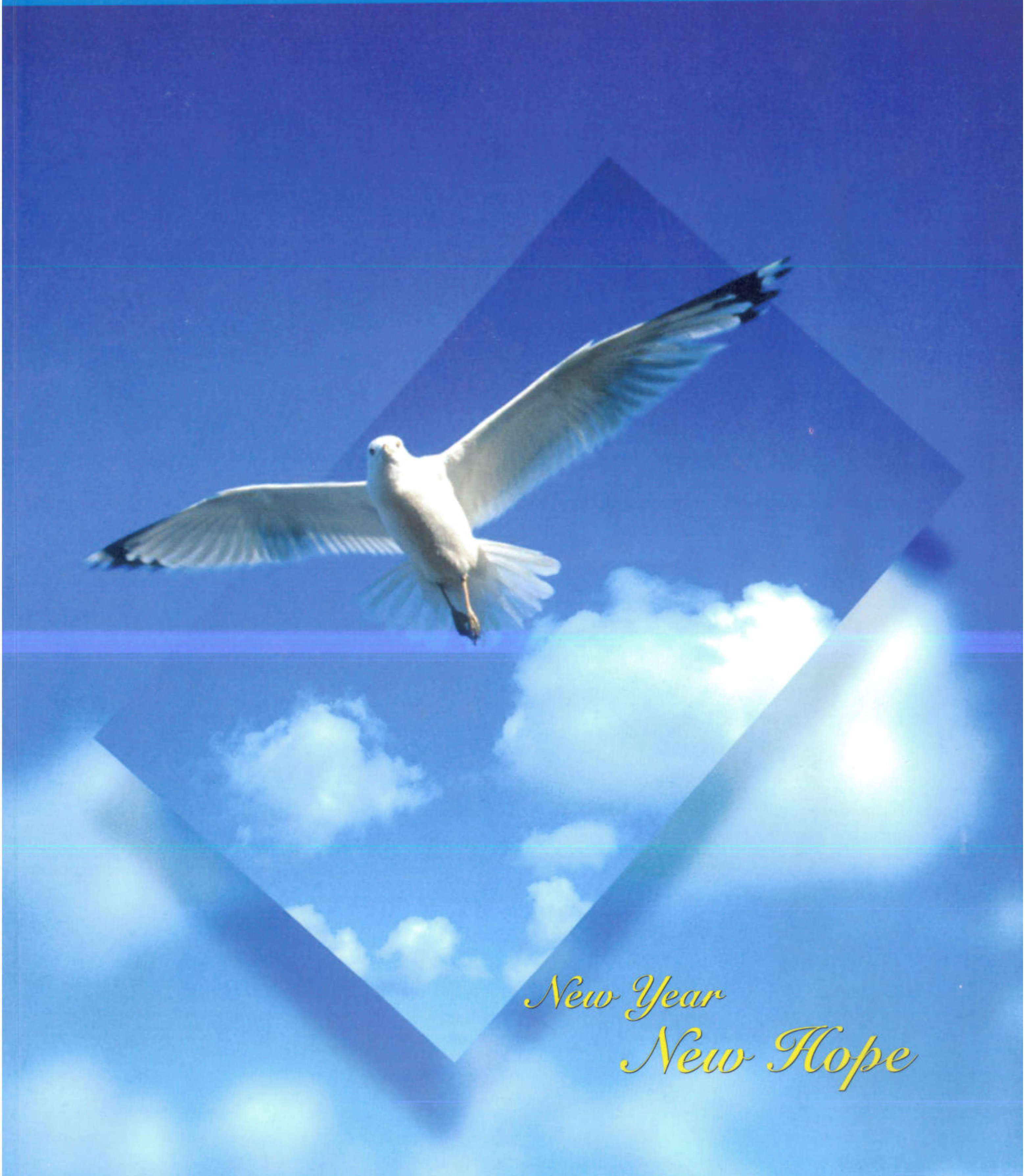
PetroFed

THE JOURNAL OF PETROLEUM FEDERATION OF INDIA

PETROFED

OCTOBER - DECEMBER 2014

VOL.13 ISSUE 4



Stop bleeding caustic: Parameters for Designing and Operating an efficient LPG treating unit

Saurabh Agarwala*, Debasis Maity, Ravi Kant Gupta, and Ganesh Prasad

Engineers India Limited, R&D Complex, Sector-16, Gurgaon

Presence of sulfur compound like H2S and Mercaptan (RSH) is undesirable in light hydrocarbon streams for their foul odor, corrosive nature and adverse health impact. Increasing use of heavy, high sulfur crude and popularity of processing heavier residue (e.g. Delayed Coker) in refineries along with more and more stringent environmental norms (as low as 20 ppm mercaptan in light hydrocarbon products) is a growing challenge for process designers and refiners. Caustic remains the primary reagent to extract mercaptans from hydrocarbon streams because it is cost effective and, more importantly, environmentally acceptable.

