [5].

The equation (2) about the formulation of natural gas hydrates shows one methane molecule is surrounded by n (approximately 6) water molecules causing Ice crystals [6]

$$(CH_4)_{(g)} + n\,(H_2O)_{(l)} \rightarrow (CH_4.NH_2O_{(s)} \quad (2)$$

1 m^3 of water may tie up to 207 Sm^3 of methane to form 1.26 m^3 of solid hydrate, while without gas same volume of pure water freezes to form 1.09 m^3 of ice. Density of methane hydrate is about 0.910 gram/cm^3 which is less than water density that is why hydrates floats on water. Formation of gas hydrates is exothermic reaction while dissociation is endothermic. [1, 6].

There are three types of Natural Gas hydrates SI, SII and SH. SI and SII are well characterized while SH less understood as discovered recently. [3, 7].

Removal of water from natural gas is known as dehydration and this process is carried out by number of ways just as absorption, adsorption, condensation and general methods.In absorption method water is absorbed in liquid desiccant. Water contents are down up to 10 ppmv in the processed stream. Liquid desiccants which are mostly used are mono ethylene glycol (MEG), di ethylene glycol (DEG), tri ethylene glycol (TEG) and tetra ethylene glycol (TrEG).[4, 8, 10, 11, 12].

In adsorption method water is trapped in the lattices available on the surface of solid desiccant. Capital cost of adsorption is 2-3 times higher than absorption also operation cost for adsorption is higher than absorption. Silica gel (gel type) activated alumina Al_2O_3 and molecular sieves (zeolites) are used for the adsorption of water from the natural gas. [4, 5, 10, 11].

Condensation / refrigeration dehydration method has a wide range of applications in the industries particularly in gas process industry [11]. Low temperature separation processes required heat rejection to the refrigeration system. The cost of the process can be found out by knowing the requirement of the power of compression and refrigerant make up cost etc.

Carnot cycle is the basic working principle for this technique. The out let stream temperature can be lowered down up to -40 °C [9][13]. Refrigeration system is used for removing of water, chilling natural gas for NGL extraction, chilling natural gas for hydrocarbon dew-point control, LPG Product storage and natural gas liquefaction (LNG) etc [10]. Refrigerant selection is based on the cooling requirements and the latent heat of vaporization of refrigerant itself. Propane is used as refrigerant.

From feed gas composition and data it is known that almost 1152 Lbs of water is available in 5 MMSCFH of wet gas and 1117 Lbs of water should be removed while hydrate point and dew point must also be less than 0 °C. As refrigeration system can be used up to -40 °C and it is recommended to be used for this study. This study will be carried out by using HYSYS software. Absorption method is not selected as in case of TEG selection minimum dew point is about -7.2 °C. Adsorption is recommended only for low water quantity while in this case water to be removed is about 1117 Lbs and it is also not recommended for hydrocarbons. General methods because of demerits are not selected.

PROCESS DESCRIPTION:

Drilled wet sour gas is processed as shown in Figure 1. After condensed liquid separation, drilled gas is introduced in to acid gas removal section where H_2S is removed by absorption into circulating methyl di-ethanolamine. Amine is converted from lean amine to rich amine. In the same section partially CO_2 is also removed. Rich amine is sent to amine regeneration unit where absorbed H_2S desorbed by heating with steam. Acid gas is sent to sulfur recovery section. Sweet gas is then sent to gas dehydration unit where water from wet gas is separated by chilling effect followed by mercury and nitrogen removal units. Prior to sweetening, gas is splitted into methane, ethane and ethane plus fractions. In sweetening merox and sulfrex processes are applied for finally removal of aromatic and sulfur compounds if any. Now dry and sweet gas is available for users, gas liquefaction and storage.

Dehydration Process Description

Gas with flow rate of 5 MMCFH, temperature of 42 °C and pressure of 5 MPa is introduced into tube side of evaporator of dehydration unit as shown in the Figure 2. Gas composition is given in Table 1. Propane is used as refrigerant, in evaporator on shell side, propane vapors gathered in knock out drum at operating pressure and temperature of 4 barg and 8 °C respectively. In knock out drum droplet or liquid of propane is collected at bottom and transferred to evaporator by pump controlled with level control valve. Only propane vapors are passed through demister prior to reach compressor suction. Compressor increased the pressure by vapor compression up to 15 barg and temperature up to 50 °C. In condenser temperature is removed by circulating cooling water and vapors are condensed to form liquid propane. Liquid propane is passed through flash valve controlled by propane level controller from evaporator. In evaporator propane is evaporated under low pressure caused cooling for natural gas up to -3 °C. Natural gas is then sent to a three phase separator where water, heavier hydrocarbons and dry gas are separated. Finally, the dry natural gas is transported to the end users.

