

# **KBR's New PURIFIER*plus*<sup>TM</sup> Process**

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# KBR's New PURIFIERplus™ Process

## **ABSTRACT**

*When the Purifier Process was invented forty years ago, the inventor envisioned a flow sheet that used a reforming exchanger instead of a primary reformer. However, at that time there was no proven design for such an exchanger and so the Purifier Process has to date used a primary reformer. In 2003 two plants started up in China that promise to fulfill the original vision of the inventor. In September 2003 the sixteenth Purifier Plant, but the first KBR Purifier Plant, a 1500 t/day unit for CNOOC on Hainan Island, started operation. In December 2003 an 1100 t/day ammonia plant owned by Shenzhen Liaohe Tongda at Panjin was started up after it had been revamped with KBR's Reforming Exchanger System (KRES™). KBR has now combined these two technologies into one flow sheet called PURIFIERplus™. This paper describes the features, experience, and benefits of this new flow sheet.*

## BACKGROUND

As has been discussed in previous papers,<sup>(1), (2)</sup> Kellogg Brown & Root LLC (KBR) has a portfolio of ammonia technology options to meet clients' needs. One of these options, the combination of a reforming exchanger coupled with KBR's Purifier Process, is our PURIFIER<sup>plus</sup><sup>TM</sup> Process. This flow sheet eliminates the expensive primary reformer and is now available for licensing from KBR in single-train capacities up to 2500 metric tons/day.

The idea of using the heat available from the effluent of a secondary reformer to supply the primary reforming radiant heat duty has been around for a long time. One of the earliest disclosures of the concept of reforming exchangers was made in two US patents published in 1969<sup>(3)</sup> and 1970<sup>(4)</sup>. Others followed suit with paper designs but nothing significant was built during the 1970s. In the 1980s, the Russian company GIAP pioneered their Tandem reformer at a synthesis gas plant in Grodno, Byelorussia. One of the predecessor companies of KBR, C F Braun & Co, entered into a licensing agreement with GIAP to offer the Tandem Reforming exchanger in conjunction with its Purifier Process.<sup>(5)</sup> However, no plants using this scheme were built.

The late 1970s and 1980s were an era of rising natural gas prices. Licensors of ammonia and synthesis gas technologies looked for ways to lower energy consumption. Many of the techniques used to lower energy use made the plants more efficient through better heat recovery. This had the effect of increasing the amount of steam export from the plants, a trend that is beneficial only if there is a use for the extra steam. Recognizing the need to counter this trend towards increasing steam export, technology licensors began actively developing reforming exchangers. These developments led to a number of demonstration and commercial units coming on line in the late 1980s and early 1990s.

It was in this timeframe that KBR developed and patented<sup>(6,7)</sup> the KBR Reforming Exchanger System (KRES<sup>TM</sup>). KRES went into commercial operation in an ammonia plant in Canada in October 1994, currently owned by Methanex. The ammonia plant produced about 850 metric tons/day of ammonia with the KRES unit making synthesis gas that is converted into 350 metric tons/day of ammonia. The balance of the synthesis gas came from methanol plant tail gas. Photo 1 shows a picture of this KRES installation. The KRES plant was shut down in late 2005 when the methanol plant went out of business.



PHOTO 1: KRES™ AT PLANT IN CANADA, WITH AUTOTHERMAL REFORMER ON THE LEFT AND REFORMING EXCHANGER ON THE RIGHT.

In 2001 KBR was awarded a project to supply technology for a revamp of Liaohe's ammonia plant in China. Part of this project included the supply of KRES technology. The existing primary reformer was demolished. Capacity is 1070 metric tons/day and the unit started up in late 2003. Photo 2 shows a picture of this installation.



PHOTO 2: KRES™ AT LIAOHE IN CHINA

The scale-up of KRES from Methanex to Liaohe by a factor of three represents a significant step forward in this technology.

Another significant milestone in the development of our PURIFIER<sub>plus</sub>™ Process flow sheet occurred in 2003, and coincidentally also in China: the first KBR Purifier Plant came on line. While it is the first Purifier Plant for KBR, it is the seventeenth Purifier Plant in total, with the prior sixteen plants being built prior to the merger of Kellogg with Brown & Root Braun. This first KBR Purifier Plant incorporates a number of new features compared to previous Purifier Plant designs which resulted in a plant with a measured energy consumption of less than 6.5 Gcal/mt. <sup>(8)</sup> This is lower than any of the earlier Purifier designs and believed to be the lowest energy consumption plant in the world.

