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ORIGINAL STUDY

Hydrogen Recovery from Refinery Units Off Gases Using Different Systems

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Abstract

Hydrogen recovery unit is so important to remove H₂S from the off gases generated, which are from various units in refinery, and recovers hydrogen. The recovered hydrogen reduces the quantity of hydrogen that produced from hydrogen production unit required for hydro-treating processes in the refinery. The off gas generated from this unit used as fuel gas. Hydrogen-rich feed streams process via adsorbent beds that trap impurities at high pressure and reject impurities at low pressure. At high pressures, the adsorbent beds effectively operate as a high efficiency filter, permitting only high purity hydrogen through to become product gas. Based on controlled sequencing, the valve arrangement changes to lower pressure and desorbing the impurities from adsorbent bed to become purge gas. This achieved at reasonable cost and with maximum protection to people, equipment, materials, and the environment. Proper operation will ensure that these goals interpolate. The required purity is (>99.9 mol%). Product routing changes required as changes in Hydrogen Recovery process occur to meet operational requirements. The product routing will be based on the PSA feed gas specification which is 38 ppmv H₂S (max.) resulting in less than 135 ppmv H₂S in the PSA tail gas. The result of the product specifications composition CO + CO₂ 10 PPMV (max.) and CH₄ 1000 ppmv.

Keywords: H₂S, MDEA amine, Off gas, Pressure swing adsorption

1. Introduction

The hydrogen recovery unit utilizes two technologies: amine-based reactive absorption and pressure swing adsorption (PSA). The amine absorption system uses methyl ethanolamine (MDEA) as a solvent for removing hydrogen sulphide gas (H₂S) and the other impurities in hydrogen-rich gas are removed using a PSA unit to produce high-purity hydrogen (Ruthven, 1984). The PSA system includes the following equipment items: feed knockout drum, PSA package and tail gas. Compression system and tail gas cooler (Skarstrom, 1960).

The pressure swing adsorption (PSA) vendor package includes programmable logic controller, adsorbent and purge gas drum. The PSA vendor

package produces a high purity (99.9 vol%) hydrogen product using proprietary technology (Yang, 1997). The vendor minimum hydrogen recovery guarantee is 87%. A backpressure controller on the PSA product gas used to hold stable HR unit operating pressure. On high feed gas pressure, the PSA bypass pressure control valve will divert PSA feed gas to the PSA tail gas header. The off gases generated from the PSA contains hydrocarbons, used as fuel gas in the refinery (Underground Sun Storage Website, 2017).

The Hydrogen Recovery unit is to produce a high purity hydrogen from the ARDS Cold Low Pressure Separator (CLPS) off-gas, ARDS Membrane Tail Gas, HCR Cold Flash Drum off-gas, CCR rich gas, HCR purge gas, KHT purge gas, and DHT purge gas. The gas mixture is contacted with amine

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Table 1. Different adsorbent packed in the single vessel.

Name	Layer	Physical properties	Chemical composition	Life time	Purpose
Aluminium oxide	1st layer from bottom	(Density: >2.0 g/cm ³) (Melting point: >400 °C) (Colour: White) (Form: Beads or Pellets)	Aluminum Oxide (non-fibrous): <97% Water: <10%	6 Years	Provide Mechanical Strength
Silicate	2nd layer from bottom	(Sp. Gr.: >1) (Melting point: >10000C) (Colour: White) (Form: Granules)	Silica Gel precipitated: <99% Water: <10%	6 Years	Ads. Of Water
Activated carbon	3rd Layer from Bottom	(Ignition Temperature: >240 0C) (Colour: Black) (Form: Granules Pellets)	Carbon 100%	6 Years	Ads. Of all Hydrocarbons (C1, C2,C3, C4,C5)
Molecular sieves	4th layer from Bottom	(Density: >2.0 g/cm ³) (Melting point: >400 °C) (Colour: Tan) (Form: Beads or Pellets)	Quartz (SiO ₂): <5%, Mineral binder: <30%, Zeolite, cuboidal, crystalline, synthetic, non-fibrous: >70%	6 Years	Ads. of Ammonia & Nitrogen

Table 2. Feed specifications data.