SIMULATION DEVELOPMENT:

Simulation model is generated by using the built-in units in the Aspen HYSYS. Firstly the components are selected as shown in Table 1 and then Peng Robinson fluid package is selected to enter the simulation environment. Peng Robinson fluid package is the most suitable fluid package for the hydrocarbons. Further our temperature range for the calculation in the simulation is >-21 °C that is why it is selected for generating the PDF in HYSYS In order to simulate the evaporator built-in heat exchanger model has been selected while for the separator a built-in three phase separator unit is used. Wet gas composition, flow rate, temperature and pressure are given in Table 1. The design case consist of only chiller and a separator as shown in Figure 3 While for the optimization a pre-cooler has been installed where the dry gas is used to cool the incoming wet natural gas to decrease the cooling load (Figure 4).

RESULTS & DISCUSSIONS:

Existing design study:

PFD is created on HYSYS by installing chiller and separator. Feed inlet conditions such as pressure, temperature, composition, and flow rate are provided as shown in Figure 3. In simulation by changing the downstream temperature the effect on the selected downstream parameters can be seen in Table 2. Graph is plotted between temperature and selected parameters and analyzed (Figure 5).

- Water separation sharply increased by decreasing temperature as decrease in vapor pressure results in condensation. This trend prominent up to 20 °C and then gradually increased.
- With cooling vapor pressure decreased and water quantity in gas decreased as well because of condensation. With decrease in temperature more and more cooling is required for decrease in vapor pressure. So cooling load is increased gradually by decreasing temperature up to -20 °C.
- Quantity of water in outlet natural gas is sharply decreased by decreasing temperature up to 0 °C and then gradually reduced.
- Dew point of natural gas remains almost linear by decreasing temperature up to 0 °C as vapor pressure up to this point is higher than partial pressure and then sharply decreased as both declined.
- Hydrate point of natural gas is remained almost linear by decreasing temperature up to 20 °C and then sharply decreased
- Heat of vaporization initially is high as mixture of gas and water but with removing water gas left behind having low heat of vaporization. Hence heat of vaporization gradually and lineally decreased with decreased in temperature.

For water in natural gas 4 – 7 Lbs/MMSCF temperature range for gas is found to be -8 to -0.5 °C. Dew point is -3.0 °C at natural gas temperature of -3.0 °C. Hydrate point is -1.2 °C at natural gas temperature of -3 °C. So set point for temperature for natural gas is -3 °C, dew point and hydrate curve can be seen in Figure 6. At set point cooling load is found to be 3871 KW and water is 6.0 Lbs/MMScf of outlet gas.

