The production of ethylene and propylene by steam cracking is a fairly mature technology. While improvements in the configuration of the pyrolysis module and the product recovery sections continue to increase the efficiency of the process, the process chemistry and fundamental flow sheet configuration have remained relatively unchanged. With rising crude oil and steel prices and global warming concerns, olefins producers face a number of challenges to remain profitable. One is to reduce greenhouse gas emissions by reducing the fuel fired in the thermal cracking of feedstocks and by lowering the energy consumption of the product recovery section. Another challenge is to lower the significant level of investment associated with new steam cracking facilities. A third challenge is to improve the rate of return on these investments by enhancing the product slate produced from thermal cracking, thereby improving the operating margins.

To help meet these challenges, Lummus Technology began a research and development programme that focused on changing the process chemistry downstream of the pyrolysis module, and on a fundamental reconfiguration of the steam cracker flow sheet. This programme has led to 16 improvements that represent the first fundamental changes in more than 25 years. These improvements include: the Front End CDHydro® system and olefins metathesis, which are the subjects of this article; tertiary refrigeration, which supplies all refrigeration...
from 40 to -140 °C in a single refrigeration system; several innovations in the pyrolysis module that lower NOx and reduce investment; and the ability to produce any quantity of propylene from ethane feedstock using dimerisation and olefins metathesis chemistry.

**Front End CDHydro**

In the conventional steam cracker flow sheet, the selective hydrogenation of C2 and heavier acetylenes and dienes is accomplished in a series of fixed bed reactor systems. As shown in Figure 1, the CDHydro process combines the hydrogenation step with the distillation step, thereby eliminating separate fixed bed reactor systems. The hydrogenation catalyst is placed in the rectifying zone of a distillation tower. The CDHydro process offers a number of advantages when compared to conventional fixed bed reactor systems. Dimers and oligomers are fractionated from the catalyst zone, which prevents catalyst fouling and the loss of catalyst activity. Spare reactor beds can therefore be eliminated. Separate green oil removal facilities are not required. Higher selectivities are achieved since the catalyst fouling rate is minimised. Since the reaction and distillation steps are combined, the equipment associated with the fixed bed reactor systems, including the reactors, feed heaters, and effluent coolers, is eliminated. Investment is therefore lowered and operation efficiency is improved.

When applied to the ethylene plant flow sheet, the CDHydro process permits the hydrogenation of the C2 through C5 acetylenes and dienes in a single reaction zone. Fractionation of the dimers and oligomers from the catalyst bed prevents the rapid fouling that occurred historically in fixed bed, ‘raw gas’ reactors. The ability to combine the hydrogenation of a wide range of acetylenes and diolefins further reduces investment. It also changes the process chemistry by removing 35% of the pyrolysis hydrogen by chemical reaction rather than cryogenic separation, thereby saving energy and investment.

The Front End CDHydro process configuration is shown in Figure 2. The cracked gas from the third stage of the charge gas compressor, after caustic wash and drying, is sent to a depentaniser tower. The depentaniser tower has a CDHydro bed in the rectification zone where C2 acetylene, MAPD, butadiene, C5 acetylene, and C6 acetylenes and dienes are selectively hydrogenated. This combined hydrogenation step is possible with the CDHydro process because the oligomers and dimers that are formed are fractionated from the catalyst zone and exit with the C6 and heavier material in the tower bottoms. The depentaniser overhead flows to a single fixed bed acetylene hydrogenation reactor to guard against acetylene breakthrough and ensure that the tight acetylene specification required in the ethylene product is achieved. Due to the much lower hydrogen content of the cracked gas, the reactor effluent can then flow either to the next stages of compression or directly to a lower pressure chilling train.

