

The Role of the Merox™ Process in the Era of Ultra Low Sulfur Transportation Fuels

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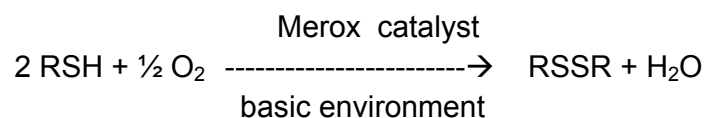
The specifications for transportation fuels, specifically gasoline and diesel, are changing significantly on a worldwide basis in this decade. In Europe and Japan by 2009, the sulfur content of gasoline must be reduced to less than 10 wppm. In the US by 2006, the sulfur content of gasoline must be reduced to less than 30 wppm on average. Similar reductions are also being mandated for diesel fuel.

In the past, refiners relied heavily upon sulfur extraction and sweetening process units, such as the Merox process, to meet gasoline and diesel product specifications. Many refiners are now turning to hydrotreating in order to meet the ultra low sulfur specifications for their transportation fuels. However, in the refining industry of the 21st century, there remains a role for Merox units. Merox applications and technology innovations are enabling refiners to reduce project capital costs to meet these future product specifications.

The Merox Process – An Overview

The Merox process was initially introduced to the refining industry more than 40 years ago. In the intervening years, on-going process and catalyst innovations have enabled the Merox process to become one of UOP's most successful processes with more than 1,700 units licensed. Even as processing objectives changed to meet impending sulfur content regulations, the Merox process has been one of the key refining technologies with more than 300 Merox units licensed since 1990.

All versions of the Merox process are characterized by the catalytic oxidation of mercaptans (RSH) to disulfides (RSSR) in an alkaline (basic) environment. The overall reaction is:



In a liquid-liquid extraction Merox process application, mercaptans in lighter feeds such as gases, C₃'s, C₄'s, LPG, and naphtha are extracted with a caustic solution, which is regenerated by oxidation with air in the presence of Merox catalyst. The resultant disulfides are separated and the caustic reused for extraction. The sulfur content of the extracted hydrocarbon is reduced.

Heavier hydrocarbon fractions such as naphthas, kerosene, jet fuel and diesel contain types of mercaptan which cannot be readily extracted from the hydrocarbon. Hence, in a fixed-bed sweetening Merox process application, the mercaptan oxidation reaction takes place in the presence of air, Merox catalyst and a basic environment, such as caustic. The mercaptans are converted to disulfides which remain in the sweetened hydrocarbon product. The overall sulfur content, therefore, remains the same. Mercaptan sweetening in a fixed bed of Merox catalyst have replaced the older liquid-liquid catalyst sweetening units. Figure 1 shows the Merox process applications for various types of hydrocarbon.

Merox Catalyst Innovations

The original catalysts for both extraction and fixed-bed sweetening Merox units were supplied in powdered form. Manual handling of the powdered catalyst proved to be inconvenient; hence more active, second generation catalysts for extraction (Merox WSTM catalyst) and for fixed-bed sweetening (Merox FBTM catalyst) were developed. These catalyst are produced as liquid catalysts which enable easier handling. Merox No. 8TM catalyst for fixed-bed sweetening was developed to make catalyst handling more efficient for refiners. Merox No. 8 catalyst is Merox FB catalyst pre-impregnated on an activated carbon support. By using Merox No. 8 catalyst, a refiner need not perform an in-situ catalyst impregnation step and therefore can be on stream faster.

Over the years, the efficiency of fluid catalytic cracking (FCC) unit operations enabled the time between turnarounds significantly increasing run lengths up to several years. To enable refiners to continue uninterrupted operations in the downstream Merox fixed bed sweetening units, UOP developed the Merox PlusTM catalyst activator. Merox Plus activator promotes the Merox FB catalyst activity. In addition, the activator helps keep the fixed bed clean of fouling contaminants which might otherwise block the catalyst active sites. The use of Merox Plus activator has enabled refiners to achieve run lengths of their fixed bed sweetening Merox units that match the run length of the FCC unit.