Feed stream	CLPS Off-gas (kg/h)	Membrane Tail gas (kg/h)	Feed gas (kg/h)	Off-gas (kg/h)	Total (kg/h)
Hydrogen	1614	1083	3451	4040	10,188
Methane	1371	4614	297	3480	9762
Ethane	1278	3100	454	1718	6550
Propane	1317	2529	657	2998	7501
i-Butane	192	331	616	2498	3637
n-Butane	693	1111	647	1440	3891
i-Pentane	0	0	143	1004	1147
n-Pentane	450	453	90.7	656	1650
i-Hexane	0	0	31	436	467
n-Hexane	0	0	15.5	152	168
Methylcyclopentane	0	0	0	212	212
CO ₂	43	26	16	26	111
Heptanes +	0	0	363	864	1227
Toluene & Aromatics	0	0	598	47	645
H ₂ O	57	42	0	296	395
H ₂ S	1935	4	0	2530	4469
Ammonia	24	0	0	9	33
Nitrogen	48	340	0	376	764
Total (kg/h)	8979	13,607	7363.2	22798.4	52,748
(kmol/h)	1043	1030.1	1796.0	2560.3	6430
Total Flow (Nm ³ /hr.)	23,377	23,107	40,254	57,387	144,125
MMSCFD	20.9	20.7	36.1	51.5	129.2
Pure H ₂ (kmol/hr.)	800.6	537.2	1711.9	2004.1	5053.8
MMSCFD	16.1	10.8	34.4	40.2	101.5
Pressure (barg)	25				

(MDEA, 45 wt%) in countercurrent manner in amine absorber to remove 50 ppm H₂S gas to an acceptable level in the overhead gas to treat in PSA (<38 ppm) (Yang, 1987). The H₂ rich gas from CCR

does not require H₂S gas scrubbing and can routed directly to PSA of HR unit, bypassing amine absorber. The mixed sweet gas is then pass through PSA unit where all other components except H₂ gas

Table 3. Hydrogen recovery unit process variables (HI Limits/Low Limits) in test run.

Process variable	Standard operating condition	Hi limit	Low limits	Units
H ₂ S in PSA feed	<38	<38	0	ppmv
Lean Amine flow to Amine Absorber	75.6	92	37.6	(m ³ /h)
Amine Absorber ΔP	Not Available	2.9	N/A	(barg)
Amine Absorber Feed Temperature Differential	11.8	14.4	7.2	°F
Tail Gas Compressor Suction Pressure	0.35	Not required	0.15	(barg)
Tail Gas Compressor Suction Temperature	104.6	116	Not required	°F

Table 4. Hydrogen recovery unit product specifications.

Composition	Hydrogen stream	PSA Tail gas stream	Analytical test method
Hydrogen, vol%	99.9 (min)	Balance	Gas Chromatography ASTM D1945
CO + CO ₂ , ppmv	10 (max.)	Balance	
CH ₄ , ppmv	1000 (max.)	Balance	

are adsorbed and pure hydrogen obtained (Ruthven, 1984). This hydrogen product from PSA sent to the hydrogen compression units and used in diesel hydrotreater unit, kerosene hydrotreater unit, atmospheric residue desulfurization units, and hydrocracker). The off gas generated from the PSA has high calorific value is compressed (to ~73 psig) and send to Fuel Gas Unit (Ruthven et al., 1994) (see Tables 1–4).

The recovered hydrogen reduces the quantity of Hydrogen needed to be produced from Hydrogen Production Units is required for Hydro-treating processes in the refinery. The off gas generated from this unit used as fuel gas. This achieved at reasonable cost and with maximum protection to people, equipment, materials, and the environment. Proper operation will ensure that these goals are met (Yang, 1997). Fig. 1 illustrates a flow chart for Full Process Diagram for Hydrogen Recovery Unit.

The feed to PSA unit, Fig. 2, is hydrogen rich gas that flows from the feed gas KO drum. During the adsorption step of the PSA cycle, impurities are adsorbed into a bed consisting of several layers (Yang, 1997).