With the successful commercialization of both of KBR's new KRES and Purifier designs, the next logical step is to combine them on a single flow sheet as originally envisioned forty years ago. We have done this, and we call the new scheme our PURIFIER<sub>plus</sub>™ Process. This paper presents the overall PURIFIER<sub>plus</sub>™ Process scheme, discusses the features and benefits of the new flow sheet to owner/operators, and describes our recent experience with the technology.

# PURIFIER<sup>PLUS</sup><sup>TM</sup> PROCESS

## Overall Scheme

The KBR PURIFIER<sup>plus</sup><sup>TM</sup> Process is illustrated in Figure 1. Desulfurized natural gas feed is split into two streams and process steam is added to each of them prior to preheating in the Process Heater. The preheated mixed feed streams flow in parallel to both the Reforming Exchanger and adiabatic Auto-thermal Reformer (ATR). About 60 to 70 percent of the feed is routed to the ATR with the remaining feed going to the Reforming Exchanger.

Process air for the ATR is compressed and preheated in the Process Heater prior to its entry in the ATR. The PURIFIER<sup>plus</sup><sup>TM</sup> Process uses about 50 percent more air than the stoichiometric requirement. In the ATR, some of the hydrocarbon is combusted, releasing the heat necessary for the endothermic reforming of the remaining hydrocarbons with steam over the nickel reforming catalyst.

The effluent from the ATR flows to the shell side of the Reforming Exchanger. The exchanger is a proprietary open-tube exchanger design. The feed plus steam enters the tube side. As the mixture flows down through the tubes, it contacts conventional steam reforming catalyst. The heat required for the endothermic reforming reaction is provided by the shell side gas, which is a mixture of the ATR effluent and tube side effluent. The mixed synthesis gas leaves the reforming exchanger shell side containing about 2.5% (dry basis) methane and is cooled by generating high pressure steam prior to shift conversion.