Low Sulfur Naphtha

As low sulfur naphtha regulations have been introduced, refiners have looked for innovative ways to meet the reduced sulfur specifications at minimal cost. Although full boiling range naphthas can be hydroprocessed there is a reduction in the octane of the naphtha product and an increase in hydrogen consumption. As such, there are advantages to splitting the naphtha into its light and heavy fractions to minimize these effects. The fractionation configuration shown in Figure 2 allows the overhead material (light naphtha cut), which contains primarily mercaptan sulfur, to be processed in a liquid-liquid extraction Merox unit at very mild conditions. This approach reduces the refiner's overall investment and operating costs by reducing the size of the associated hydrotreater while eliminating the octane losses and reducing the hydrogen consumption associated with hydroprocessing a highly olefinic light FCC naphtha fraction. The bottoms material from the naphtha splitter (heavy naphtha cut) can be processed in a gasoline desulfurization unit, such as the ISAL™ process. In the ISAL™ process, the lower octane naphtha components are reconfigured through octane-enhancing reactions to minimize the octane loss due to olefin saturation.

The mercaptan content of light FCC naphtha can be reduced by more than 95% through application of the liquid-liquid extraction Merox process without any yield or octane loss. The higher the endpoint of the FCC naphtha fraction that is processed, the lower the percentage of mercaptan sulfur present relative to the total sulfur content. Therefore, when applying the liquid-liquid extraction Merox process, maximum desulfurization of light FCC naphtha is achieved by optimally cutting the end point of the light fractions. Since thiophenes begin to boil at around 65° C, fractionating the FCC naphtha such that these thiophenes remain in the heavy FCC naphtha is recommended when maximum desulfurization is desired.

Process Innovations

There have been several process innovations in the Merox process which can assist the refiner in meeting process specifications while minimizing capital costs.

Liquid-Liquid Extraction Merox

The flow scheme for a liquid-liquid extraction Merox unit is shown in Figure 3. Maximum removal of the mercaptans is achieved in a single vertical extraction

column using proprietary high velocity/high efficiency jet deck extraction trays. The naphtha feedstock flowing up the extractor column is counter-currently extracted with a circulating caustic solution. Depending on the feedstock properties and the required product specifications, as many as six or more stages of extraction are incorporated into the Merox unit extraction column design. This ensures maximum desulfurization with a minimum caustic circulation rate and reduces capital costs compared to other processes that can only achieve a single stage of extraction per contacting vessel.

If hydrogen sulfide (H_2S) is present in the feed, the extractor column is preceded by a caustic prewash for (H_2S) removal. Removal of H_2S prior to mercaptan extraction provides for a more efficient operation. By removing H_2S the circulating mercaptan extraction caustic is not contaminated which allows for more efficient usage and minimizes disposal of the circulating caustic. Additionally, the efficiency of the mercaptan extraction is maximized by eliminating the H_2S which otherwise interferes with the mercaptan extraction efficiency and regeneration of the circulating caustic.

Following the extractor column is an optional caustic settler to help further minimize the already low potential for caustic carryover. The treated naphtha then flows through a sand filter coalescer to reduce the sodium (Na) content of the naphtha to less than one weight part per million (< 1 wt-ppm Na^+).

The Merox unit also contains a caustic regeneration section where the mercaptan-rich caustic solution from the bottom of the extraction column flows to an oxidizer column where extracted mercaptans are oxidized to disulfides. Air is injected upstream of the oxidizer.

A wash oil, generally hydrotreated naphtha or hydrotreated kerosene, is injected upstream of the oxidizer. Wash solvent is usually included in the flow scheme when extracting naphtha range feedstocks in order to minimize the product re-entry sulfur, which is the disulfide contained in the regenerated caustic that re-enters the hydrocarbon phase and increases the sulfur content of the extracted product.

Merox WS catalyst is added periodically to the circulating caustic to maintain the required catalytic activity. The oxidized solution exiting the top of the oxidizer column flows to the disulfide separator where spent air, disulfide oil/wash solvent, and caustic solution are separated. The spent air is usually vented to an existing fired heater near the site, while the disulfide oil/wash solvent stream is decanted and sent to a hydrotreating unit. The caustic stream leaving the disulfide separator is circulated back to the extraction column.

Innovation Delivered – Improved Extraction Merox Design

As seen in the previous section, the hydrocarbon section of the liquid-liquid extraction Merox unit consists of four basic operations, H₂S removal, mercaptan extraction, caustic settling and caustic coalescing, each operation accomplished in a separate vessel. UOP's process innovation is to combine these various operations into a single vessel. This innovative flow scheme is shown in Figure 4.

