

CATALYSTS FOR BETTER

Technology Providers Seek Higher Yields, More Feedstock Flexibility

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All over the world, cars and trucks are requiring higher performing engine oils and transmission fluids to meet demands for better fuel economy and to ensure lower volatility and better oxidation stability. Lubricant formulators are meeting those demands in part by shifting from API Group I base oils to higher grades such as Group II and III.

Group I base oils are generally produced by solvent refining, a technology that has been around since the 1930s. The first step is solvent extraction, wherein a solvent such

as furfural or NMP (n-methyl pyrrolidone) is added to remove 50 to 80 percent of impurities, including aromatics, polar compounds and compounds that contain sulfur and nitrogen. The resulting product from the extraction is referred to as a raffinate.

Aromatics are removed because they are more likely to react with oxygen, and this can lead to side reactions that dramatically shorten the life of the base oil. Removing aromatics also improves the oil's viscosity index, or VI – a measure of the extent to which viscosity changes given a change in temperature.

For base oils with a higher viscosity index, the viscosity changes less with changing temperature. This allows lubricants to be easily circulated when the engine is initially cold and yet provide sufficient lubricity to protect the engine at its high operating temperatures.

The second step in solvent refining is solvent dewaxing, which removes waxy molecules so that the lubricant will flow at colder operating temperatures. Wax is removed by diluting the raffinate with a solvent, chilling the mixture and then filtering the precipitated wax.

The solvent lowers the viscosity of the mixture to improve the low-temperature filtration. Common solvents for this purpose include MEK (methyl-ethyl ketone)/toluene or MEK/MIBK (methyl-isobutyl ketone).

Some base oil manufacturers employing solvent refining have used a final finishing step to provide further stability so the base oil lasts longer before needing to be replaced. Clay treating has been used to soak up polar components such as polynuclear aromatic components to further improve the oxidation stability and color.

BASE OILS



The base oil plant at Sinopec's refinery in Gaoqiao, China, uses Chevron Lummus technology.

Photo courtesy of Sinopec

DAWN OF HYDROTREATING

Hydrotreating was developed in the 1950s and first used by Amoco and others in the 1960s for base oil manufacturing. Hydrotreating is a catalytic process run at pressures above 3,500 kiloPascal in the presence of hydrogen that reduces levels of aromatics and impurities such as sulfur and nitrogen. Hydrotreating can be used for both VI upgrading and for finishing.

Hydrocracking is a more severe form of hydrotreating, operating at pressures above 7,000 kPa. It reduces aromatics levels even more

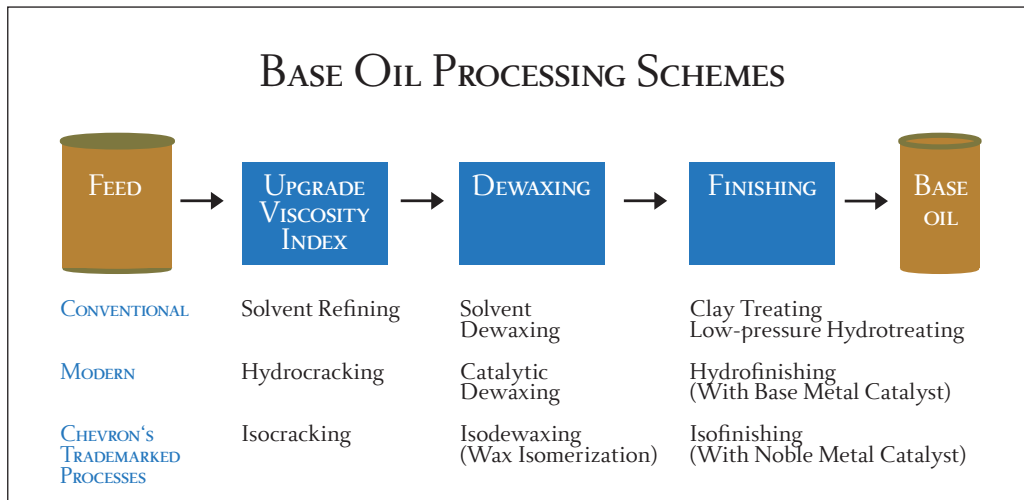
and removes almost all of the sulfur and nitrogen. The process reshapes some molecules to form isoparaffins, which contribute to high VI and low pour points. The first hydrocracker for base oil manufacture was commercialized in the 1950s by Gulf Oil, which is now part of Chevron, in Idemitsu Kosan Company's Chiba, Japan, refinery. This was followed by Sun Oil Company's Yabucoa Refinery in Puerto Rico, which started up in 1971 and which also used Gulf technology.

