MEMBRANE MATRIMONY

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Petroleum refiners are facing significant changes and challenges to the way they operate refineries. Transportation fuels are becoming ever more restrictive in the components they contain: allowable sulfur content is approaching zero; oxygenates are in one day and out the next; benzene and other aromatics are restricted; vapour pressures must be controlled. These restrictions require that the petroleum fractions previously used directly in refinery products must now be treated both to remove impurities and to convert them to more desirable compounds (that increase fuel performance while eliminating restricted compounds from the refinery products). These changes have increased refiners' dependence on hydroprocessing, hydrotreating and other cracking/ converting processes that produce a variety of purges and other streams. These streams contain a variety of valuable gases (hydrogen, propane, butane), but they are of no use except as fuel because they are in a dilute mixture. Unfortunately, the new refinery processes often produce more fuel than a refinery can use. The historical method of dealing with excess fuel is flaring, which is now becoming restricted. As a result, refiners must consider alternative methods to deal with excess fuel. The fortunate refiner may be able to sell the excess fuel to external users, including petrochemical plants (for fuel), hydrogen producers (for reformer feed) or natural gas supplies (to augment their gas supply). When none of these options are available to handle excess fuel, a refiner could be forced to modify the operation of the refinery to produce less waste gas. This will result in inefficient operation and, in the worst case, could require the refinery to reduce production.

Figure 1. Membrane permeation rates.

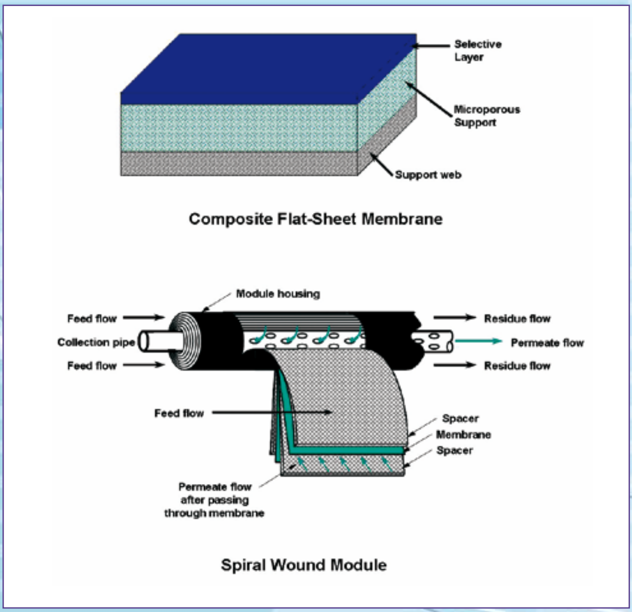

Figure 2. Flat sheet membrane and module.

An obvious alternative is to remove and recover the valuable components from the waste streams, leaving a smaller fuel gas stream that can be fully used in the refinery. If the hydrogen can be recovered and concentrated, it can be reused in the refinery to supplement rising hydrogen consumption due to recent sulfur restrictions. Recovered hydrocarbon components (C_3+) could be reused in the refinery for fuel production or sold as LPG. The remainder in the waste stream is primarily methane and ethane, plus any inert components (nitrogen and CO_2), and would be used as fuel within the refinery. Conventional technologies cannot economically recover these waste stream components; new solutions are needed.

One new technology is membrane separation. Membranes are currently used to recover hydrogen in some refinery streams, but are often not economical due to low concentrations found in many waste streams. Other membranes are currently used to recover hydrocarbons from petrochemical waste streams, but have not been economical for refinery waste streams. Membrane Technology and Research, Inc. (MTR) based in the USA, has been providing hydrocarbon recovery membranes to petrochemical plants for the past 10 years. The company recently began providing hydrogen recovery type membranes, putting the company in the unique position of being able to supply these two different types of membranes. This article discusses the advantages of combining these two different membranes to achieve an improved process that is economical for refinery waste streams