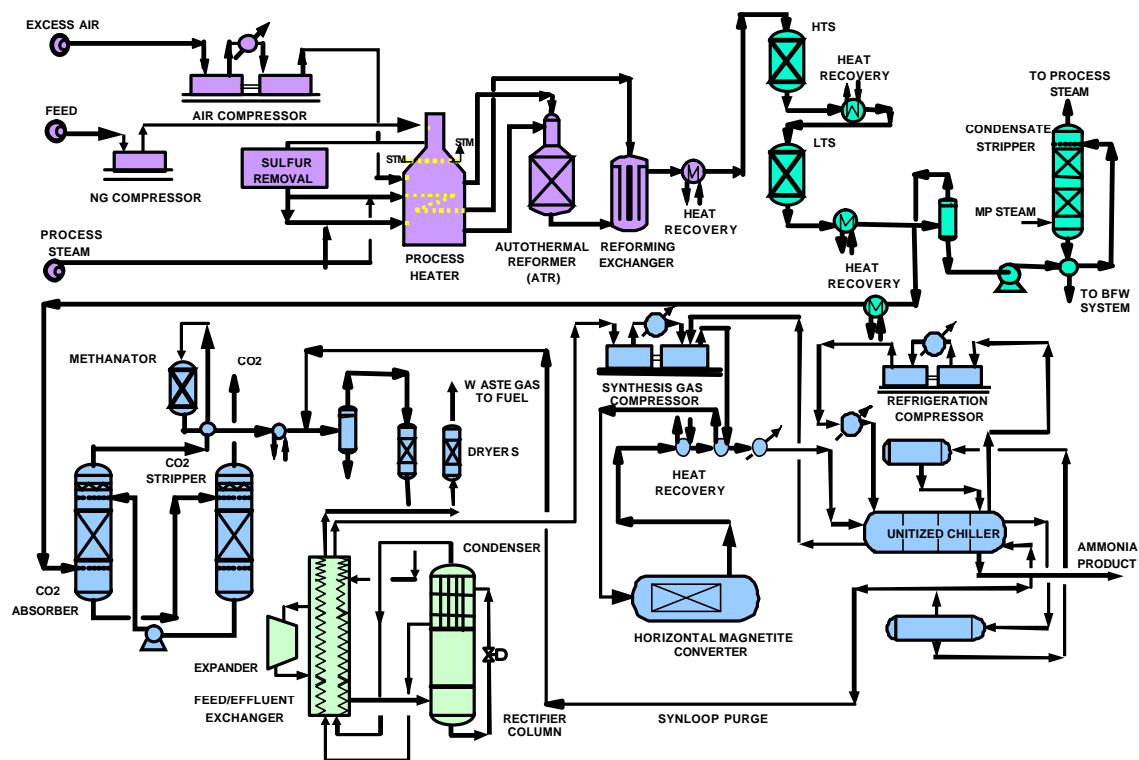


FIG. 1: PURIFIER PLUS™ PROCESS FLOW SCHEME WITH REFORMING EXCHANGER IN PARALLEL WITH THE AUTO THERMAL REFORMER

Shift conversion uses the traditional two-stage high and low temperature reactors. Carbon dioxide is removed by proven processes licensed from third parties such as UOP or BASF. Process condensate is recovered, stripped with medium pressure steam in the Condensate Stripper, and recycled as process steam to the reforming section. The synthesis gas from the CO<sub>2</sub> absorber overhead is heated in a feed/effluent exchanger and then passed over methanation catalyst to convert residual carbon oxides to methane.

In preparation for drying, the methanator effluent is cooled by heat exchange with methanator feed and cooling water. The methanator effluent then combines with the recycle synthesis loop purge gas and is further cooled with ammonia refrigerant to about 4°C. The chilled gas from the condensate separator drum goes to the syngas dryers. Two dryers are provided. They contain mol sieve desiccant and operate on a 24-hour cycle. Exiting these dryers, the total of water, CO<sub>2</sub> and NH<sub>3</sub> content is reduced to less than 1.0 ppmv. Regeneration of the molecular sieve dryers is done with the waste gas from the Purifier.

The cryogenic Purifier provides the final purification of the raw synthesis gas. The system consists of three pieces of equipment: a feed/effluent exchanger, a low speed expander, and a rectifying column with an integral overhead condenser. The dried feed to the Purifier with H/N ratio of about 2.0 is first cooled in the top part of the feed/effluent exchanger by exchange with the purified gas and waste gas. It then flows through a turbo-expander where energy is recovered to develop the net refrigeration required for the cryogenic unit. The expander effluent is further cooled and partially condensed in the bottom of the exchanger and then enters the rectifier column.

All of the methane, about 60 percent of the argon and all the excess nitrogen coming to the Purifier are removed as rectifier “bottoms.” Liquid from the bottom of the rectifier is partially evaporated at reduced pressure in the shell side of the rectifier overhead condenser to provide reflux for the column. It is further reheated by exchange with Purifier feed gas and then leaves as a waste gas to regenerate the molecular sieve dryers. The waste gas is then used as fuel in the process heater. The synthesis gas containing about 0.25 percent argon and an H/N ratio of 3.0 is reheated by exchange with Purifier feed and then goes to the suction of the synthesis gas compressor.

The purified gas is compressed to about 150 bars while combining with unreacted recycle gas. Compressor discharge is heated by feed/effluent exchange and enters the horizontal converter. In the converter ammonia conversion is raised from about two percent to over nineteen percent while passing over three beds of magnetite catalyst. Converter effluent is cooled by generating high pressure steam, by feed/effluent exchange, with cooling water, and finally in KBR’s proprietary “Unitized Chiller.” A conventional refrigeration system provides the necessary chilling. A small purge stream is recycled to upstream of the dryers in order to recover the hydrogen and nitrogen. Ammonia product is exported from the synthesis loop as either a warm product for further processing or a cold product to storage.

## **Features & Benefits of PURIFIER<sup>plus</sup>™ Process**

### *KRES™ PROCESS FEATURES & BENEFITS*

KBR’s KRES reforming exchanger operates in parallel with the autothermal reformer, as illustrated in Figure 1. This is different than other proposed reforming exchanger designs, most of which operate in series with the ATR. Parallel operation has several advantages:

- System pressure drop is lower than for operation in series.
- The single train capacity limit is much higher as only part of the hydrocarbon feed flows through the reforming exchanger.
- The process is more flexible as a degree of freedom is added with the ability to vary the split of feed between the ATR and the reforming exchanger.
- Parallel operation means that each methane molecule has only one chance at being reformed into synthesis gas, thus increasing the likelihood of higher methane slip. However, with a Purifier downstream, high methane slip is not a concern.

