Ammonia Manufacture from Refinery Gas

Although operating costs are relatively high, this South African facility
has demonstrated high performance and production levels, partly due
to use of alternate feedstocks

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In a world where the reserves of natural gas are rapidly being depleted and shortages are developing, manufacturers of ammonia are turning to alternative feedstocks such as higher hydrocarbons and coal. In certain areas where the balance of oil refinery products is such as to produce an excess of off gas, it is possible that this by-product offers the most economic raw material for the manufacture of ammonia.

South Africa is a country with neither natural gas nor oil and has therefore been in the unhappy position to have to look to unorthodox feedstocks for some time. In the 1960's, two ammonia plants were commissioned in South Africa based on refinery off gas. One of these is owned by AE&CI at Umbogintwini, near Durban, and our experience over eight years of operation may be of value to others who are considering this type of raw material.

The Umbogintwini ammonia plant was commissioned in 1967 and is basically an orthodox Kellogg 600-short ton/day naphtha unit of the "new generation" type. A block diagram of the plant is given in Figure 1.

The differences from an orthodox naphtha unit are the gas compression stages and the ability to fire both gas and naphtha on all major furnaces, including the plant's auxiliary boiler. The decision to design the plant for both gas and naphtha usage was based on an anticipated shortfall of gas in the early years of operation and on the need to run the plant during refinery shutdowns. Although there are ammonia plants in the world using refinery gas without a naphtha back-up, we regard some sort of feed-fuel back-up as essential to good plant operation and on-line time.

Gas is received from two refineries via separate gas pipelines 13 km. long. One refinery supplies approximately 300 ton/day of low-sulfur, hydrogen-rich gas suitable for both feed and fuel use. The other supplies 300 ton/day of higher sulfur material suitable for fuel purposes only. Thus both refineries have to be fully operational for the ammonia plant to run on gas only. Naphtha is introduced as feed or fuel to make up for any shortfall below the current plant limitation. This naphtha is supplied by road tanker.

Differences between this and naphtha plants

The choice of feedstock being refinery gas of the composition shown in Table 1, the additions to the conventional naphtha ammonia plant are as follows: a) gas pipelines from refineries to plant; b) gas compressors for feed and fuel gas; c) larger diameter reformer tubes; d) special burners for gas/
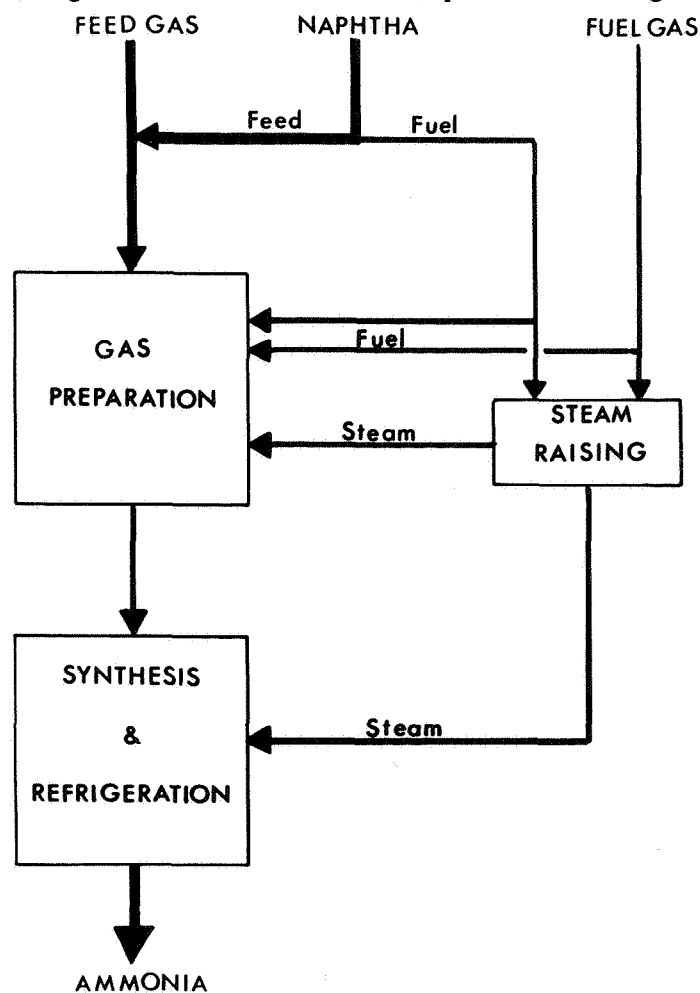