Membranes for gas separation

Since the early 1980s membranes have been used for gas separation, originally for hydrogen recovery, and later to separate N_2 from air and CO_2 from natural gas. In these applications the separation is accomplished primarily by differences in diffusion rates according to variations in molecular size. These 'size selective' membranes are made from polymers that have a rigid structure ('glassy' polymers). In 1995 MTR commercialised a new membrane, called VaporSep, for separating hydrocarbons

Table 1. Current purge conditions and estimated performance of the membrane systems configurations for the hydrocracker

	Current purge to fuel	Purge to fuel with **LPG only design**	Purge to fuel with **enhanced LPG recovery**	Purge to fuel with **enhanced H_2 recovery**
Composition (vol%)				
Hydrogen	44.8	51.4	22.6	10.0
Methane	25.3	28.5	55.6	51.1
Ethane	9.7	9.3	13.4	18.4
C_3+	17.7	8.5	6.5	17.6
H_2S	2.5	2.3	2.0	3.0
Total flow rate (Nm^3/hr) **LPG recovery**	**2000**	**1700**	**740**	**800**
Bpd	~	140	200	140
Annual value (@ US$ 20/bbl)	~	1 million	1.4 million	1 million
H_2 recovery				
Purity (vol%)	~	~	88	88
Total flow rate (Nm^3/hr)	~	~	820	915
Annual value (@ US$ 0.10/Nm^3)	~	~	600 000	700 000
Total annual value (US$/yr) **Utility requirements**		**1 million**	**2 million**	**1.7 million**
Compressor power (kW)	~	290	310	290
Annual power cost (@ US$ 0.05/kW-h)	~	120 000	130 000	120 000
System price (US$)	~	1.4 million	1.9 million	1.6 million
Simple payback (yr)	~	1.6	1.0	1.0

from N_2. In contrast to the conventional membranes described above, the VaporSep membrane separates according to differences in solubility. It behaves in a counter-intuitive manner by allowing large hydrocarbon molecules to permeate much faster than smaller molecules such as nitrogen, hydrogen or methane. This behaviour is due to the higher solubility of large hydrocarbon molecules in the membrane polymer compared to the light gases. This membrane is made from a polymer with a flexible structure (a 'rubbery' polymer) that can move to accommodate the larger hydrocarbon molecules. The relative permeation rates for both membrane types are shown in Figure 1.

Gas separation membranes can be produced in several forms, the most common being a composite flat sheet packaged in a spiral wound module (Figure 2), or a hollow fibre packaged in a 'shell and tube' type module (Figure 3). The choice of configuration depends primarily on the mechanical properties of the polymer that is chosen for a particular separation. For hydrogen recovery membranes a hollow fibre configuration is normally used. This allows higher membrane area for a given module volume, which is needed in this application because the glassy polymers used normally have a low permeation rate. For MTR's solubility selective membrane, the rubbery polymer that provides the desired separation is not strong enough to make hollow fibres, and therefore is made as a composite flat sheet. Fortunately, rubbery membranes have high fluxes, compensating for the lower packing density of the spiral wound module. MTR supplies membrane based systems as complete, skid mounted packages. The skid can include simply the membranes and their pressure vessels, or additional components such as rotating equipment (compressors and pumps), heat exchangers, gas/liquid separators and other items necessary for optimal performance. The systems are compact and contain few (if any) moving parts, making installation simple and inexpensive. Figures 4 shows a typical membrane skid utilising flat sheet membranes.

Both membranes are robust but should be protected against particles and liquids. Pretreatment usually includes filtration and heating (to raise the dewpoint for size selective membranes) or cooling (solubility selective membranes provide better separation at lower temperatures). The VaporSep membrane is not damaged by any compound normally found in refinery streams. However, greater care is required for the hydrogen membranes as these can accept only limited levels of ammonia, amines and aromatics.

Two case studies are presented: the first is the purge gas from a hydrocracker, and the second is excess refinery fuel gas. These case studies demonstrate the synergy of combining these two very different membranes.