The first catalytic dewaxing and wax hydroisomer-

ization technologies were commercialized in the 1970s. Shell used wax hydroisomerization technology coupled with solvent dewaxing to manufacture base oils with extra-high VI in Europe. Exxon and others built similar plants in the 1990s. Plants with wax hydroisomerization plants had the disadvantage of having low yields of base oils. Mobil, later acquired by Exxon, used solvent extraction coupled with a catalytic dewaxing technology that selectively cracked wax molecules into smaller molecules outside of the base oil boiling range.

In 1984, Chevron became the first to commercialize an all-hydroprocessing scheme at its Richmond Lube Oil Plant (RLOP) in California. RLOP used Chevron's Iso cracking process followed by catalytic dewaxing and Chevron's Isofinishing process. The latter utilized noble metal catalysts to saturate polynuclear aromatics (PNAs), providing excellent stability and improved product color to base oils over an extended catalyst life.

This new all-hydroprocessing route allowed Chevron to produce premium base oils from crude oils deficient



in high VI components, such as those from Alaska's North Slope. This development allowed the production of premium base oils from a large pool of crude oils, many of which had previously not been suitable for base oil production.

CHANGING WAX FOR THE BETTER

Then in 1993, Chevron commercialized a new catalytic dewaxing technology that it called Isodewaxing. It represented a breakthrough improvement in hydroprocessing technology. Instead of removing wax molecules (as in solvent dewaxing) or cracking them to light hydrocarbons,

ranging from C₃ to C₈ (as in classic catalytic dewaxing), the Isodewaxing catalyst isomerizes the wax molecules into base oil. Chevron began to license the technology and it has since been used in Group II and III plants around the world.

Wax isomerization significantly improved base oil yields because it transforms some feedstock components that would be removed by conventional solvent processing. Improvements in catalyst technology have also increased the yield and selectivity of hydrocracking systems. These combined improvements to the all-hydroprocessing route have led to lower capital and

operating costs compared with solvent processing. The Group II or Group III base oils produced from hydroprocessing have lower levels of sulfur, nitrogen, aromatics, and polycyclic aromatics, so they are more stable and require lower additive dosages.

This combination of benefits has led to the steady increase of Group II and Group III production worldwide. In the United States, those categories now represent over 60 percent of paraffinic base oil capacity. The trend toward Group II and III production brought competition in processing technology. Exxon-Mobil developed Mobil Selective Dewaxing, which is

used in an all-hydroprocessing route in the company's Singapore refinery and which is also actively licensed.

Chevron turned over licensing of its technology to Chevron Lummus Global, a joint venture with engineering firm CB&I. Since 1994, CLG has licensed about 65 percent of the hydroisomerization base oil capacity worldwide, with approximately 8 million t/y in operation or in design and construction. In addition, CLG has been awarded catalyst reloads in base oil units that were not originally designed using CLG's technology.

TECHNOLOGY MOVES FORWARD

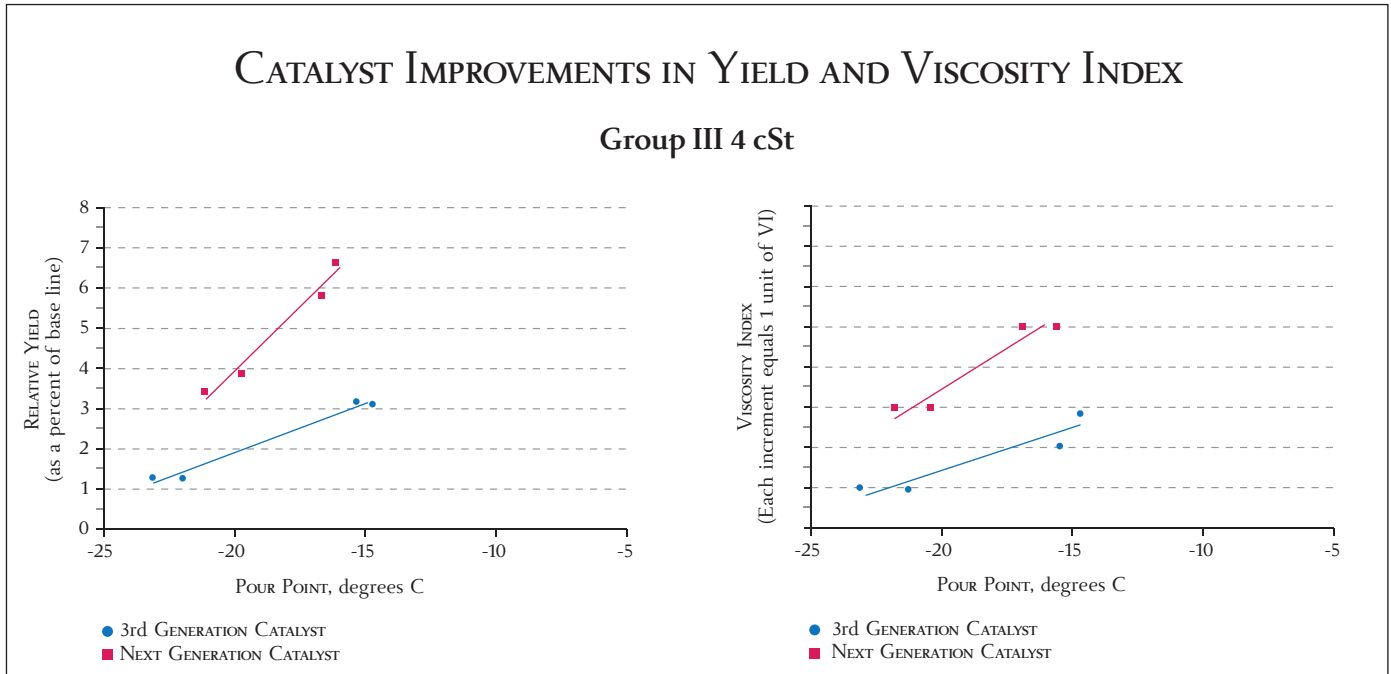
As refiners increased capacity of base oil units in recent years in order to take advantage of strong margins, they often purchased additional feedstocks to supplement their normal supplies. Refiners have less control over the quality of these supplemental feeds, which may contain higher polycyclic aromatics (PCAs) (from unconverted oils containing coker gas oils), higher levels of nitrogen, and other contaminants including seawater and corrosion products from shipment.

