Figure 1. A standard combination natural gas and steam atomization liquid oil burner operating on No. 2 fuel oil in a down-fired ammonia reformer, set at 0.5 lb. of steam/lb. of oil at a heat release of 2.5 million B.t.u./hr.

Figure 2. Allied Chemical's normal operating mode, with all burners in the row, including the one shown in Figure 1, set at 2.5 million B.t.u./hr. but with atomizing steam increased to 1 lb./lb. of oil.

Figure 3. VFO fuel on a 1,000 ton/day down-fired reformer. Two burners at the left rear are on VFO with non-luminous flame. Burners at the right are on natural gas. Each of the burners is at 2.5 million B.t.u./hr. heat release.

Firing Oil On an Ammonia Reformer

In addition to operating on burners designed for natural gas, the Vaporized Fuel Oil System has lower operating costs than liquid oil steam atomizing burners.

E. R. Johnson, Allied Chemical Corp., Hopewell, Va.

Allied Chemical Corp. originally made syngas from coke, but with the advent of natural gas-steam reforming in the 1940s our plants were converted from coke to this more efficient and lower cost technology. The process was low pressure, about 15 lb./sq. in. gauge, and the reforming reaction took place in 8 in. diameter catalyst tubes fired at temperatures in excess of 1,800°F.

The efficiency was rather low in comparison with modern high pressure reforming because, at the low operating pressure it was impossible to remove the latent heat in the residual steam in the converted gas at any useful temperature level other than for building heating. However, the process was a long step forward from syngas preparation from coke to the extent that it reduced the cost of ammonia by 30%. Thus, in 1950 we were among the first to install natural gas reforming units.

Our first installations were at the Hopewell, Va., and South Point, Ohio, plants. These reformers were fired with radiant gas burners mounted in the side walls, but they were also provided with oil-firing capability through steam atomizing oil burners in the end walls of each reformer.

The reason for our plan to fire oil as well as natural gas as early as 1950 was that the Hopewell plant was located on the "big inch" pipeline, which could not supply our reforming fuel needs during the winter, as well as those of the large metropolitan areas such as Washington just north of the plant.

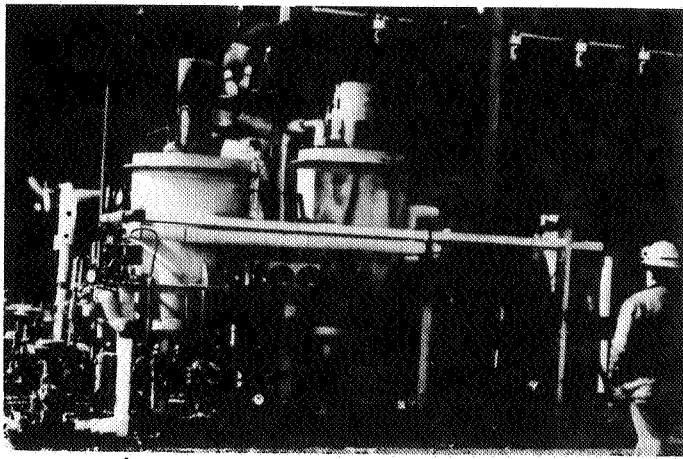We also provided for gas or oil firing on the gas reform-

Figure 4. Allied's skid-mounted VFO oil rig in operation on a 500-ton/day radiant wall reformer. VFO fuel is piped to the second row of burners.

ing units at South Point, Ohio, but for a different reason. That plant is adjacent to the company's Semet-Solvay Coke Oven Div., and a large part of our fuel needs were, and still are, met by coke oven gas from this operation. However, an Armco Steel plant just across the river from South Point would occasionally require large volumes of CO gas in the form of our coke oven gas during the winter months. Thus we had to make up for this winter time fuel deficiency by occasional use of fuel oil.

Both the Hopewell and South Point installations were set up to burn Bunker C oil in horizontally mounted steam atomizing oil guns in the end walls of each cell of the reformer, firing between parallel rows of vertical tubes. The Bunker C oil supply was heated and fed to the oil guns, then looped back to storage to maintain temperature in the stream-traced and insulated oil line. This system worked fairly well, being used periodically in the winter months when gas was short.