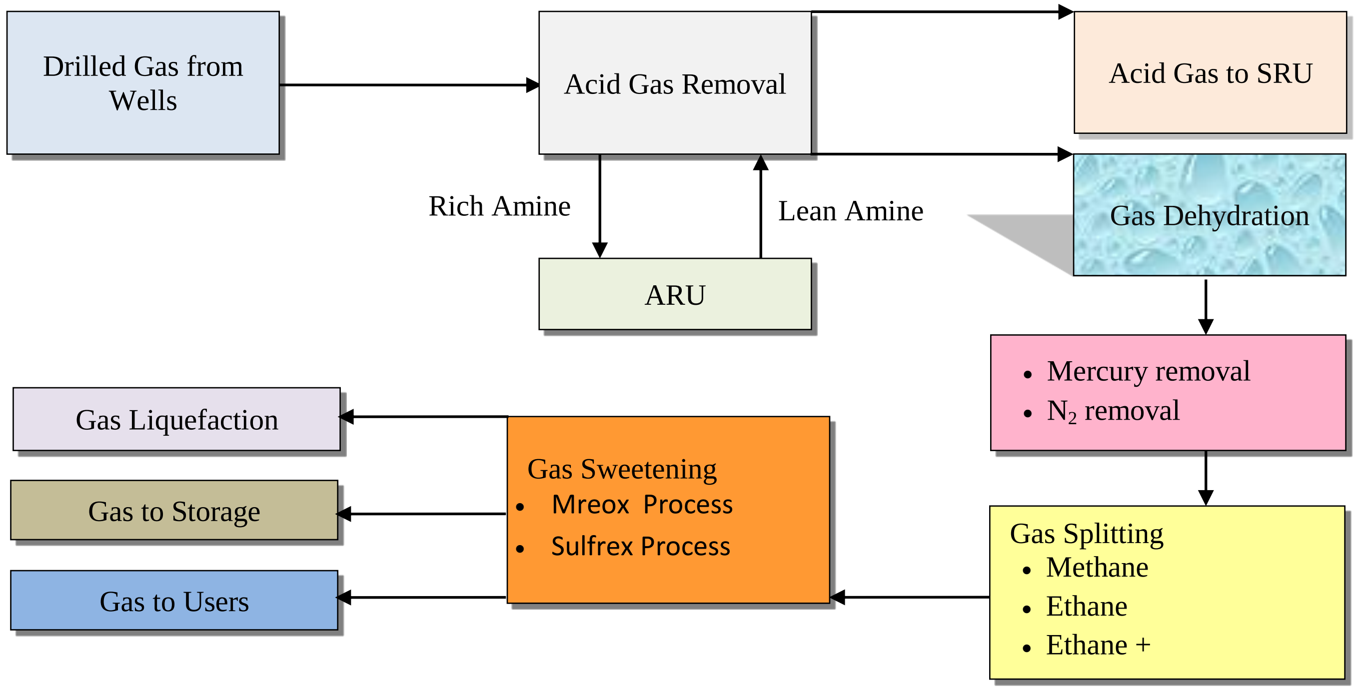


Figure 1: Gas processing plant

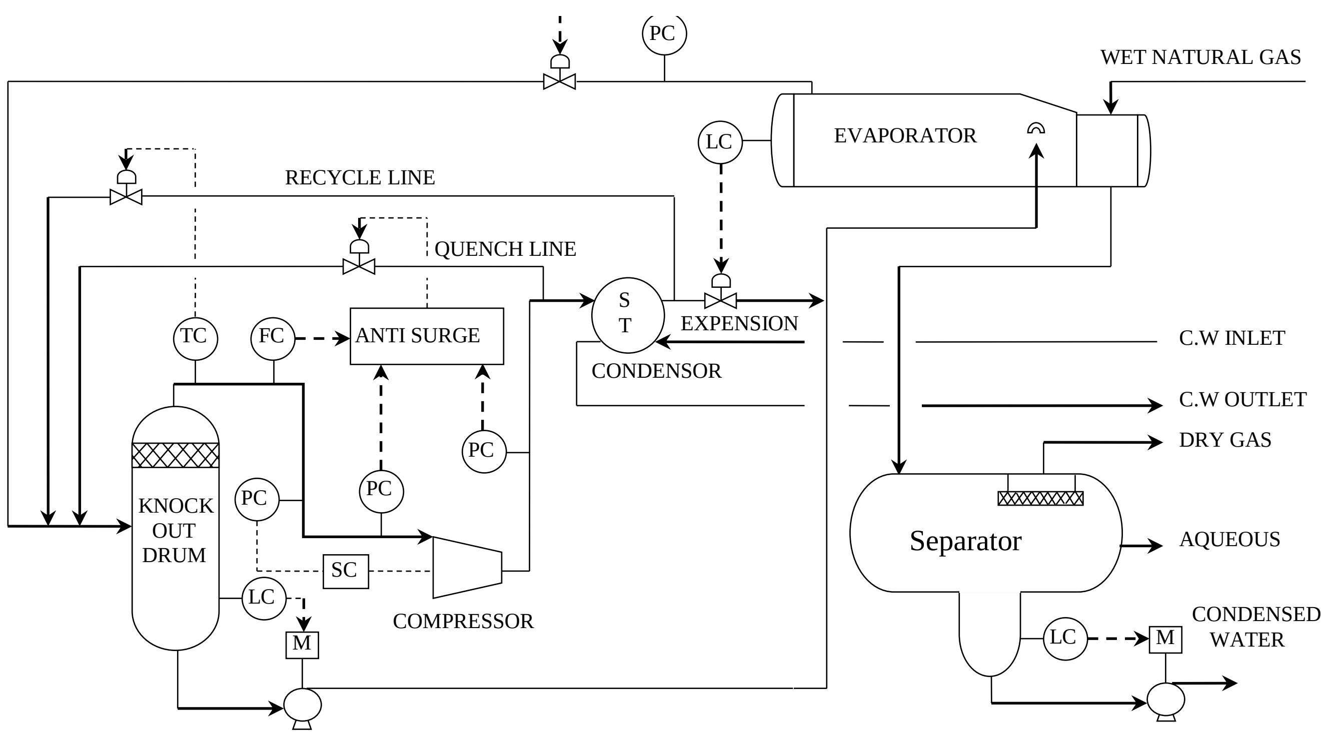
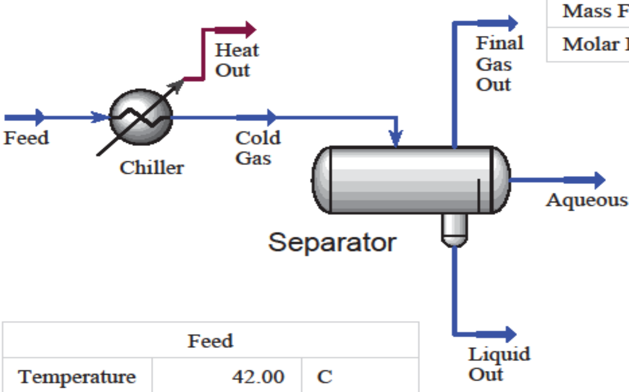