The Five Steps Pressure Swing Adsorption Process can be described as follow:-

1.1. Adsorption

Feed gas enters the PSA skid at the feed battery limit and flows through the feed header to valve, enters adsorber from the bottom and flows upwards through the adsorbent bed. Impurities are adsorbed and purified gas flows into the product line through valve. The purified gas delivered to the product battery limit at a pressure slightly below the feed pressure (Ruthven, 1984).

1.2. Provide equalization

During this step, the pressure in adsorber decreases while gas used to re-pressurize adsorber whose pressure increases from 4.97 barg to 10.77 barg. Gas leaves adsorber over top through valve and enters adsorber from the top through valve. The equalization is cut-off, i.e. at the end of the step,

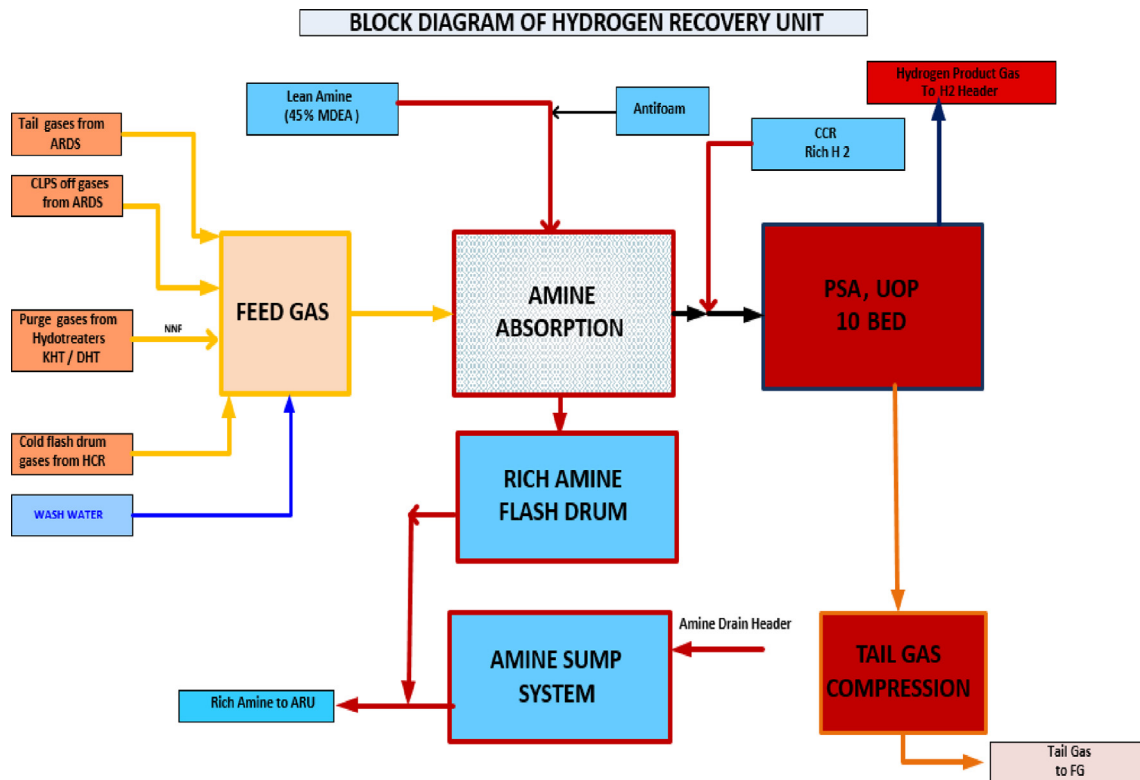


Fig. 1. Full process diagram for hydrogen recovery unit.

