Hydrocracking Design Fundamentals

by

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Introduction

Hydrocracking is one of the oldest hydrocarbon conversion processes. Development on this process started in Germany dating back to 1915 as a means of securing a supply of liquid fuels derived from coal. This was a catalytic process operating at very high pressures in the range of 200 to 700 bar and high temperatures from 375°C to 525°C[1]. The first hydrocracking plant was put into operation in Germany in 1927.

After Word War II, hydrocracking lost its importance and further development was discontinued. The hydrocracking process that we are familiar with today was established in the early 1960's. The original process was designed to upgrade low valued distillate feedstocks such as light cycle oils and thermally cracked coker gas oils into gasoline and lighter materials. Feeds that were difficult to process in an FCC found a home in the hydrocracking process. These feeds were typically aromatic in nature and contained high concentrations of organic nitrogen and sulfur. The naphtha product from a hydrocracker, processing these feeds is a component that can be blended directly into the gasoline pool or is a good reformer feed.

As the demand for high quality middle distillates increased in the 1970's, the hydrocracking process was further developed to meet the changing market demand to convert higher boiling point feedstocks into high quality middle distillate. Over a twenty year period the 90 % point of the feed increased from 400°C to over 600°C[2]. Major advances have been made in hydrocracking in two primary areas, catalyst and process. The focus of this paper is on the hydrocracking process.

Hydrocracking Refinery Configuration

One example of a refinery configuration integrating a hydrocracker and an FCC unit is presented in Figure 1.

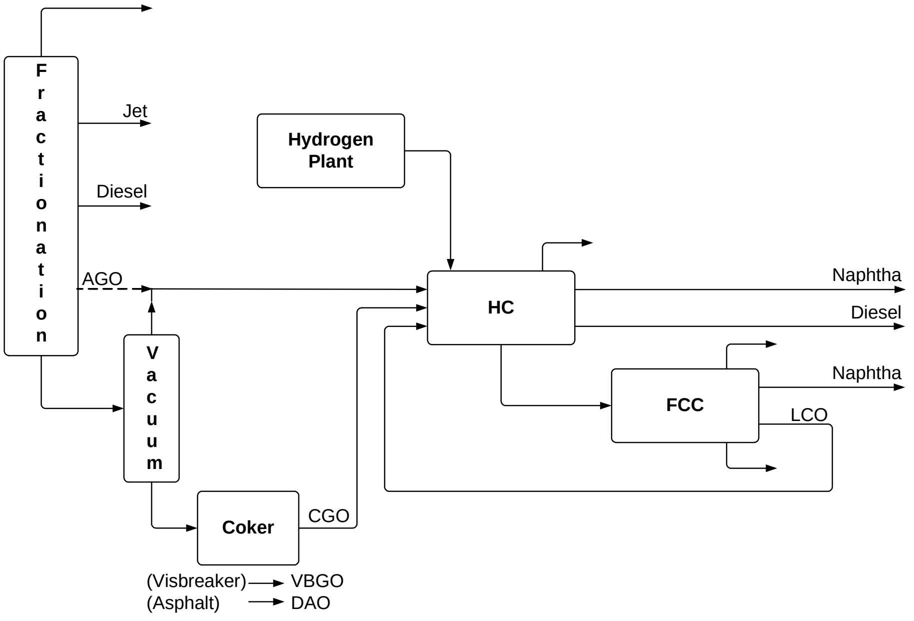

Figure 1: Refinery with FCC and HC – block flow diagram

A typical hydrocracker feed is vacuum gas oil boiling in the range of 350°C to 550°C. Lower boiling point feeds can be used depending on the specific needs of a refinery. This can include conversion of naphtha to LPG or conversion of material in the diesel boiling range such as LCO to produce naphtha. Higher boiling feeds such as DAO can also be processed in hydrocracker. Other more aromatic hydrocracker feeds include light and heavy gas oils form conversion units such as delayed coker and visbreaker.

In a refinery with both a hydrocracker and a FCC, the LCO from the FCC can be sent to the hydrocracker. The LCO is a low value stream that is often used as a cutter stock; however it is an excellent hydrocracker feed. The hydrocracker converts the LCO to a valuable heavy naphtha stream that is high in cyclic compounds and is a very good reformer feed, while the diesel produced contains almost no sulfur and typically has a cetane number of 45 to 50[3].

While the by products of the FCC are good feeds for the hydrocracker, the unconverted oil from the hydrocracker makes an excellent feed for the FCC. The paraffinic, high hydrogen and low nitrogen content of the unconverted oil can be readily converted in the FCC. The poly aromatics content of the unconverted oil tends to be low, thus the yields from the FCC are relatively high. Compared to untreated feed, the unconverted oil from a hydrocracker can increase the gasoline yield in a FCC unit by 10 vol% and about a 6 vol% increase in C_3/C_4 olefins[3]. This can be a tremendous increase in revenue for the refinery. Additionally because the FCC feed is low in sulfur, the naphtha produced from the FCC can meet future low sulfur fuels specification while the SO_x emissions from FCC flue gas are substantially reduced. In addition to low sulfur and nitrogen, the unconverted oil is also low in metals that can poison the FCC catalyst.