Figure 1. Block diagram of Umbogintwini ammonia plant shows use of naphtha and of refinery gas as feed.

Table 1. Composition of feed gas

	Maximum density	Average density	Minimum density
Specific gravity	1.18	0.80	0.55
Hydrogen, %	26.9	48.2	62.6
Methane, %	6.7	5.9	5.6
Heavier hydrocarbons, to n-pentane	66.4	45.9	31.8
Olefins	trace	trace	trace
Mean molecular weight	34.4	23.2	16.1

naphtha operation; and e) extra instrumentation.

The following items may then be of reduced capacity: naphtha storage; naphtha vaporization/preheating furnace; and CO_2 absorption unit.

The gas pipelines have the following characteristics: The fuel gas line from the Mobil refinery is 13.7 km. long and 400 mm. (16 in.) in diameter; and the feed gas line from the Shell refinery is 11.2 km. long by 500 mm. (20 in.) in diameter. They follow a fairly complex path through residential and light industrial areas, and they also traverse some marsh lands below sea level. The depth generally is about 3 m. Syphons (reservoirs for collection of condensate) are situated at low points, and they are drained weekly. Pigging equipment was provided but never used until May, 1976.

The two gas compressors are characterized as follows. *Feed gas*: centrifugal; 3,000-hp.; 15,000 kg./hr. throughput; suction pressure 2.5 bar; discharge pressure 40 bar.; gas density range (relative to air) 0.6 to 1.1. *Fuel gas*: rotary screw; 600 hp.; 14,000 kg./hr. throughput; suction pressure 1 bar; discharge pressure 3.3 bar; gas density range (relative to air) 0.9 to 1.4.

The reformer design is characterized by having tubes of larger than normal diameter; being 4 in. ID. The reformer is otherwise a conventional down-firing furnace, apart from having dual fuel burners.

The CO_2 removal system uses the Giammarco Vetrocoke solution for absorption (arsenic-activated potassium carbonate solution). It has been the plant limitation when using the originally specified ceramic saddles. Installation of polypropylene pall rings proved the worth of changing the packing. An incident in which these were melted by steam led to stainless steel pall rings being installed in May, 1976.

In the 1960's, the raw material cost position in South Africa made refinery gas and naphtha the raw materials giving lowest capital cost for ammonia manufacture.

Consider a 600 ton/day plant. Then compare the costs of making this quantity of ammonia from refinery off gas or from naphtha. This balance sheet is drawn up with hind-sight since some of the factors were unknown in the 1960's when the plant was designed. It should also be noted that the cost figures are *not* 1976 costs.

Capital and production costs

Table 2 is a list of additional capital items necessary for a dual feedstock gas/naphtha unit over and above a purely naphtha-based unit. Some items where capital savings are made because of dual feedstock are also included.

Assuming a feed/fuel usage of 57 Gigajoules (540 Therms)/ton ammonia and costs of $0.40/Gj. for gas and $0.65/Gj. for naphtha, the difference in the cost of an annual

$$160,000 \times 57 \times (0.65 - 0.40) = \$1,368,000/yr.$$

In practice, an uninterrupted gas supply cannot be expected and the above difference must be reduced, on Umbogintwini experience, to $1,100,000 to allow for a 30,000-ton/yr. shortfall in gas.

The figure of $1,100,000 is a broad approximation because it assumes an equal thermal efficiency for gas and naphtha operation which is found to be reasonable in practice.