Technical and economic problems

The two main drawbacks to heavy oil firing were economic and technological. The economic problem was two-fold: Bunker C cost about 50% more than natural gas and required approximately one pound of atomizing steam per pound of oil.

The main technological disadvantage was that the ash in the oil would periodically plug up the reformer convection section. The major problem location was at the inlet to the flue gas waste heat boiler where this ash would reach its fusion point and slag out on the tubes. However, the use of steam lances enabled us to keep the tubes clear enough to run full rate on 100% Bunker C fuel oil firing.

Operation continued this way during the winter for several years, when suddenly in 1956 many reformer tube failures of a different nature began to occur. In the first years of operation there had been an occasional bulged or cracked tube, but the new problem was the start of many failures from corrosive attack. A lengthy investigation led to the determination that the impurities in the Bunker C oil had gradually increased in vanadium and sodium content to the point where these metals were attacking the tubes. Earlier supplies of Bunker C had contained less than 2 parts/million vanadium and less than 5 parts/million of sodium. The vanadium forms an oxide, probably the pentoxide, which attacks the catalyst tubes. Further, when sodium is present the sodium oxide acts as a fluxing

agent to remove the protective chrome oxide film on the reformer tubes and increase the rate of vanadium attack.

To stay with relatively low-cost Bunker C oil, we looked at ways of removing impurities. The sodium could be removed from the oil with a water wash in a high speed centrifuge. However, we could find no economic way to remove the vanadium and we tried various additives such as dolomitic limestone without much success.

As the rate of tube failure increased, it was decided that the cheapest solution to the problem was to burn No. 2 oil in place of Bunker C when gas was being curtailed. In the last year during which Bunker C was burned, the vanadium and sodium attack resulted in failure of 56% of the tubes in both plants. After the cause of the corrosion was uncovered, we found that we could plot the increase in vanadium and sodium content against the rate of tube failures in the reformers for the preceding few years of operation on Bunker C oil. Accordingly, the switch to No. 2 oil was made, and is still used at the South Point plant during gas curtailment.

With the advent of more efficient high-pressure gas reforming in the early 1960s, we elected, in 1964, to replace the low pressure natural gas reformers in the plant at Hopewell with high pressure reforming technology. Historically, our natural gas supply had been curtailed each winter. Therefore, the new reforming furnace at Hopewell was provided with burners that could handle natural gas or oil separately or concurrently.

These burners worked quite well, and with No. 2 oil there were no problems with corrosion or with slagging in the convection section. However, there was still the same problem with the older oil guns: when oil was used, we required between 1/2 and 1 lb. of steam/lb. of oil. This doesn't sound like a very large amount, but when you consider that it takes about 1/3 of a ton of oil as fuel to pro-
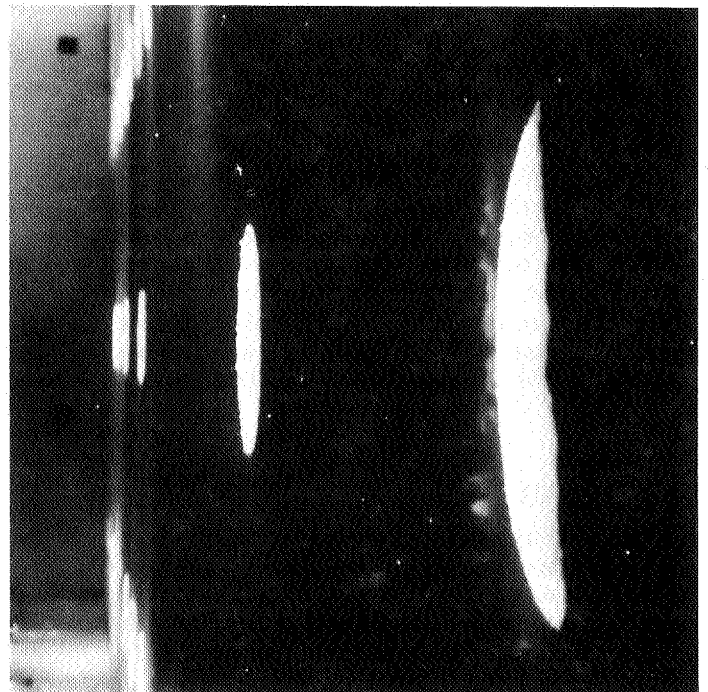

