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RECYCLE PURGE GAS FOR ADDITIONAL AMMONIA PRODUCTION FROM AN EXISTING AMMONIA PLANT
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SUMMARY

Installation of a purge gas recovery (PGR) unit is the modern trend for additional production from an existing ammonia plant. Shriram has placed an order for PGR unit for their 600 TPD ammonia plant at Kota in India. The installed cost for complete unit will be about Rs. 20 million & additional ammonia production shall be 17 TPD. The PGR unit is scheduled to be commissioned in the first quarter of 1985. Meanwhile, as a first step towards achieving additional production, 1000 NM^3/hr of purge gas from synthesis loop was recycled into primary reformer exit gases. In actual practice over a period of seven days, additional ammonia production was 6 TPD and no detrimental effect was observed anywhere in the plant. It costs Rs. 0.05 million for installing the purge gas recycle system. This paper gives steady state mass balance both for the base plant & the plant with purge gas recycle. It explains how additional ammonia production is achieved by recycling purge gas.

PURGE GAS RECYCLE

Ammonia is produced by synthesis of a gaseous mixture containing hydrogen and nitrogen in the ratio of approximately 3:1. In producing this synthesis gas by steam reforming of naphtha, methane is also formed. Make-up synthesis gas besides containing methane, also contains argon. This comes along with air which is added in the secondary reformer.

Methane and argon present in synthesis gas do not take part in any reaction in ammonia converter whereas N_2 and H_2 are continuously getting converted to ammonia. As a result of this, methane and argon build up in the synthesis loop and are to be purged out to operate at a constant inert level. This gas which is purged out contains nitrogen and hydrogen also. At Shriram Fertilizers & Chemicals, Kota plant, this gas along with fuel naphtha was being burnt in the primary reformer to recover fuel value of hydrogen and methane till the idea of recycling this purge gas to secondary reformer was conceived. In this arrangement 1000 NM^3/hr of purge gas is recycled to secondary reformer resulting in an additional production of about 8 TPD.

By recycling purge gas to secondary reformer, most of the methane contained in this gas gets reformed. The argon of course is not affected. In addition to this, some more argon is added along with the additional air added in the secondary reformer. By recycling 1000 NM^3/hr of purge gas, the net effect is addition of H_2, N_2, methane and argon at the rate of 42, 14, 1.3 and 2.6 kg moles/hr respectively in the make-up synthesis gas.

By the addition of purge gas at primary reformer outlet, the temperature of secondary reformer inlet as well as outlet drops by about 7° C for 1000 NM^3/hr of recycle gas (Table I), as the recycle purge gas is at 40° C after scrubbing of ammonia in a wash tower. This results in a comparatively higher methane slip from secondary reformer. Estimated increase for Shriram plant is about 0.03% over and above the design of 0.29%. This effect can be reduced by preheating the recycle purge gas.

ADDITIONAL AMMONIA PRODUCTION

With increased inert level in the make-up synthesis gas, higher purge at the rate of 4404 NM^3/hr instead of 3951 NM^3/hr (Base Plant figure on dry basis given in Table III) is to be kept. This higher purge is less than the additional hydrogen and nitrogen in the make-up gas, thus resulting in a higher nitrogen and hydrogen availability for ammonia production. It can be seen from the mass balance (Table I) that consumption of nitrogen and hydrogen in the synthesis loop goes up by about 10 and 30 kg moles/hr respectively resulting in a higher production at 8 TPD of ammonia.

NAPHTHA AND POWER CONSUMPTION

Due to this purge gas recycle, net gas available for burning in primary reformer reduces by 14.55 kg moles/hr of H_2 and 4.83 kg moles/hr of methane (Table III). This means 1.8 M Kcal /hr which is equivalent to about 4 TPD of naphtha. Thus, for producing 8 TPD of additional ammonia, 4 TPD of naphtha is required instead of about 6.5 TPD (9.83 T/T ammonia for base plant) required for producing it in the normal manner.

Additional power required for this 8 TPD ammonia is 866 Kwh/t (Table II). In the base plant power requirement for production of ammonia is 930 Kwh/t on ammonia.

ACTUAL RESULTS OBTAINED

In actual practice at Shriram plant at Kota, additional ammonia production over a period of seven days with 1000 NM^3/hr of purge gas recycle was 6 TPD and there was no detrimental effect observed anywhere in the plant.