At Umbogintwini there is an additional penalty when running on naphtha as our feed gas contains some 30 ppm. of sulfur, whereas raw naphtha contains some 700 ppm. (as liquid). This means that about 107 ton/yr. of additional sulfur must be removed if we were to run solely on naphtha. The cost of this additional zinc oxide catalyst would be $20,000/yr.

The Umbogintwini plant runs with a crew of seven men/shift (including the foremen). An all-naphtha plant could probably operate with less. Additional labor costs

Table 2. Economics of ammonia production: capital cost (in $ thousands)

Gas pipelines from refiner	1,500
Gas compressors	350
Additional burners	50
Pipework and instrumentation	50
Reduced naphtha storage	−50
Reduced preheat capacity	−5
Total additional capital	**1,800**

Table 3. Economics of ammonia: production cost

Annual production, tons	160,000
Feed/fuel usage, Gj/ton	57
Gas cost, $/Gj	0.40
Naphtha cost, $/Gj	0.65
Increased cost, on naphtha, $160,000 \times 57 \times (0.65 - 0.40)$, in $/yr.	1,368,000
Or. $1,000,000/yr. less shortfall.	

Table 4. Balance sheet: operation on gas instead of naphtha ($ thousands/yr.)

	Credit	Debit
Feedstock savings	1,100	——
Additional ZnO	20	——
Additional labor	——	40
10% interest on additional capital	——	180
Excess	——	900
Totals	**1,120**	**1,120**

Thus, advantage in using gas feed instead of naphtha is $900,000/yr.

are thus $40,000/yr.

An abbreviated annual balance sheet is given in Table 4. From this it may be seen that the incentive is to use refinery off gas to the tune of $900,000/yr.

It should be born in mind that the above comparison assumes equal production whether on naphtha or gas. The Umbogintwini plant was designed primarily to use gas feed. and it loses production when on naphtha. As we have normally run in a production limiting environment, we have suffered large financial losses due to low production on naphtha feedstock. We recommend that nay dual feedstock plant should be designed to give the required output on naphtha as well as on gas.

How the feed and fuel streams are monitored

A radio telephone/telemeter link between both refineries and the plant provides communication, and also some predictive information. Figure 2 shows the systems. Flow rates of gas at both refineries are indicated and also for the feed gas: density (related to hydrogen content) and H_2S content *at the refinery end of the pipeline*.

When the refinery is operating well, feedstock gas contains about 20 ppm. sulfur. This can, however, go up to some thousands of ppm. during a refinery upset. It is essential therefore to have this sulfur monitoring if premature saturation of the desulfurizing catalyst is to be avoided.

We have had instances of olefin breakthrough into the gas supply, and the first sign has been a rise in temperature in our cobalt/molybdenum sulfur hydrogenating catalyst. The answer to this problem is careful design of the gas reticulation system at the refinery.

In a plant of this nature, the feedstock varies in composition and calorific value over the long term (weeks) according to the crude oil being processed and the refineries own production priorities.

In the short term, if the refinery is subject to an upset such as a power failure the ammonia plant may have to switch its firing or feed load to naphtha within 15 min.

In general, the plant is operated with the density (relative to air) of the gas as criterion for the operation of the "front end." This density varies with the quantity of hydrogen in the feed , and is used to determine the "carbon feed rate,"
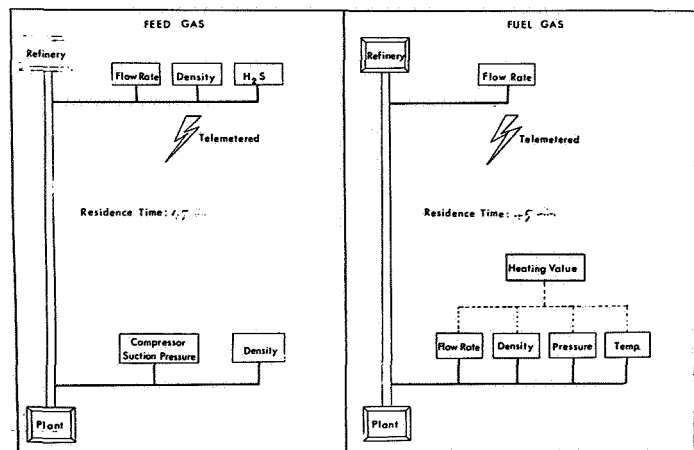

