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## HYDROGEN PURIFICATION IN HYDROPROCESSING (HPH<sup>SM</sup> TECHNOLOGY)

**YUV R. MEHRA & ALI H. AL-ABDULAL**  
PROCESS & CONTROL SYSTEMS DEPARTMENT  
**Saudi Arabian Oil Company (Saudi Aramco)**  
Dhahran, Saudi Arabia

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### Abstract

Saudi Aramco has recently patented<sup>1</sup> a process technology to significantly increase the partial pressure of hydrogen in hydroprocessing processes. In a representative application of the Hydrogen Purification in Hydroprocessing (HPH<sup>sm</sup>)<sup>2</sup> technology to the hydrocracking process, the flashed gases from the high pressure separator (containing typically about 78-83 mol% H<sub>2</sub>) are fed to the bottom of an absorption column where the entering gases are counter-currently contacted with a lean solvent. The lean solvent absorbs away the contained methane, H<sub>2</sub>S, ethane, propane, butanes and pentanes from the contained hydrogen. The absorbed components in the rich solvent are separated from the lean solvent by reducing pressure. The heatless flash regenerated lean solvent is pumped and returned to the top of the methane absorber column. In doing so, hydrogen purity of the overhead gases leaving the absorber increases to 96-98 mol%. This purified, recycled hydrogen stream is mixed with the make-up H<sub>2</sub> to produce a combined stream with an overall purity in the range of 96 to 99 mol% H<sub>2</sub>. This improvement in hydrogen partial pressure significantly increases the overall throughput and efficiency of the hydro-processing unit. Similarly, the HPH technology can be effectively utilized for improved performance from the hydrotreating, hydrodesulfurization, hydrodenitrogenation, and hydrodealkylation reactor processes.

Saudi Aramco has physically demonstrated the H<sub>2</sub>-C<sub>1</sub> separation by absorption for most HP separator flash gas compositions over a wide array of operating pressures common to hydroprocessing applications. This demonstration has confirmed that absorption can be effectively used to recover and purify hydrogen. Saudi Aramco is currently developing its commercialization plan for the HPH Technology.

## INTRODUCTION

Hydroprocessing processes are quite common to refining operations. These processes either enhance value to lower-value heavier, residual fuel oils (i.e. vacuum gas oil) or treat contaminant-laden refinery products (e.g. kerosene, diesel and gasoline). In hydroprocessing processes, the heavier or contaminated hydrocarbon products are co-processed with hydrogen to produce either higher-value products (such as gasoline from residual fuel oils) through hydrocracking operation or upgrade refinery products like diesel and gasoline to meet higher-quality, lower-contaminant specifications for such products through various hydrotreating processes.

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<sup>1</sup> U.S. Patent No. 6,740,226 issued May 25, 2004.

<sup>2</sup> "HPH" is an intended service mark of the Saudi Arabian Oil Company for its proprietary Hydrogen Purification in Hydroprocessing technology portfolio.

## WORLDWIDE HYDROPROCESSING<sup>3</sup>

Saudi Aramco owns and operates five refineries within the Kingdom of Saudi Arabia (KSA) for a total hydroprocessing (*hydrocracking + hydrotreating*) throughput of 291,800 barrels per day (BPD). Each of these refineries has some form of hydroprocessing as follows:

REFINERY	HYDROPROCESSING TYPE
Ras Tanura Refinery	Hydrocracker Naphtha Hydrotreater
Riyadh Refinery	Hydrocracker Naphtha Hydrotreater Kero-Unibon Hydrotreater Diesel Hydrotreater ( <i>under construction</i> )
Yanbu Refinery	Naphtha Hydrotreater Kero-Unibon Hydrotreater Diesel Hydrotreater ( <i>under construction</i> )
Jeddah Refinery	Naphtha Hydrotreater
Rabigh Refinery	Diesel Hydrotreater

