

Coke Oven Light Oil (COLO) Hydrotreating and Aromatics Recovery Technology

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Summary

COLO (Coke Oven Light Oil) is a by-product of steel industry, obtained during the thermal conversion of coal to coke. It is a highly aromatics material composed primarily (~90%w) of benzene, toluene, and xylenes. It also contains high levels of sulfur, such as thiophene (0.3-0.6 %w), nitrogen, such as pyridine (0.25 %w) contaminants and significant quantities of olefinic aromatics, such as styrene (1.5-2.5 % w). Removal of thiophene, pyridine, styrene from raw COLO feedstock by simple fractionation are not feasible since their boiling ranges are too close to that of the (desired) aromatics products to allow for precise separation. Precautions have to be taken to saturate the di-olefinic aromatics such as styrene prior to complete fractionation, since they readily undergo polymerization upon heating and vaporization in the presence of oxygen.

The COLO Hydrotreating section is designed for pretreatment of COLO feed (prior to aromatic recovery) to remove undesirable contaminants, such as thiophenes, pyridines, styrene and C9+ (indenes) from the COLO feedstock, without excessive aromatics loss (saturation). To produce nitration grade benzene, toluene and xylenes, the olefins content must be lowered to a diene level of 1 gm/100 gms; heteroatom contaminants must be reduced to levels < 1 ppmw.

LyondellBasell have incorporated many commercially proven reactor design features which have been custom designed for each licensed unit; features such as:

- Proper reactor sizing
- Improved liquid distribution
- High contacting efficiency
- Vaporization Control
- Premier dense loading technique
- Effective pressure drop control
- Temperature control



LyondellBasell uses a combination of a Nickel/Molybdenum (Ni/Mo) catalyst in the (mixed-phase) first stage reactor, followed by a Cobalt/Molybdenum (Co/Mo) catalyst (or a combination of Ni/Mo and Co/Mo) in the (vapor phase) second stage reactor, to achieve the desired results. Thus, the costs for catalysts used in LyondellBasell system are lower than many of the competitor systems that use precious metal catalyst for the first stage (di-olefin removal) or competitors which require vapor phase in the first reactor.

LyondellBasell has licensed many Reformate/Py Gas aromatics extraction units all over the world since the '70s. Their first licensed COLO/Extraction unit complex was for Kawatetsu Chemicals (Japan) which was started up in 1982. The second COLO feed based unit was for Adchemco Corp. (Japan) which started up in 1995. With the fifteen years of commercial experience and associated pilot studies in COLO hydrotreating, LyondellBasell are able to quantify the influence of all major operating variables, and also provide continuous technical & catalyst improvements to new and existing licensees.

Process Description

The COLO hydrotreating unit is generally comprised of a feed pretreating section, a hydrotreating reaction section, a product stabilization section and a MEA (gas treatment) section (refer to slide #23.)

The feed pretreating section (see slide #24) is mainly a simple vacuum fractionator designed to remove C9+ (148°C+) components including any polymer already present due to reactions with the reactive di-olefins common to these COLO feeds. Heavy C9+ material (if not removed) will tend to increase both, catalyst aging and the required reaction severity.

COLO hydrotreating (see slide #25) has to be carried out in two stages: In the first stage, a moderately low temperature (~ 200°C) hydrotreater is used to selectively saturate the highly reactive styrene (to ethylbenzene) to eliminate reactor fouling and plugging due to (uncontrolled) polymerization reactions. The saturation of these di-olefins is monitored by noting a reduction in the bromine number and by gas chromatographic (GC) analysis.

In the second stage, a moderately severe (300-400°C) hydrotreatment is used to remove undesirable sulfur and nitrogen containing contaminants, saturate all remaining olefins (mono -type), while minimizing aromatics saturation. Both of these stages are operated at a much lower pressure than is typical of thermal/cracked naphtha hydrotreating (< 35 Kg/cm²g vs. 50-70 Kg/cm²g) to reduce the potential for aromatics saturation.

To remove undesirable byproducts of H₂S and NH₃ from the hydrotreated COLO, the reactor effluent is flashed and stripped (stabilized) in an atmospheric tower.



A MEA (recycle gas) treating is carried out using ethanolamine absorption columns to remove H₂S from hydrocarbon streams, if available. Otherwise, a slipstream of chilled stabilized product is used to absorb H₂S. Wash water injection (with steam condensate) is used before the final reactor effluent cooling to prevent NH₄SH salt precipitation in the effluent exchangers.