Others <sup>(9)</sup> have written that they will not offer a flow sheet with a reforming exchanger for new plant designs. The claimed reason is that it causes problems with the steam balance. KBR studies conclude differently. By selecting the proper choice of services for heat recovery into the high pressure steam system, coupled with the appropriate choice of drivers for the compressors, the PURIFIER<sup>plus</sup><sup>TM</sup> Process can accommodate a wide variety of plant steam balances.

KBR studies indicate that placing a reforming exchanger in a conventional (non-Purifier) flow sheet necessitates an air separation unit, which would add five to eight percent to the plant capital cost. However, placing a reforming exchanger into the Purifier flow sheet has the opposite effect—it lowers the plant capital cost by three to five percent. Flow sheets that use a reforming exchanger require extra heat release in the secondary reformer or ATR in order to make the heat balance work. So unless the flow sheet includes a Purifier to remove excess nitrogen, an air separation plant is required. Air separation plants are expensive.

#### *KRES<sup>TM</sup> MECHANICAL FEATURES & BENEFITS*

Figure 2 is a sketch of the open tube reforming exchanger. It has the following unique design features:

- Simple, open-tube arrangement allows each tube to expand individually. This results in a very low stress on the tube sheet since only the weight of the bundle is present. In addition, the presence of a single tube sheet and open tube arrangement eliminates any thermal stresses which result from differential tube to shell temperatures.
- The bundle is completely removable to allow easy inspection or replacement with a minimum of facility downtime.

- The tube sheet is located at the cold end of the exchanger, which results in higher allowable material stresses.
- The tube sheet is a hanging type, which allows the flanged joint to operate at a uniform and practical temperature.
- The shell is refractory lined with a proven dual layer internal refractory. In addition, the shell is externally water jacketed to assure uniform lower operating temperature and an added protection to allow an orderly shutdown in the event of a refractory failure.
- The ATR effluent is uniformly distributed across the bundle field by use of a perforated plate distributor. This design has been optimized by the use of computational fluid dynamic (CFD) analysis. The reformed gas exiting the open tubes is mixed with the ATR effluent by use of a perforated end cap, which is designed specifically to promote mixing with the shell-side fluid.
- The design eliminates the need for a complicated concentric tube design, pigtails, complicated closure at the hot end, and a second tubesheet which must be at the hot end.
- Pressure in the tubes is about the same as on the shell side, resulting in thin-wall tubes and higher allowable operating pressures than in primary reformers.