The CDHydro process effectively accomplishes raw gas hydrogenation of the acetylenes and dienes without the severe catalyst fouling and loss of selectivity to olefins that has caused earlier attempts at raw cracked gas hydrogenation to fail. With the Front End CDHydro process, the selectivity to hydrogenate the acetylenes and dienes is significantly improved over conventional hydrogenation. It achieves 80% conversion of acetylene to ethylene and 95% conversion of the methyl acetylene and propadiene to propylene.

The Front End CDHydro process also reduces investment cost while lowering maintenance costs and improving plant reliability. 40 pieces of equipment, or approximately 12% of the ISBL equipment piece count, are eliminated from the conventional flow sheet by combining the various hydrogenation reactors into a single system. Spare reactors are also eliminated. Total investment cost savings are approximately 7% of the ISBL investment. The process chemistry downstream of the cracking heaters is also changed, as less pyrolysis hydrogen needs to be removed by cryogenic separation. In addition, it permits many of the back end towers to operate at higher pressure since the dienes and acetylenes are no longer present to foul the tower bottoms. These changes in the process chemistry combine to reduce ethylene plant compression power by 10%, lowering greenhouse gas emissions and reducing operating costs.

The process chemistry downstream of the cracking heater may be further changed by using the butenes that are produced in the Front End CDHydro system or that are produced in conventional fixed bed selective hydrogenation reactors as feed to a metathesis unit, integrated with the ethylene plant.
Metathesis and isomerisation chemistry applied to the ethylene flow sheet

Metathesis is the reaction between two olefins where the double bond of each is broken and new olefin products are formed. Isomerisation is the shifting of the double bond within the olefin molecule to produce a more favourable metathesis reaction or a more valued product.

By using the butenes that are produced by the Front End CDHydro system as feed to metathesis and isomerisation reactors, a number of more valuable byproducts, including propylene, butene-1 and hexene-1, can be produced. Lummus Technology offers two isomerisation and metathesis processes: Olefins Conversion Technology (OCT) for the production of propylene and Comonomer Production Technology (CPT) for the production of butene-1 and hexene-1.

By using OCT for the production of propylene, the following two reactions are key:

\[
\text{Butene-1} \rightarrow \text{Butene-2} \\
\text{Butene-2 + ethylene} \rightarrow \text{Propylene + pentene-2}
\]

This reaction consumes 720 kg of butene-2 and 300 kg of ethylene to form 1000 kg of propylene and 20 kg of C5 and heavier olefins. The value added to the byproduct slate results from upgrading the C5 olefins, which are typically valued higher than feedstock but well below propylene, to propylene value.

The reaction of butene-2 and ethylene to form propylene can be applied to the ethylene plant material balance in two ways. The first application is to optimise the design of a conventional, mid to low severity steam cracker with a propylene-to-ethylene product ratio of 0.5 - 0.7. The second is to maximise the propylene production from the steam cracker. In this case, the maximum propylene-to-ethylene product ratio can be increased from 0.7 to as high as 1.1.

Table 1 summarises the impact of applying metathesis chemistry to the ethylene plant material balance to achieve a conventional, low severity, propylene-to-ethylene ratio of 0.67.

Two cases are presented in Table 1: a steam cracker only, without metathesis, and a steam cracker integrated with an OCT unit. As shown in the table, at a constant net ethylene and propylene production of 1 million tpy and 670 000 tpy respectively, the steam cracker integrated with the OCT unit considerably improves the overall plant material balance. Compared to the standalone steam cracker, the integrated case consumes 2% less fresh feedstock while producing 50% more benzene and only 60% of the remaining, lower valued pyrolysis gasoline.