Catalyst Systems & Process Variables

Typical catalysts employed for hydrotreating are sulfided (stable activity) forms of either NiMo or CoMo metals supported on highly porous gamma alumina (aluminum oxide). Typical amounts of metal oxides present on the catalyst are 10-20 % w for molybdenum oxide and 2-5 % w for the cobalt or nickel oxides. CoMo is generally preferred for HDS activity, while NiMo is utilized for minimizing hydrogen uptake when processing unsaturated fuels such as products from thermal cracking operations)

It is generally believed that Co and Ni act as promoters by increasing the activity of the Mo, while secondarily stabilizing the monolayer of aluminum oxide, Al₂O₃. If the fresh or newly regenerated CoMo catalyst is not properly presulfided, a significant penalty in activity of 10-20% may result for nitrogen removal. This activity loss is generally found to be even greater for NiMo catalysts.

Tungsten sulfides, promoted with nickel, act in an analogous fashion to Ni-Mo catalysts, but are more difficult to activate (presulfide). NiW has marginal activity advantage over the Ni/Mo but such advantages are generally outweighed by higher cost. High nickel only catalysts are also used in hydrotreating some thermal naphthas (such as Py Gas), but their higher saturation activity (in their reduced metal state) is off-set by their being very sensitive to sulfur poisons.

The first stage reactor - Ni/W catalyst or Ni/Mo catalysts exhibit high activity for olefin saturation, (i.e. saturation of styrene to ethylbenzene). The olefin saturation reactions are highly exothermic nature, and can be influenced by the operating variables such as: (1) an increase in temperature results in enhanced styrene saturation, (2) a reduction in space velocity affects a higher styrene saturation and (3) a higher hydrogen to oil (feed) ration will increase the styrene saturation.

The second stage reactor- high activity Co/Mo (or a combination of Ni/Mo and Co/Mo) catalyst for hydrodesulfurization and hydrodenitrogenation. The conversion of sulfur compounds to H₂S and sulfur-free hydrocarbon is highly exothermic. When desulfurizing a 2000 wppm sulfur feed to < 10 wppm sulfur product, the heat release due to the desulfurization reaction will contribute about a 18-23°C to the catalyst bed temperature rise.

The denitrogenation reactions are also highly exothermic. When denitrogenating a gas oil containing 1400 ppmw nitrogen compounds to 20 ppmw, the heat release due to the denitrogenation reaction will contribute an additional 3-6°C to the catalyst bed temperature rise. The rates of desulfurization and denitrogenation increase with



increasing H₂ partial pressure and reaction temperature. A temperature rise of 18-20°C will cause a doubling of the desulfurization rate whereas a temperature increase of 22-28°C will cause a doubling of the denitrogenation rate. A two-fold increase in hydrogen partial pressure typically results in a two-fold increase in the rate of denitrogenation.

The saturation of benzene can also significantly effect the reactor temperature raise and total reactor pressure. Approximately 1.75 to 2.75% w of the benzene in the feed to the second-stage is saturated at the optimum design conditions (i.e., low temperature and low pressure). Increasing temperature can drastically increase benzene saturation to a level of 4.5 to 6.7% w or more. At higher pressures (say over 50 Kg/cm²g), benzene saturation of over 5% can be observed. Along with these increases in aromatic (benzene) saturation, the (chemical) hydrogen consumption observed will also increase upon increasing reactor temperature or total pressure. This is due to the fact that most of the chemical hydrogen consumption is mostly due to the level of aromatics saturation.

Catalyst Loading

LyondellBasell have always specified a dense loading for these reactors via such procedures as ARCO's premier catalyst oriented packing (or COP). Without a suitable dense loading, the amount of catalyst actually loaded into the reactor will be reduced by up to 15% lower than expected. This type of loading (non-dense or sock) greatly increases the possibility of bed slumping and is likely to significantly effect pressure drop and contacting efficiency. This reduction in available catalyst (due to the use of sock loading) will necessitate a slightly higher initial weight average bed temperature (WABT). A higher initial WABT means somewhat shorter catalyst life.

Hydrotreating Reactor Design Basis

LyondellBasell's COLO feed based design calls for use of down-flow reactors which are the most cost-efficient and practical system to operate, and are commonly used in hydrotreaters service. The second stage reactor is generally designed with multiple internal catalyst beds, with a gas quench between the beds, to enable better control of critical reactor temperature. The most important reactor design parameters are:

- Mixed-Feed 1st Stage Reaction
- Feed vaporization (1st Stage)
- Minimum H₂ partial pressure
- Liquid mass velocity (Minimum)
- Maximum pressure drop per bed
- Manageable bed delta T.