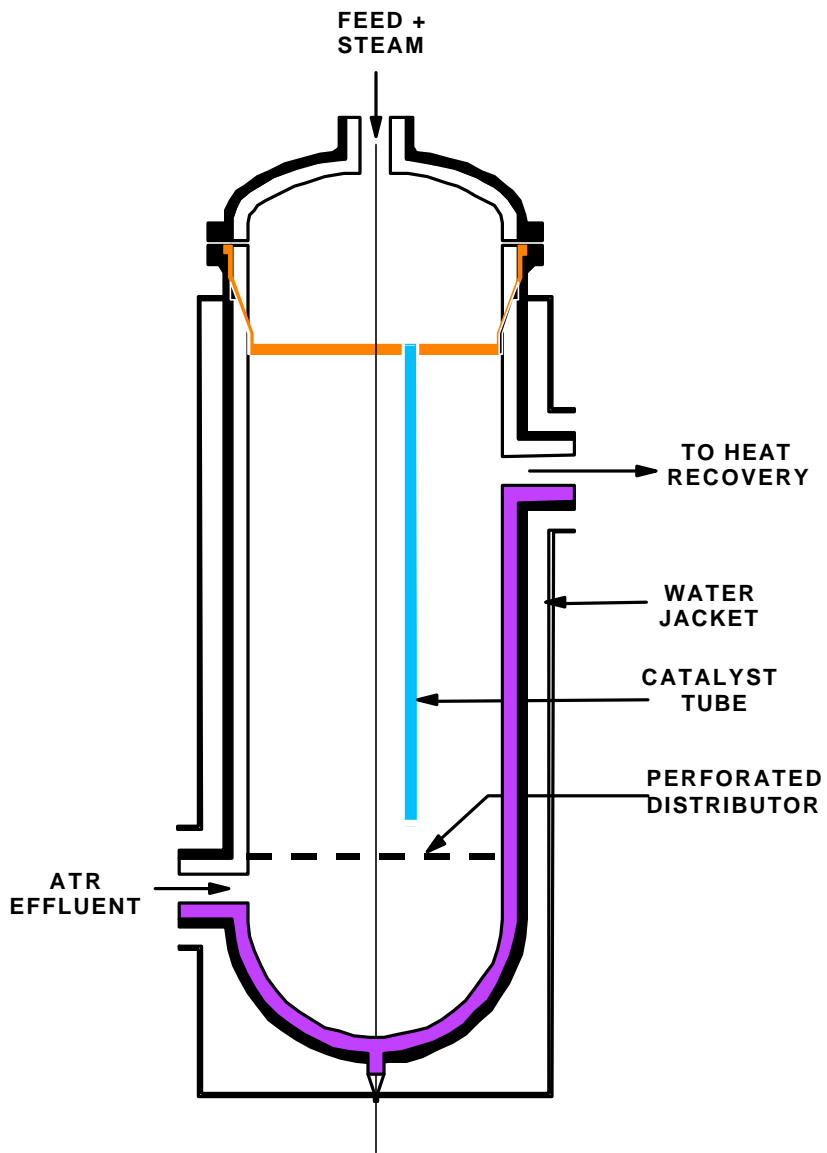


FIG. 2: OPEN TUBE REFORMING EXCHANGER

## PURIFIER PROCESS FEATURES & BENEFITS

Figure 3 shows a sketch of the Purifier system.

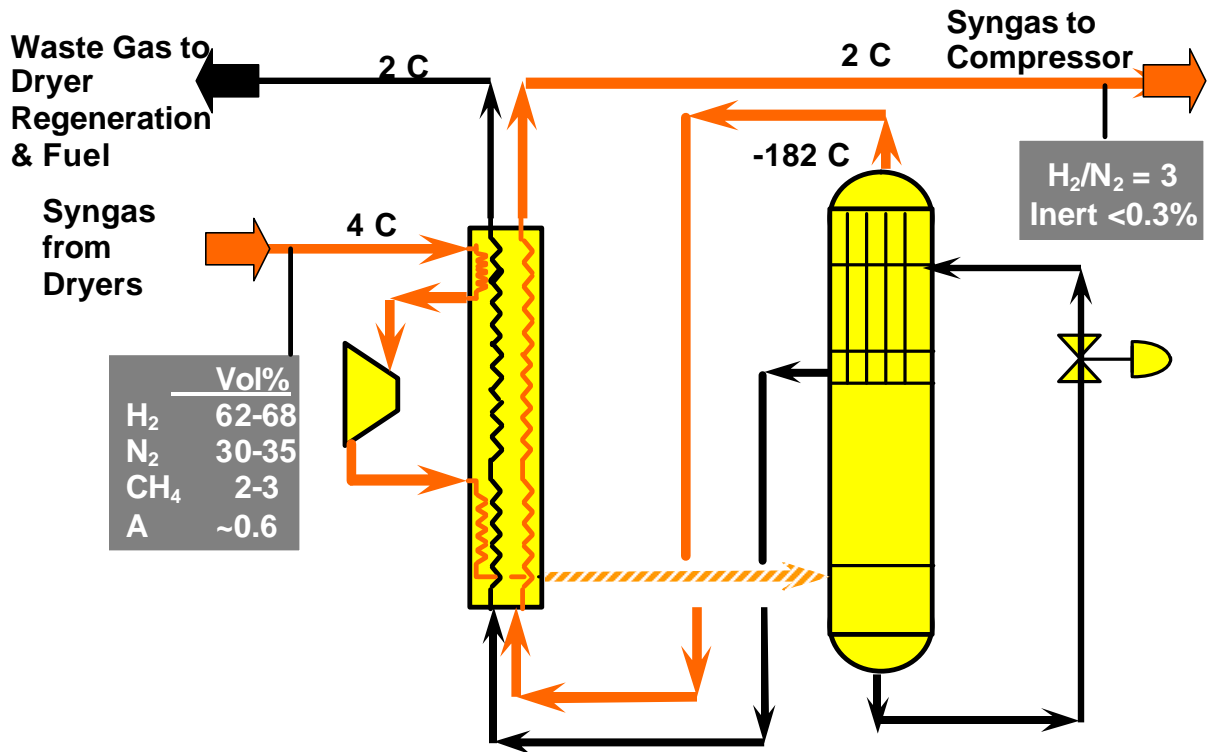


FIG. 3: SKETCH OF KBR PURIFIER CRYOGENIC PROCESS

The key process features of the cryogenic Purifier are:

- Removal of all the methane, excess nitrogen, and 60 percent of the argon from the incoming synthesis gas
- Control of the H/N ratio at 3/1 via the let-down valve in the line that routes the liquid from the bottom of the column to the overhead condenser
- Control of the system energy balance by varying the amount of work extracted via the expander.