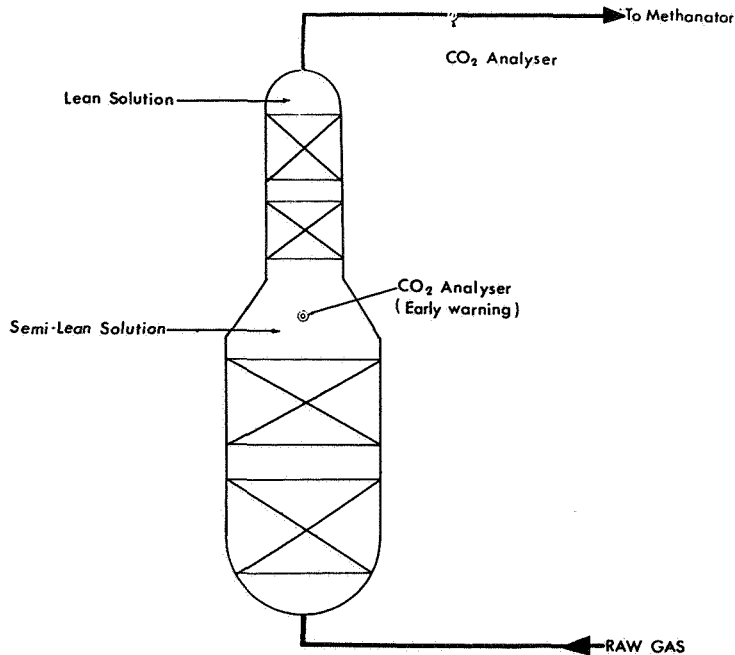Figure 2. Monitoring of the gas supplies.

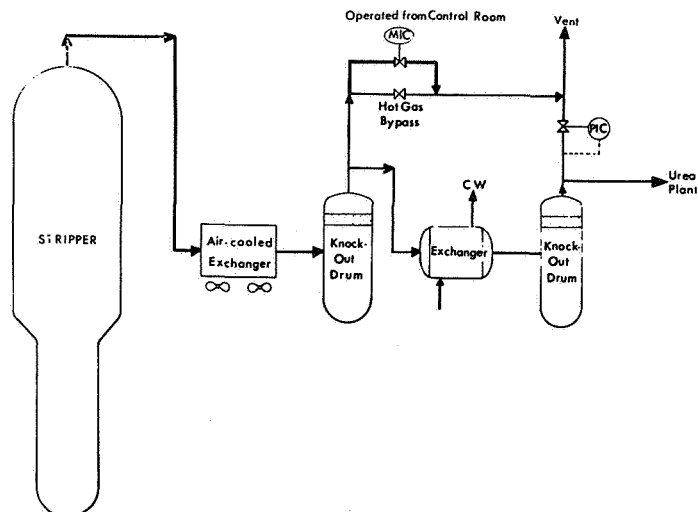**Figure 3. Carbon dioxide absorption, showing analyzer locations.**

Figure 4. Remote-operated hot gas by-pass system for carbon dioxide removal water balance.

i.e., the molar rate of carbon in the hydrocarbon gas; by which the reforming steam rate is set. The design steam/carbon ratio is 3.5, but this is normally run slightly higher for reasons set out below.

The effect of a "density swing" through the plant may be explained as follows. See Figures 3 and 4. Suppose the density changes from 0.8 to 0.60 in 10 min. This would be considered fairly normal, although not frequent. It would first indicate on the telemetered charts some 40 min. before arrival at the plant.