The most important criteria is in maintaining good liquid (feed) and solid (catalyst) contact efficiencies throughout the entire catalyst system. If the feed vaporization is too great, then the liquid mass velocity will drop well below the desired minimum rate. A minimum liquid phase (40-60% w) is maintained in the first stage reactor to assure the transport of any polymeric material which might be formed through the first-stage and to the proprietary Vaporizer unit. This minimum liquid phase level is favored by low reaction temperatures and reduced hydrogen to oil ratios. These lower reaction temperatures also reduce the possibility of polymer formation, aromatics saturation, and subsequent coking of the catalyst.

Again, the LyondellBasell process maintains a mixed phase in the low temperature first-stage reactor, to avoid the potential problem of polymer formation which could lead to coking/fouling and eventual plugging of the fixed-bed downflow reactor. The unconverted intermediates product, particularly styrenic & DCPD materials can form polymers & gums, so it is important to control the temperature and maintain the liquid phase of these materials.

The first stage reactor effluent is vaporized by direct contact with a hot hydrogen recycle stream in LyondellBasell unique proprietary Vaporizer unit. This vaporizer will force the reactor liquid effluent to a superheated condition, avoiding the dew point condition. Thus when the first-stage effluent goes over to the second stage reactor, it is a superheated vapor. Those styrenic & DCPD materials would lead to polymer formation and they are easily removed in the bottoms of the vaporizer, such that no additional fouling and plugging would occur in the vapor phase second-stage reactor.

The COLO vapor is then processed in the second-stage reactor where essentially complete hydrosulfurization and hydrodenitrogenation and olefin saturation occurs. The effluent undergoes separation into a hydrogen rich gas phase and a liquid phase, containing primarily aromatics with an expected aromatics recovery of > 97.0%. Subsequent stabilization of the hydrotreated aromatics (liquid) phase results in a contaminant-free COLO that is fed to the aromatic extraction unit.

The saturation of styrene and other aromatics accounts of approximately 60-80% of the total hydrogen uptake calculated and the remained 20% for the minor levels of hydrodesulfurization and hydrodenitrogenation. The total (chemical) hydrogen consumption is ~ 35-40 Nm³/m³.

Proper Reactor Sizing & Material of Construction

For a given feed rate, smaller diameter reactor vessels will tend to increase the liquid mass velocity and thus improving the overall contacting efficiency. However, this same reduction in reactor diameter has the opposite effect on the pressure drop through the reactor (which is increased). Since it in most hydrotreating operations, cycle length is directly related to pressure drop limits, minimizing reactor pressure drop is considered to be a most critical parameter with respect to size. It is therefore, most desirable to use as large a diameter reactor as possible without violating the minimum liquid mass



velocity criteria. Still, comparing a mixed-phase 1st stage versus a vapor phase 1st stage, the reactor size and required catalyst amount are indeed smaller.

Reactor internals and fabrication preferences are custom-designed and determined based on the latest development and operating experience, some key areas are:

- Liquid Distributors
- Trash Baskets
- (Hydrogen) Quench Spargers
- Thermocouple Locations
- (Catalyst) Dump Nozzles

Due to the high H₂S partial pressure and H₂ rich environment associated with COLO feed based hydrotreaters, alloyed steels (like 1 Cr-1/2 Mo) are required for proper corrosion protection. The reactor internals should be further constructed with stainless steel cladding to provide for maximum corrosion allowance. The choice of base reactor vessel metallurgy must also take into consideration the fact that NiMo or NiW and CoMo hydrotreating catalysts usually require presulfiding temperatures as high as 343 to 370°C (final soak) at full hydrogen partial pressure to get full activity.

Reactor Design

A good COLO Hydrotreater reactor design calls for a high L/D, down flow reactors, which is the most cost-efficient and practical system, and is commonly used in refinery hydrotreaters. With the “OptiTrap” catalyst bed filter and other design features of the LyondellBasell system, up flow reactors are not needed. A “COP or dense” loading procedure of catalysts would also be applied.