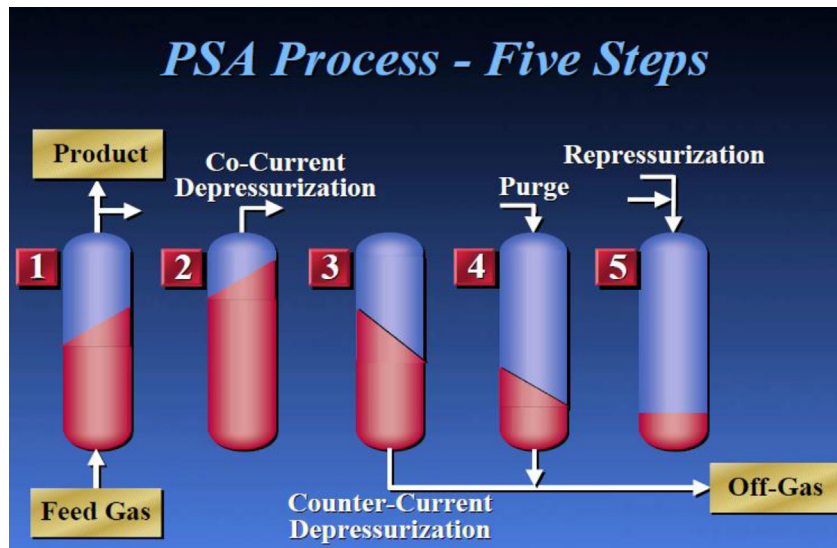


Fig. 2. The five steps pressure swing adsorption process (Yang, 1997).

there is a remaining pressure differential between both adsorbers. Valve XV close as soon as the end pressure of the step has reached in the adsorber on depressurization (Ruthven, 1984).

1.3. Isolation

During the isolation step, the pressure in the adsorber does not change, since during this time the adsorber does not receive any gas from the feed side nor from any of the other adsorbers. The adsorber pressure should remain constant at 17.48 barg; this means that any pressure change during an isolation step can be used to detect the presence of a leaking valve. In order to optimize the opening and closing time as well as the valve lifetime, valve XV remains open during the isolation step (Skarstrom, 1960).

1.4. Provide purge

During this step, the pressure in adsorber decreases from 6.02 barg to 2.49 barg while gas used to purge other adsorbers at low pressure. Adsorber depressurizes over top through valve and provides gas to adsorbers receives provide purge gas from the top through valve. Adsorbers receives provide purge gas from the top through valve. Adsorbers receives provide purge gas from the top through valve (Skarstrom, 1960).

1.5. Blowdown

The pressure in adsorber decreases from 2.49 barg to 0.55 barg. Adsorber depressurizes from the

bottom through valve into the tail gas drum. Valve PV controlled in such a way that the blowdown flow is coming smoothly out of the adsorber and that the pressure in adsorber has dropped to the tail gas pressure at the end of the step (Yang, 1987).

1.6. Purge

During Purge, adsorber at a pressure of approx. 0.55 barg is being purged from top to bottom with hydrogen from another adsorber on provide purge. The hydrogen enters the adsorber from the top through valve and desorbs the impurities that leave the adsorber through valve to the tail gas drum. During Purge, valve is fully open to maintain low pressure in the adsorber. Adsorber is purged with provide purge gas coming from adsorber. Providing Purge gas leaves adsorber over top through valve and enters adsorber from the top via valve. Adsorber is purged with provide purge gas coming from adsorber valve is sent the command to close a few seconds before the end of step (Voss, 2005).

1.7. Receive equalization

During this step, the pressure in adsorber increases from 0.47 barg to 4.97 barg while gas received from adsorber whose pressure decreases from 11.02 to 6.02 barg. Gas leaves adsorber over top through valve and enters adsorber from the top. The equalization is cut-off at the end of the step, there is a remaining pressure differential between both adsorbers (Yang, 1997).

1.8. Final Re-pressurization

During Final Re-pressurization, adsorber re-pressurized to the adsorption pressure. Adsorber re-pressurized by valve using a slipstream of the feed gas. Valve controlled in such a way that the re-pressurization flow is constant in order to minimize fluctuations in the feed and product gas streams. The Final Re-pressurization step completed when the adsorber has reached a pressure that is almost equal to the adsorption pressure (Montgareuil and Domine, 1964). Fig. 3 show the Pressure Changed through Pressure Swing Adsorption Process.