Figure 2 Dehydration Unit

Heat Out		
Heat Flow	1.394e+007	kJ/h
Power	3871	kW

Final Gas Out		
Temperature	-3.000	C
Pressure	4800	kPa
Molar Flow	5905	kgmole/h
Mass Flow	1.126e+005	kg/h
Molar Entropy	147.7	kJ/kgmole-C



Aqueous		
Temperature	-3.000	C
Pressure	4800	kPa
Molar Flow	43.98	kgmole/h

Feed		
Temperature	42.00	C
Pressure	5000	kPa
Molar Flow	5977	kgmole/h
Mass Flow	1.151e+005	kg/h

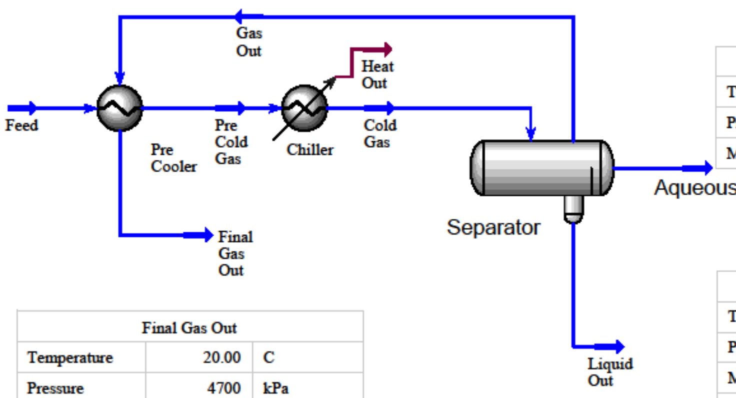
Liquid Out		
Temperature	-3.000	C
Pressure	4800	kPa
Molar Flow	28.29	kgmole/h
Mass Flow	509.7	kg/h

Figure 3: PFD for existing design case

Feed		
Temperature	42.00	C
Pressure	5000	kPa
Molar Flow	5977	kgmole/h
Mass Flow	1.151e+005	kg/h

Heat Out		
Heat Flow	7.054e+006	kJ/h
Power	1959	kW

Gas Out		
Temperature	-3.000	C
Pressure	4750	kPa
Molar Flow	5905	kgmole/h
Mass Flow	1.126e+005	kg/h
Molar Entropy	147.8	kJ/kgmole-C
Heat Of Vapourization	8076	kJ/kgmole



Aqueous		
Temperature	-3.000	C
Pressure	4750	kPa
Molar Flow	43.47	kgmole/h

Liquid Out		
Temperature	-3.000	C
Pressure	4750	kPa
Molar Flow	28.28	kgmole/h
Mass Flow	509.5	kg/h

Final Gas Out		
Temperature	20.00	C
Pressure	4700	kPa
Molar Flow	5905	kgmole/h
Mass Flow	1.126e+005	kg/h
Molar Entropy	152.0	kJ/kgmole-C