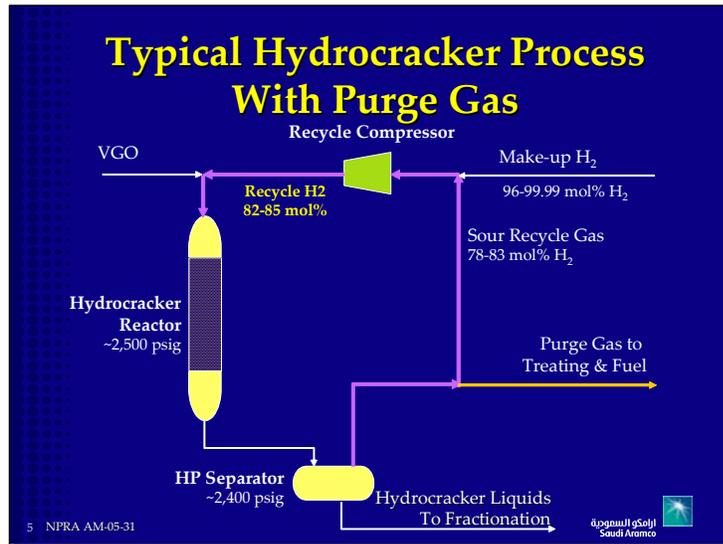
In addition, Saudi Aramco retains an ownership interest in various joint ventures (JV) that have a combined hydroprocessing capacity in excess of 1,436,300 BPD. A breakdown of major worldwide hydroprocessing capacities is as follows:

COUNTRY	HYDROCRACKING + HYDROTREATING
United States (Excluding SA JV's)	13,533,170 BPD
Germany, Italy, France and UK	6,169,700 BPD
Japan	4,491,700 BPD
Russia	2,228,020 BPD
Rest of the World	22,308,790 BPD
Total Worldwide	45,967,350 BPD

<sup>3</sup> Worldwide Refineries-Capacities as of Jan I, 2005 from *Oil & Gas Journal* Dec 20, 2004.

## TYPICAL HYDROCRACKING PROCESS

In a typical hydrocracking process, as shown in the schematic diagram, vacuum gas oil (VGO), and if desired other heavier components, enters along with a hydrogen stream having purity in the range of 82-85 mol% H<sub>2</sub>. The combined VGO-H<sub>2</sub> feed enters a high pressure hydrocracking reactor operating at about 2,500 psig and 750°F. By flowing the combined feed over a selective catalyst, the entering VGO is converted to lighter hydrocarbons and higher-value hydrocarbons such as naphtha and diesel. Typically, the reactor effluent is cooled by cross-exchanging heat with the fresh



VGO feed and ambient air coolers. The liquid hydrocracked products from the cooled reactor effluent stream are separated from the non-condensable hydrogen-rich gases in the indicated high pressure HP Separator which operates at about 2,400 psig. The separated hydrocracker liquids flow to low pressure separator and eventually to fractionation section for further processing.

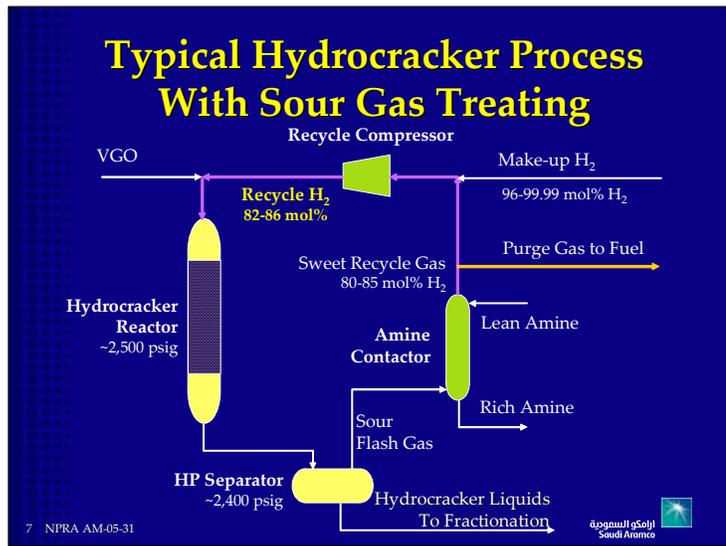
The separated gases from the HP Separator contain about 78-83 mol% H<sub>2</sub>. Since these gases contain a significant amount of hydrogen, they are recycled to the reactor as part of the hydrogen feed. Unfortunately, these gases are of lower purity than the hydrogen feed because they contain lighter hydrocarbon gases like methane, ethane, propane, butanes and pentanes. Any H<sub>2</sub>S formed or present in the reactor feed generally also ends up in the HP separator gases. In order to prevent build-up of these components, which are formed during the hydrocracking process, a portion of these gases (10 -15%) is purged to the fuel gas system or to a PSA unit from which about 20% is lost to fuel gas system. After purging, the remaining separated H<sub>2</sub>-rich gases are mixed with the make-up hydrogen, compressed and recycled back to the top of the hydrocracking reactor. Depending upon the source of make-up H<sub>2</sub>, the make-up hydrogen stream is typically available at 96 to 99.9 mol% H<sub>2</sub> purity.