In the main mode of operation, there are always two adsorbers in adsorption, while the others are in depressurization, regeneration or re-pressurization. During the adsorption step of the PSA cycle, impurities adsorbed into a bed consisting of several layers of solid adsorbent and the purified hydrogen leaves the unit at a purity of 99.9%. About 87% (in normal operating mode) of the hydrogen present in the hydrogen rich gas recovered. Impurities adsorbed at high pressure and then desorbed at low pressure. At high pressures, the adsorbent beds effectively operate as a high efficiency filter, permitting only high purity hydrogen through to become product gas. Based on controlled sequencing, the valve arrangement changes to lower pressure and desorbs the impurities from adsorbent bed to become purge gas. Each adsorber goes through the same cycle of adsorption and regeneration without change in temperature, except for the heat of adsorption and desorption.

2. Experimental

2.1. Material used in pressure swing adsorption unit

UOP LLC, USA, supplies the adsorbent, which used in the adsorbers. A different layer of adsorbent

used to remove different components present in the product hydrogen. A list provided in the following table of the different adsorbent packed in the single vessel, which is a representative of all other vessels (European Commission, 2019).

2.2. Process conditions description

High purity hydrogen (99.9% vol.) which is sent to the refinery hydrogen network to supply the make-up hydrogen demands of the refinery (European Commission, 2019). Tail gas, which compressed in tail gas compressor and sent to the fuel gas network (Gatzen, 2022). PSA unit, consists of 10 adsorber column each with identical design and adsorbent. Each adsorber in PSA system go through the process of adsorption and regeneration without change in temperature (Yang, 1987), The Pressure Swing Adsorption (PSA) process purifies hydrogen-rich feed streams via adsorbent beds that trap impurities at high pressure and reject at low pressure. At high pressures, the adsorbent beds effectively operate as a high efficiency filter, permitting only high purity hydrogen through to become product gas (Ruthven, 1984). Based on controlled sequencing, the valve arrangement changes to lower pressure and desorbs the impurities from adsorbent bed to become purge gas (Yang, 1987). PSA unit is designed for producing high purity 99.9% H₂ (<1000 ppmv, CH₄, No H₂S slip. Vide design basis, slip in product is expected to be “Zero” (McCabe et al., 1993). Critical component determining product purity is CH₄. Tail gas recovered from the PSA& sent for fuel gas system. Vendor guarantees include a minimum 87% hydrogen recovery (10 Bed Mode) (Ruthven, 1984). Nominal PSA unit feed capacity is 87,701 SCFM, (140,977 Nm³/hr). Pressure: 21.5 barg, (ΔP across PSA 1.2 barg). PSA unit is designed for operation in 10 bed (Normal), 8 bed and 6 bed mode.

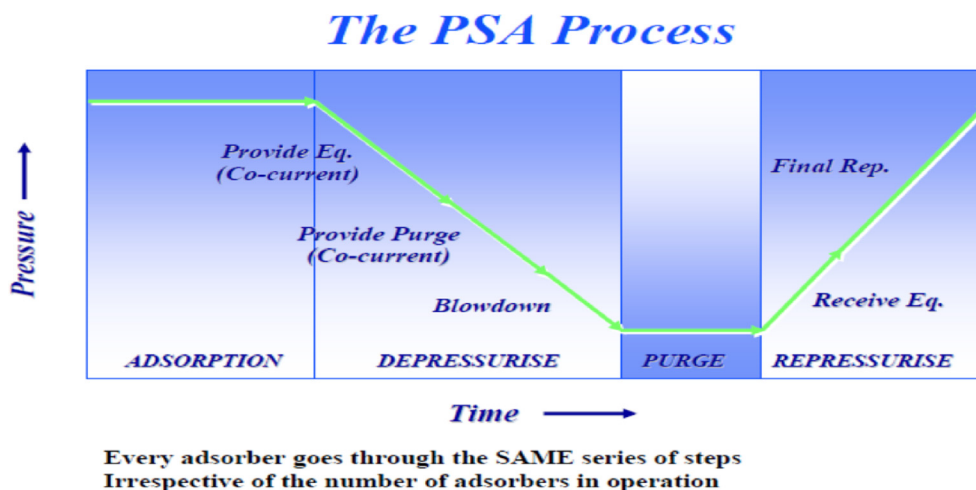


Fig. 3. Pressure changed through pressure swing adsorption process (Underground Sun Storage Website, 2017).