Figure 4 : PFD for optimized case

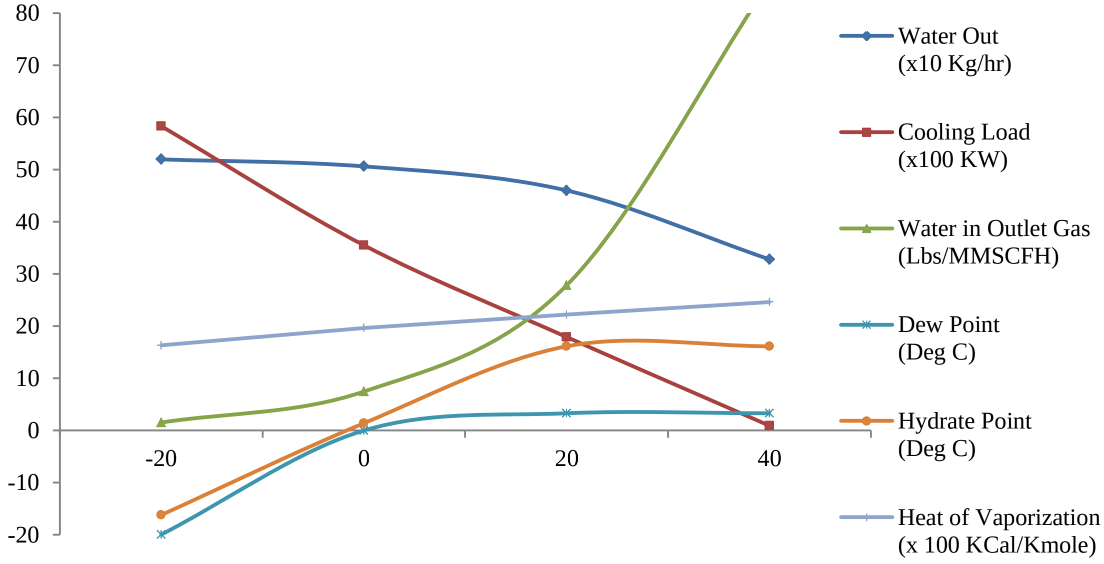
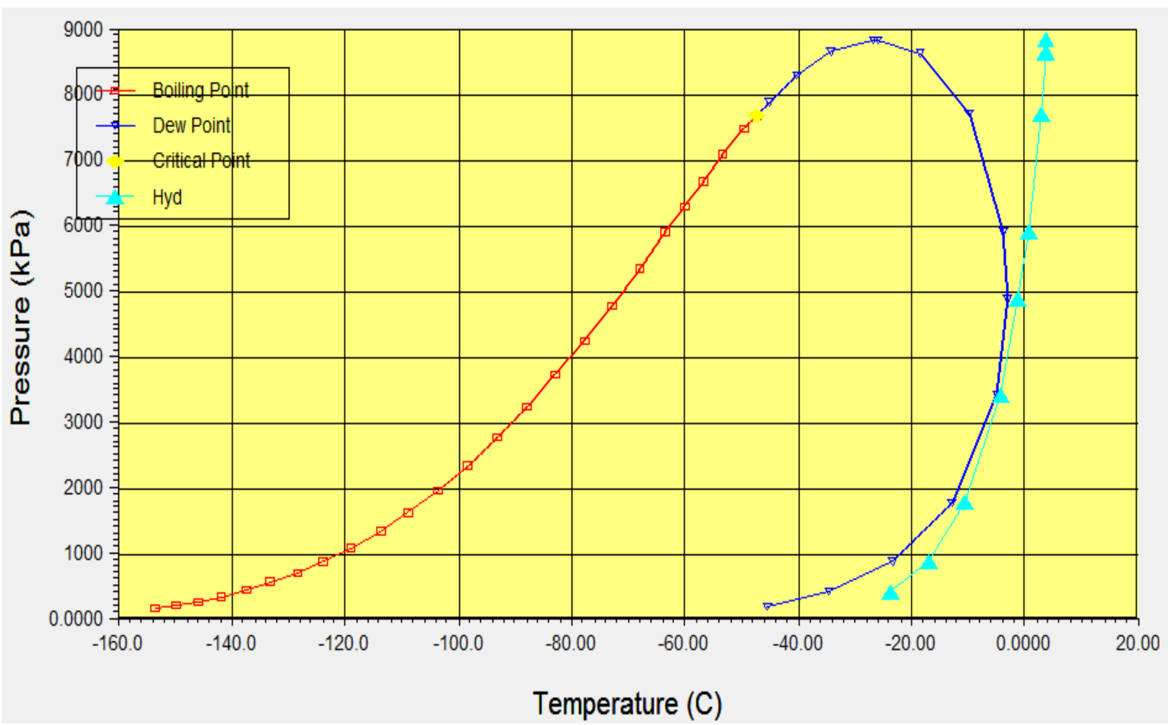


Figure 5: : Temperature vs Downstream Parameters in Existing design case



Figue 4: Graph between pressure, temperature, dew point, hydrate point and boiling point in design case