The performance of any hydroprocessing process, be it a hydrocracking or hydrotreating application, is limited by the hydrogen partial pressure at the inlet to the reactor. The higher the hydrogen partial pressure, the better the hydroprocessing reactor performance. With higher hydrogen partial pressures, some of the realized benefits may be summarized as follows:

- Longer Catalyst Cycle Life
- Higher Throughput Capability
- Better Distillate Quality
- Heavier Feed Processing Capability
- Higher Conversion Capability
- Purge Gas Elimination

Since the make-up hydrogen is essentially pure (96-99.9 mol% H<sub>2</sub>), to realize benefits from the higher hydrogen partial pressure, one has to either increase the operating pressure of the hydroprocessing reactor or increase the purity of recycled hydrogen to the reactor.

When H<sub>2</sub>S is present in the flashed gases from the HP Separator, some facilities have utilized an amine contactor in the recycle hydrogen loop to improve the hydrogen purity or to address metallurgical concerns. Because of the relatively low content of the H<sub>2</sub>S in the separated gases, the hydrogen purity is slightly improved from 78-83 mol% H<sub>2</sub> in separator gases to 80-85 mol% H<sub>2</sub> leaving the amine contactor.



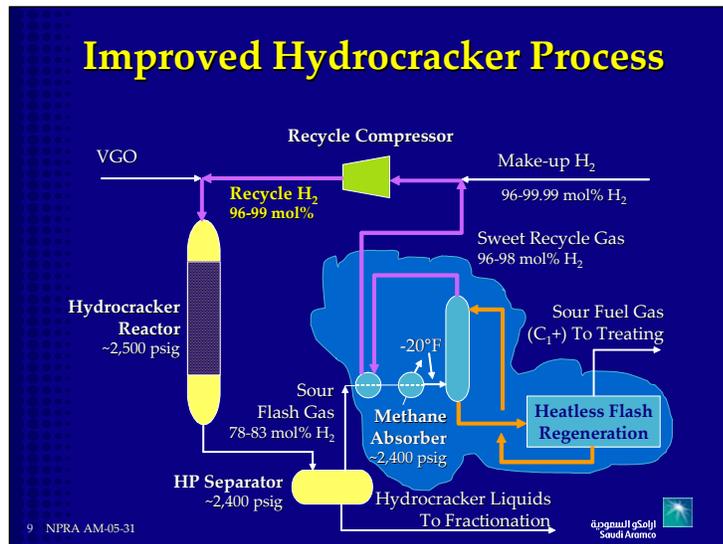
The above hydrogen purity increase is limited because the amine treating system does not remove the contained lighter hydrocarbon gases.