LPG treatment

Mercaptans in LPG are extracted by caustic washing, which is also known as sweetening process. The extraction based sweetening process is often divided in two steps, starting with extraction using fresh caustic and finishing with oxidation of the rich caustic. The lighter mercaptans are first extracted by caustic solution forming water and sodium mercaptide salts. In the second stage, these salts (NaSR) are oxidized by air injection in the presence of a catalyst and produce an organic disulfide (RSSR) phase that separates by gravity from the aqueous solution. After decantation of disulfides, the regenerated lean caustic solution is recirculated back to the top of the extractor to continue extracting mercaptans. The overall reaction stoichiometry produces 0.5 mol water per mole of mercaptan converted. Therefore, the caustic solution being recirculated becomes weaker due to the water generated during every cycle, which keeps accumulating in the solvent recirculation circuit. Hence, the caustic strength at any given time is a function of number of cycles the solvent has completed, feed mercaptan concentration, and the volume of recirculation loop.

Chemistry of LPG treatment

Caustic Wash

$$H_2S + 2NaOH \longrightarrow Na_2S + 2H_2O \quad (1)$$

$$RSH + NaOH \longrightarrow NaSR + H_2O \quad (2)$$

Caustic Regeneration

$$2Na_2S + H_2O + 2O_2 \longrightarrow Na_2S_2O_3 + 2NaOH \quad (3)$$

$$2NaSR + 1/2\ O_2 + H_2O \longrightarrow RSSR + 2NaOH \quad (4)$$

Parameters that matter

Design considerations as well as operating conditions should gel perfectly to run a unit efficiently. The refinery operators and designers tend to overlook some parameters which are listed below:

Know your LPG: Feed quality and product specification

LPG from different production units is often contaminated with acidic components such as hydrogen sulfide (H_2S) , carbon dioxide (CO_2), carbonyl sulfide (COS), carbon disulfide (CS_2), methyl- , ethyl- and butyl- mercaptans, sulfur-dioxide etc. Ammonia (NH_3) may also be present when sources of LPG are hydrocracker, HDS, hydrotreater or thermal cracker like DCU. H2S and RSH distribution is critical in designing the caustic wash system.

Source of LPG

The amount of impurities in LPG feed is dependent on the crude processed and the source unit of LPG. The higher amount of mercaptans may require multiple stages of caustic washing. Typical values of impurities from different production units are presented below:

	CDU/VDU	FCCU	DCU
H_2S	7500 ppm	50000 ppm	85000 ppm
Mercaptans	1000 ppm	2000 ppm	2800 ppm
COS	-	70 ppm	-

Product Specification:

The product specifications are getting stringent due to environmental concerns. But another important consideration is the ultimate use of LPG produced. For LPG in domestic use, RSH content should be 20 ppmw to provide odour in case of leakage. LPG going to downstream petrochemical unit shall have RSH content of 5 ppmw in order to avoid poisoning of catalyst used in those units. Total volatile sulfur content is also to be kept under check and specifications prescribe 150 ppmw maximum.

How operating parameters effect?

- The ease of removal of a mercaptan from hydrocarbon phase by an aqueous alkaline solution is markedly dependent on the molecular weight of the mercaptan and, to a lesser extent, on its configuration. The lighter and the straight-chain mercaptans are more readily extracted than the heavier and branched-chain members.
- An increase in the sodium hydroxide concentration improves the extraction of mercaptans but not in proportion to the increased hydroxide concentration, and beyond a given range (2 to 3 N sodium hydroxide), the extraction may actually become poorer. As the sodium hydroxide concentration in the aqueous phase increases, the improvement in the extraction of mercaptans becomes less than might be expected from the higher caustic concentration. This is due to the salting-out of the non-neutralized mercaptan from the aqueous phase by the sodium hydroxide.
- A decrease in the extraction temperature increases the degree of removal of mercaptans from the hydrocarbon phase.

Right Treatment at the right place:

LPG treatment has undergone many developments right from mixing valves to packed columns to now highly efficient fiber-based technology (CFC technology jointly developed by IOCL & EIL). Hydrotreatment is expensive and thus needs serious consideration of refinery capacity and configuration. Amine absorption and molecular sieve absorption are capable of removing H_2S but not mercaptans efficiently.