The benefits of the Purifier have been well documented in the literature over the years. The main benefits are:

- Direct control over the composition of the make-up synthesis gas as it enters the synloop. Other process technologies need to vary the amount of air to the secondary reformer to control H/N at 3/1, which also causes process conditions in the entire front end of the ammonia plant to vary.
- The Purifier stabilizes the synloop operation. Regardless of the process conditions upstream of the Purifier, the composition of the make-up gas to the loop is always constant.
- Catalyst deactivation is less important in a plant with a Purifier. As reforming and shift catalyst age, the amount of methane and carbon monoxide in the synthesis gas increases. The carbon monoxide is methanated and in technologies that do not use a Purifier, the methane content in the synloop increases, which can limit production. With a Purifier the operation is stable and improved. All the methane is removed and sent to the fuel system while the synloop continues to operate in a methane-free environment.
- The Purifier removes any traces of water that pass through the dryers. It also removes carbon monoxide that did not get methanated. Therefore, the synthesis loop is free of poisons. Synthesis catalyst in a Purifier Plant has never had to be changed due to poisoning in over 300 plant-years of operation.

#### *PURIFIER MECHANICAL FEATURES*

The Purifier equipment and its connecting piping are enclosed in a cold box, insulated with perlite, and the box is pressurized with nitrogen to keep air out. Photo 3 is a picture of a recent installation.

The feed/effluent exchanger is fabricated of brazed aluminum. The column can be either aluminum or stainless steel. The overhead condenser is integral with the column and is a shell and tube unit. The expander is a low-speed machine, often coupled to a generator to recover the energy removed from the process. For an ammonia plant capacity of 2000 tons/day, the expander power is typically about 200 kW.



PHOTO 3: KBR PURIFIER COLD BOX AT A RECENTLY BUILT PLANT

## **EXPERIENCE**

All the features of the PURIFIER*plus*<sup>™</sup> Process are completely proven. The following paragraphs provide an overview of this experience for the key process steps – KRES and Purifier.

### **KRES<sup>™</sup> Experience and Reliability**

The first KRES unit operated from 1994 to 2005 at the Methanex plant in Kitimat, British Columbia, Canada. KBR's experience with our first KRES unit design was reported in a joint paper by the client and KBR.<sup>(10)</sup> These unique features have been primarily responsible for a long, sustained, and successful run of the KRES exchanger at Methanex. These features are scalable to larger capacity units.

An inspection was performed in October 1996 by pulling the bundle and removing and reloading the catalyst in three tubes. All elements of the reforming exchanger were in a new-like condition. There was no evidence of metal dusting. The catalyst was found to be in good condition. Details of this inspection are discussed in the literature.<sup>(11)</sup>

In late 1999 the pressure drop across the tube side of the reforming exchanger began to rise. Also, the temperature approach to equilibrium for methane reforming began to rise. The decision was made to change the catalyst. During a scheduled turnaround in May 2000, Methanex replaced the 5 1/2-year old catalyst with a new loading. It was noted that some of the original load of catalyst had broken over time leading to the high pressure drop across the tubes, as discussed in an earlier paper.<sup>(12)</sup> The second charge of catalyst operated without incident until the plant shut down and was mothballed in December 2005. In its eleven plus years of operation, the reforming exchanger has been 100 percent available. In other words, the KRES unit never caused a plant outage at Methanex.

All of the groundwork in KRES development helped KBR win its second license of a KRES unit. In the fall of 2001, KBR was awarded a contract to supply KRES technology for Shenzhen Liaohe Tongda Chemical Co. Ltd.'s ammonia plant revamp project. Liaohe operates a nameplate 1000 mt/d plant at its site in Liaoning Province. When they could get enough natural gas, the plant could produce 1070 t/d.

In order to overcome the shortage of natural gas, Liaohe installed KRES to reduce their fuel requirement. The heat previously used to generate high pressure steam will now be used to heat the reforming exchanger. The lost steam production is made up by generating steam in a coal-fired boiler.