## PROCESSES FOR RECYCLE HYDROGEN PURIFICATION

To further increase the recycle gas' hydrogen purity, the industry has previously considered and rejected the direct use of available cryogenic, pressure swing adsorption, membrane systems and oil sponge system processes within the high pressure recycle gas loop for the following reasons:

Hydrogen Purification Process	Significant Limitations & Features
Cryogenic	<ul style="list-style-type: none"> <li>Extremely Cold Temperatures &lt;-250°F</li> <li>Operating Pressure &lt; 1,000 psig</li> <li>Low Flexibility for Composition Changes</li> </ul>
Pressure Swing Adsorption	<ul style="list-style-type: none"> <li>Low H<sub>2</sub> Recovery (80 to 85%)</li> <li>Operating Pressure &lt;600 psig</li> </ul>
Membrane Systems	<ul style="list-style-type: none"> <li>Extremely High Pressure Drop</li> <li>Lower Purity and Recovery (~90%)</li> </ul>
Oil Sponge Systems	<ul style="list-style-type: none"> <li>High Circulation Rate from High MW Oils</li> <li>Ineffective for Methane (C<sub>1</sub>) Absorption</li> <li>Limited Purity Improvement ~ +2 mol% H<sub>2</sub></li> </ul>

## IMPROVED HYDROCRACKING PROCESS

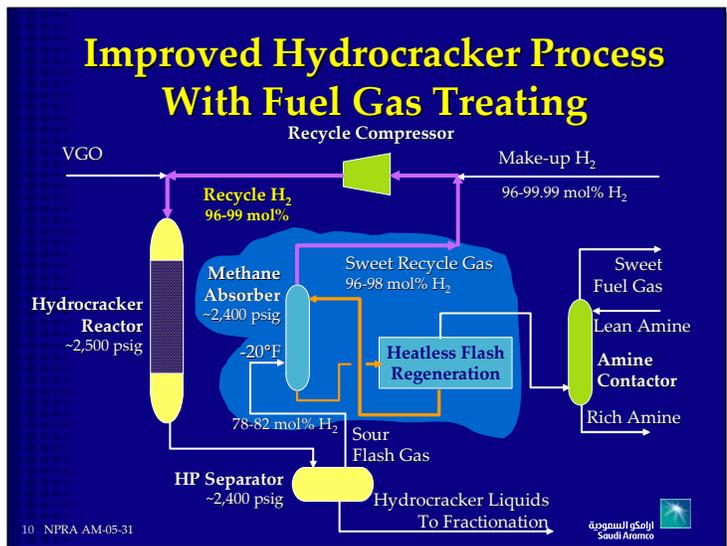


In the improved hydrocracking process, subject of U.S. Patent No. 6,740,226 entitled "Process for Increasing Hydrogen Partial Pressure in Hydroprocessing Processes," the sour flashed gases leaving the HP Separator at 78-83 mol% H<sub>2</sub> purity are counter-currently contacted with a lean solvent to absorb the methane and heavier hydrocarbons away from the contained hydrogen. The separator gases are chilled by cross-exchanging with a

colder, purified, recycled hydrogen stream followed by propane refrigeration to about -20°F. To prevent any water freezing, ethylene glycol (EG) is injected on the tube side of these exchanges and an EG-H<sub>2</sub>O stream is separated in a three-phase coalescer/separator prior to chilled gases and condensed liquids entering the methane absorber column. Most of the H<sub>2</sub>S present in the flashed gases is also absorbed away from hydrogen.

The rich-solvent from the bottom of the methane absorber column is let down in pressure to separate the absorbed methane, ethane, H<sub>2</sub>S, propane, butanes-plus hydrocarbons and produce a lean solvent, which is essentially the heaviest fraction, i.e. butanes-plus present in the HP separator gases. This flash regeneration of lean solvent is essentially a heatless process. The regenerated lean solvent is pumped and temperature controlled to remove the heat of pumping before entering near the top of the methane absorber column. The separated sour fuel gases (C<sub>1</sub>+) are sent for further treating within the refinery.

As shown in the alternative configuration with fuel gas treating, the sour gases leaving the heatless flash regeneration module may be sweetened by an amine contactor. Interestingly though, the size of the amine contactor required for the improved hydrocracking process is significantly smaller because the gas volume through the amine contactor is < 22% of the gas volume treated in the amine contactor of the existing hydrocracking processes.