The combination of the hydrocracker and FCC also provides the refiner with a lot of flexibility to meet changing market demands. As the market demand swings form gasoline to diesel, the hydrocracker severity and conversion can be increased to make low sulfur diesel. At times of peak gasoline demand, the conversion in the hydrocracker can be reduced, thus maximizing FCC feed and ultimately maximizing gasoline yield from the FCC.

Hydrocracking Process Configurations

Single Stage

Single stage hydrocracker configuration shown in Figure 2, is the most common design configuration for high conversion hydrocracking units and is typically the most economical design. This design utilizes a treating reactor that is immediately followed by a cracking reactor. In some cases a single amorphous based catalyst (for treating and cracking) can be used for maximizing middle distillate yield when processing low nitrogen, straight-run feed stocks.

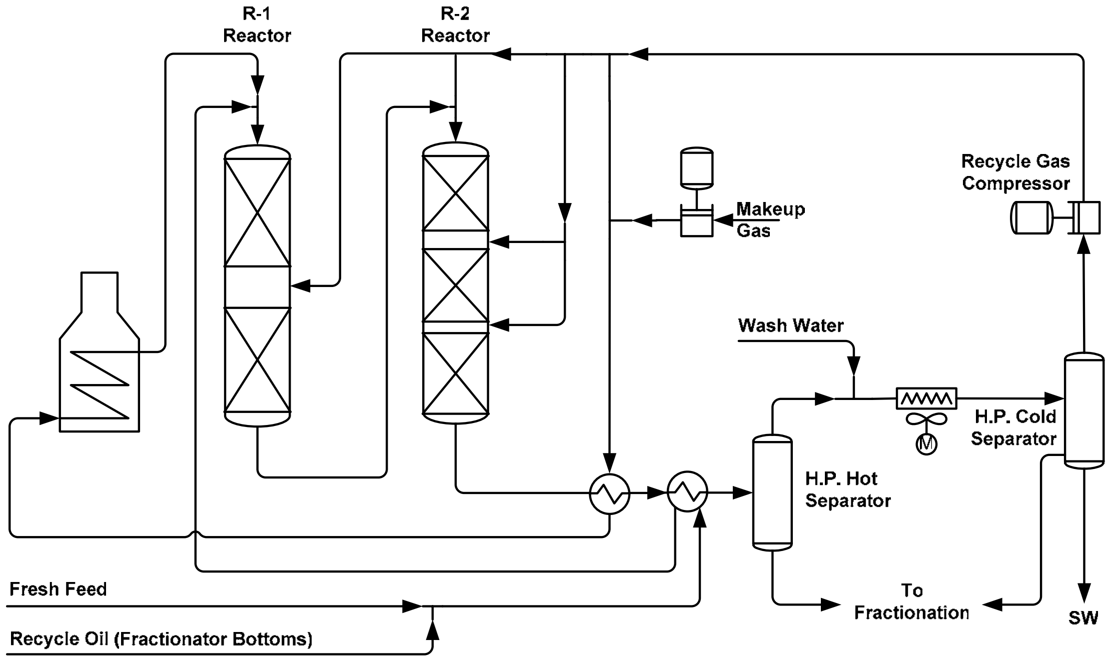

Figure 2: Typical single stage hydrocracker – process sketch

The treating reactor converts the organic nitrogen and sulfur compounds to hydrogen sulfide and ammonia. Ammonia is an inhibitor of the hydrocracking catalyst activity but its effect is much less than that of organic nitrogen compounds in the feedstock. Saturation of aromatics will also occur in the treating reactor. Cracking in the treating reactor is minimal and primarily results from conversion of sulfur and nitrogen containing molecules.

Most of the cracking occurs in the second reactor over the cracking catalyst. In the single stage configuration, the total effluent of the hydrotreaters including the H_2S and NH_3 passes into the hydrocracking section. The presence of the H_2S requires the cracking catalyst to operate in a sulfided form. The presence of the NH_3 reduces the cracking catalyst acid site cracking activity. Organic nitrogen compounds have the highest deactivating influence on the cracking catalyst. The proper selection of catalyst and operating conditions can be used to produce a wide range of products including LPG, naphtha, turbine fuels, and diesel fuels. Initially amorphous based cracking catalyst were employed, but unless absolute maximum selectivity to heavy diesel is required, zeolite based catalyst are frequently employed.

The single stage multiple catalyst-multiple reactor scheme permits optimum removal of organic nitrogen and sulfur compounds and allows the independent control of treating and cracking.

The effluent from the cracking reactor is cooled, separated, and sent to fractionation. A process sketch of a typical mid barrel unit fractionation section is presented in Figure 3. The unconverted oil from fractionation is recycled back to the feed surge drum. Alternate designs include recycle of the unconverted oil directly to the cracking reactor since the unconverted oil requires no further treating. The recycle oil rate typically ranges from 25 vol% to 70 vol% of the fresh feed rate.

