PROCESS AND CATALYST INNOVATIONS IN HYDROCRACKING TO MAXIMIZE HIGH QUALITY DISTILLATE FUEL

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INTRODUCTION

Steady worldwide economic growth continues to drive demand for transportation fuels, and in particular, diesel. Consumption of low-sulfur, high-quality diesel is projected to grow at a faster rate than both fuel oil and gasoline over the next 10 years. Growth in demand and stricter product quality requirements requires increased conversion and upgrading of heavy low-quality feeds such as vacuum gas oil, heavy coker gas oil and deasphalted oils (DAO). Hydrocracking and hydrotreating technologies and catalyst innovations, have taken on an increasingly prominent role in many refinery configurations. UOP’s outstanding commercial experience in delivering hydrocracking process and catalyst technology solutions has lead to process innovations incorporated in an enhanced two-stage UOP Unicracking™ process design, providing a significant increase (up to 5 – 7 wt%) in distillate yields while processing difficult high-nitrogen heavy feedstocks.

MARKET SITUATION

Refined Products Demand

The growth of refined products demand varies geographically (Figure 1). The growth rates are slowest in the Americas, Europe and the developed countries in Asia. However, rapid economic
development in China, India and the Middle East will help total refined products demand grow nearly 14 million barrels per day, a 1.7% average rate, over the next 10 years. This 10-year demand represents an average worldwide growth rate essentially the same as has been seen over the past 10 years. It is worth noting that worldwide demand for diesel has exceeded the gasoline demand since 2000 and that this trend is projected to continue through 2015.

**Figure 1: Worldwide Refined Products Demand**

![Bar chart showing worldwide refined products demand from 2007 to 2017.](image)

**Total Refined Products Demand**
2007: 78 million BPSD
2017: 92 million BPSD

**Environmental Regulations**

Motor fuel specifications have changed significantly over the past 10 to 15 years and are continuing to evolve. The World Wide Fuel Charter Initiative is helping to set advanced emission control requirements, and thus drive fuel qualities. Sulfur and aromatics contents are being reduced in most developed countries and the trends are spreading to other regions. The most notable changes govern the sulfur content of both gasoline and diesel fuel. Tier II regulations in the U.S. have driven gasoline sulfur down to < 30 ppm. Europe has reduced sulfur
to 50 ppm with further tightening to 10 ppm scheduled to take place later this decade. Japan already has very low sulfur levels in its gasoline while other countries are moving in the same direction, but most at a slower pace. The evolution of gasoline sulfur specifications is shown in Figure 2².

![Figure 2: Changing Gasoline Sulfur Standards](image)

Diesel fuel sulfur content is being reduced at a similar pace to gasoline with Germany mandating maximum sulfur levels of 10 ppm in 2003, the U.S. mandating 15 ppm in 2006, Japan planning to go to 10 ppm, and several other European countries voluntarily switching to 10 ppm sulfur in diesel ahead of a 2009 deadline (Figure 3³).

![Figure 3: Changing Diesel Sulfur Standards](image)
By the end of the decade, 80% of the world’s gasoline consumption will be ultra-low sulfur (< 50 ppm). Currently, ~65% of the world road diesel is refined to low and ultra-low sulfur diesel. This percentage is projected to rise to approximately 75% by 2015.

**UNICRACKING PROCESS FLOW SCHEMES**

UOP has offered hydrocracking processes since the inception of commercial hydrocracking. There are several Unicracking process flow schemes presently offered to meet individual refinery needs and project objectives. The basic flow schemes considered are single-stage or two-stage design.

Two-stage flow schemes can be employed in specific situations. UOP two-stage Unicracking process flow schemes can be a separate hydrotreat or a two-stage Unicracking process as shown in Figure 4. In the separate hydrotreat flow scheme the first stage provides only hydrotreating while in the two-stage Unicracking process the first stage provides hydrotreating and partial conversion of the feed. The second-stage of the two-stage design provides the remaining conversion of recycle oil so that overall high conversion from the unit is achieved. These flow schemes offer several advantages in processing heavier and highly contaminated feeds. Two-stage flow schemes are economical when the throughput of the unit is relatively high.
The design of hydrocracking catalyst changes depending upon the type of flow scheme employed. The hydrocracking catalyst needs to function within the reaction environment and severity created by the flow scheme that is chosen. As indicated in Figure 4, two-stage flow schemes provide a unique reaction environment for the second-stage hydrocracking catalyst. The second-stage reaction environment is cleaner and significantly boosts the cracking activity of the catalyst.

**Enhanced Two-Stage Unicracking Process**

During the early years of hydrocracking, refiners were mainly interested in maximizing production of naphtha for reforming to high octane gasoline. UOP has designed many two-stage units for the North American market for this purpose. However with advancements in hydrocracking catalyst technology, and the demand for maximizing distillate yields from heavier feedstocks, two-stage design offers a cost-effective option for a larger capacity maximum distillate unit operation. As part of continual renewal and advancement of technology, UOP has recently advanced the two-stage Unicracking process.
As shown in Figure 5, a typical two-stage hydrocracking design consists of the first stage that provides hydrotreating and hydrocracking of the feed using two types of catalysts in one or two reactors. The feed is hydrotreated and hydrocracked followed by separation of gas and liquid effluents. The hydrocracked liquid effluent is fractionated into products and unconverted oil. The unconverted oil is recycled to the second-stage hydrocracking reactor. The second-stage reactor provides hydrocracking of unconverted oil so that overall conversion from the unit can be as high as 100%.

**Figure 5: Two-Stage Unicracking Flow Scheme**

![Two-Stage Unicracking Flow Scheme Diagram]

A major difference between the first and second stage hydrocracking reactor reaction environments lies in the very low concentrations of ammonia and hydrogen sulfide in the second-stage. The first-stage reaction environment is rich in both ammonia and hydrogen sulfide generated by hydrodenitrogenation and hydrodesulfurization of the feed. This significantly impacts reaction rates, particularly cracking reaction rates, leading to different product selectivity and catalyst activity between the two-stages. The catalyst system can be optimized to obtain a highly distillate selective overall yield structure. Optimum severity can be set for each stage to
achieve catalyst life target with minimum catalyst volume. Overall, the two-stage design allows optimization of conversion severity between the two stages, maximizing overall distillate selectivity.

New advances in the two-stage Unicracking process design include several innovations in each reaction section of the design. The pretreating section uses a high activity pretreating catalyst that allows hydrotreating at a higher severity, providing good quality feed for the first-stage hydrocracking section and enabling maximum first-stage selectivity to high quality distillate. The second-stage is optimized by use of second-stage hydrocracking catalyst that is specifically designed to take advantage of the cleaner reaction environment. The second-stage catalyst is designed so that the cracking and metal functions are balanced. At the same time the second-stage hydrocracking severity is optimized so that maximum distillate selectivity is obtained from the second-stage of hydrocracking.

**CONCLUSIONS**

Growth in demand combined with stringent quality requirements for transportation fuel make hydrocracking a technology of choice. Hydrocracking of heavier and highly contaminated feedstocks require optimal technical solutions that include catalyst and flow scheme consideration. Renewal of technology like the two-stage Unicracking process has demonstrated significantly improved total distillate yields, 5 – 7 wt%, while processing difficult feedstocks and producing excellent product qualities. UOP is developing process design and materials science innovations that demonstrate our understanding of complex process reaction chemistry and the challenges facing the industry, resulting in solutions that advance the success of our customers.
REFERENCES