Effective Pressure Drop Control

Depending on the catalyst particle sizes and shapes (i.e. trilobe, cylinders, sphere), and the physical properties of the liquid and vapor phases within the reactor, one can use the Ergun equations to estimate the pressure drop based on COP (dense) loading. To account for possible accumulation of dirt, scale, and coke which could increase the bed pressure drop through the catalyst cycle, one can generally assume an end of run (EOR) pressure drop is approximately equal to the “clean” pressure drop multiplied by a factor of 2.

Temperature Control

The heat release associated with the various exothermic reactions can be calculated to predict the total temperature rise across the reactor. Then one can choose a temperature control scheme that relies on properly sized multiple catalyst beds to maintain “manageable” bed delta T’s. It is best to limit the individual bed delta T to around 17-20°C due to the adverse effect of higher temperatures.



For the second stage, which is operated in an all vapor environment, H₂ quench is used to manage the temperature rise to 17-20°C and limited the reactor effluent temperature of the second stage to prevent the common problem of byproduct H₂S reacting with trace olefins to form mercaptan sulfur compounds in the COLO product.

Reactor Conditions

The design operating conditions is tabulated below:

	<u>First Stage</u>	<u>Second Stage</u>
WABT, °C	150-250	300-400
LHSV, 1/hr	~2	1-2
Hydrogen Rate, Nm ³ /m ³	50-100	400-500
Pressure, Kg/cm ² g	~ 30	~ 30
Catalyst	Ni/Mo or Ni/W	Co/Mo

In order to obtain maximum flexibility for unit design, a typical turndown operation at 50% is assumed when customizing the reactor internals design.

Catalyst Aging/Poisons

The catalyst activity is monitored by checking the change in saturation of styrene in the first stage and the sulfur and nitrogen compounds removal in the second stage. LyondellBasell's experience has shown that coke laydown is about 15-20% w at end of run. Like most hydrotreating operations, they adjust (raise) temperatures during the cycle to compensate for activity loss. Once a maximum temperature is reached, a decision must be made whether to regenerate or replace the aged catalyst. However, most of the time the pressure drop reaches the maximum allowable level long before the maximum temperature or EOR activity is observed

Heavy meals are non-regenerable and (if present) will lay down on the catalyst as permanent poisons. These should be limited to < 1 wppm to obtain the required run length. Of particular concern is arsenic which is commonly present in COLO feeds. Arsenic should be limited to < 0.5 wppm. Nitrogen compounds or organic chloride are not expected to poison the catalyst, but their associated by-products of NH₃ and HCl can combine to form a NH₄ClH precipitate salts that can foul downstream heat exchangers. These can be washed out with proper injection of wash water (steam condensate). Free water is undesirable, since it tends to inhibit heteroatom conversion and olefin saturation.

In-Situ/Ex-Situ Regeneration

Once the catalyst has reached the end of its cycle, a decision must be made to regenerate (in-situ) or replace (with either fresh or off-site regenerated) catalyst. Two different in-situ regeneration procedures are generally used: steam-air and inert gas (nitrogen). Steam-air regeneration has been used more frequently. However, because



of pollution considerations, many installations have switched to inert gas in-situ regeneration. Properly conducted, both procedures will remove most of the coke. Note however, that high temperatures in a steam atmosphere is considerably more detrimental to catalyst activity than high temperature in a dry gas environment. Hence, regeneration in the presence of steam results in substantially lower activity restoration for NiMo catalyst than CoMo catalyst.

Catalyst in-situ regeneration can generally obtain activity recoveries of 90% for the first regeneration. Subsequent regenerations can be considerably less. The usual minimum acceptable activity recovery is 70%. This, however, would be far too low for COLO Hydrotreater Service. Off-site (ex-situ) regeneration is a standard practice, performed by experienced contractors under very controlled conditions.

Hydrogen stripping is also a normal practice on Pt or Pd-catalyst (recommended by some COLO Hydrotreating processes), but NiMo and CoMo catalysts do not generally respond as well and may (at best) gain only a short term activity boost to extend a run for a short time (1-2 month).

Flexibility for Pyrolysis Gasoline Processing

LyondellBasell's COLO Hydrotreating Unit can be designed with the flexibility to process 100% COLO feed and if necessary, a mixture of COLO and Pyrolysis Gasoline or Aromatics Reformate streams. For this feature, the maximum amount of Pygas or Reformate in the feed mixture is approx. 35.0 wt%, on a 100% COLO feed Unit capacity design basis.