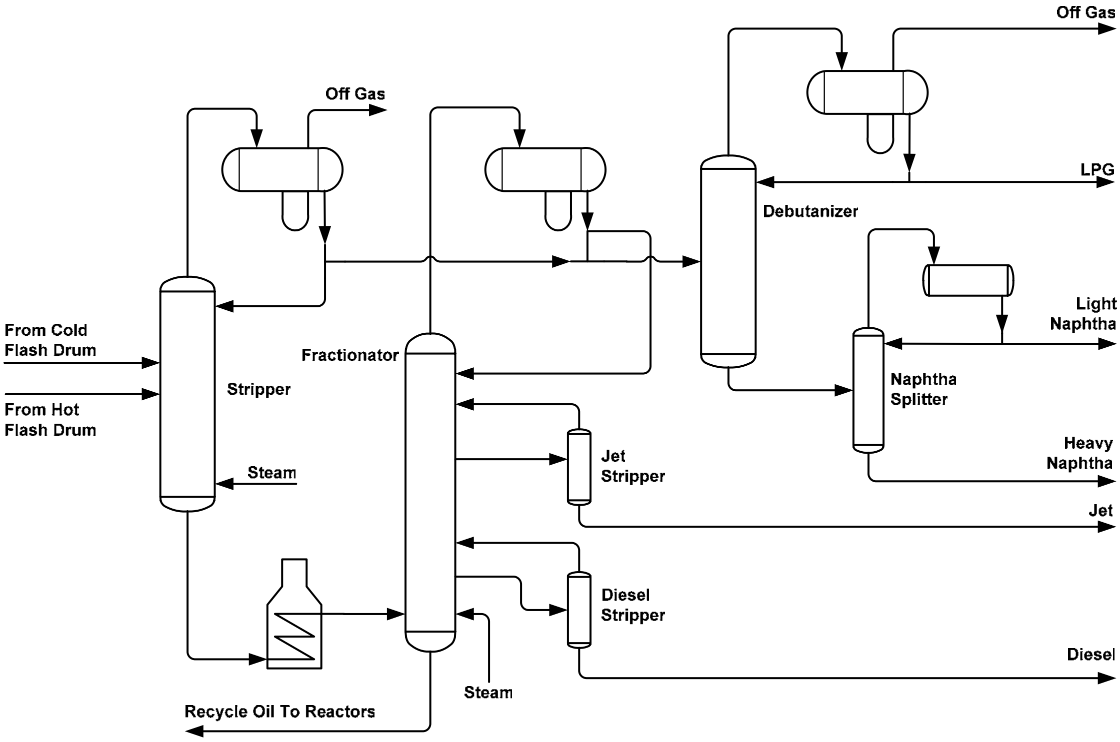

Figure 3: Typical middle distillate hydrocracker – fractionation section process sketch

The single stage unit design can be used for conversions up to 100%. However with high boiling feedstocks, a small slip stream or bleed of the recycle oil is taken so as to control the concentration of heavy polynuclear aromatics (HPNA) in the recycle oil. High concentrations of HPNA can cause catalyst deactivation, loss of selectivity as well as fouling of air coolers and heat exchangers.

The single stage process can be used to produce greater than 90 vol% middle distillate yield with high cetane diesel and high smoke point kerosene. Better yields are obtained as the recycle oil rate is increased relative to the feed rate. However, at higher recycle oil rates the unit cost increases.

Maximum capacity for a single reactor train is 65,000 bpsd fresh feed plus recycle.

This case will serve as the base case and all other process configuration will be compared to this design.

Once-through

The once-through configuration is a single stage with out recycle of the unconverted oil from the fractionator. A process sketch of the high pressure section of a typical once-through unit is presented in Figure 4. Because the recycle is eliminated, the capital investment at a given fresh feed rate is reduced. Thus this scheme has the lowest capital investment of all the schemes.

This configuration is utilized typically when the unconverted oil is one of the principal desired products. One example of this is the production of high VI lube base stocks. Hydrocracking allows production of high VI lube base stocks from wide range of feeds. Compared to solvent extraction, hydrocracking has higher flexibility in feeds that can be processed, has higher yield of high VI lube base stocks and has a more environmentally acceptable route for the manufacture of lube base stocks. Due to the high level of hydrogenation and ring opening capacity of hydrocracking, low VI components such as poly aromatics and naphthenes can be converted to high VI products. Higher conversions typically result in higher product VI up to conversion of about 85% to 90%. Above this conversion range, the VI of the unconverted oil will drop. A further extension of once-through hydrocracking is dewaxing for which a specialized dewaxing catalyst is utilized in the second reactor.