As before, the naphtha feed is first introduced into the H₂S removal section. However, in the improved extraction Merox design, the H₂S section is incorporated into the bottom portion of the single vessel. Efficient H₂S removal is maintained by a continuous circulation of 10° Be caustic.

What was the caustic settler and sand filter are now replaced with a coalescer which is “installed” at the top of the extraction vessel. The extraction vessel will maintain:

- High mercaptan extraction efficiency
- Low re-entry disulfide in the treated product
- Low overall caustic consumption
- < 1 wt-ppm sodium in the treated product.

Most importantly, a reduction in the unit capital cost of up to 30% can be achieved with the improved extraction Merox design. This cost savings is realized via the reduction in the number of vessels required and corresponding plot space reduction.

Sweetening Merox Process

As shown in Figure 1, fixed-bed sweetening Merox process is applied to pentane and heavier hydrocarbon streams. The MinalkTM design of the fixed-bed sweetening Merox process is shown in Figure 5. The primary application for the Minalk process is for treating naphtha.

The Minalk process utilized a simple design consisting of a single reactor filled with a fixed bed of activated charcoal impregnated with Merox FB catalyst. Dilute caustic, to maintain alkalinity, is continuously injected into the feed naphtha along with air. The naphtha is then passed downward through the fixed bed where the mercaptan is oxidized to disulfide. The disulfide, being oil soluble, remains in the hydrocarbon (naphtha) phase. The design of the Minalk unit reactor and reactor collection system allows for efficient caustic

separation from the naphtha such that the treated naphtha will contain < 1 wt-ppm sodium without need for a separate coalescing media.

The process benefits associated with the Minalk process include:

- Production of a “Doctor negative” product while minimizing removal of phenols from the naphtha
- Long catalyst life (which can further be extended by use of Merox Plus catalyst activator)
- Minimum of operator attention required
- A very small continuous discharge of dilute spent caustic
- Low capital and operating costs

Innovation Delivered - SweetFrac™ Flowscheme

As mentioned earlier, the primary role for the Minalk process is in sweetening naphtha. However, there are innovative applications for the Minalk process in the production of low sulfur naphtha. One of these applications has the Minalk unit located upstream of the naphtha splitter. This is an alternative to splitting the full boiling range naphtha into light and heavy fractions, and then treating the light FCC naphtha fraction [LCN] by a liquid-liquid extraction Merox unit, as seen in Figure 2. This new processing scheme, named SweetFrac, sweetens the full boiling range FCC gasoline in a fixed bed Minalk unit upstream of the naphtha splitter column as shown in Figure 6. The mercaptans in the naphtha are converted to disulfides. These disulfides have a much higher boiling point than the mercaptans and are easily fractionated into the heavy naphtha cut. Since the full range FCC naphtha is fractionated into light and heavy cuts after being sweetened, only the heavy FCC naphtha fraction requires desulfurization in a hydrotreating unit.

The advantages and benefits of SweetFrac are:

- Less sulfur in the LCN product after fractionation (no unextracted mercaptan sulfur and no re-entry disulfides) since the need for a liquid-liquid extraction Merox unit on the LCN can be eliminated.
- The size of the hydrotreater and hence the resulting hydrogen consumption and octane penalty can be reduced significantly.

There are eight Sweetfrac flowschemes in operation.

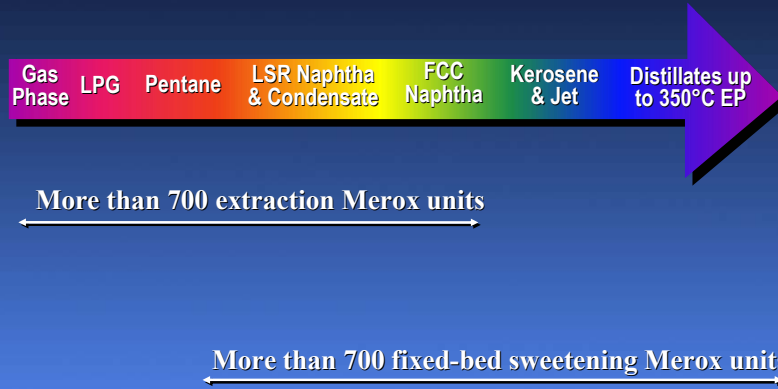
Innovation Delivered – Treating Recombinant Mercaptans from Hydrotreating Units

As more FCC gasoline selective hydrotreating units are placed on stream, the frequency of hydrotreating units whose products have recombination mercaptans are increasing. Levels of 10 to 60 wt-ppm mercaptans are being found in some units. Whereas the heavy naphtha cut may, in some instances, still meet the overall total sulfur specification, the presence of these mercaptans may cause the naphtha to fail the “Doctor test”. Hence, another application for Minalk units, as shown in Figure 7, is to sweeten the recombinant mercaptans in the naphtha cut so that a “Doctor Negative” test result can be achieved. In many cases, a refiner may be able to reuse existing Minalk units for this service.

