A CATALYTIC CRACKING PROCESS FOR ETHYLENE AND PROPYLENE FROM PARAFFIN STREAMS
THE ADVANCED CATALYTIC OLEFINS (ACO) PROCESS

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Publication / Presented:
Prepared for Presentation at the 2007 Spring National Meeting - Houston, Texas
KBR Internal Reference Paper 2015

Date:
April 23 - 26, 2007

Notes:
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Abstract: SK Corporation and KBR have developed a new and innovative catalytic cracking technology called the Advanced Catalytic Olefins (ACO) process to produce ethylene and propylene from predominantly paraffinic streams, such as straight run naphtha. This technology holds promise for replacing the conventional hot ends area of liquid crackers. Moreover, ACO can produce a propylene/ethylene ratio of about 1/1, thereby filling the regional propylene gap with a commonly available feedstock. In this paper, we present the principles for this new technology, supplemented by data from trials and leveraged by commercial experience.
A Catalytic Cracking Process for Ethylene and Propylene from Paraffin Streams
The Advanced Catalytic Olefins (ACO) Process

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Steam cracking is mainstay and backbone of the petrochemicals industry for the last 85 years. Driven mainly by the polymers and fibers industries, the manufacture of ethylene and propylene has produced many significant but evolutionary changes in the thermal cracking of paraffinic feeds. One of the first patents for the commercial production of ethylene is credited to Union Carbide in 1922 (1). Just three years later, the first commercial plant for ethylene product was built in West Virginia in the United States.

Since then, the olefins industry has gradually evolved. Starting with “worldscale” ethylene plants in the early 1950’s with capacities of around 20,000 to 50,000 MTY, plants have become bigger, more energy efficient, and more environmentally friendly. The nameplate capacity for today’s worldscale crackers can well be over 1,000,000 MTY of ethylene. KBR’s Saudi Kayan ethylene plant is now being designed for 1,350,000 MTY.

Steam crackers using feeds other than ethane generally also produce propylene as a byproduct (among other byproducts). Indeed, as the ethylene market grew, so did the propylene market. In recent years, the growth in propylene exceeded the growth in ethylene, opening up other technology opportunities focused primarily on propylene. These “propylene-on-purpose” technologies have and will fill a niche need in the propylene market. However, most of these technologies depend on the availability of certain niche feeds, which may not be generally be the case. As such, there is a need for a new technology that can address any propylene gap or shortage in the future, but with more commonly available feeds.

This paper discusses the olefins market and trends, with an emphasis on propylene. It also covers briefly available technologies for “propylene-on-purpose”, but also addresses a new technology developed jointly by KBR and SK Corporation called the Advanced Catalytic Olefins (ACO™) process. Unlike steam crackers which predominately make ethylene or “propylene-on-purpose” technologies which make propylene, the ACO process produces about equal amounts of ethylene and propylene.

Trends in Steam Cracking and the Olefins Market

Olefins Growth and Other Trends

In the past few years there has been a resurgence in ethylene plant activity, dominated by activity in mainly the Middle East and Asia. Figure 1 (2) shows that ethylene is driven by the polyethylene market and ultimately by the consumer end products such as plastics and fibers. The aggregate annual growth rate (AAGR) for ethylene demand was 3.5% from 2000-05 and projected to be 4.3% from 2005-2010. During these periods, however, propylene
demand was much higher, with an AAGR of 4.7% and 4.8%, respectively, in those same periods. Overall, propylene growth rate is roughly 1% higher than ethylene growth rate.

- Ethylene driven by polymers and fibers markets.
- Overall global growth rate ~4%.
(Source: CMAI)

**Figure 1 – Ethylene Demand Growth**

- Propylene also driven by polymers and fibers markets.
- Overall global propylene growth rate is ~5%, higher than ethylene.
(Source: CMAI)

**Figure 2 – Propylene Demand Growth**

This higher propylene growth of course, poses a dilemma, as most of today’s propylene is a byproduct form steam cracking. As both the historic and predicted ethylene growth rates lag propylene growth rates, steam cracking alone will not keep up with propylene demand. The bottom line is there is healthy growth in both ethylene and propylene until at least 2010 but propylene is especially attractive.

**Steam Cracking Feed Issues**

The Middle East remains an advantaged location for ethylene production because of its abundance of cheap natural resources, both gas and crude oil. Because of the relatively low price for ethane, Saudi Arabia (and other nearby countries) have dominated the recent ethane cracking market. As supplies for ethane are being consumed, Middle East crackers have
included additional light gas feeds such as propane and butane in the feed slate. However, even the propane and butane can be obtained at discounted prices making these also attractive as steam cracker feedstocks. With this, the Middle East is projected to increase its share of global ethylene production from its current 10% to about 18% within a span of 5 years.