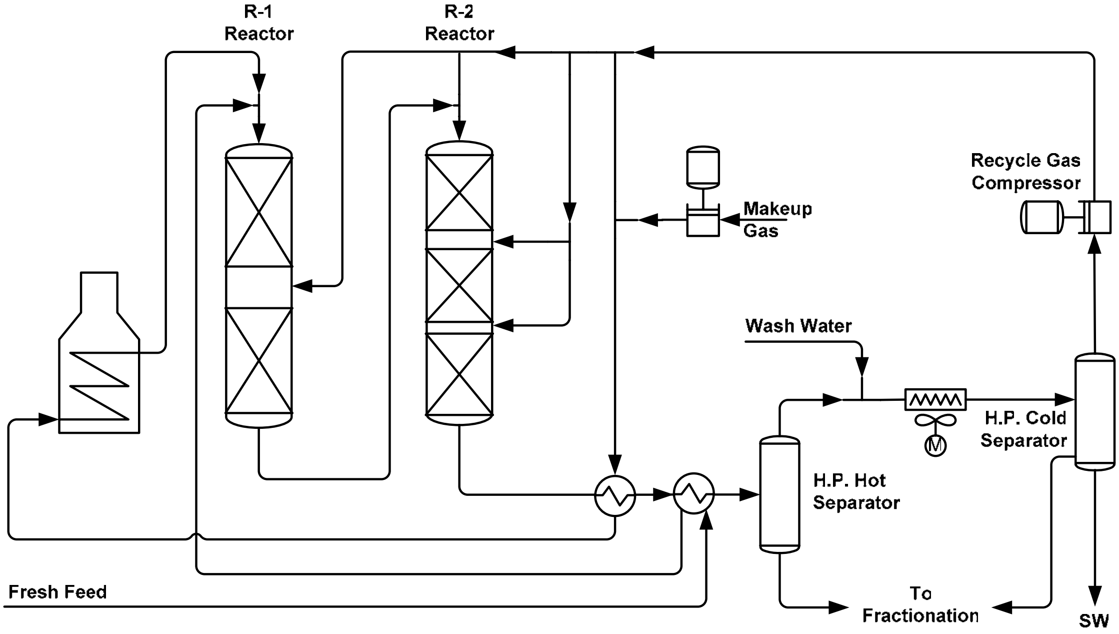

Figure 4: Typical once-through hydrocracker – process sketch

Once-through hydrocracking is also used to upgrade FCC feed. Favorable FCC yield structure is obtained when processing unconverted oil from the hydrocracker as discussed previously.

Unconverted oil from a hydrocracker is an excellent ethylene plant feed. The highly hydrogenated, paraffinic unconverted oil has a high BMCI which correlates with high ethylene yield.

For certain low boiling point feeds such as LVGO and with proper choice of cracking catalyst, a once-through hydrocracker can produce Ultra Low Sulfur Diesel and jet products at 100% conversion.

A partial conversion once-through hydrocracker can generally process higher end point feeds than a full conversion. Feeds such as deep cut HVGO, HCGO, and DAO can be processed in a once-through hydrocracker. There is no concern of HPNA buildup in a once-through configuration.

Typical conversion in a once-through unit is 30 to 80 volume percent to diesel and lighter. Higher conversions up to 95% are possible, but over cracking can occur and diesel yield will decline.

One negative aspect of this configuration is the poor quality middle distillates (low smoke point jet and low cetane diesel) in low pressure unit because the products often contain higher quantities of aromatics. Another disadvantage is the reduced flexibility to vary product yield structure compared to plants designed for recycle. Additionally the product yield structure is not as favorable as the recycle operation. Especially at high conversions, the once-through configuration will produce more light ends. Topsoe has a unique partial conversion process that addresses some of the concerns of a low pressure once-through units.

Separate Hydrotreat

In the separate hydrotreat configuration, the first stage typically has a single reactor to only hydrotreat the feed. No cracking catalyst is used downstream of the treating reactor. The product from the treating reactor is then cooled and sent to fractionation. The unconverted oil from the fractionation section is then sent to a dedicated separate stage, where the required cracking takes place. The cracking stage could share a common recycle gas compressor with the treating stage. A process sketch of the high pressure section of a typical separate hydrotreat – hydrocracking unit is presented in Figure 5.