TABLE I

ADDITIONAL AMMONIA PRODUCTION WITH PURGE GAS RECYCLE

1. <u>Temperature drop in Secondary Reformer</u>

    By introducing purge gas recycle available at 40° C, secondary reformer inlet gas temperature reduces by about 7° C. Calculations are as given below:

Primary Reformer outlet design	- Flow	= 5021 kg moles/hr
	- Temp.	= 784° C
Purge gaz recycle	- Flow	= 44.64 kg moles/hr
	- Temp.	= 40° C

$$\text{Drop in gas temperature °C} : 784 - \frac{5021 \times 784 + 44.60 \times 40}{5021 + 44.65}$$

$$: 784 - 777.4$$

$$\text{Say} : 7° C$$

Since Primary Reformer exit temperature drops by 7° C, secondary reformer exit temperature is expected to drop by little more than 7° C because reformer exit gases now contain some nitrogen (due to purge gas recycle) and as a consequence air addition to the secondary reformer shall be less than proportionate. However, on a conservative basis, taking that secondary reformer outlet gas temperature will also reduce by about 7° C, Secondary Reformer outlet will be 960-7 = 953° C. From equilibrium methane % graphs (Topsoe's operation manual-ammonia plant), it is estimated that methane percentage at secondary reformer outlet will increase by about 0.031% for a 7° C drop in outlet temperature.

Methane slip-in base plant	= 0.2967%
-after purge gas recycle	= 0.2967 + 0.031
	= 0.3277%

2. <u>Mass balance calculations (dry basis)</u>

    A steady state mass balance has been worked out for base ammonia plant with 1000 NM^3/H of purge gas recycle. It is given in Table IA. Let X kg moles/hr of methane be reformed:

$$CH_4 + H_2O = CO + 3 H_2O$$
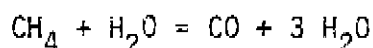
From the steady state mass balance, we have

Component	Primary Reformer Outlet	Purge Gas Recycle	Air addition (1019.16 kg moles/h) and H_2 combustion	CH_4 Reforming	Secondary Reformer Outlet	
H_2	1672	26.61	- 427.80	+ 3 X	1270.81+3X	1999.45
CO	266	-	-	+ X	266 + X	508.88
CO_2	425	-	-	-	425	425
CH_4	249	6.25	-	- X	255.25-X	12.37
N_2	6	9.15	795.21	-	810.36	810.36
A	-	2.63	10.05	-	12.68	12.68
TOTAL:	2618	44.64	377.46	+ 3 X	3040.10+3X	3768.74

$$\% \text{ of } CH_4 = 0.3277 = \frac{255.25 - X}{3040.10 + 3 X}$$

Therefore, X = 242.88

Value of X is substituted to get kg moles/hr of H_2, CO, CO_2, CH_4, N_2 & A at the Secondary Reformer exit. These are given in last column of the above table.

- After secondary reformer, shift conversion reaction ($CO+H_2O = CO_2+H_2$) takes place in HTS & LTS.

- CO_2 is absorbed in HPC Absorber after which gas goes to methanator inlet. Composition is given in table below:

Component	Methanator Inlet	Methanator Outlet	Make up Gas	Recycle to FSRU** and losses
H_2	1999.45-10*+508.88-14=2484.33	2484.33-42-12= 2430.33	2360.36	69.97
CO	14	-	-	-
CO_2	3	-	-	-
CH_4	12.37	29.37	28.52	0.85
N_2	810.36-4*=806.36	806.36	783.14	23.22
A	12.69	12.69	12.31	0.38
TOTAL:	3332.74	3278.74	3184.33	94.42

*10 kg moles/hr of H_2 and 4 kg moles/hr of N_2 get dissolved in HPC solution in CO_2 Absorber.

**Final Sulphur Removal Unit.

To arrive at a steady state condition, total inerts (CH_4 + A) in the make up gas have to be same as the total inerts leaving the synthesis loop as purge gas. There is some dissolution loss also. On this basis, purge gas flow rate works out to be 196.61 kg moles/hr with the following composition.

Component	kg moles/hr.	%
H_2	117.18	59.6
N_2	40.31	20.5
CH_4	27.52	14.0
A	11.60	5.9
TOTAL :	196.61	100

3. <u>Additional ammonia production calculations</u>

From the above mass balance, we have

- Nitrogen consumption

    = 783.14 - 40.31
    = 742.83 kg moles/hr

- Hydrogen consumption

    = 2360.36 - 117.18
    = 2243.18 kg moles/hr

- With purge gas recycle, additional consumption of.
    - N_2 in the loop

        = 742.83 - That in base plant
                    (Table III)
        = 742.83 - 733.04
        = 9.79 kg moles/H

    - H_2 in the loop

        = 2243.18 - That in base plant
                    (Table III)
        = 2243.18 - 2213.16
        = 30.02 kg moles/H

- Additional ammonia production
    - On N_2 consumption basis

        = 9.79 x 2 x 17 x 24
        = 7988 kg/D

    - On H_2 consumption basis

        = 30.02 x $\frac{2}{3}$ x 17 x 24

    - Or Say 8 TPD.