The Liaohe plant was restarted in December 2003. The performance test was successfully passed in 2004. Table 1 shows data taken from the plant before the revamp and during the performance test. The result of the revamp allows Liaohe to reduce their natural gas consumption per ton of ammonia by about 30 percent.

	<b>Gcal/MT-LHV</b>	
	<b>Before</b>	<b>After</b>
<b>Natural Gas Feed</b>	<b>5.4</b>	<b>6.2</b>
<b>Natural Gas Fuel</b>	<b>3.8</b>	<b>0.3</b>
<b>Total Natural Gas</b>	<b>9.2</b>	<b>6.5</b>
<b>Steam Import</b>	<b>0.0</b>	<b>2.1</b>
<b>Total (Excl. ASU)</b>	<b>9.2</b>	<b>8.6</b>

TABLE 1: COMPARISON OF ENERGY CONSUMPTION AT LIAOHE BEFORE AND AFTER KRES™ REVAMP.

Since Liaohe was subject to gas curtailments, especially in the winter time, the the revamp allows them to divert gas from fuel to feed and keep their production rate up. Details of this revamp project are described in several papers.<sup>(13,14)</sup>

## Purifier Experience and Reliability

The first Purifier Plant went on-stream in the United States in 1966. Since this time fifteen more Purifier Plants have come on-line. The seventeenth Purifier Plant, a 2200 metric ton/day unit for BFPL in Australia, will start up in early 2006.

The latest Purifier Plant to start up is the 1500 ton/day unit for CNOOC on Hainan Island, China. This plant features an improved design. The overhead condenser has been redesigned and demonstrated improved performance with less surface area. The surface area of the feed/effluent exchanger has also been reduced, resulting in a more compact cold box where all equipment is inside one enclosure. Finally, the pressure has been raised by about seven bars, which makes the system operate better.

The CNOOC plant started up in late 2003. The performance test was run in 2004 and some results of the test are shown in Table 2. The measured numbers are from the test data and the expected numbers are from the process flow sheets.

	<b>Gcal/MT-LHV</b>	
	<b>Measured</b>	<b>Expected</b>
<b>Natural Gas</b>		
<b>Feed</b>	<b>6.25</b>	<b>6.32</b>
<b>Fuel</b>	<b><u>1.93</u></b>	<b><u>1.91</u></b>
<b>Subtotal</b>	<b>8.18</b>	<b>8.23</b>
<b>Export Steam</b>	<b>-1.72</b>	<b>-1.75</b>
<b>Net</b>	<b>6.46</b>	<b>6.48</b>
<b>Electricity</b>	<b><u>0.03</u></b>	<b><u>0.03</u></b>
<b>Total Energy</b>	<b>6.49</b>	<b>6.51</b>

TABLE 2: COMPARISON OF CNOOC ENERGY CONSUMPTION MEASURED AT PERFORMANCE TEST VS. EXPECTED VALUES FROM THE FLOW SHEET

Table 2 demonstrates two things--that the plant consumes very little energy and that KBR-designed plants perform as expected.

Purifier-based ammonia plants have proven to be the most reliable design in the industry. Data from a recent survey<sup>(15)</sup> indicate that Purifier Plants have a four percent higher on-stream time than non-KBR ammonia plants. The longest reported runs between shutdowns have been reported by Purifier Plants – runs of 1395 days, 960 days, and 920 days. But this reliable track record should not be a surprise. The Purifier Process is clearly a more flexible process than other designs, which makes it “user friendly.” KBR expects its PURIFIER*plus*<sup>TM</sup> plants to be even more reliable because the primary reformer is eliminated.

## **SUMMARY**

KBR has combined KRES and Purifier, two well-proven technologies, into one flow sheet called PURIFIER*plus*<sup>TM</sup>. This new process offers the following benefits to ammonia producers:

- Low operating cost
  - ✓ very low energy consumption
  - ✓ reduced maintenance costs
  
- High reliability
  - ✓ well-proven commercial designs
  - ✓ greater operational flexibility
  - ✓ ease of handling process upsets
  
- Lower capital cost
  - ✓ Eliminates the primary reformer
  - ✓ Eliminates the purge gas recovery unit
  - ✓ Has smaller synthesis loop and refrigeration system due to high purity make-up gas
  
- Smaller plot space
  
- Reduced emissions

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