As the lower density enters the feed compressor, the speed will increase (The feed gas compressor operates at maximum governor speed at all times to allow the speed to increase when the gas density drops. This is to prevent surge at low density.) The temperature exit the feed preheater furnace may swing because the heat capacity change. The temperature exit primary and secondary reformers will increase because of a different reforming reaction and gas velocity. Already the air mix is off-specification although

it does not show yet, apart from the secondary reformer top temperatures. The shifters may hiccup, but the bottle-neck on the plant, CO_2 removal, will show the greatest effect: less slip for low density, worse for high density (or naphtha). Any change in slip will show in the methanator temperature. Finally the H_2/N_2 ratio in the loop will change.

Large increases in CH_4 during an upwards density swing will require increased purging of the "syn" loop to keep the converters at the correct temperature. This is aggravated by the fact that while an increase in density gives an increase in CH_4, it also results in an air-rich syn loop gas mixture. Even the refrigeration section will swing.

Understanding, feel, and anticipation for the effects of any given condition is an essential part of an fully competent operator in this plant.

Feed rate control method

The feed gas compressor operates with maximum steam rates to the turbine. Gas pressure is controlled by a kickback valve which has a trip open mechanism for surge protection. At very low densities (spec. grav. 0.4) the kickback has to be opened at the expense of partial loss of feed to prevent surge.

The flow controller for gas feed rate has a linearized indication which is corrected for temperature, pressure, and density to operate a steam/carbon ratio computer (pneu-matic). Hence an increase in density will cause a higher mass flow to be indicated, although a molar carbon feed rate is not proportionally higher. Automatic flow controller action would, however, reduce the effective plant (molar) feed rate. Manual valve positioning has been found to be the more stable mode of operation.

Reformer temperatures can vary considerably with the difference in reforming reactions. Remote control fuel valves often have to be helped by lighting up or dousing arch burners.

Determination of correct air rate with varying composi-tion feed stock is difficult. An error here may not show till some time later in the synthesis loop when the hydrogen/ nitrogen ratio goes out of specification. It took some years of operation before it was realized that if primary reforming was good, the rate of air addition could be roughly controlled by keeping a constant mixing zone temperature in the sec-ondary reformer.

Two points of interest are to be found in CO_2 adsorption (vetrocoke). To help anticipate the changes in CO_2 load due to the vary ing feedstock, it has been found advantageous to install a CO_2 monitor midway (semi-lean entry tray) in addition to the normal one at the exit. This gives some warning before CO_2 slip occurs. It also allows some feel for the "balancing" of the absorption in the top and bottom sections. See Figure 5.

The other innovation is a remote-controlled "hot gas" bypass in the CO_2 system. See Figure 6. Since there is normally an excess of CO_2 over that required by the down-stream urea plant, it is possible to vent some of the wet CO_2 exit the stripper in between the air-cooled heat exchanger and

SAS DENSITY   SAS FEED RATE   NAPHTHA RATE   REFORM STEAM / SAS INTO REFORMER   AIR RATE TO SECONDARY   SYN LOOP PRESS
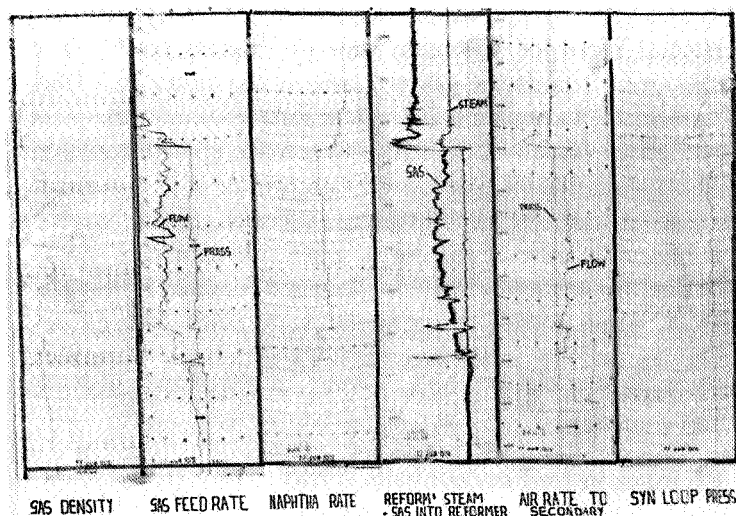
Figure 5. Chart readings for three operating vari-ables to help anticipate changes in carbon dioxide load due to feedstock variations, three charts at left); the remaining three charts on right are for operating variables in remote-controlled hot gas by-pass in the carbon dioxide system.

the final water-cooled exchanger/knockout drum.