CONCLUSIONS

UOP remains committed to the on-going development of Merox process technology and to servicing the many Merox units in operation around the world. Catalyst and catalyst activator innovations improve catalyst life and on-stream efficiency. Engineering design improvements reduce process capital and operating costs. Innovative process applications allow refiners to reduce costs by using existing equipment and reducing the sizing required for new hydrotreating units. As a result, the Merox process continues to play an important role in meeting the ultra low specifications of the refining industry’s transportation fuels.

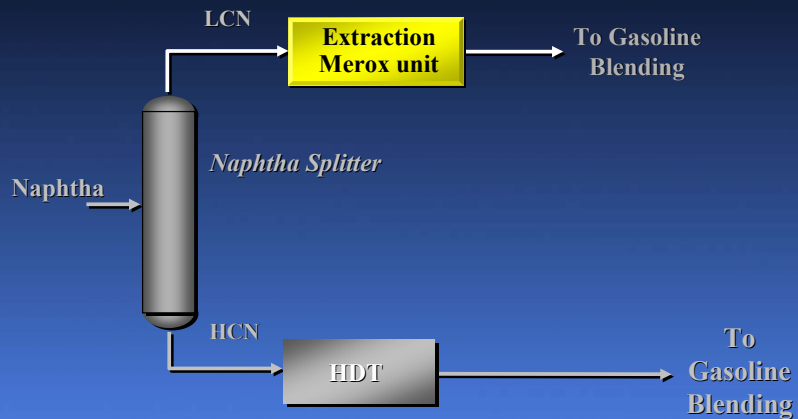
Figure 1
Mercox Process Applications



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Figure 2 - Extraction Mercox Process for Low Sulfur Gasoline Production



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Figure 3
Extraction Merox Process

