Petroleum Coke Gasification Based Ammonia Plant

Coffeyville Resources operates the only petroleum coke gasifier in North America that produces ammonia. The gasification of petroleum coke allows the plant to be independent of the volatility of natural gas prices. This paper will give an overview of the GE Energy hydrogen production process and will discuss some of the benefits, difficulties, and issues related to the process. A discussion of reliability and safety will be included.

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Introduction

Construction began on the Coffeyville Nitrogen Plant in Coffeyville, Kansas, U.S.A. in January 1998. The Process Information Package for the hydrogen production facility (gasification and hydrogen purification) was developed by GE Energy (formerly Texaco Development Corporation). The EPC for the gasifier and ammonia facility was Black & Veatch Pritchard. Much of the equipment for coke handling, gasification and syngas cooling was relocated from Daggett, California where it was part of a U.S. Department of Energy sponsored integrated gasification combined cycle power plant demonstration project known as Coolwater. Initial ammonia production began in late 2000.

The facility was built and initially operated by Farmland Industries, Inc. In March of 2004, the facility was sold to an investment group and named Coffeyville Resources.

Process Description [see block flow diagram, figure 1]

Petroleum coke is received by truck from Coffeyville Resources Refining and Marketing or an outside source to a storage pad where it is allowed to dewater for two to three days. It is then loaded into a hopper by a front end loader where it goes through a feeder breaker to size it to approximately 4 inch (102 mm) pieces and then to a hammer mill where it is further reduced in size to about ½ inch (13 mm) or less. The crushed coke is stored in a 6,000 ton silo for feed to the process.

The coke is fed through one of two belt conveyors where a fluxing agent is added to the coke. It then feeds into one of two rod mills where water containing recycled solids are added to form a slurry of a 60 – 65% solids concentration. The slurry is stored in an agitated tank prior to being charged to the gasifier with plunger style pumps. Two pumps are normally in operation and the controls are such that if one pump trips or needs repair, the other one ramps up to control the process flow.

Oxygen is provided by BOC Gases as an across-the-fence contract. They also provide nitrogen for the ammonia plant and retain liquid argon for sale. The oxygen is provided at 850 psig (60 bar) and combines with the slurry in a feed injector at the top of the gasifier vessel.
Figure 1: Gasification Block Flow Diagram
Coffeyville Resources has two GE Energy designed gasifiers which are alternated to provide continuous syngas and to facilitate periodic maintenance on the refractory lining. Each gasifier is 900 cubic feet in volume and is lined with a specialized refractory that resists the intense temperatures and corrosive slag that is produced from the metal impurities in the petroleum coke.

The spare gasifier is normally in a hot-standby condition. That is, it is preheated with natural gas or purge gas and is ready to be switched into service if necessary. To put a gasifier into service, the preheat burner is removed and a feed injector is inserted. The feed lines are bolted up and the gasifier is ready for light off. There is more about the startup and safety systems later in this paper.

The gasifier operates at 620 psig (43 bar) and 2500°F (1370°C). Oxygen flow is controlled to maintain the temperature. The reducing conditions form carbon monoxide (CO), hydrogen (H₂) and carbon dioxide (CO₂) at essentially equilibrium concentrations. Most of the sulfur in the coke is converted to hydrogen sulfide (H₂S) with a small amount of carbonyl sulfide (COS). The fluxant (primarily silica) and metal impurities form slag on the refractory where it flows downward to the throat area above the quench chamber. The hot gas and slag are quenched with water in the quench chamber and the cooled syngas goes to the carbon scrubber. The solids, primarily slag and unconverted carbon settle out and are removed through a lockhopper system at the bottom of the quench chamber. A drag conveyor separates the slag from the water. [see figure 2 for a diagram of the gasifier and quench chamber]
Black water containing carbon and fine slag is also removed from the bottom of the quench chamber and goes though a series of solid settlers at reduced pressure. The concentrated recycle solids stream is sent to the rod mill for slurry preparation. The clean water is sent back to the quench chamber.

The carbon scrubber contains water wash trays to remove the last traces of soot and carbon prior to going to the sour gas shift converters. The gas stream contains approximately 50% carbon monoxide which is shifted to carbon dioxide and hydrogen through two catalyst beds with waste heat recovery. The catalyst also hydrolyzes most of the carbonyl sulfide to hydrogen sulfide. The gas is then cooled and the process condensate is recovered and recycled back to the quench chamber.