Hydrocracker purge stream

In hydrocracking, heavy petroleum components are catalytically reacted into more useful components. The process is performed by combining the hydrocarbon liquid with moderate purity hydrogen (90 - 99 vol% H_2) and passing the mixture over a catalyst in a high pressure reactor. After exiting the reactor, the hydrogen gas is separated from the product hydrocarbons and recycled to the inlet of the reactor. However, besides useful compounds, the cracking process also produces unwanted light hydrocarbon and other gases (C_1, C_2, H_2S). These gases build up and dilute the hydrogen stream, lowering the hydrogen partial pressure in the reactor, and adversely affect the hydroprocessor performance. To remove these unwanted gases and maintain hydrogen partial pressure, a purge stream is taken off and sent to fuel. However, this purge also contains significant amounts of C_3+ hydrocarbons, which are lost when the stream is burned as fuel. The composition and conditions of the purge gas are provided in Table 1.

Recovery systems

Option 1: LPG recovery

To recover these valuable C_3+ hydrocarbons, a membrane based recovery system can be used to treat the purge stream before sending it to the fuel gas header. MTR's VaporSep process, which combines compression, condensation and membrane separation, is appropriate for this recovery application. As shown in Figure 5, the purge stream is compressed to 33 bar G and cooled to 35 ˚C, partially condensing the C_3+ hydrocarbons. The condensed C_3+ hydrocarbons (or LPG) is recovered and returned to the refinery. The remaining gas, which still contains significant amounts of hydrocarbons, enters MTR's solubility selective membrane. The C_3+ hydrocarbons permeate across the membrane faster than the lighter gas components, resulting in a C_3+ hydrocarbons enriched permeate stream and a C_3+ hydrocarbons depleted residue stream. The permeate is recycled to the compressor suction and the residue is sent to the fuel header. This process recovers approximately 60% (140 bpd) of the LPG currently lost in the low pressure purge stream.

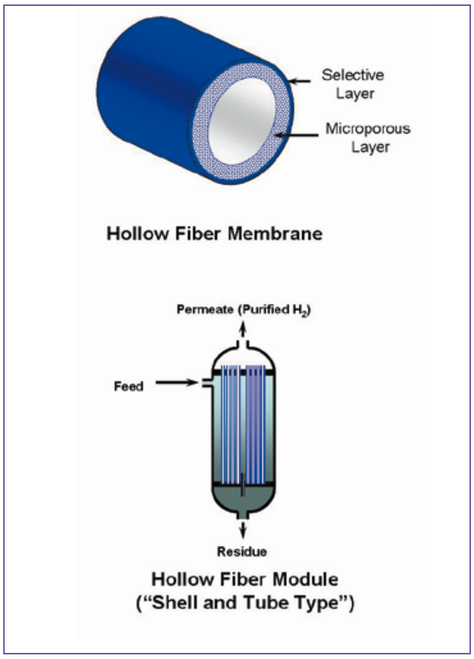

Figure 3. Hollow fibre membrane and module.

Option 2: Enhanced LPG recovery

As shown in Table 1, the hydrocracker purge stream also contains a significant concentration of hydrogen (44.8 vol%). The presence of the hydrogen makes it more difficult to condense and recover the LPG from the purge stream. Reducing the hydrogen content in the purge stream prior to the condensation step would enrich the C_3+ hydrocarbons and improve LPG recovery by the VaporSep System. One method for removing hydrogen is to use a size selective (or hydrogen selective) membrane for pretreating the purge stream. Figure 6 shows this modified VaporSep system.

Figure 4. Membrane skid with spiral wound modules.

The size selective membrane reduces the hydrogen concentration from 44.8% to 14.4% before this treated stream is sent to the same VaporSep system as used above for LPG recovery. This design recovers an additional 60 bpd of LPG (80% total recovery). In addition, the hydrogen selective membrane recovers 820 Nm^3/hr of enriched hydrogen (at 88 vol% purity), which can be reused in the hydrocracker.

Option 3: Enhanced H_2 recovery

The Enhanced LPG Recovery system described above shows increased LPG recovery, but also produces a permeate stream that is enriched in hydrogen (approximately 88 vol%). This hydrogen purity is sufficient for use elsewhere in the refinery. Reusing this hydrogen can potentially add considerable value to the overall process economics. Therefore, MTR examined its design to determine if it could further increase hydrogen recovery as a third design option.