The hydrogen purity of the overhead recycle gases leaving the methane absorber column is substantially increased to the 96-98 mol% H<sub>2</sub>. Additionally, the pressure drop across the absorption-based system is < 30 psi. Because the C<sub>1</sub>+ contaminants from the recycled hydrogen are removed by the absorption unit, there is no need to purge a part of the recycled hydrogen stream. Consequently the hydrogen loss through purge, common to conventional processes, is eliminated. The overall hydrogen recovery across the absorption module is 96-98%.

Because of this improvement in the recycled hydrogen purity, the hydrogen purity of the combined recycled plus the make-up hydrogen streams is 96-99 mol%. For a typical hydrocracking process, the improvement from the current 82-86 mol% H<sub>2</sub> purity to the 96-99 mol% H<sub>2</sub> under the improved hydrocracking process of the HPH technology portfolio, hydrogen partial pressure is increased by 327 psia.



- *Purge Gas Elimination*
  - ❖ Typical Purge Gas Rate 5% → 0%
- *Higher Conversion Capability*
  - ❖ Improved Conversion +2%
- *Better Distillate Quality*
  - ❖ Improved Cetane Number +3 to 4
  - ❖ Improved Aniline Point +13 to 17°F
- *Heavier Feed Processing Capability*
  - ❖ Feeds Suitable for Processing De-Metalized Oil (DMO)  
De-Asphalted Oil (DAO)  
Coker Gas Oil  
FCC Decanted Oil

The improved economics depend upon several factors as follows:

- Unit size impacting overall capital costs
- If retrofitted into an existing facility:
  - ❖ Configuration of existing system
  - ❖ The ability to utilize existing amine contactor for methane-plus component absorption and installing a significantly smaller contactor for treating fuel gases
- Site location and accessibility
- Operating margins for feed, products and hydrogen
- Utilities availability and pricing

For most applications, a payback period between 2 to 4 years is expected.

## HPH TECHNOLOGY PORTFOLIO

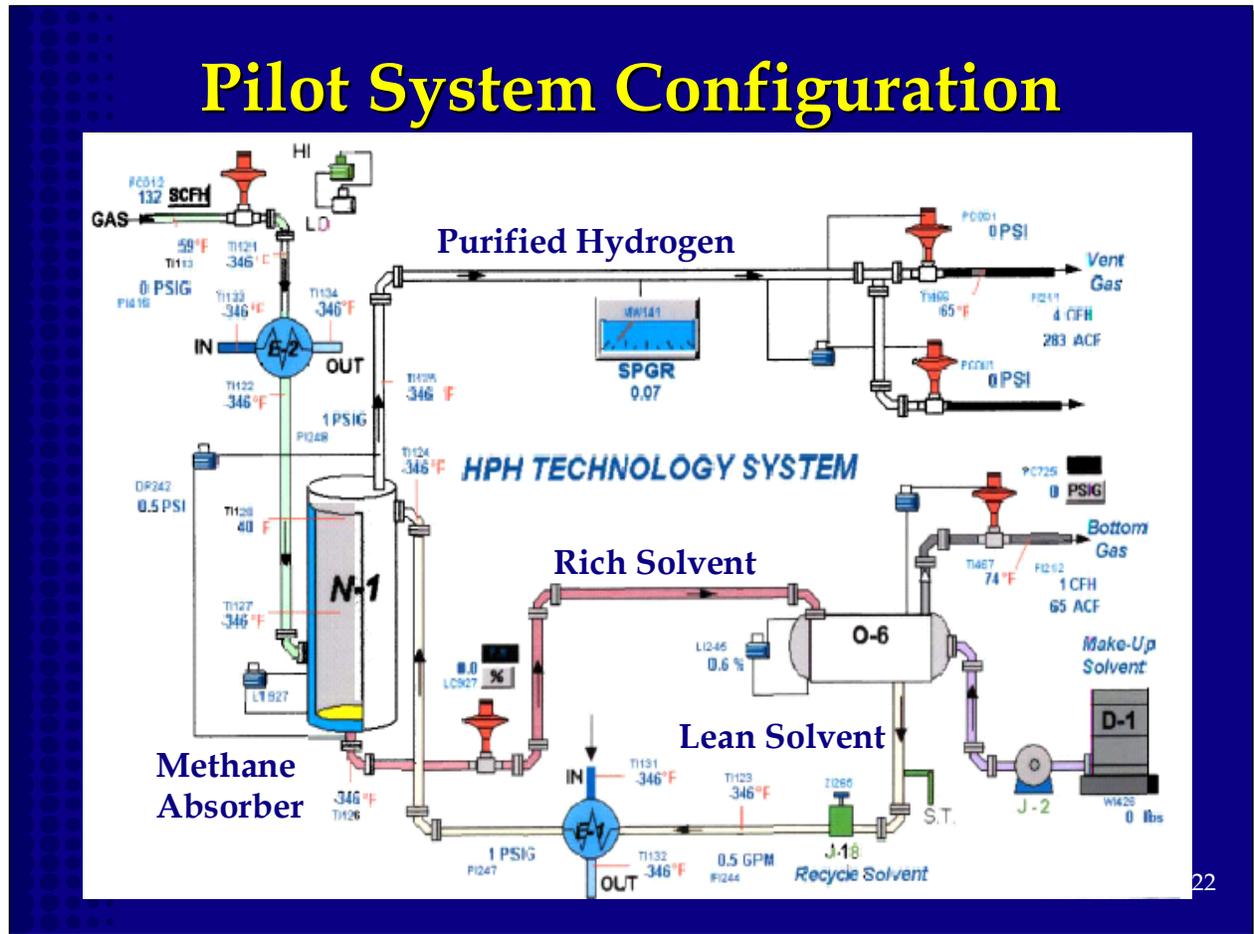
The HPH technology portfolio is subject of issued patents and/or filed applications in the United States, Canada, Mexico, and Australia; selected countries within South America, European Union, and the Middle East; and the Asian countries of China, India, Japan, South Korea, Philippines, Indonesia, Malaysia and Thailand.