Unfortunately, ethane cracking does not typically give enough propylene to be recovered. The amount of propylene recovered from propane, butane or even naphtha is less than half that of the ethylene yields as shown below in Figure 3.

Not only will new ethylene plants be unable to keep up with propylene demand growth rate, the amount of propylene is less than what is needed by the marketplace. As noted the Propylene/Ethylene (P/E) averages only about ~0.5 with these common feeds. Hence, with the shift of ethylene production capacity to the Middle East with its light feed slates, steam crackers will not be able to keep up with propylene demand (given that propylene growth rate is higher than ethylene growth rate). It is expected that the world wide P/E demand will approach over 0.6 by 2010.

**Regional Issues**

Overall, there are two regions of importance with regards to ethylene and propylene, namely the Middle East and Asia (primarily China and Southeast Asia). This is because Middle East is the source of cost advantaged (cheap and/or discounted) feeds that make this region a dominant player in the construction of ethylene plants. Asia complements the Middle East, as Asia is one of the fastest growing regions with a very high demand for consumer products made from ethylene and propylene.

The market message is clear with regards to olefins production: Go to where there is abundant and cheap feed (Middle East) and go to where olefins-based products are in high demand (Asia). As a result, ethylene market share will increase in the Middle East and Asia, Figure 4 (2).
Ethylene
- The region of greatest growth is the Middle East due to its advantaged feeds.
- The second region showing growth is Asia Pacific, with its high consumption of olefins-based products.
(Source: CMAI)

Figure 4 Regional Ethylene Supply

Although both the Middle East and Asia will gain in ethylene market share, there will still be a gap in propylene supply especially in Asia. As Figure 5 (3) shows, the required P/E ratio in Asia is about 0.9.

Propylene
- Propylene demand is greatest in Asia Pacific.
- Middle East will not meet the global propylene demand.
- Opportunities exist for “Propylene-On-Purpose” (POP) technologies in Asia Pacific.
(Source: Nexant)

Figure 5 Regional Incremental Olefins Demand

These market trends are best summed up as follows.
- Propylene demand growth is higher than ethylene.
- As a result, steam crackers will not keep up with propylene demand.
- This is exacerbated by the shift to lighter feeds, which do not make appreciable propylene.
- Overall, there is a need for alternative propylene technologies, especially in Asia.

Propylene-On-Purpose Technologies

Feed Sources for Propylene
Currently, steam cracking and refinery operations constitute over 95% of the propylene produced today. Clearly, alternative routes to propylene will gain prominence as producers seek to leverage their existing assets and available internal steams to find an optimum solution.
for meeting the demand for propylene. A recent paper (4) gives an overview of the various routes to propylene, as a function of feed source and as summarized below.

- **Methane** - There are no economic direct routes of converting methane to propylene despite the enormous amount of monies expended on this topic. Interest in the direct conversion of methane to olefins remains high, in fact Dow Chemical recently announced research funding for such routes to promising processes (5). Currently, however a couple of indirect routes exist. Both processes use an intermediary feed, methanol or dimethyl ether (DME), and converts such feeds to propylene. The methanol/DME routes to propylene are not yet commercially proven, although designs have been announced. The key to such Methanol To Olefins (MTO) processes is the value for the natural gas feed (methane), which needs gas priced at much less than world fuel prices. This alone makes MTO a niche opportunity in most cases.

- **Ethylene as a Feed** - Metathesis is the reaction of ethylene with butene-2 reacts to yield propylene. The world’s first commercial metathesis unit was started up in the 1980’s in Channelview, Texas and more recently installed at a site in Port Arthur, Texas and elsewhere. Although this process has been commercial for a long time, it was also considered a niche technology, as the economics dictate that ethylene should sell at less than the price of propylene for metathesis to be attractive. However, there are cases when ethylene is in excess supply (because of the market or idle units) and metathesis could make economic sense. For new plants employing metathesis, the ethylene plant must have a higher nameplate capacity to supply the needed ethylene for the propylene reactions, driving up some parts of the plant costs.

- **Propane** - The economics of dehydrogenation of propane to propylene depends heavily on the price of propane. Most of today’s activity in dehydrogenation is centered in the Middle East with its attractive propane pricing structure. For the most part, long term availability of low price propane precludes this technology as an option in Asia.

- **C2-C10 Paraffin Feed, Steam Cracking** - By far, conventional steam cracking provides most of today's propylene. It must be recognized that propylene is still a byproduct with higher growth rates than ethylene, as discussed earlier.