In the previous design, a size selective membrane was used upstream of the solubility selective (VaporSep) membrane to reduce the hydrogen concentration in the low pressure purge stream and enrich the hydrocarbon concentration. As a result, additional LPG is recovered. Conversely, the solubility selective membrane can be placed upstream of the size selective membrane and used to pretreat the purge stream to reduce the hydrocarbon content and enrich the hydrogen concentration. As a result, the size selective membrane recovers purified hydrogen more effectively. This recovery system configuration is shown in Figure 7. The first part of the process is identical to the original VaporSep System design (LPG recovery only). The residue is then heated to 70 ˚C and enters the size selective membrane, where it is separated into a purified hydrogen permeate and a methane enriched residue stream. Although heating is not necessary to lower the dewpoint since the stream is already depleted in hydrocarbons by the VaporSep membrane, it does improve the performance of the size selective membrane. The purified hydrogen is reused in the refinery, and the residue is sent to the fuel header. By reversing the order of the membranes, hydrogen recovery is increased from 80% to 90% (while maintaining purity at 88 vol%). However, LPG recovery decreases to 60% (the same as the performance of the first design option).

Recovery system comparisons

The performances of the previously described design configurations are compared in Table 1. All three options use identical membrane areas and only differ in the membrane configuration. Although Option 2 requires two compressors, the total power requirement of all three options is essentially the same. By placing the size selective membrane upstream of the solubility selective membrane, LPG recovery increases. Conversely, placing the solubility selective membrane upstream of the size selective membrane results in recovering additional purified hydrogen, but at the expense of the enhanced LPG recovery.

As shown in Table 1, all three options yield a reasonable payback. However, the recovery systems featuring the combination of the two membranes (Options 2 and 3) show a significantly better payback based on the LPG and hydrogen values used in MTR's economic evaluation. The two combined systems demonstrate very similar economic performances. However, with different economic conditions (i.e. LPG and H_2 market values) this result would be different, with one option clearly providing the better economic performance. The preferred option depends on the current and future economic conditions. Presently, the customer is evaluating these to determine their preferred option.

Excess fuel gas stream

MTR also considered the previously described recovery system configurations for treating excess fuel gas at a different refinery. In this case, the flow rate of the stream was larger and the initial hydrogen concentration lower. Table 2 shows the stream composition and conditions of the fuel gas. The recovery system designs are similar to those used for the hydrocracker purge stream, but with the following differences:

- The fuel gas stream is compressed up to 40 bar G.
- The compressed gas stream is cooled to 5 ˚C to condense the LPG.
- Larger membrane areas (both solubility selective and size selective) are required.

Table 2 shows the performance comparison for the three design configurations. Similar to the previous case, the addition of a size selective membrane upstream of the solubility selective membrane

Table 2. Current purge conditions and estimated performance of the membrane system configurations for the refinery fuel gas

	Current fuel gas stream	Fuel gas stream with	Fuel gas stream with	Fuel gas stream with
		LPG only design	**enhanced LPG recovery**	**enhanced H_2 recovery**
Composition (vol%)				
Hydrogen	25.0	31.2	21.9	14.2
Methane	40.0	48.0	59.4	59.2
Ethane	20.0	16.8	15.6	21.4
C_3+	15.0	3.3	2.2	4.3
Total flow rate (Nm^3/hr)	**18 000**	**13 600**	**10 000**	**10 400**
LPG recovery				
Bpd	~	1400	1500	1400
Annual value (@ US$ 20/bbl)	~	9.8 million	10.5 million	9.8 million
H_2 recovery				
Purity (vol%)	~	~	84	86
Total flow rate (Nm^3/hr)	~	~	2400	3200
Annual value (@US$ 0.10/Nm^3)	~	~	1.7 million	2.3 million
Total annual value (US$/yr)		**9.8 million**	**12.2 million**	**12.1 million**
Utility requirements				
Compressor power (kW)	~	3000	3400	3000
Annual power cost (@ US$ 0.05/kW-h)	~	1.3 million	1.43 million	1.3 million
System price (US$)	~	5 million	6 million	5.5 million
Simple payback (yr)	~	0.60	0.55	0.50