Acid Gas Removal [see figure 3 for Selexol block flow diagram]
The syngas then goes to the CO₂ absorber where it is contacted with semi-lean and lean solvent to remove CO₂ down to about 4% v/v. The clean syngas which is now about 93% hydrogen goes to the UOP designed pressure swing absorption (PSA) unit. This unit is a ten bed system. Absorption times are adjusted to maintain less than 5 ppm CO in the hydrogen stream to the ammonia plant. The PSA reject gas is compressed and recycled back to the second shift convertor. A small purge stream is used to preheat the spare gasifier or is flared.

**Ammonia Plant** [see figure 4]

The ammonia synthesis unit was designed by Black and Veatch Prichard and utilizes an Ammonia Casale three bed intercooled convertor. The feed hydrogen and nitrogen, at ratio, are fed to the syngas compressor, heated and sent to the convertor. The loop operates at 1,850 psig. (129.5 bar) The gas exit the convertor is cooled in a steam superheater, 600 psig (42 bar) waste heat boiler and boiler feed water preheater. Ammonia is condensed with cooling water and ammonia chillers prior to syngas recycle. Due to the high purity of the nitrogen and hydrogen, no high pressure purge is needed. Any traces of impurities are removed as dissolved gases in the low pressure ammonia refrigeration system purge. The refrigeration compressor, in addition to condensing the product ammonia, also handles the vapors from the Selexol chillers.

After the final flash, the CO₂ is heated with steam to increase dispersion prior to venting to the atmosphere.
UAN Plant [see figure 5]

Coffeyville Resources upgrades the majority of the ammonia produced into urea-ammonium nitrate (UAN) solution utilizing a Weatherly designed integrated plant. CO₂ from the purifier is compressed in three stages to 3800 psig (266 bar) and combined with excess ammonia in the urea plant. The pressure is reduced and some of the ammonia is sent to the nitric acid plant. Some excess ammonia is recycled to the urea plant and the excess carbamate is decomposed to provide ammonia to the ammonium nitrate neutralizer. The urea solution and ammonium nitrate solution are combined to make the product 32% N UAN.

Safety Systems

Coffeyville Resources uses the GE Energy proprietary safety systems for the startup sequence and critical controls for the gasifiers. After the process feed injector is inserted in the preheated gasifier and the piping connections are tight, the system is purged with nitrogen to remove any oxygen. Slurry is pumped up to the injector deck and circulated back to the slurry feed tank. Startup oxygen flow is established out through the vent. These are established at the proper feed ratio. Oxygen is prevented from entering the feed injector by a double block and nitrogen buffer. When all of the interlock parameters are met, the operator initiates the startup sequence and the valves open so that slurry reaches the gasifier prior to oxygen. The reaction lights off of the hot refractory.

The critical controls system looks at oxygen to carbon ratio and adjusts pump speed and/or oxygen to maintain control. All critical control parameters are monitored through a two-out-of-three voting algorithm as part of the Triconex computer soft-
ware. This software also has high speed data collection which captures predetermined events. If the safety limits are exceeded, the slurry and oxygen valves are tripped close and purges automatically occur to make the gasifier safe. In the five years this facility has been in operation, there have been no trips that were not warranted.

The gasifier shell is designed for 800 °F (426 °C) and is monitored continuously by a system developed by Sensa (see: http://www.sensa.org/technology_principles.asp for more information on fiber optic temperature sensing). It utilizes an optical fiber which is wrapped around the gasifier shell. A laser signal is shot through the fiber and converted to an average temperature over a small section of the shell. The operator looks at the temperature graphically and can be alerted when the temperature exceeds a predetermined point, usually 550 °F (287 °C). This system gives an early indication of refractory loss. A hand held infrared camera is also used by the operators to determine more precise temperature variations.

The facility has four separate flare systems to handle startup, shutdown and upset conditions for each plant area. The four flares prevent hazardous releases from impacting the nearby community.

The gasifier flare handles the startup gas flow exit either carbon scrubber. This same flare also handles syngas inlet Selexol, exit Selexol or exit the PSA. In addition, all process relief valves are connected to the flare. This flare prevents the uncontrolled emission of hydrogen sulfide.

The ammonia plant has a separate flare to handle ammonia plant synthesis gas and any venting from the refrigeration system. The storage tank has a flare to handle boil off when the holding compressors are unable to maintain pressure. The fourth flare is on the UAN plant and can handle ammonia containing process gas during startup and shutdown.