2.3. The catalyst

The adsorbents deactivated temporarily during adsorption cycle, various components present along with Hydrogen (such as Methane, Ethane, Propane, i-Butane, n-Butane, i-Pentane, n-Pentane, i-Hexane, n-Hexane, Methyl Cyclopentane, Cyclohexane, Heptane, Toluene & Aromatics, H₂O, H₂S, NH₃, Nitrogen) are adsorbed and bed is exhausted of its adsorption capacity beyond which it will lead to product hydrogen obtained from PSA unit with a lower impurity. This aspect is taken care in the design of the cycle time by PSA vendor (Ruthven, 1984).

2.4. Reactions

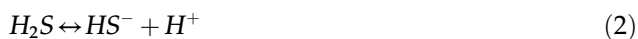
Reactions for acid gas absorption in amine solution (amine absorber):

One of the mechanism postulated for H₂S dissociation and ionic reaction in water based amine solution described below (Ruthven, 1984):

Dissociation of water:



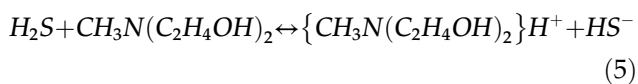
Dissociation of H₂S in water:



Dissociation of amine in water:



The overall Reaction of H₂S with Amine can be described:



3. Results and discussion

The design operating capacity of the hydrogen recovery unit is 144,125 Nm³/h of feed gas. This flow rate based on the following data.

Hydrogen recovery unit will routing the PSA hydrogen product or PSA tail gas based on feed gas specification which is 38 ppmv H₂S (max.) resulting in less than 135 ppmv H₂S in the PSA tail gas. When the quality of the feed gas to PSA is met normal process variable, the recovered hydrogen stream from the PSA unit will be routing to the Hydrogen Compression 1st stage suction, in addition, the PSA tail gas stream is compressed, cooled and routed to

the fuel gas system via Tail Gas Compressor (Yang, 1997). In case of High H₂S from amine absorber, High alarm will generate and treated hydrogen quality will be affected considerably. In this case, we must check delta P across the tray in both absorbers. In addition, check delta T between Feed gas and lean amine temperature to make the difference between them identical to the normal limit value (Ruthven et al., 1994). If H₂S value in PSA feed exceeds High limit for more than 12 h without any improvements, in this case unit should go for shutdown for an extended period, the residual impurities in the adsorber vessel will diffuse towards the top of the vessel. Therefore, at a subsequent restart of the unit, it will produce hydrogen of considerably lower quality for several cycles and reduced (CCF to 80) for 4 h. After 4 h, start the unit (Press the start button). After that, monitor the normal operation of the process variables during the initial sequencing of the unit and check the adsorber pressure profiles (Yang, 1997). Also monitor the product quality. When the CH₄ content is within specification, open the product block valve to draw off product. Make sure the sample line is flushed sufficiently before taking the sample. The cycle time should be slowly lengthened by slowly increasing CCF to 100 in steps of maximum 5%. when the desired product purity is almost reached, adjust CCF in very small steps. Wait at least 2 complete cycles between 2 step changes of CCF. As soon as the hydrogen section is commissioned, the tail gas compressor can be started and routed tail gas to the fuel gas header (Montgareuil and Domine, 1964).

The amine contactor because of more surface area. In below figure, minimum CO₂ concentration 2 ppm can reach with 25 trays (Montgareuil and Domine, 1964) (Fig. 4).

The product recovery of hydrogen recovery unit is the comparison of pure hydrogen (min. 99.9 vol %) of products produced compared with the total hydrogen entering from the feed stream to the unit (shown as "vol. %"). Table below lists the calculated product recovery of the hydrogen recovery Unit (Skarstrom, 1960) (Fig. 5).

In this figure shows H₂ changes in adsorption cycle to the bed diameter. This figure shows that the hydrogen concentration increase with increasing of the bed diameter for a constant bed length. This part of results provides the PSA operations based on the off gas specification's through PSA cycles sequences.