The HPH technology encompasses the hydro-desulfurization, hydro-cracking, hydro-denitrification, hydro-dealkylation and hydro-treating applications. Suitable feeds may include naphtha, kerosene, diesel, light & heavy vacuum gas oil, demetalized oil, coker gas oil, resid, fuel oil, aromatics and the like.

## PILOT DEMONSTRATION OF H<sub>2</sub>-C<sub>1</sub> SEPARATION BY ABSORPTION

Given the worldwide applications of the HPH technology portfolio, the fact that the vapor-liquid equilibrium data for hydrogen-methane systems is well understood and known, and yet H<sub>2</sub>-C<sub>1</sub> separation by absorption is new, Saudi Aramco

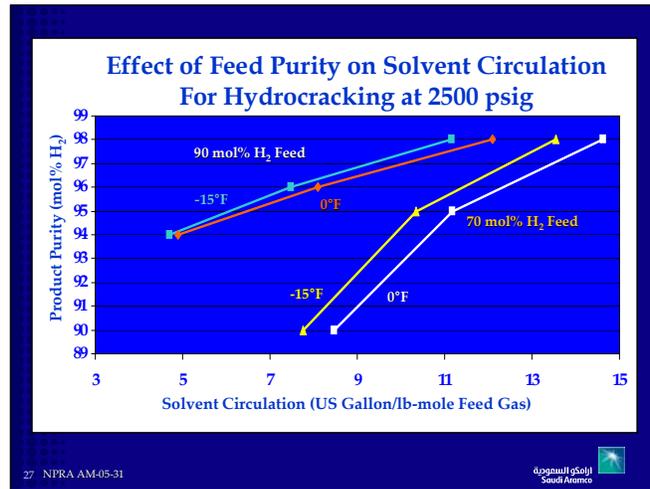
### Pilot System Configuration



undertook physical demonstration of this feature of its proprietary technology in 2002-2003. Through its Houston-based subsidiary Aramco Services Company, Hydrocarbon Technologies, Inc. was contracted to build a pilot unit at its Lawrenceville, NJ, USA facility to collect experimental data and verify the expected performance related to hydrogen purification by absorbing methane-plus hydrocarbons.