Throughout the gasifier process area there are area personnel monitors for carbon monoxide and hydrogen sulfide. These can alert the operators in the field and in the control room in the event of a process leak.

Many other safety features were incorporated into the original detailed design of the facility. One of note is the double wall, double integrity design of the 20,000 ton refrigerated ammonia storage tank. This was designed and built by Chicago Bridge and Iron.

**Maintenance**

Gasification maintenance has a significantly higher cost than natural gas based ammonia plant maintenance. Some of this is due to the extensive solids handling equipment, but some is unique to the gasifier itself. The following paragraphs outline some of the unique issues encountered.

**Refractory** [see figure 6]

Each gasifier vessel is lined with refractory brick. The refractory and insulation system consists of insulating fire brick, ruby back up brick and the chrome hot face brick. The hot face brick is primarily chromium and areas of the refractory system have up to 90% chrome brick. The gasifier lining is made up of separate zones so only the area that is worn can be removed. The zones consist of cone and throat, wall and dome. The dome is not supported by the hot face of the wall, so it can be changed separately, likewise, the cone in the bottom does not support the wall.

The highest wear occurs in the cone and throat area at the bottom and this brick will wear from the original six inch thickness to one to two inches in a period of 90-120 days. Wall brick lasts 300 days or more and the dome can last up to two years. Part of the backup to the dome and the cone consist of castable refractory, which requires a long curing time. Downtime for refractory change out averages two to four weeks depending on which area is changed. The high chromium brick is relatively expensive and a total change out costs in excess of $1,000,000 US.
Grey water

The black water and grey water from the gasifier contains large amounts of slag, which is essentially fine sand. When the pressure is reduced on streams containing slag, there tends to be high levels of erosion of the valves and piping. Some sections of pipe are lined with ceramics and some of the controls valves have exotic trim materials such as tungsten carbide. The grey water system is configured so that sections can be taken out of service for short periods of time (two to four hours) for pipe repair or valve replacement without affecting the production of syngas.

Because of the hydrogen sulfide dissolved in the circulating water, extra precautions need to be taken when performing maintenance to prevent personnel injury. This includes flushing with clean water and in some cases using supplied air respirators.

Ammonia Steam superheater

In the description of the ammonia plant, it was mentioned that there is a steam superheater on the ammonia convertor exit gas. This exchanger caused a great deal of downtime in the early operation of the plant due to tube leaks. The exchanger originally had Inconel 600 finned tubes. Due to a combination of excessive stress and small amounts of boiler solids from the steam generator, caustic stress corrosion cracking was occurring. The problem was solved by re-tubing with bare Inconel 690 tubes and installing a high efficiency steam separator. These bare tubes have resulted in less than design superheat temperature so the unit will be replaced with a u-tube style bundle having more surface area at turnaround. This will result in improved thermal efficiency.

Refrigeration compressor drive

The refrigeration compressor chosen for the facility is powered by a 9000 horsepower variable frequency electrical drive. The variable frequency drive was selected due to the wide range of refrigeration load from only Selexol to the ammonia plant at full rates and all cold product. There were two early failures of the motor due to overheating. It was determined that the variable frequency drive was creating an excessive amount of current harmonics which were manifesting themselves as heat in the rotor. The solution to this problem involved installing a VAR compensator and putting heavier rings and bars in the rotor to dissipate the heat better.

Urea plant corrosion

Another issue that caused problems was in the urea plant. The original design of the carbon dioxide purifier made is difficult to control the temperature to the zinc oxide bed. During a low temperature excursion, sulfur migrated to the urea plant and caused accelerated corrosion in the primary urea reactor. In the current design, enough hydrogen is added to the CO₂ to get the proper reaction tem-
perature in the oxidation catalyst bed so that the zinc oxide is hot enough to remove all of the sulfur. As an added safeguard, the passivation oxygen is kept at 1% v/v.

Environmental

The facility water supply comes from the Verdigris River. The water is clarified and filtered for use as cooling tower makeup. The clarifier generates a sludge that is processed through a press. The subsequent lime cake is landfilled. The boiler feed water is treated in a reverse osmosis system. Water wastes from the facility consist of cooling tower blowdown, sand filter backwash and boiler blowdown. These are sent to a municipal water treatment plant for disposal. There is no process water discharged from the plant. Because all of the hydrogen comes from water, the plant uses wash down water and contaminated storm water as makeup to the grinding feed system or to supplement quench water. The small amounts of chlorides that come in from the water makeup or the coke are removed with the wet slag.