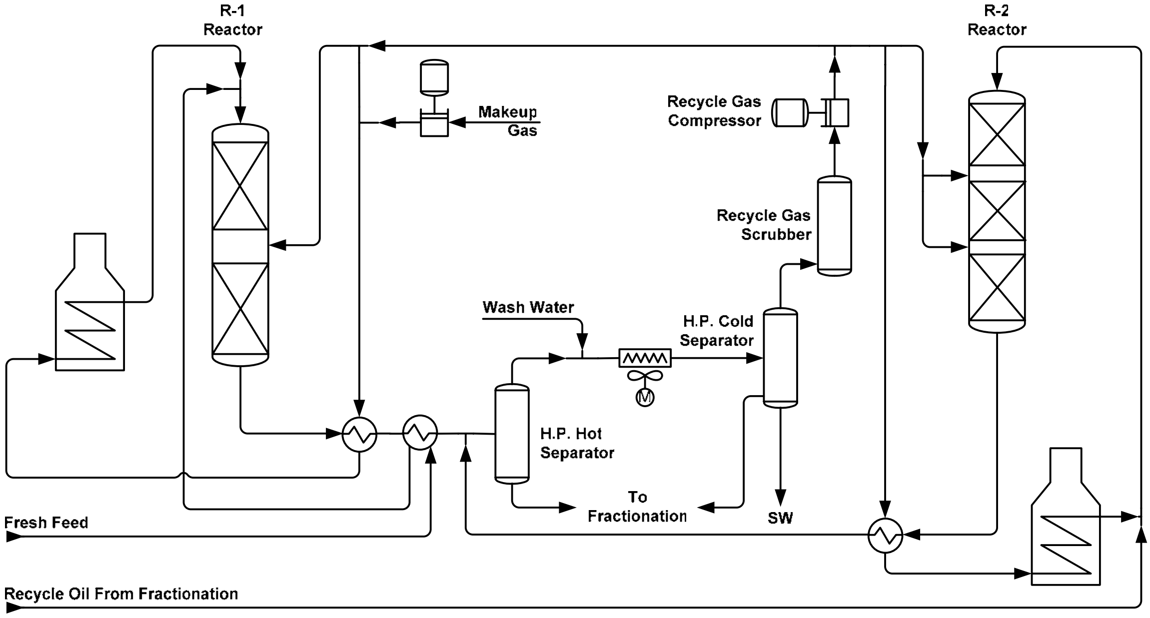

Figure 5: Typical separate hydrotreat – hydrocracker – process sketch

By separating the stages, the ammonia produced in the treating stage is eliminated from the cracking stage. Additionally if the unit has a scrubber or a separate recycle loop, then the H_2S can also be eliminated from the cracking reactor. This has the advantage that a noble metal catalyst can be used in the second stage or the desired H_2S and NH_3 environment can be maintained by spiking the feed and or bleeding in sour gas.

This type of configuration is not commonly used. The capital investment for this configuration is the highest compared to all other hydrocracking configurations. This configuration would be utilized when the feed nitrogen is very high and it is uneconomical to do any amount of cracking in the treating stage due to the very large quantities of cracking catalyst that would be required. This configuration can also be justified if the feed contains a high percentage of material in the boiling range of the desired product. For this situation the first stage is used to improve the quality of the product that is in the feed while preparing feed for the second stage. There are two main advantages to separating out the product before going to the second stage. This includes avoiding over cracking of the product in the feed and reducing the feed rate and thus the size of the equipment in the cracking stage.

Two-stage

The two-stage configuration is similar to the separate hydrotreat configuration with the exception that cracking catalyst is added in the first stage down stream of the treating reactor to do some cracking. The effluent from the first stage is routed to fractionation and the unconverted oil is fed to the second stage. The second stage can share some of the equipment with the first stage including compressors, high pressure and low pressure separators, some of the high pressure exchangers, and fractionation section. A process sketch of the high pressure section of a typical Two-stage hydrocracking unit is presented in Figure 6.

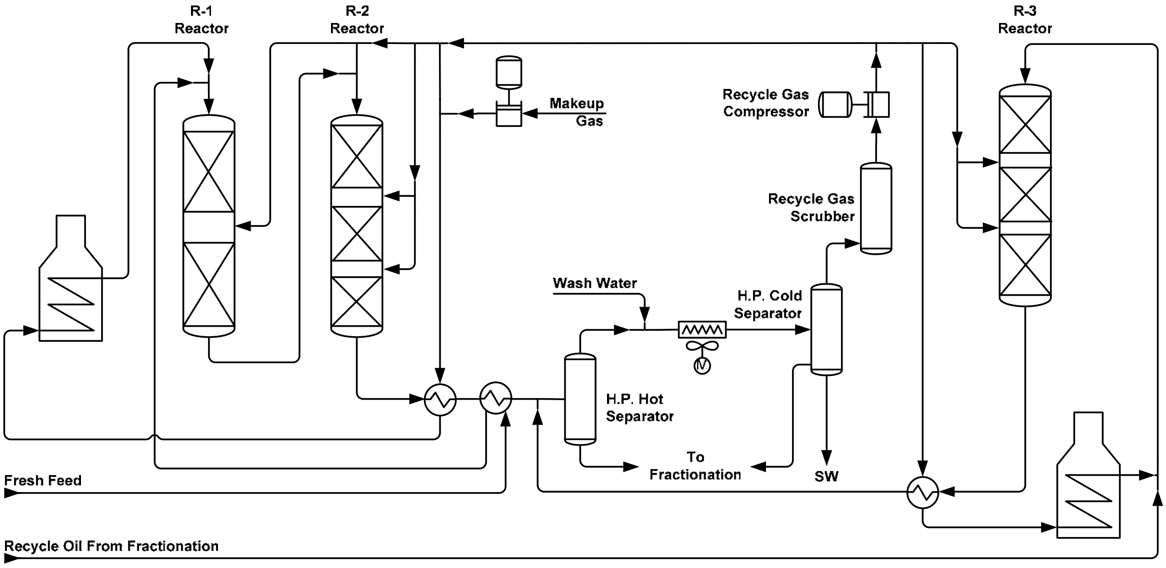

Figure 6: Typical two-stage hydrocracker – process sketch

This configuration has the same advantages as the separate hydrotreat configuration with the added advantage that by accomplishing some amount of cracking in the first stage the feed rate to the second stage is reduced.

As with the separate hydrotreat configuration, a two-stage unit can be utilized if reactor size constraints are exceeded. It is also used when feed rate is too high for a single train single stage configuration. As an example a two-stage configuration may be considered with a feed rate of 50,000 bpsd unit. The cost of a parallel train single stage configuration is comparable to a two-stage design. However the two-stage design has more processing flexibility.