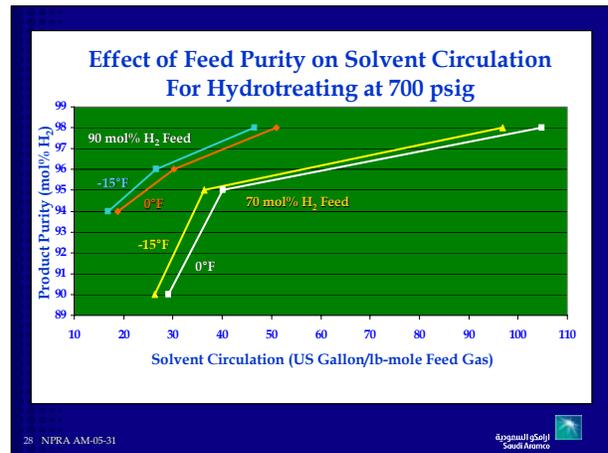
Installed equipment in the shown pilot system configuration was used to collect experimental data for following combinations:

Scope of Data Collection	
Hydrogen Purification Applications	Hydrocracking, Hydrotreating and Fuel Gas Recovery
Feed Gas H <sub>2</sub> Composition Range	50 mol%, 70 mol% & 90 mol%
Operating Pressure Range	400 psig, 700 psig & 2,500 psig
Operating Temperature Range	0°F, -15°F & -20°F
Hydrogen Product Purity Range	90 mol%, 95 mol% & 98 mol%
Number of Data Sets	52



Once the initial HP flash gas at 78-83 mol% H<sub>2</sub> is purified to 96-98 mol% H<sub>2</sub> and recycled back to the reactor inlet, the hydrogen content of subsequent flash gas begins to increase. After a few iterations, the hydrogen content of HP separator flash gas stabilizes at about 90 mol% H<sub>2</sub>. The impact of feed purity on the required solvent circulation rate is shown in the figures for both the improved hydrocracking and hydrotreating processes.

The relative effect of temperatures 0°F and -15°F on solvent circulation rate to achieve the 96 to 98 mol% H<sub>2</sub> purity is also shown in the figures. As expected, lower pressure operation common to a hydrotreating process requires higher circulation rate than the hydrocracking process, but the energy required for the HC or HT pumps is about the same since the pressure increase from solvent pump in HT system is lower than in the HC system.



The following few pictures illustrate the extent and scale of the demonstration unit that was used to collect experimental physical data to verify the performance of hydrogen-methane separation by absorption:

### Monitoring Online Performance



23

### Methane Absorber Column N-1



Looking Up the Column

24

### Solvent Circulation Pump



25

### Packaged Refrigerant Chiller



26

### Refrigerant Fluid Pump



29

### Chilled Liquid To/From Pilot Unit



31

With this first-of-a-kind demonstration, Saudi Aramco has shown that non-cryogenic absorption can be successfully utilized for separating hydrogen from methane-plus hydrocarbons. In doing so, the hydrogen purity of a stream is significantly improved. Some of the features of the heatless flash regenerated absorption system are:

- ❖ Capability of operating at very high pressures ~2,500 psig
- ❖ Achieves 96+% H<sub>2</sub> Recovery
- ❖ Produces 96+ mol% H<sub>2</sub> Purity
- ❖ Minimal pressure drop < 30 psi
- ❖ Very high flexibility towards feed gas composition changes
- ❖ Utilizes standard low temperature carbon steel metallurgy
- ❖ Requires EG injection for dehydration

## CONCLUSIONS

Saudi Aramco has successfully demonstrated the H<sub>2</sub>-C<sub>1</sub> separation by non-cryogenic absorption which offers significant advantages for the hydroprocessing industry. This development overcomes a major limitation to boost the performance of conventional hydroprocessing processes.

Having secured the intellectual property rights for the HPH Technology Portfolio, which is the subject of a significant worldwide patent coverage, Saudi Aramco is working towards identifying first commercial application within the hydroprocessing industry. Saudi Aramco intends to grant licenses for the use of its HPH technology.