- **C4-C8 Olefinic Feeds** - Newer catalytic routes using ZSM5 type catalysts have shown promise recently, by converting C4-C8 olefinic feeds into as much as 40% propylene. An example of this technology is SUPERFLEX™ technology (6).

- **Gas Oil and Resid Feeds** - Second to only steam cracking, the refinery FCC unit is the next largest producer of propylene in the world. Historically, most FCC units were designed to produce either gasoline of distillates. Significant improvements in FCC design, hardware, and operating severity in FCC units can boost the propylene yield, but currently technology limits the overall yield to about 25%.
For the most part, the “propylene-on-purpose” technologies with substantial propylene yields are MTO (discounting the water in the effluent product slate), metathesis, propane dehydrogenation, and olefins cracking. These technologies in essence require a niche feedstock whether it be methanol, propane, or olefinic feeds that may be difficult to procure regionally or expensive. This points to a need for a new technology that can use widely available feedstock, such as straight run naphtha. And that is the impetus for the development of the ACO process, not only for large amounts of propylene but also for equal amounts of ethylene, both very important commodity products in the future.

The Advanced Catalytic Olefins (ACO) Process

Why Naphtha Feed

Naphtha is the predominate feed for steam crackers, Figure 6 (7), hence any producer looking at a naphtha cracker (mainly in Asia and China) should also be interested in ACO. ACO holds the promise of substantial propylene increase, but still with significant ethylene produced, using the most common feedstock available, straight run naphtha. To put it another way, ACO is not a niche “propylene-on-purpose” technology dependent on the right type of feed. ACO uses readily available straight run naphtha and as such can supply large amounts of propylene (and ethylene) whenever this feed is available.

ACO Catalyst

A very important key to ACO is the formulation of catalyst that is selective for light olefins (ethylene and propylene) but optimized for paraffinic feeds. A team of scientists at SK Corporation and KRICT (Korea Research Institute of Chemical Technology) have been developing such a catalyst which show roughly the same ethylene yields as steam cracking but with twice the propylene, all at substantially lower temperatures compared to pyrolysis furnaces.

Similar to typical FCC catalysts, ACO catalyst is microsphere-containing zeolite and can be manufactured with conventional spray drying facility. To ensure higher olefin yields, ACO process is operated under temperature between 600°C and 700°C with addition of steam in the riser, which requires good hydrothermal stability of the catalyst. By controlling the composition of key components, ACO catalyst achieves good hydrothermal stability as well as low attrition.
Although formulated for paraffinic feeds, the ACO catalyst also shows good performance for olefinic feeds as is required in the SUPERFLEX process. As such, it is quite feasible to recycle crack all the C4-C6 Non-Aromatics components back to the reactor for extinction conversion to more valuable products in the ACO process.

**The ACO Reactor**

The ACO process uses a KBR proprietary fluid bed catalytic cracker called the Orthoflow™ configuration, Figure 7, which is a single vessel with a stacked reactor disengager on top of the regenerator. This design builds upon over 65 years of refinery FCC experience in process design and hardware innovations but now applied to the production of petrochemicals.

Some of the unique features of the ACO reactor system include the dual riser, closed cyclones, third stage separator, patented catalyst well for continuous fuel firing (7), and patented catalyst removal system (8). Some of these features are described briefly below.

- **Dual Risers** - The use dual risers in FCC units was quite common during the early stages of FCC development. The first KBR FCC unit in 1942 had dual risers, and KBR has built 14 additional dual riser units since 1950. The primary reason for dual risers at that time was one of scale-up, that is, design commercial risers that had similar flow characteristics as tested in the pilot plant. There are several advantageous process reasons for using the a dual riser in ACO application.

- **Closed Cyclones** - Closed cyclones minimize the residence time of hydrocarbon vapor and catalyst in the disengager, thereby eliminating post-riser thermal and catalytic cracking. Less valuable products are destroyed, leading to more valuable products, as shown in Figure 8.

- **Third Stage Separator** - In regions where there is a stringent particulates emissions requirement, the KBR proprietary third stage separator has proven to be quite effective (Figure 9).

- **Heat Balance** - Like the SUPERFLEX process, the ACO process is endothermic. As such, to maintain heat balance, fuel must be imported into the reaction system. KBR’s patented catalyst well design with continuous fuel firing has now been commercially proven.
• **Catalyst/Hydrocarbon Separation** - Although the cyclones are quite efficient, invariably some catalyst fines will carry over with the reactor effluent. KBR’s patented catalyst fines removal system has now been commercially demonstrated and applicable to ACO technology also.