This adjustment to the water balance of the system enables control to be maintained in some instances where solution strength would otherwise rapidly become dilute. This valve is adjusted from the control room.

Some difficulties are encountered in the setting of purge rate exit the synthesis loop. The amount of inerts is largely set by reformer operation, but obviously slips of CO_2 exit the absorber will lead to appreciable methane levels in the make-up gas after the methanator.

The operation of the purge is largely set by "feel," with an eye for analysed methane level, converter tempera-tures, synthesis loop pressure, and circulating rate. This is a section of the plant that is under review in the present climate of high feedstock costs.

Operation on naphtha and mixed feed

At Umbogintwini the raw naphtha storage is 1,800 tons. The suppliers have always managed to meet the fluctuating demand for naphtha caused by varying supplies of gas.

Operation on pure naphtha feed is reasonably straight-forward. There are none of the feed variations that are a normal part of refinery gas operation.

However, there are two areas of the plant which are some-what of a bottleneck. The first is the feed preheater furnace, where a limit in heat transfer and firing is reached on high-rate naphtha feed (120% of design carbon feed rate). An attempt is being made to overcome this by installing steam-heated exchangers to take the naphtha to its (operating pressure) boiling point and thus reduce the heat load required in the furnace.

The second bottleneck is the CO_2 absorption system which quickly reaches its limit because of the heavier carbon load in the feed.

Production on full naphtha feed has seldom exceeded 590 ton/day.

37

The refinery gas supply has decreased lately, and the normal mode of operation now is "mixed feed." The maximum amount of gas available is fed to the unit (this prouces the most ammonia) and the difference up to the plant bottleneck (usually CO_2 removal) is made up with naphtha. This means that the plant can always operate at its maximum capacity under the circumstances, although production cost is higher because of the use of expensive naphtha.

The "moment of glory" for the plant occurred in August, 1974, when special arrangements were made with the refineries, and the plant was run at 129% of design gas rate plus 8% naphtha for a daily make of 720 ton. The design make is 545 ton/day.

Changes in feed occasionally tricky

The change of feed from mainly gas to all-naphtha feed is again a tricky procedure. The accompanying process charts indicate some of the points to be made. The effects are similar to that of bad density swings. These are very much more wild in the event of a "crash-down" on the refineries.

Fortunately at Umbogintwini the fairly long gas pipelines gives sufficient time for a change to naphtha to be made— provided operators are on their toes and some naphtha is already being used as fuel. If an ammonia plant is being built next to a refinery, we would recommend some form of gas storage.

Part of the problem in changeover lies in the phenomenon of the naphtha not being "seen" until some 20 min. after its introduction as feed. It is surmised that this is in some way connected with a "hold-up" of vaporizing liquid naphtha in the preheater furnace tubes or desulphurizer vessels.

The naphtha used contains sulfur compounds in the order of 700 ppm. in the liquid. This is largely organic sulfur and the reaction over "CoMox" catalyst therefore requires hydrogen.

Under straight-naphtha conditions this would be supplied by recycle of synthesis gas, but it will be obvious that hydrogen-rich feed gas will do the job as well. This is, in fact, a standard plant procedure, and synthesis gas is only recycled if feed gas is in very short supply. Substantial

savings are incurred here since the following volume of make-up gas is much reduced, and higher feed rates may be used.

There are a considerable number of items that have suffered because of the varying feed stock.