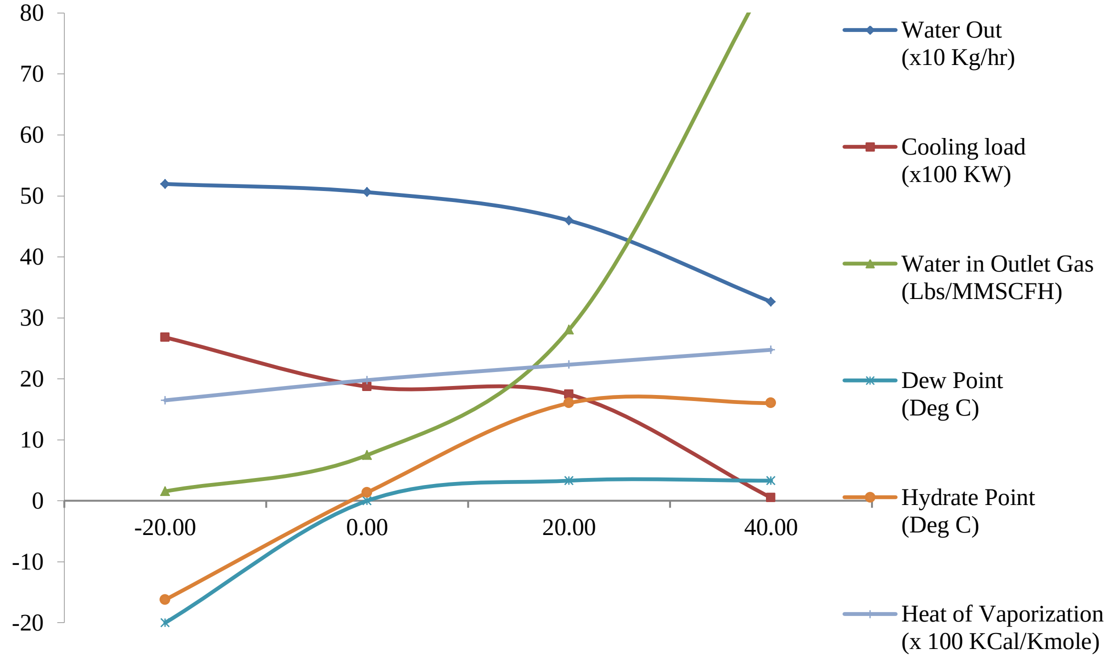


Figure 6: Temperature vs downstream parameters in optimized case

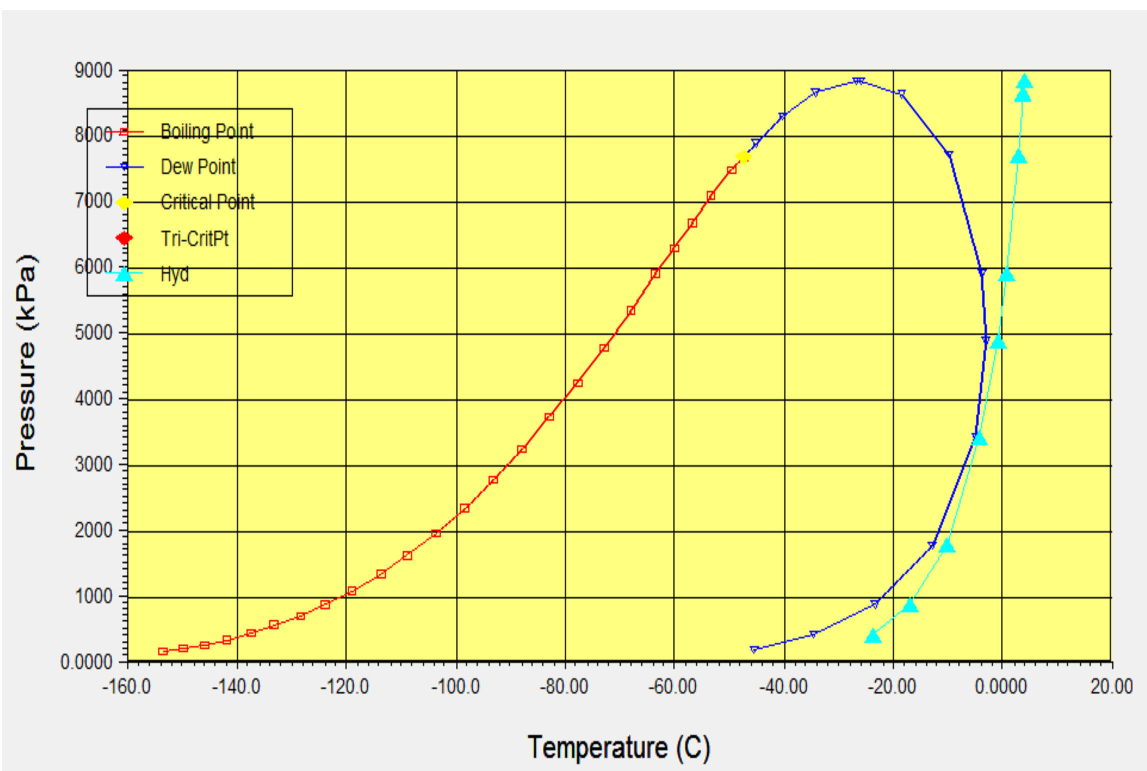


Figure 5: Graph between pressure, temperature, dew point, hydrate point and boiling point in optimized case