Figure 5. VFO fuel on a radiant wall reformer. Center row of burners on VFO with oil and low steam-to-oil ratio. Top and bottom rows are on natural gas. Each burner is at 0.5 million B.t.u./hr.

duce a ton of ammonia, then 1 lb. of steam/lb. of oil at current energy costs represents about $1 million/yr. in additional operating cost for a 1,000 ton/day ammonia reformer.

The photos in Figures 1 and 2, although they are not as sharp as they might be, do show the effect of increased atomized steam on burner flame. Both figures show a standard combination natural gas and steam atomization liquid oil burner operating on No. 2 fuel oil in a down-fired NH_3 reformer. In Figure 1, the burner at the rear, center, has been set at 0.5 lb. of steam/lb. of oil at 2.5 million B.t.u./hr. heat release. Note the typical broad, luminous, high emissivity flame typical of liquid oil steam-atomizing burners.

Figure 2 shows Allied's normal mode of operation with all burners in this row, including the burner shown in Figure 1, set at 2.5 million B.t.u./hr. heat release but with atomizing steam increased to 1 lb./lb. of oil. Note how the flames from the burners in Figure 2 resemble those produced by natural gas. As mentioned earlier, this operation costs about $1 million annually for a 1,000 ton/day NH_3 plant. However, the aggregate 100% fuel gas curtailment was about three months each year at that time, and the burners were already installed. Therefore, we accepted this $250,000/yr. operating cost penalty for lack of a better solution.

We were unaware, however, of events then transpiring that would later expose our Gulf Coast operation to extremely high financial penalties due to changing fuel availabilities.

In 1965, about the same time the high-pressure gas reformer was installed in the Hopewell plant, we constructed facilities at Geismar, La., about 25 miles south of Baton Rouge. In the Louisiana area, natural gas was 18¢/million B.t.u. And according to the gas suppliers as well as our experts, there was no end in sight for gas availability. Accordingly, the Geismar 1,000 ton/day ammonia plant was designed with the capability for only gas firing on the primary reformer.

Both the gas-fired Louisiana unit and the oil or gas-fired Hopewell unit started up in the early spring of 1967. The situation was uneventful until 1974 when forecasts of gas curtailment threatened the Gulf Coast area. We then undertook to engineer, design, and procure materials required to convert the Geismar reformer to oil or gas firing by replacing the gas burners with combination oil or gas burners like those originally installed at Hopewell. But when all the equipment was delivered and we were in the critical-path planning stage for the installation, we received a shock. The liquid fuel oil conversion would require extended downtime on the unit to replace the tiles, burners, piping, and arch refractory, which would result in a production loss of more than $1 million.

A new approach

At this point Allied management said, "Try something else." In response, we undertook to develop a system that could burn oil in the existing equipment. The target was a system that could burn oil and/or gas in the existing burners and tiles with no need to replace either.

Initial pilot plant research work used a single vertically-fired burner exactly the same as those originally installed on the Geismar reformer. This research was successful, and oil was fired in this gas burner without any modification. Further, the tests showed we had developed a system that could burn oil at utility consumptions lower than those required by the standard liquid oil or pressure-forced draft burners.