Primary reformer tubes were changed after only four years of operation. This was in part due to the "bumps" experienced from density swings. The secondary reformer burner head has been a source of trouble since inception. The varying feed means that temperatures in the mixing zone can go very high unless carefully watched. The auxiliary boiler has suffered through vibrations occurring during heavy firing on naphtha and an incorrect change to bricking of the walls instead of casting and guniting.

Primary and secondary reformer catalysts were initially changed annually, although two-year runs are now achievable. Sulfur poisoning and carbon laydown are occasionally a problem in the primary reformer, usually arising from some feed upset.

An extra CoMox bed in the first-stage desulphurizer has given better utilization of the zinc oxide.

Secondary reformer catalyst is subject to fusing and channeling. A potash-free catalyst is being used successfully in the bottom of the primary reformer tubes to minimize potash migration and thus reduce fouling of waste-heat boilers and shifters.

Shifter catalysts are reasonably long-lived and give little trouble out of the ordinary.

The methanator catalyst has served very well, despite regular temperature excursions and a number of high-temperature trips due to the overloaded CO_2 absorption system.
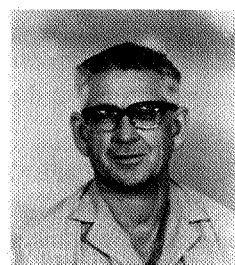
Conclusion

Despite the comparatively high costs of operation on refinery products, this plant has performed excellently and has one of the highest productions of ammonia for a standard plant of its type. This is in part due to the ability to use alternative feedstocks for operation continually at the limit. The yeat 1975 was the best so far. with a production of 206,000 metric tons (227,000 short tons) of ammonia.   #

CARTER, K.A.   **LONSDALE, H.**   **KLOPPERS, J.J.**   **MARTENS, G.J.**

DISCUSSION

JOHN WEISZ, Standard Oil Co. (Ohio): Do you clean the gas up, (such as with hydrodesulfurization)? What kind of catalyst do you use to keep from having coking of the high molecular weight hydrocarbons? Are you getting this type of coking or do you have a special steam reforming catalyst that can reform higher

molecular weight naphtha fractions?
MARTENS: That is one of the problems. In other words, the steam carbon ratio goes down, then you get coking.

There is also the possibility of getting other things from the refinery and this has also caused us coking

problems in the reformer.

BOB OSMAN, Exxon Chemical Co.: Your mention that you use a gas density analyzer for monitoring your feed gas. Could you tell me what type of analyzer for monitoring your feed gas. Could you tell me what type of analyzer you use, and whether you've had good service with it?

MARTENS: Both refinery gas streams have a density analyzer on them and I think it's a Kent meter. I could come back to you on that. I know that it depends on the gas viscosity—it has two spinners and the difference in torque between the gas and the air indicates the density. We've had pretty good service on the refinery gas, the feed stock stream—the fuel gas stream is a very dirty gas and has a lot of H_2S in it with iron sulfide and the like. That analyzer has given us a lot of problems.

OSMAN: You also mentioned that you had problems with the secondary reformer air distributor? Could you tell me generally what type of distributor you are using?

BADREL DIN, Petrochemical Industries, Co., Kuwait: Do you have the same fluctuations in your fuel gas also, and how do you control your burners—do you keep trimming them all the time when you have such large fluctuations on fuel gas?

MARTENS: Yes, the fuel gas can also have density fluctuations. You have in fact answered the question— we do just manually trim the burners to keep the furnace on line. Your will appreciate if the feed starts going up and down, it's pretty much a manual operation to keep the furnaces in trim anyway.

MARTENS: Up to 1974 we used a burner designed by Kellogg. It has a double walled nose cone. The air distributes itself down through the double wall, cooling the tip and then goes inside and comes out through 55 holes. And it has a sort of finned distributor around the side. That's the one that gave us problems. We have now gone on to a burner designed by ICI, which is basically 2 concentric rings fed from a central pipe, and these have simple holes in them.

OSMAN: And did you attribute your problem to the cyclic nature of the secondary reformer operation, due to change in gas composition?

MARTENS: Yes, I think it's pretty much totally due to that.