CLG has developed a combination of catalytic systems, designs, and operating practices to mitigate the impacts of poor quality feeds on catalyst activity and life. The robust dewaxing catalyst system includes a guard layer which maintains stable activity with relatively high nitrogen feed and decreases the rate of deactivation caused by higher PCAs.

API BASE STOCK CATEGORIES			
Group	Sulfur (percent by weight)	Saturates (percent)	Viscosity Index
I	> 0.03	and/or < 90	≥ 80 - < 120
II	≤ 0.03	and ≥ 90	≥ 80 - < 120
III	≤ 0.03	and ≥ 90	≥ 120
IV	All Polyalphaolefins (PAOs)		
V	All base stocks not included in Groups I-IV (Naphthenics and synthetics other than PAOs)		

Source: API

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Source: Chevron Lummus Global

As the market has moved toward Group II and III base oils, competing technologies using the all-hydroprocessing route have been developed, requiring CLG to continue to develop new generations of Isodewaxing catalyst. CLG is now commercializing the fourth generation of Isodewaxing catalyst technology and an improved Isofinishing catalyst. Testing of the new Isodewaxing catalyst shows significant improvements in yield and VI on light, medium, and heavy neutral feeds to make Group II and Group III products.

For example, the chart above shows the relative yield and VI improvements when using a commercial feedstock to make Group III 4 centiStoke base oil in one of CLG's licensed units. The fourth generation dewaxing catalyst increased yield by 3 percent and raised

VI by two, relative to the third generation catalyst. The new catalyst also reduced yields of lower value by-products such as light gases and naphtha.

The latest Isofinishing catalysts also provide improved color and lower aromatics, while also operating at lower temperatures. Hydrofinishing adds hydrogen to saturate aromatics, thereby stabilizing product and improving color. CLG's noble metal hydrofinishing catalysts can work at a relatively low temperature, which make them very effective for finishing hydrocrackates. These catalysts also have a low deactivation rate, meaning they last longer.

The improved product qualities, higher throughput and longer run lengths achieved by the new Isofinishing catalyst all offer opportunities for base oil producers to increase profits.

Along with catalyst developments, CLG has also developed new process flow schemes that save capital costs. New plants at a GS Caltex refinery in Yeosu, South Korea, and a Bharat Petroleum refinery in Mumbai both use integrated CLG equipment in the hydrocracker and dewaxing/hydrofinishing units. An integrated design was also employed by a joint venture between Neste and Bapco, which plans to open a plant in Bahrain next year.

TRENDS CONTINUING

The base oil market can be expected to continue to push for higher base oil quality as engine manufacturers and lubricant providers strive for longer drain intervals, lower emissions and higher fuel efficiency. At the same time, the worldwide refining market is experiencing pressures from a slowdown in the glob-

al economy, and the operating units within these refineries that are producing base oils are subject to these same market conditions.

Predicting the future is challenging, but it appears clear that, in the long term, refiners will continue using technology to increase supply of Group II and III base oil. This will be accomplished through the construction of new units, debottlenecking of existing units, and the modification of existing Group I units. Meanwhile, new catalyst systems will continue to be developed that allow for greater feed variations while providing higher yields and VI. ❖

The authors are all employees of Chevron Lummus Global, a refining technology joint venture between Chevron and CB&I. For more information see www.clg-clean.com