To get long range operating plant data on the use of this system, we constructed a skid-mounted rig that could be
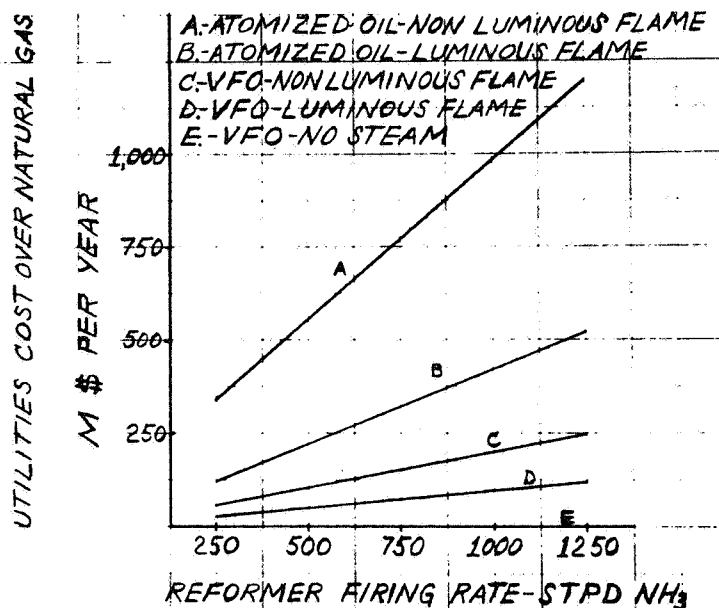

Figure 6. Effects of VFO in reducing operating costs.

moved to various plants to supply oil fuel to various types of gas burners under actual operating conditions. During the plant testing we further advanced the technology to the point where we could burn oil in our existing natural gas burners with no steam requirement at all.

At this point we knew that not only had we found a solution to the problem of conversion of existing units but that the system would be preferred on a new installation due to its lower operating cost.

The oil-atomizing combination oil-gas burner system procured originally for the Geismar reformer remains in a warehouse; we can't afford the cost of installing it. The new oil firing system is called VFO, an acronym which derives from its project name, Vaporized Fuel Oil.

The photographs in Figures 3, 4, and 5 show the VFO oil firing system burning oil on units designed only for gas firing.

We have demonstrated "tailor-made" flame patterns and emissivities with VFO that can be used on kilns, open hearth furnaces, and gas turbines, in equipment designed to burn only natural gas, while avoiding the problems of localized overheating often experienced with liquid oil burners.

In addition to operating on burners designed for natural gas, the VFO system has lower operating costs due to its lower utilities consumption when compared with liquid oil steam atomizing (or assist) burners. Figure 6 shows the reduced operating cost on VFO fuel.

We are currently converting two ammonia plants from gas to oil firing by this new technology. One plant was started up earlier this year, and the other one is in the engineering and design stage. #
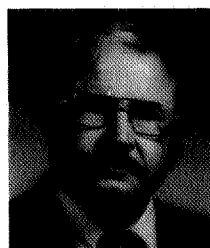
E. R. Johnson, presently project manager for the Agricultural Div., Allied Chemical Corp., earned his B.S.Ch.E. from Polytechnic Institute of Brooklyn. He has been a consultant to the Korean and Iranian governments regarding fertilizers, holds patents in the area of urea manufacture and, more recently, managed Allied's engineering offices in New York and Paris.

DISCUSSION

Q. I would like to discuss the period when you were burning bunker C. I had a chance to review your paper before you started talking, and apparently the bunker C oil contained about 2 parts to the million vanadium and 5 parts to the million sodium.

JOHNSON: That was the maximum level, yes.

Q. Well my question is really directed in that vein. Is it your sense that if I had oil with a maximum of 2 ppm vanadium and 5 ppm sodium that it would not have a fuel ash problem.

JOHNSON: The fuel ash problem experienced with fouling of the convection system was caused by the total ash or mineral content of the bunker "C" oil, while the vanadium and sodium, in their oxidized forms, caused the catalyst tube corrosion. Initially, our bunker C oil back in the early 1950's had less than a part per million vanadium and almost no sodium. When we started to experience corrosion problems we were up to two parts per million vanadium and it seemed as though this was a very significant area, that somewhere less than one ppm of vanadium probably would be satisfactory, while two ppm or more would cause high catalyst tube corrosion rates.

Q. Second question, if I may just take a minute. In the VFO system is it possible to use bunker C there?

JOHNSON: The test work we have completed is for No. 2 oil and this is the basis upon which we are designing our current gas-oil fuel conversion systems.

Q. No. 2 oil?

JOHNSON: Correct! We have underway test work which we are not ready to publish yet, using heavier oils including petroleum.

Q. That's very interesting, thank you.