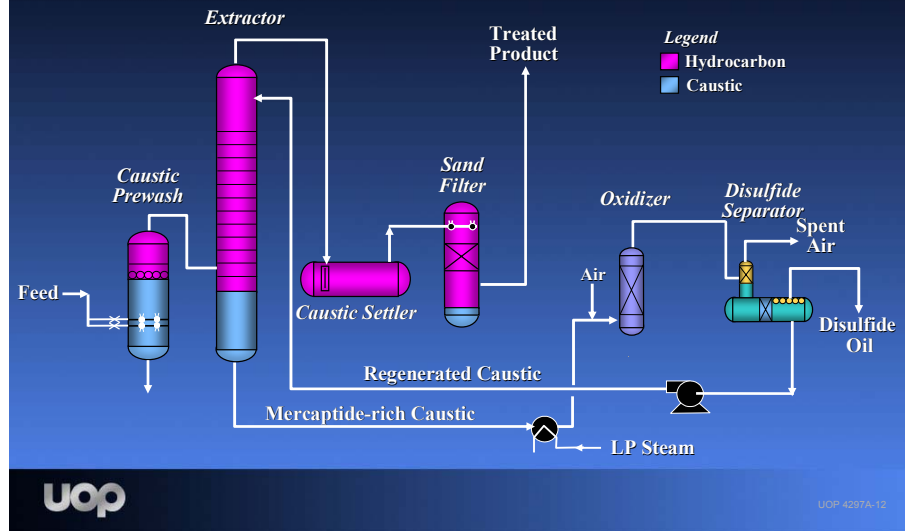
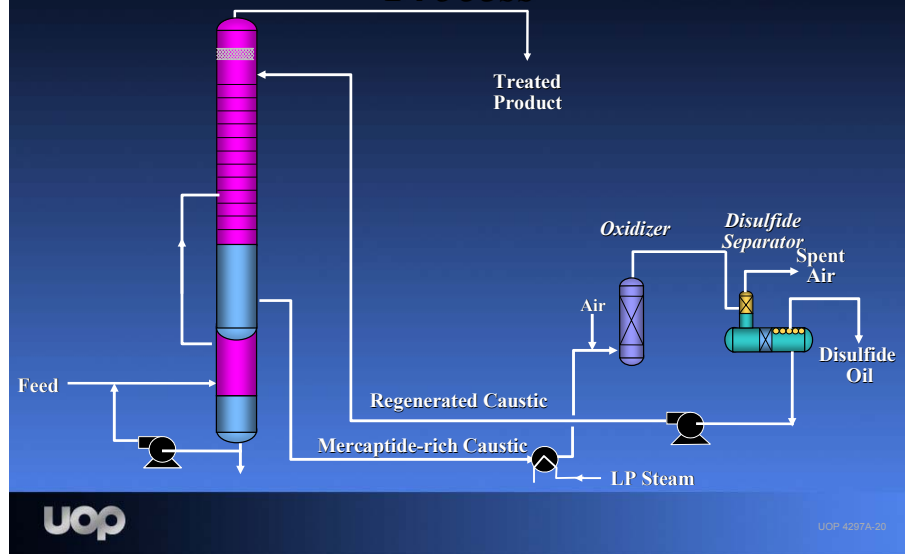
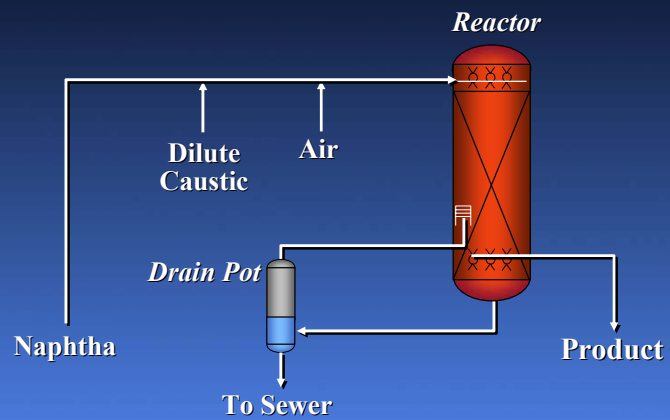


Figure 4 - Improved Extraction Merox Process



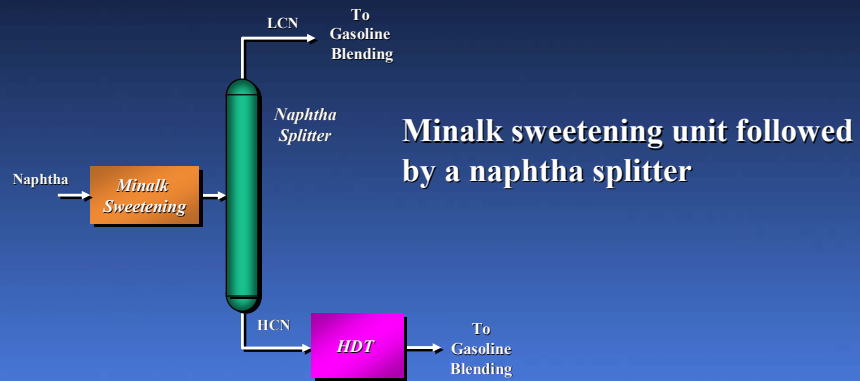
**Figure 5 - Minalk Process
Fixed Bed Sweetening**



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**Figure 6 - SweetFrac Pre-treatment
For Low Sulfur Gasoline Production**

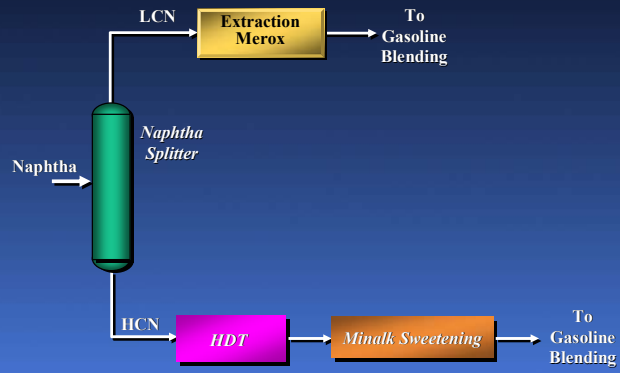


Minalk sweetening unit followed by a naphtha splitter

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**Figure 7 - Minalk Merox Process
For Low Sulfur Gasoline Production**



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