Table 1: Stream Input Data:

Available Natural Gas	
Component	Mole Fraction
Methane	0.7945
Ethane	0.1500
Propane	0.0102
i-Butane	0.0041
n-Butane	0.0061
i-Pentane	0.0043
n-Pentane	0.0043
n-Hexane	0.0025
H_2O	0.0218
CO_2	0.0009
Nitrogen	0.0013
H_2S	0.0
Flow rate	5 MMCFH
Temperature	42 °C
Pressure	5 MPa

Table 2 Downstream parameters vs temperature in existing design case

Temp	Water Separated	Cooling Load	Water in Outlet Gas	Heat of Vaporization	Dew Point	Hydrate Point	Hydrate Form
°C	Kg/hr	KW	Lbs/ MMSCF	KJ/Kgmole	°C	°C	
-20	519.8	5833	1.53	1633	-19.95	-16.2	Yes/Type II
0	506.3	3550	7.47	1965	0	1.4	Yes/Type II
20	460.1	1791	27.85	2220	3.3	16.14	No
40	328.1	91.55	86	2464	3.3	16.14	No

Table 3: Downstream parameters vs temperature in optimized case

Temp	Water Separated	Cooling Load	Water in Outlet Gas	Heat of Vaporization	Dew Point	Hydrate Point	Hydrate Form
°C	Kg/hr	KW	Lbs/ MMSCF	KJ/Kmole	°C	°C	
-20	519.78	2679	1.55	1648	-20	-16.23	Yes/Type II
0	506.215	1872	7.52	1979	-0.6	1.3	Yes/Type II
20	459.56	1745	28	2233	3.3	16.14	No
40	326.39	50.9	86.7	2476	3.3	16.14	No

Optimized design study:

Many studied are carried out to reuse the waste energy by plant modifications. In existing plant cold dry gas from three phase separator is sent to plant even though this stream is at very low temperature. In this study a pre cooler is installed in the same PFD created on HYSYS for existing design study. Cold dry gas is at -3 °C so this cold stream is used in pre-cooler to pre-cool the wet feed gas. Dry gas outlet temperature is set at 30 °C as outlet gas temperature. Now feed is entering the chiller comparatively at low temperature as shown in the Figure 4. In simulation by changing the downstream temperature the effect on the same selected downstream parameters are obtained and shown in Table 3. Graph is plotted between temperature and selected parameters and analyzed (Figure 7).

- With decreased in temperature water vapor pressure decreased so quantity of water separation sharply increased but as quantity of water in gas is decreased more cooling is required so separation is gradually increased after 20 °C.
- Cooling load is increased gradually by decreasing temperature up to 0 °C and then sharply increased.
- Quantity of water in outlet natural gas is sharply decreased by decreasing temperature due to reduction in vapor pressure up to 0 °C and then gradually reduced.
- Dew point of natural gas remained almost linear by decreasing temperature up to 0 °C as vapor pressure up to this point is higher than partial pressure and then sharply decreased as both declined.
- Hydrate point of natural gas remained almost linear by decreasing temperature up to 0 °C and then sharply decreased.
- Heat of vaporization initially is high as mixture of gas and water but with removing water gas left behind having low heat of vaporization. Hence heat of vaporization gradually and lineally decreased with decreased in temperature.

For water in natural gas 4 – 7 Lbs/MMSCF temperature range for gas is found to be -8 to -0.5 °C.
Dew point is -3.0 °C at natural gas temperature of -3.0 °C. Hydrate point is -1.2 °C at natural gas temperature of -3 °C. So set point for temperature for natural gas is -3 °C, dew point and hydrate curve can be seen in Figure 8. At same set point cooling load is found to be 1959 KW and water is 6.08 Lbs/MMSCF of outlet gas.

CONCLUSION:

This study is performed in simulation with Peng Robinson package by refrigeration method for two cases such as existing design case and optimized design case.
The motive was to get the optimization of cooling load for maximum dehydration of natural gas. By changing downstream temperature the effect on different parameters are calculated and for better understanding the effect of temperature on parameters studied by graphs. Rate and trend in both the graphs are almost same. The difference is only in the graph between temperature change vs cooling load requirement. Here trend is same for both cases but quantity is different. The installation of a pre-cooler prior to chiller in an optimized design case resulted in a temperature drop of 22 °C. Further, an almost 50% reduction is energy requirement is observed.