In addition, the energy consumption of the integrated steam cracker/OCT unit is 13% lower. The reason for this reduction is that less olefins are produced by thermal cracking in the integrated case, thereby lowering the fired duty of the cracking heaters and the energy consumed in the recovery section. That is, in the steam cracker only case, 1.67 million tpy of ethylene and propylene are produced by thermal cracking. In the integrated case, 1.495 million tpy of ethylene and propylene are produced by thermal cracking, with the remaining propylene being produced by the energy neutral metathesis reaction. The 13% reduction in energy consumption results in a 13% reduction in greenhouse gas emissions. This level of reduction is significant and, as such, could be one of the major contributing routes to meeting olefin industry goals of lower greenhouse gas emissions from steam crackers. The lower energy consumption also improves the operating margin. Combined with the economic benefits of the improved material balance, the lower energy costs improve the operating margin of the integrated steam cracker/OCT unit by 8% when current feed, byproduct, and energy costs are applied.

Investment costs are also lower. As shown in Table 1, capital costs are reduced by 6% in total ISBL and OSBL costs. The investment costs associated with the ISBL ethylene plant are reduced due to lower plant throughput, lower fired duty, and a significant reduction in the size of the propylene fractionator system, which is the single most costly tower system in the ethylene plant. The reduction in load of each plant system is shown in Figure 3.

The investment cost of the pyrolysis gasoline hydrotreater is reduced due to less throughput and lower diolefin/olefin content. The investment cost of the aromatics extraction unit is also lowered, since the...
aromatic content of the pyrolysis gasoline is higher. Finally, OSBL costs are reduced due to the 13% reduction in energy consumption. The savings associated with these units more than offset the investment costs associated with the OCT unit, resulting in a 6% reduction in overall investment.

Isomerisation and metathesis of the butenes can also be utilised to maximise propylene production. Operation of the steam cracker at a propylene-to-ethylene ratio of 0.67 will produce sufficient butenes to increase the propylene-to-ethylene ratio to 1.12. That is, a 1 million tpy ethylene plant can produce up to 1.12 million tpy of polymer grade propylene. Of this, 745 000 tpy of propylene is produced by thermal cracking and the remaining 375 000 tpy is produced by energy neutral metathesis.

Metathesis and isomerisation chemistry can also be applied to upgrade the steam cracker C₄'s to the comonomers butene-1 and hexene-1. Utilising Lummus Technology’s CPT, the reactions of interest to produce these comonomers are:

\[
\begin{align*}
\text{Butene-2} & \rightarrow \text{Butene-1} \\
\text{Butene-1 + butene-1} & \rightarrow \text{Hexene-3 + ethylene} \\
\text{Hexene-3} & \rightarrow \text{Hexene-1}
\end{align*}
\]

Starting with steam cracker C₄s that have been selectively hydrogenated using either conventional fixed bed reactors or the Front End CDHydro process, the isobutene is removed and the butene-2 is isomerised to butene-1. The butene-1 is then recovered via fractionation and can be used to meet the butene-1 demands of the complex and/or as feed to an energy neutral metathesis reactor, where the butene-1 reacts with itself to produce 750 kg of hexene-3 and 250 kg of ethylene for each 1000 kg of butene-1 reacted. Hexene-3 is then sent to an isomerisation reactor, where it is isomerised to hexene-1 and hexene-2, and then to a fractionator, where comonomer-grade hexene-1 is produced. Unconverted hexene-2 and hexene-3 are recycled from the tower bottoms back to the isomerisation reactor where 80 - 85% is ultimately converted to hexene-1.

The main advantage offered by CPT is the ability to produce both the butene-1 and hexene-1 comonomer from a single processing unit, leading to lower investment, higher reliability, and lower maintenance costs. In addition, these high value comonomers are produced from the steam cracker C₄s rather than by polymer grade ethylene, resulting in lower energy consumption, lower greenhouse gas emissions, and improved return on investment.

**Conclusion**

The ability to change the process chemistry downstream of the cracking heaters provides the benefits of producing more valuable byproducts with lower energy consumption and lower investment. These advantages should help meet the changing needs of the olefins industry in the coming decade.

**Notes**

1. CDHydro is a registered trademark of CDTECH, a partnership between Lummus Technology, a CB&I company, and Chemical Research & Licensing Co., a CRI company.