In this figure clearly shows area needed versus feed pressure. The figure shows that the needed area decreases with increasing feed pressure (Fig. 7) because of increase in the differential pressure as a driving force (Voss, 2005).

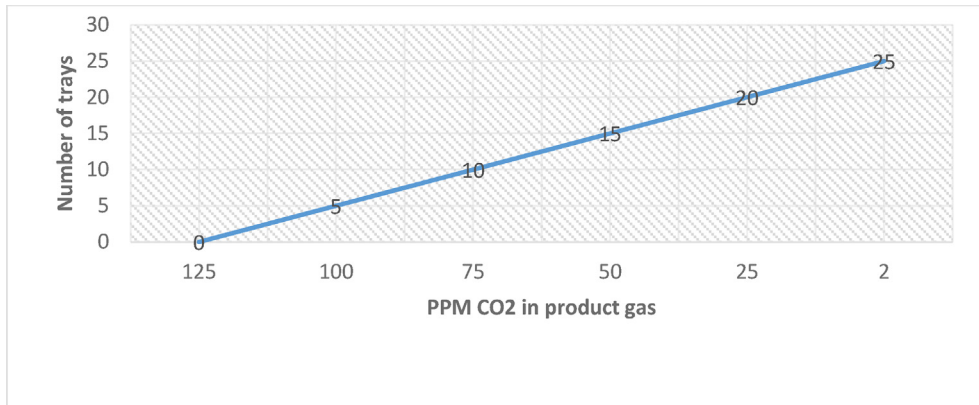


Fig. 4. Effect of number of trays on CO₂ mole fraction in the MDEA contactor.

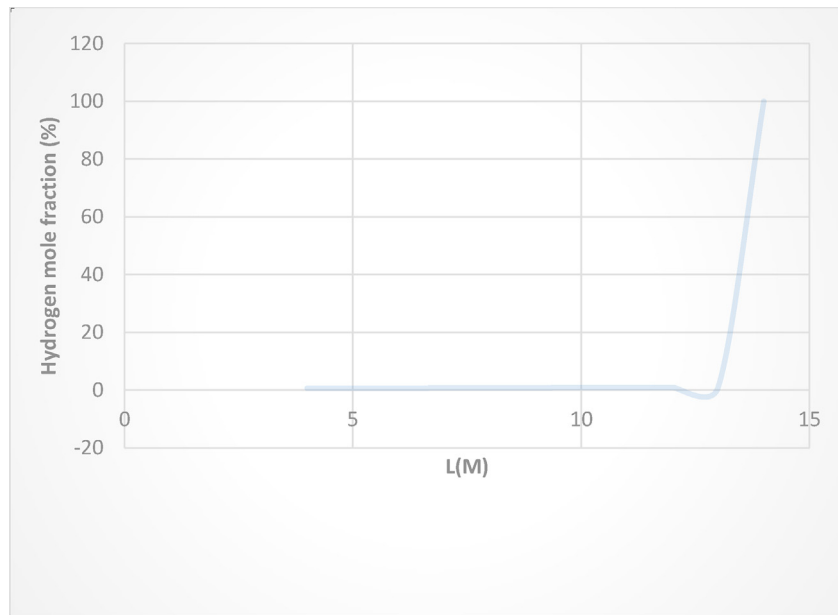


Fig. 5. Effect of the bed length on hydrogen mole fraction in adsorption step with a constant diameter (Fig. 6).