Aromatics Extraction Process Technology

There are many different processes offered for the extraction of aromatics from a variety of coal-liquid and petrochemical sources. By far the most popular of these is liquid-liquid extraction using sulfolane as the extracting solvent. The process was developed more than forty years ago and has been improved upon over the years, and despite the introduction of other extraction flow schemes and various different extraction solvents, the sulfolane-type of system as offered by LyondellBasell (and UOP, etc.) is still the most preferred.

Sulfolane -- a Preferred Solvent

Around the world, sulfolane is accepted to be a safe, reliable material for extracting aromatics. It has low toxicity, non-explosive, and is produced by many manufacturers world-wide and readily available. The very selective and high boiling point of sulfolane (285°C) enables its use over a large range of feedstocks, including xylenes & C9 aromatics mixtures. When the extraction unit and regenerator are operated as designed and the starting sulfolane material is clean (free of impurities), a sulfolane-type Aromatics Extraction Unit can operate with a very low solvent make-up requirement.



Based upon LyondellBasell's experience in licensing Aromatics Process for all sorts of extraction units, it is clear that non-sulfolane extraction and extractive-distillation units are much more difficult to start up and to maintain a steady-state operation.

N-Formylmorpholine (NFM) is also widely used as an extraction solvent and has the advantage of being more thermally stable than sulfolane.

Regardless the solvent, licensors have optimized the required solvent ratios and operating and design conditions to ensure efficient separation of aromatics and non-aromatics, while minimizing new unit capital costs and on-going operating costs.

Flexibility for BTX Production

A liquid-liquid Sulfolane Extraction unit can be easily designed to produce very high purity benzene, toluene and xylene products *simultaneously*. The proportion of each aromatic component, and the ratio of aromatics to non-aromatics, can be varied over a broad range, with minimal changes in operating conditions; certainly no physical change in hardware would be required. This feature maximizes revenues when compared to competing process technologies.

LyondellBasell has both owned and licensed Aromatics Extraction Units (over thirty units now); operating today on coke oven light oils, as well as hydrotreated pyrolysis gasoline, reformat, and various mixtures of these. In fact, the Kawatetsu and Adchemco Plants in Japan are able to operate on COLO either alone, or in mixture with Pyrolysis Gasoline.

Like many licensors, LyondellBasell, through its engineering partner, Mustang Engineers and Constructors, L.P. creates a customized process design for each new Aromatics Extraction Unit, to build in as much flexibility as each new licensee may require.

Licensed and Operating Unit Improvements

LyondellBasell own hands-on operating experience gives a distinct advantage over other licensors in that they can provide troubleshooting expertise through their own operating units. In addition, LyondellBasell has a strong need to keep abreast of the technological advances in Aromatics area and how to implement these advances into commercial practice. Any improvements or advancements in the technology will be furnished (granted back) to their licensees.

Since the '90's, the improved designs of licensors and their operations have been incorporated into all newly-designed LyondellBasell units. One main example of this is the design and operation of the extractor column to be operated at lower temperature than other sulfolane processes, and to utilize a lower solvent-to-feed ratio than previously possible. Both of these benefits directly affect operating costs: lower temperature is directly related to lower utility requirements, while the lower solvent-to-feed ratio results in less of a make-up solvent requirement. In addition, Lyondell offers a



unique method of regenerating and purifying the re-circulating sulfolane solvent, to minimize corrosion - therefore, the unit can be designed using low-cost carbon steel material which can be fabricated in China and need not be imported from overseas.

Conclusions

A good COLO hydrotreating /Aromatics Recovery Process recovers the maximum possible quantity of benzene from COLO feeds with minimum aromatics loss due to saturation. Each plant should be customized with the latest reactor design practices and greater flexibility. Through LyondellBasell's on-going relationship with existing hydrotreating and aromatics extraction licensees, and continuing catalyst evaluation programs with various catalyst manufacturers (Criterion, Procatalyse, Zeolyst, etc.), LyondellBasell will continue making process technology improvements and identify better catalyst(s), providing improved HDS/HDN performance, less aromatic saturation activity (improved selectivity), and enable very high recoveries at a modest hydrogen gas to feed ratios, minimize solvent usage, and Utility requirements.

These process technology advancements include more efficient and robust designs, thus reducing the capital cost (improving the economics) for new units and/or existing unit improvements, while maintaining or minimizing operating costs.

This is a main goal of all COLO Hydrotreating Aromatics Recovery technology licensors. And most commercially available technologies are well-known and have a number of operating units from which to draw knowledge and improvements. LyondellBasell does have the advantage of being an Operating Company with associated research facilities as well.