Needless to say, the reactor hardware design is as important as the catalyst performance in the overall process, with continuing process improvements as the technology develops. One significant advantage of the Orthoflow converter is economy of size with regards to olefins capacity. As a comparison, the maximum commercially demonstrated capacity for a single cell liquids pyrolysis furnace in steam cracking is about 200,000 ethylene. With an 0.5/1 P/E ratio, these is equivalent to about 300,000 MTY olefins. By contrast, the world’s largest Orthoflow converter (if similarly sized to the world’s largest commercial FCC unit today) can make about 4-5 times more olefins, or up to 1,500,000 kta ethylene + propylene all in a single converter train.

**The ACO Flow Scheme**

The ACO process produces both polymer grade ethylene and propylene. Much of the process flow scheme is in line with typical olefins plant recovery, however, there are some unique features. For example, the amount of acetylene can be almost two orders of magnitude lower than a typical cracker. Further, there are trace impurities such as nitrogen oxides, oxygen, and other trace impurities that must be removed. These and other issues are addressed in the ACO process flow scheme, which features front end depropanizer, Figure 10.
**ACO Commercialization**

SK Corporation is a Korean-based conglomerate with 2006 sales over US$24 billion. SK owns and operates two naphtha crackers in Ulsan with a total ethylene capacity of about 800,000 MTY. Studies and plans are currently underway to integrate the ACO converter system at the SK Number 1 Ethylene Unit in Ulsan, which cracks naphtha feedstock. Most or all of the pyrolysis furnaces will be replaced with a single ACO converter, utilizing much of the downstream ethylene plant recovery unit, revamped as appropriate for the new flow rates and compositions. At least one pyrolysis furnace will be retained to crack the ethane/propane made by the ACO converter. With the implementation of the new reactor and revamp of the existing recovery end by 2010, SK Corporation will be the first commercial adopter of the ACO process.

**The ACO Process – An Example**

The combination of a robust and selective catalyst, coupled with the optimized design from the Orthoflow converter give quite a flexible ACO process. In general, with increasing temperatures, the P/E from the ACO process varies from about 1.1/1 to about 0.7/1. Per pass yields are higher than for steam cracking, with lower tail gas make. Further, the C4-C6 non-aromatic portion can be recycled directly to the reactor without hydrogenation or additional treating. SK and KBR have tested both light straight run (LSR) and full range naphthas, with plans to extend the feed slate.

As an example, LSR can be cracked in pyrolysis furnaces to give ethylene and propylene, along with the tail gas, pyrolysis gasoline, and fuel oil. By comparison, the use of the same LSR feed in the ACO process will yield slightly less ethylene, but about two times more propylene. And with the recycle of the C4-C6 Non-Aromatic hydrocarbons back to the reactor, the only other byproducts from the ACO process are tail gas and gasoline. There is no appreciable fuel oil made with the ACO process. Figure 11 gives a comparative analysis of the overall product yield structure from a steam cracker an the ACO process for LSR naphtha.

![Figure 11 Steam Cracker and ACO Yields](image)

- Typical ultimate LSR steam cracker light olefins yields are ~50%.
- ACO ultimate yields are much higher at ~60-65%
- Overall, ACO will give more ethylene and propylene
The ACO process makes about 15-25% more ethylene plus propylene on a relative basis, depending on the operating conditions. In the example above, the total ethylene plus propylene product yield is about 17% higher than a steam cracker. Further, the ACO process has a higher concentration of BTX in the gasoline fraction, resulting in about 20-25% higher absolute aromatics yield from the ACO process.

One means of comparing the ACO process to a steam cracker is to look at the Cost of Production (COP) of ethylene. In this type of analysis, the feed and operating costs are offset by the byproduct costs. Other costs include indirect and overhead costs and depreciation (10%) and profit is added (10%) to arrive at an overall COP. Based upon a constant feed to either a steam cracker or an ACO unit, the ACO process is favored by lower COP of about $25-30/MT of ethylene. Further improvements current underway could reduce the ACO COP even further.

Summary

Steam cracking of naphtha and distillates is constrained in the amount of propylene and total olefins that can be made. For typical naphthas, the overall olefins yields from a steam cracker are about 50% with a P/E of 0.5. By contrast, the ACO process can yield roughly 65% olefins with P/E ratios up to 1/1. With the growing need for propylene and the abundance of naphtha worldwide as a petrochemical feedstock, the ACO process can be a viable alternative technology for propylene production. Rapid commercialization of the ACO process is on track with a planned implementation of the ACO converter at the Number 1 Ethylene Unit of SK Corporation in Ulsan, South Korea by 2010.
References

2. CMAI, 2006 World Light Olefins Analysis