By utilizing different cracking catalyst in each stage the refiner can have increased product yield flexibility. As an example some refiners utilize maximum distillate type of catalyst in the first stage while using maximum naphtha type of catalyst in the second stage. Thus when diesel demand is high the cracking in the first stage can be increased relative to the second stage and vice a versa when gasoline demands is high. This can also be done with a flexible cracking catalyst in a single stage design but the selectivity is not optimized. Another example is the low ammonia environment allows the use of low activity amorphous catalyst which improves selectivity to heavy diesel with out sacrificing product properties since reactor operating temperatures are still relatively low. Middle distillate selectivity can also be adjusted using desired quantities of H_2S and NH_3 in the second stage cracking reactor.

In addition to optimizing yields, product properties can also be optimized with the flexibility of the two-stage design. Due to the lower operating temperatures of the second stage, aromatics saturation can be higher in the second stage to produce better quality jet fuel.

The primary disadvantage of the two-stage process is the capital cost when the feed rate is low enough to utilize a singe train single stage configuration. The operating cost is also higher with a two-stage unit due to pressure let down and cooling from the first stage and repressurization and reheating into the second stage. Additional potential disadvantage with the two-stage design is that zeolite based cracking catalyst make more light ends in the low ammonia environment than in a single stage high ammonia environment.

Another disadvantage is the complexity of the system. The control of a single stage is simpler than two-stage. In a two-stage unit, the second stage needs to be adjusted for even small changes occurring in the first stage. Small variations in first stage performance can have a great impact on operation of the second stage. It can take a long time to line out this complex hydrocracking system which may result in a loss of on grade product during start ups and upset conditions.

Processing Requirements

Processing requirements will set the design of the hydrocracking process. This includes feed rate and feed quality as well as makeup gas quality and availability. Product requirement will include the desired product which can range from LPG to unconverted oil and the required yield which can set the conversion requirements.

Another key processing requirement is the product properties. For middle distillate units the focus has been on jet smoke point and diesel cetane. Increasingly the focus has also been on product sulfur and aromatics along with required improvements in product pour point and cloud point. Product aromatics are a strong function of feedstock quality and hydrogen partial pressure. Also as the run progresses the product aromatics content will increase, thus the design of the unit will be dictated by meeting product specs at end of run. The choice of catalyst is also important for product quality such as aromatics. Product aromatics tend to be higher with amorphous catalyst than zeolite catalyst. Amorphous catalysts have higher start of run temperature and can reach aromatics equilibrium limitations quicker. Thus for highly aromatic feeds, zeolitic catalyst should be selected when targeting low product aromatics specifications.

The cycle length requirement will play a large role in required catalyst volumes.

Feed Properties and the Impact on Hydrocracking

Since the hydrocracker is capable of processing a variety of feeds, the properties of the feed play an important role in determining the process requirements of a hydrocracking unit. Key feed properties and their impact on the hydrocracker design is presented.

Nitrogen

High feed nitrogen will impact the amount of hydrotreating and hydrocracking catalyst that is required. Organic nitrogen decreases conversion and causes higher rates of deactivation of the cracking catalyst. Organic nitrogen is converted to ammonia in the treating reactor which then retards the activity of the cracking reactor in a single stage or once-through design. Very high feed nitrogen content would directionally favor the separate hydrotreat or the two-stage configuration. Feed nitrogen content can also significantly impact wash water requirements and metallurgical decisions.

Sulfur

Feed sulfur will be converted to H_2S in the treating catalyst. Build-up of H_2S will reduce the hydrogen partial pressure of the unit and ultimately lower conversion. At very high feed sulfur concentrations a scrubber can be used to remove the H_2S. Feed sulfur must also be considered for metallurgical requirements.

Density, Aromatics, and Hydrogen Content

Feed density is an important consideration in determining the refractivity of the feed. Catalyst volume requirement is directly impacted by feed density. The aromatics content of the feed is an indication of the refractive nature of the feed. As with high end point feeds, higher aromatics feeds will have higher propensity to form coke as well as HPNA. Higher hydrogen partial pressures as well as larger catalyst volumes will be required for activity as well as stability compensation. Product aromatics requirement will be influenced by the feed aromatics. Higher hydrogen partial pressures and lower end of run operating temperatures are some ways to compensate for higher aromatics feeds.

Distillation

The full feed distillation needs to be considered when setting unit severity. The front end of the distillation sets the quantity of product in the feed and directly impacts the conversion requirements. The back end of the feed plays an important role in determining the conditions required to maintain stable operation. High end point feeds will tend to have higher propensity to coke. This can be combated to some extent by higher unit pressure. End point will also impact other properties such as asphaltenes, con carbon and metals. High end points will also translate to higher propensities to build HPNA. Some refiners control HPNA formation by limiting the end point of the feed. Feed hydrogen content is a function of the feed aromatics content and is used in the calculation of chemical hydrogen consumption requirements.

Metals

Metals including nickel and vanadium are permanent poisons. Typical limit is set at about 2 ppm. One method of combating feed metals is with a layer of demet catalyst upstream of the treating catalyst.