(Option 2) increases LPG recovery. Total LPG recovery increases from approximately 1400 bpd (84%) to 1500 bpd (92%). Reversing the configuration of the membranes (Option 3) results in increasing hydrogen recovery from 2400 Nm^3/hr (47%) to 3200 Nm^3/hr (64%). Hydrogen purity also increases slightly from 84 vol% to 86 vol%. In contrast to the hydrocracker purge application, Option 2 provides only a minimal increase in LPG recovery for this excess fuel gas application in comparison with Option 1. This is due to the fuel gas composition, which includes smaller amounts of H_2. Its removal will, therefore, have less impact on LPG recovery than it did in the hydrocracker purge application.

A comparison between Options 3 and 2 also shows a significant increase in enriched hydrogen recovery with Option 3. As shown in Table 2, the initial concentration of hydrogen in the fuel gas stream is approximately 25 vol%. As a result, recovering enriched hydrogen with the size selective membrane is rather difficult. However, after first removing the LPG using the solubility selective membrane, hydrogen concentration increases to 31 vol%. At the higher concentration, the efficiency of the size selective membrane is much higher, significantly increasing the hydrogen recovery.

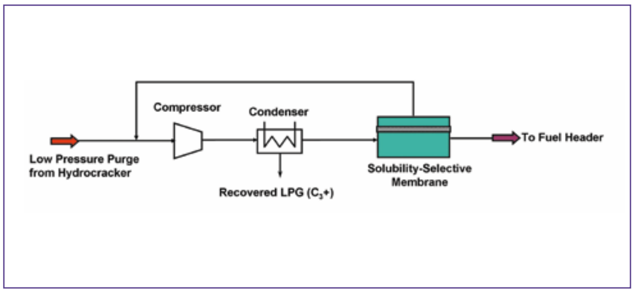

Figure 5. VaporSep system (Option 1).

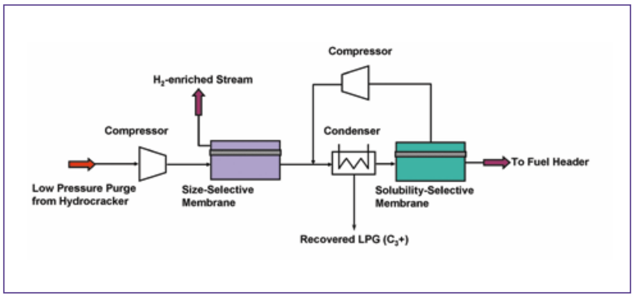

Figure 6. Enhanced LPG Recovery system (Option 2).

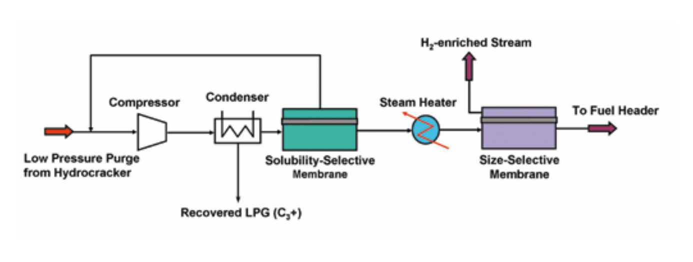

Figure 7. Enhanced H_2 Recovery system (Option 3).

Table 2 shows all three options provide reasonable payback times. While the economics of the membrane recovery system were attractive, the refiner was fortunate to find a nearby natural gas pipeline that would accept the excess fuel gas. Although the expected revenue from this option is lower than MTR's proposed options, the refiner chose to sell the excess fuel gas due to lower capital expense.

Conclusion

The case studies presented demonstrate that membrane based recovery systems can be economical for treating refinery waste streams. These systems can be designed to recover LPG or hydrogen or both LPG and hydrogen. Furthermore, the economics for recovery are enhanced when a combination of two different membranes is used. How the membranes are best combined depends on the specific process and economic conditions at each individual site. In general, membrane based recovery systems for LPG and hydrogen provide opportunities for refiners to reduce waste and recover/recycle valuable raw materials that are currently lost to fuel or to the flare. ■