The slag from the gasifier that is removed through the lockhopper contains vanadium, nickel and chromium. Because the gasifier operates under reducing conditions the metals are in the reduced, non-leaching state. Furthermore, the metals are encapsulated in the silica that is used as a fluxing agent. The slag also contains considerable amounts of unconverted carbon and some water, but is very low in sulfur. The carbon content gives it some value and it is currently used to supplement fuel to a Portland cement plant as kiln fuel. Also, due to the extreme temperatures and reducing atmosphere in the gasifier, any long chain or cyclic aromatics are reduced to hydrogen and carbon monoxide so they do not constitute a hazard in the slag. The slag passes the United States Environmental Protection Agency (USEPA) Toxicity Characteristic Leaching Procedure (TLCP) and thus is considered non-hazardous.

The facility produces five to ten times fewer priority pollutants than a similarly sized natural gas based ammonia plant. In the United States, priority pollutants are SOx, NOx, CO and PM10. Nearly all of the SOx emissions occur during startup when the process gasses are vented to the flare prior to introduction to the Selexol unit. This lasts for one to three hours on average for each startup. The NOx comes from the combustion of hydrogen and CO that purges out the flare, the combustion of natural gas or purge gas for the gasifier preheat burner and the few hours each year that the ammonia startup heater is used. Some CO slips with the CO2 vent and from the combustion of purge gas. The PM10 emissions are from coke handling, although this is minimized through the use of enclosed conveyors and baghouses.

In addition to the priority pollutants, small amounts of hazardous air pollutants are emitted. These are carbonyl sulfide via the CO2 vent and hydrogen sulfide from fugitive sources. Because of the multiple flares, ammonia emissions are also very low.

There are currently no regulations limiting carbon dioxide emissions in the United States, however all of the CO2 created from the petroleum coke is used either in the urea plant or is vented as a pure stream which could be compressed and sequestered without additional scrubbers or control equipment.

Performance

The plant first made ammonia in July of 2000 and has steadily increased on-stream performance and instantaneous rates since. The design was to produce 1100 stpd of ammonia. Currently the plant routinely makes 1240 stpd. In calendar year 2004, excluding turnaround, the gasifiers made hydrogen 95% of the time. In 2005 this was 98% and ytd 2006 the plant is producing at 98.5% on stream. The reliability increases have been realized through a concerted effort at the plant level to evaluate all weaknesses in design, equipment and procedures and then applying appropriate reme-
dies. Production increases have been primarily through debottlenecking of the Selexol unit. Increased amounts of carbon dioxide removed result in less reject gas or alternatively, the ability to send more feed to the PSA.

The UAN plant was designed for 1500 stpd but was able to produce about 1700 stpd from day one due to some excess capacity in the design. The CO₂ compressor has been modified slightly to increase volume and pure oxygen is supplemented to the nitric acid plant gauze. Current rates are 1950 to 2000 stpd.

Figure 7 - Plant Performance

Conclusion

Everyone in the nitrogen fertilizer industry recognizes the relationship between natural gas prices and ammonia production costs. Natural gas is the single largest component in the cost structure for a conventional natural gas based plant. In the petroleum coke gasification based plant, the cost of coke is only about 20% of the ammonia cost. The largest operating cost is electricity. For instance, the Coffeyville facility uses 60 MW of power including the air separation plant. As refineries target heavier crude slates and continue to add coking capacity to make their operations more efficient, the supply of petroleum coke is expected to keep pace with demand. Consequently, the price of coke is expected to stay competitive compared with other fuels such as coal. Recognizing that most of the other costs for a gasification facility are essentially fixed, the on-stream factor is the single most important variable in keeping production costs low.

Given the current price of natural gas, and the high on-stream factor, Coffeyville Resources is the low cost producer of ammonia and UAN in North America.
About the author

Neal Barkley started his career as a Process Engineer for Cooperative Farm Chemicals Association, a joint venture between Farmland Industries and MFA, in Lawrence, Kansas. He held several technical positions with Farmland, and in 1995, Mr. Barkley became the Plant Manager at the Dodge City Kansas nitrogen fertilizer plant. When construction was underway at the Coffeyville nitrogen fertilizer plant, he moved into the project manager role for the facility. Once construction was complete, Mr. Barkley was named Plant Manager. He is registered professional engineer in Kansas and a member of the American Institute of Chemical Engineers. Mr. Barkley holds a B.S. in Chemical Engineering from the University of Nebraska - Lincoln.