Con Carbon and Asphaltenes

Feed con carbon and asphaltenes content are indicators of the propensity of the feed to form coke. Typically the asphaltenes target is set at less than 500 ppm. Higher asphaltenes and con carbon will lead to higher catalyst deactivation rate and thus more catalyst will be required.

Process Variables

Once the processing requirements are set, the process engineer has a number of process variables that need to be established.

Process Configuration

The first choice that needs to be made is the type of hydrocracking process whether it will be the conventional single stage or one of the other choices that has already been discussed. The unit fresh feed quality and rate can play an important role in determining the process configuration selected. If the unconverted oil is to be recycled then the conversion per pass will have to be set. This can be set by capital cost limitations, and product yield structure requirements since lower conversion per pass lead to better middle distillate selectivity.

Catalyst

The catalyst that will be utilized will have to be determined. The catalyst selection process includes the requirement for grading at the top of the lead reactor to control pressure drop and demet catalyst to handle metal contaminants in the feed.

For the main bed catalyst, Topsoe typically recommends the use of both hydrotreating and hydrocracking catalyst. The selection of hydrotreating catalyst will have to be made but typically this will be our highest HDN activity catalyst. For the hydrocracking catalyst, the first decision will be to use amorphous or zeolitic catalyst. The compromise of activity and selectivity will need to be determined. The reactor size limitations or catalyst volume availability in existing reactors may determine the activity level of the catalyst.

For revamps, where pressure drop is a concern, then catalyst size and loading process (dense or sock) may also come into play as a variable.

LHSV

The space velocity (LHSV) is the ratio of feed rate to catalyst volume. This is one of the key parameters in the design of the unit. Feed impurities, conversion requirement and cycle length requirements and catalyst activity will dictate the required LHSV. Typically the LHSV is in the range of 1 to 3 for the treating and cracking catalyst in single stage and once-through units.

Hydrogen Partial Pressure

Hydrogen partial pressure is one of the key process parameters. Hydrogen partial pressure plays an important role in catalyst stability. Feed impurities such as nitrogen content and feed end point are key parameters that are used for setting this required pressure. At high hydrogen partial pressures catalyst coking tendencies are reduced, thus increasing catalyst stability. Minimum hydrogen partial pressure can also be set by the level of conversion requirement in a once-through unit. Product quality requirement that depend on high hydrogenation activity requirement for aromatics saturation such as jet smoke point can also govern the hydrogen pressure of the unit.

Hydrogen partial pressure is a combined effect of unit pressure and recycle gas purity. Recycle gas purity is impacted by makeup gas quality, the presence of a scrubber in combination with feed sulfur content, and the unit lay out with respect to the presence of a high pressure hot separator (HPHS). If a HPHS design is used with low purity makeup gas then the recycle gas purity will be substantially lower. Typical designs will utilize PSA quality makeup gas in combination with a HPHS for improved heat integration. The use of the HPHS also reduces the size of the air cooler and cold separator and is beneficial in preventing the HPNA from fouling the effluent air coolers. The HPNA level in the unconverted oil can be controlled with a bleed. The requirement of a bleed stream can set the overall conversion that can be achieved.

Higher unit pressures will however increase the ammonia partial pressure which retards the cracking activity. The iso to normal ratio of light paraffins also decreases with increasing ammonia partial pressure due to the lower catalyst activity. However, the beneficial impact of higher hydrogen partial pressure out weighs the negative impact of higher ammonia partial pressure and the net effect of higher pressure is increased conversion and improved product quality. Typical operating pressure of a hydrocracker can range from 60 to 200 bar.

Reactor Temperature

Reactor temperature is the primary means of conversion control. A 10°C increase in temperature will double the reaction rate. Reactor temperature is adjusted to compensate for the loss of catalyst activity. This can be done until peak operating temperature is reached or when product quality deterioration dictates catalyst change out. Hydrocracking reactor operating temperatures can range form 300°C to 450°C.

The required SOR to EOR temperature difference will be largely dependent on the cycle length requirements.

Recycle Gas Rate

Another key operating parameter is the recycle gas rate or the hydrogen to oil ratio. Recycle gas serves three functions. The primary function of the recycle gas is that it provides the needed hydrogen for all of the reactions that take place in the treating and cracking reactors. Recycle gas is also used to quench the exotherm in each reactor bed. The mass of the recycle gas also limits the extent of temperature rise in each bed. The hydrogen to oil ratio can range from 500 to 1700 Nm^3/m^3. The gas rate selected will be dependent on the hydrogen consumption and the expected reactor exotherm.

The layout of the fractionation system will depend on product yields. A typical fractionation system for a mid barrel unit is presented in Figure 3.

Reactor Design and Operation

One of the key pieces of equipment in the hydrocracker is the design of the reactors. Reactor design starts with the total catalyst volume requirements. The ratio of hydrotreating to hydrotreating catalyst to be used for design requires some optimization. Targeted nitrogen slip from the treating reactor to the cracking reactor can be varied until an economic solution is reached. The cost of the reactor as well as the cost of the catalyst needs to be considered. Ideally the treating and cracking catalyst will run out of activity at the targeted cycle length.