Process	Merits	Demerits
Amine Absorption	• Low capital and operating cost compared to molecular sieve process • No COS formation during processing with H_2O and water • Used in refineries for bulk removal of H_2S	• Does not remove mercaptans • Removal of COS is low • Removal of traces of sulfur compound is not possible • Dispersive system where available surface area is low
Molecular Sieve Absorption	• Chemical affinity of molecular sieve: $H_2O>H_2S>CO_2$. So dehydration along with sweetening is possible • Selectivity of H_2S over CO_2 • Removal of mercaptan and COS is possible	• Large capital and operating cost involved • In presence of H_2O, COS is formed • It can't meet current stringent specification of LPG
CFC Technology	• Complete removal of H_2S and mercaptans to lowest extent in product • Caustic consumption is minimum with continuous regeneration • Energy consumption is less compared to other two processes • Available surface area is much higher	• For heavier mercaptans like butyl mercaptans (usually absent in LPG feed) caustic circulation will be high. • Only 50% of NaOH consumed due to presence of H_2S in LPG is regenerated.
Packed Bed	• Number of equilibrium stages can be easily added	• Being a counter current dispersive contactor, caustic carryover is high
Hydrotreating LPG	• Treats all kind of sulfur compound	• Operating and Capital cost is very high

Significance of choosing the right technology cannot be emphasized more than in the article presented by HPCL-Mumbai Refinery, during 16th RTM-2011, about using CFC technology. Praising the efficient technology, HPCL-MR revealed that the unit is helping them make savings in terms of reducing caustic consumption by 75% (caustic regeneration unit has been provided along with caustic wash unit) and thus Rs. 115 Lakhs per annum! The actual savings shall be even higher as spent caustic to ETP would approximately cost another Rs. 25/ Kg of sulfide for treatment. (*Reference:* "Replacement of conventional LPG treating with CFC technology" presented at 16th RTM, Kolkata)

Designing the right mix:

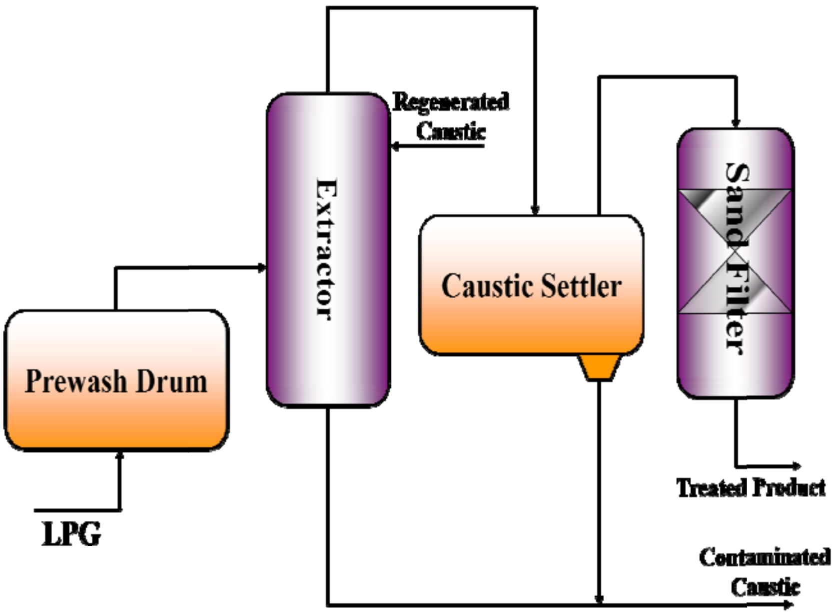
A combination of above mentioned technologies can be used to optimize caustic consumption. Amine treatment unit upstream of caustic wash is a popular choice for Indian refineries. Amine treating (usually DEA or MDEA) takes care of high amounts of acid gas present in LPG.

A designer's duty is to carefully consider all the factors and strike the right balance between operating and capital cost. The different configuration in which EIL has offered the units is given below:

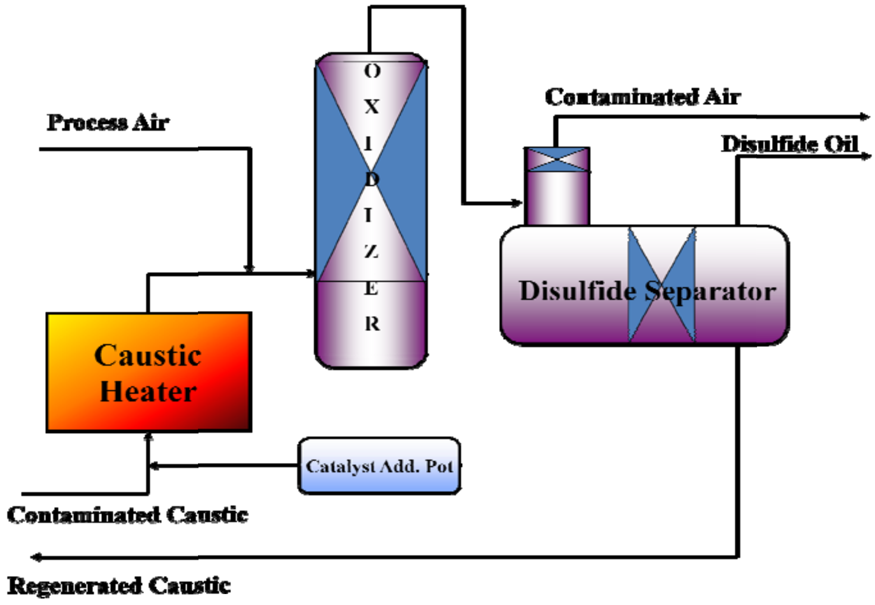
Stand-alone wash unit: Ideal for units with low LPG throughput and low impurity levels. In this case regeneration is not considered for caustic consumption is expected to be low. Fresh caustic batch is filled in the unit and recirculated till it gets depleted.

Caustic wash and regeneration: The rich caustic from wash section is oxidized in presence of catalyst and regenerated. Disulfide oil (RSSR) formed as a result is removed using Heavy Naphtha as a solvent. The advantage of these units is low caustic consumption as well as reduced load on ETP.

If the LPG feed is mercaptan rich (>1000 ppmw) along with small amount of H_2S, it is better to have a pre-wash column. In such a column, caustic circulation is not required and LPG just passes through pool of caustic. The advantage is that caustic can be depleted to about 2wt% strength and preferentially remove H_2S. Thus the caustic used for mercaptans removal can be completely regenerated.



Typical Caustic wash section



Typical Caustic regeneration section

In the End

Balancing between right design and efficient operation can result in an environment friendly LPG treatment unit. The environmental norms are getting more stringent both with respect to sulfur removal and caustic disposal. Caustic discarded from extractive treating (with regeneration unit) is small in volume and is not classified as hazardous waste. It can either be neutralized on site and then processed in the refinery wastewater treating system or sent to companies specializing in sulfidic caustic disposal.

Tips for designers: The designers are entrusted with a great responsibility of delivering product with right specification using optimum amount of resources. For LPG treating unit, the designers should have an eye on following **3Cs**:

Cost: Both the operating and capital cost is to be considered. Though using the latest technologies is always alluring, a designer needs to avoid fancy equipment & instrumentation if it comes at high cost. For example: using structured packing instead of ripple trays in pre-wash column.

Contact: LPG treatment with caustic is essentially a mass transfer with chemical reaction case. It is essential to provide effective reaction space between the two species. CFC ensures a close contact between LPG and caustic even though the two move in co-current fashion and hence eliminating issues of carryover. Mixing valves, traditionally used for providing contact, have proved to be energy inefficient.

Caustic Consumption/ circulation: In conventional systems like caustic spray columns and mixing valves, the Caustic-LPG ratio was kept very high. In today's efficient technologies the circulation rate is reduced and shall be monitored/ controlled closely. The designer should make it a point to provide good turn-down capacity to save energy and caustic.

Tips for refiners: Operations group own the unit designed and they should study the process scheme minutely. Operation group shall be involved during the design review stage as well as safety studies like HAZOP. The refiners should monitor these **3Qs**:

Quality of LPG feed: The unit is designed considering a particular crude (as design case) and alternative feed (as check case). But the crude quality, over a time period, changes. Also, with fluctuating crude prices, refineries tend to get an economical mix of crude which changes feed components considerably. It is a good practice to keep checking feed composition and control operating parameters accordingly.

Quality and quantity of Caustic: If LPG feed predominantly consists of acid gas, then the caustic can be allowed to deplete up to 2wt% strength as the reaction between H2S and caustic is instantaneous. A mercaptan rich feed will need caustic strength upwards of 7 wt%. Operators should monitor the decay rate if unit is running in batch mode. For units with caustic regeneration facility, a purge stream should be taken out of the system to remove salts and excess water. During turndown conditions or low impurity feed, caustic circulation should be reduced to save energy.

Quality of LPG product: The best indication and perhaps the first one about the performance of the unit, comes from monitoring the product quality. Slippage of mercaptans and carryover of caustic are the indications of non-performance of the unit. Caustic circulation and the interphase levels should be maintained to avoid such problems.