APPENDIX

Lbs	= Pounds mass
MPa	= 10^6 Pascal pressure
MMSCF	= Million Standard Cubic Feet
Sm^3	= Standard cubic meter
SCF	= Standard cubic feet
STP	= Standard Temperature Pressure
ppm (v/v)	= Parts per million in volume
°C	= Degree centigrade
K	= Kelvin
KJ	= 10^3 Joule energy
KW	= 10^3 Watt power
Kg	= 10^3 Grams mass
NGL	= Natural Gas Liquids
LNG	= Liquefied Natural Gas
LPG	= Liquefied Petroleum Gas
ARU	= Amine Regeneration Unit
LC	= Level Controller
PC	= Pressure Controller
TC	= Temperature Controller
SC	= Speed Controller
M	= Motor
SRU	= Sulfur Recover unit

ACKKNOWLEDGEMENT

First of all, I would like to express my sincere gratitude to my advisor Prof. Dr. -Ing. Naveed Ramzan for his patience, motivation, enthusiasm, support, guideline and understanding throughout my study at department of chemical engineering, university of engineering and technology, Lahore, Pakistan.
Besides my advisor, I would like to thanks the members of Faculty of Chemical Engineering who helped me throughout the study and because of their proper teaching and guidance I am able to cover this land mark.
Last but not the least; I want to dedicate this research work to my family and brother who always backed my spirits up.

REFERENCES

[1] Y. F. Makogon, S. A. Holditch, T. Y. Makogon, *"Natural gas hydrates, A potential energy source for the 21st century"*, 3rd October 2005. P 15, 18-19
http://research.nigc.ir/files/info_res/articles/86025ag_r13.pdf
[2] Michelle Michot Foss, *"Interstate natural gas Quality specifications and interchangeability"*, Sugar Land, Texas, (December 2004). P 16
http://www.beg.utexas.edu/energyecon/lng/documents/CEE_Interstate_Natural_Gas_Quality_Specifications_and_Interchangeability.pdf
[3] John Carroll, *"Natural gas hydrates",* A guide for engineers, 2nd edition, 2009. P 17-20, 151
https://books.google.com.sa/books?id=TRSXPEPghAwC&printsec
[4] Michal Netusil and Pavel Ditl *"Natural gas dehydration"*, Chapter 1, 2012. P 4-6
http://cdn.intechopen.com/pdfs-wm/36624.pdf
[5] Arthur J. Hidnay and William R. Parrish *"Fundamentals of natural gas processing"* , 2006. P 43, 134, 136, 150
http://dualibra.com/wp-content/uploads/2011/06/Fundamentals_of_natural_gas_processing.pdf
[6] Tarun Grover, *"Natural Gas Hydrates – Issues for Gas Production and Geomechanical Stability"*, Texas A&M University, August 2008, Chapter II, P 6
http://repository.tamu.edu/bitstream/handle/1969.1/86049/Grover.pdf?sequence=1

[7] Peter Brew and Edward Peltzer III, "Effects of Hydrate Formation on Gas Composition: A physical chemistry and environmental science question", Deanna Donohouse, Augustana Colloege, Summer, 2000, P 2-4, http://www.mbari.org/education/internship/00interns/00internpapers/deanna.pdf

[8] Dan Laudal Christensen, *"Thermodynamic Simulation of the water/glycol mixture"* K10 – Aalborg University Esbjerg, February 2009. P 8-10, 16-17. http://www.gas.uni-miskolc.hu/publics/Tananyag_Gas_Dehydration.pdf

[9] Robin Smith and Sonia Farrokhpanah *"Low Temperature Separation Systems"* University of Manchester, U,K, Volume 12, 2007, P 14 http://www.aidic.it/cet/07/12/002.pdf

[10] Thomas Forde *"Drying of natural Gas"*, Trondheim, 09/10/2008, Slides 28, 37-40, 48 http://www.ipt.ntnu.no/~jsg/undervisning/naturgass/lysark/LysarkFoerde2008.pdf

[11] A. Rojey and C. Jaffret, *" Natural gas Production Processing Transport"*, 1997. P 208, 265, 272. https://books.google.com.sa/books?id=7P_OlHoaReIC&printsec

[12] Karl Kolmetz, *"Gas Dehydration (Engineering Design Guideline)"*, May 2012. P 7, 11-12 http://kolmetz.com/pdf/EGD2/ENGINEERING_DESIGN_GUIDELINES_gas_dehydration_systems_rev_web.pdf

[13] A. Bhatia, B.E. *"Fundamentals of Mechanical Refrigeration Systems"*, 2012. P 2 http://www.pdhcenter.com/courses/m244/m244content.pdf