Once the treating and cracking catalyst volumes are set then reactor diameter must be determined. Mass velocity is a major consideration in setting the reactor diameter. Some flexibility is allowed and this can be used to fit the required treating catalyst in a single reactor and the required cracking catalyst in a second reactor.

The number of beds then needs to be set for the treating reactor and the cracking reactor. The number of beds is dictated by limitations on temperature rise and bed lengths.

Bed grading at the top of the treating bed is specified for pressure drop control. Using bed grading in place of scale baskets has become an industry standard. Demetallation catalyst is added down stream of the grading for feeds containing metals.

The demetallation catalyst is followed by the required number of beds of the treating catalyst and the required number of beds of the cracking catalyst in a single stage or once-through design. The operating philosophy for temperature control of each of these beds is shown graphically in Figure 7. The Average Bed Temperature (ABT) of the treating catalyst is used to control the nitrogen content of the cracking reactor feed. Ideally equal bed outlet temperatures are set for treating beds. The cracking catalyst ABT is set by the conversion requirement. Equal bed outlet temperatures are also set for the cracking beds. The peak temperature at SOR and EOR determines the available temperature for catalyst deactivation. Some times the number of beds can be increased to increase the temperature span available during the cycle. This can be an economic decision.

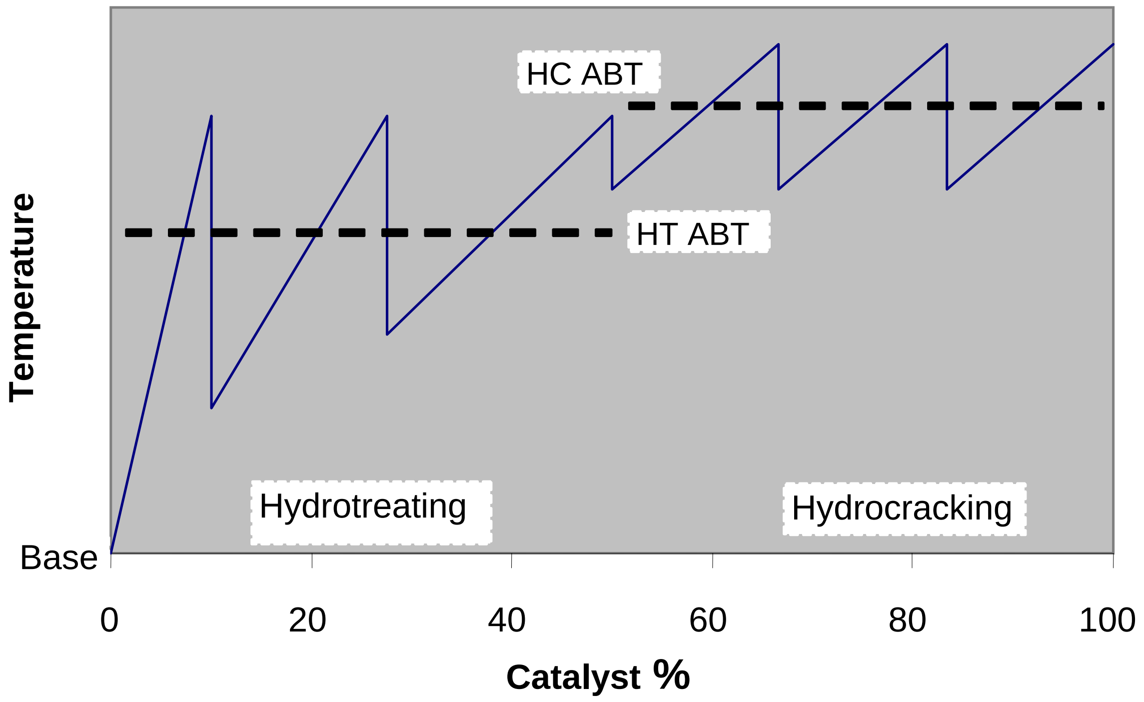

Figure 7: Typical hydrocracker reactor temperature profile

The cracking catalyst is typically followed by a small layer of post treating catalyst. The post treating catalyst serves the purpose of treating the mercaptans that are formed in the cracking catalyst at elevated temperatures. If the mercaptans are not removed then the naphtha product can fail the doctor test.

Reactor internals design is an important part of the total reactor design topic. This is covered in a separate paper.

Reactor thermometry also needs to be considered for proper monitoring of reactor performance. This is especially true in hydrocracking applications where prevention of temperature runaways is an important safety consideration. For this reason flexible thermocouples are specified for the inter bed thermometry. Some of the older designs that used bayonet designs have switched to the flexible thermocouples. Flexible thermocouples have allowed increased coverage of temperature measurement points with minimal intrusion. Reactor nozzle size requirements are minimized with the use of flexible thermocouples. As an example more than a dozen thermocouples can fit into a 3 inch nozzle on the reactor.

Conclusion

This paper has presented an overview of the hydrocracking process. The potential process flow configuration options have been presented along with a discussion of some key design parameters for selection of the various options.

Process requirements have been considered and the importance of various feed properties have been presented. The process engineer has numerous process parameters that need to be considered for an optimal design. The design of the reactor was discussed in more detail.

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