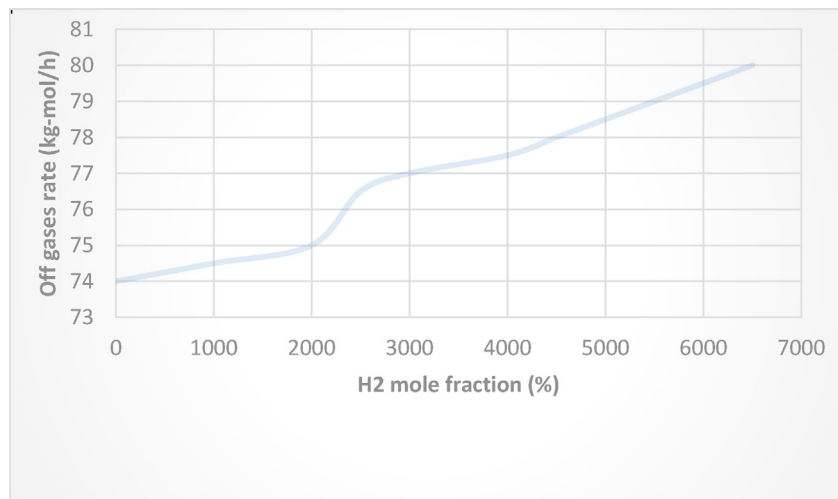


Fig. 6. Effect of adding off gas as feed into the existing hydrogen recovery unit.

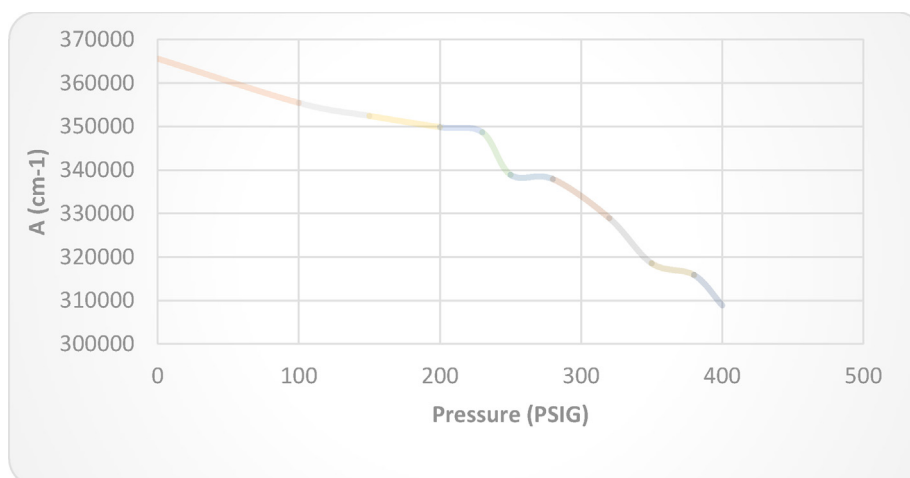


Fig. 7. Effect of feed pressure on PSA adsorbers.

4. Conclusion

Product routing changes required as changes in hydrogen recovery process. The product routing will be based on the PSA feed gas specification to meet operational requirements. Which H_2S is 38 ppmv (max.) resulting in less than 135 ppmv in the PSA tail gas. In case of high CO_2 concentration in outlet MDEA contactor, checked the quality of lean amine coming from lean amine unit and increase lean amine flow to both absorbers up to 120% of design capacity until achieved the normal CO_2 value. If required change the source of lean amine (CO_2 bearing amine), then reduce the unit throughput (feed as flowrate to absorbers).

When the quality of the feed gas to PSA met as described above, the recovered hydrogen stream from the PSA unit will flow to the hydrogen compression first stage suction. The PSA tail gas stream is compressed, cooled and routed to the fuel gas system via Tail Gas Compressor. During periods where H_2S excursions exceed PSA unit limitations, a PSA unit bypass directs the amine absorber overhead to either the fuel gas system.

Credit statement

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The content of this paper was conceptualized, researched, and written by the authors mentioned above. The authors are solely responsible for the research conducted, data analyzed, and conclusions drawn in the paper.

Prof. Dr. Mohammed M. El-Halwany proposed the method and developed the overall framework for the paper. He also supervised the development of the mathematical optimization method.

Prof. Dr. Mahmoud Mahmoud contributed to the development of the mathematical calculations. Additionally, he was reviewing for the process descriptions.

Prof. Dr. Mohamed Gar Alalm was responsible for conducted the literature review and wrote the introduction, abstract and conclusion.

Eng. Abdullah Abdullah was responsible for to the double check the results obtained and wrote the summary and double check on the types methods that used. Also helped in the editing and revision of the manuscript.

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I confirm that I have not received any financial support or research, authorship or publication my article.

Conflicts of interest

I confirm that I have note declared any potential conflict of interest in connection with the research, authorship, or publication of my article.

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