<u>MATERIALS & UTILITIES CONSUMPTION FIGURES PER TON ADDITIONAL AMMONIA PRODUCED WITH PURGE GAS RECYCLE</u>

There shall be improvement in specific consumption of both naphtha & power with purge gas recycle as compared to that of base ammonia plant.

AMMONIA PLANT WITH PURGE GAS RECYCLE-MASS BALANCE

TABLE I-A

PRIMARY REFORMER

PROCESS AIR

Kg Moles/Hr
N_2 = 795.21
O_2 = 213.9
A = 10.05

PURGE GAS RECYCLE

	Kg.Moles/Hr	Mole %
H_2	1672	63.86
CO	266	10.16
CO_2	425	16.23
N_2	6	0.24
CH_4	249	9.51
TOTAL	2618	100.00

	Kg.Moles/Hr	Mole %
H_2	2484.33	74.54
CO	14	0.42
CO_2	3	0.09
CH_4	12.37	0.37
N_2	806.36	24.20
A	12.68	0.38
TOTAL	3332.74	100.00

	Kg.Moles/Hr	Mole %
H_2	69.97	74.12
N_2	23.22	24.59
CH_4	0.85	0.90
A	0.37	0.39
TOTAL	94.41	100.00

RECYCLE GAS TO F.S.R.U

	Kg.Moles/Hr	Mole %
H_2	2360.36	74.12
N_2	783.14	24.59
CH_4	28.52	0.90
A	12.31	0.39
TOTAL	3184.33	100.00

SECONDARY REFORMER

SHIFT CONVERSION & CO_2 ABSORPTION

METHANATOR

Kg.Moles/Hr
H_2 CONSUM.=2243.18
N_2 CONSUM.= 742.83

	Kg.Moles/Hr	Mole %
H_2	26.61	59.6
N_2	9.15	20.5
CH_4	6.25	14.0
A	2.63	5.9
TOTAL	44.64	100.00

	Kg.Moles/Hr	Mole %
H_2	1999.45	53.06
CO	508.88	13.50
CO_2	425.00	11.27
CH_4	12.37	0.32
N_2	810.36	21.51
A	12.68	0.34
TOTAL	3768.74	100.00

	Kg.Moles/Hr	Mole %
H_2	2430.33	74.12
N_2	806.36	24.59
CH_4	29.37	0.90
A	12.68	0.39
TOTAL	3278.74	100.00

SYNTHESIS

PURGE GAS

WATER WASH

AMMONIA PRODUCT

PURGE GAS TO H.D.S & FUEL

	Kg.Moles/Hr	Mole %
H_2	90.57	59.60
N_2	31.16	20.50
CH_4	21.27	14.00
A	8.97	5.90
TOTAL	151.97	100.00

	Kg.Moles/Hr	Mole %
H_2	117.18	59.60
N_2	40.31	20.50
CH_4	27.52	14.00
A	11.60	5.90
TOTAL	196.61	100.00

——— PURGE GAS RECYCLE-LINE

——— BASE PLANT

TABLE II

Item	Unit	Base Plant	With purge gas recycle (Addl.)
- NH$_3$ Production	M.T.	600	8
- Per ton ammonia			
- Naphtha	M.T.	0.830	0.506
- Power	Kwh	930	866

The details of 0.506 T/T & 866 Kwh/T for additional 8 TPD ammonia production are given below.

Naphtha efficiency calculation

		Unit	Base plant	Plant with purge gas recycle
In fuel gas	- H$_2$	kg moles/H	105.12	90.57
	- Methane	"	26.10	21.27
	- Heat of combustion	Kcal/kg mole		
	- H$_2$		57,800	57,800
	- Methane		191,760	191,760
	- Total heat value	M Kcal/h	11.08	9.31

Therefore, - additional heat to be supplied : $(11.08-9.31) \times 10^6$

                                                      : 1.77×10^6 Kcal/H

           - equivalent naphtha   : $\dfrac{1.77 \times 10^6}{10500}$

                                                      : 168.57 kg/hr.

           - Additional ammonia production : 8 T/D

           - Naphtha per Ton addl. ammonia : $\dfrac{168.57 \times 24}{1000 \times 8}$

                                                        : 0.506 Ton

Power requirement calculations

Kwh/Ton

Basis: Power consumption in base ammonia plant -

		Kwh/Ton
- Processing gas from HDS to synthesis compressor section	=	130
- Process air compression	=	200
- Synthesis gas compressors and refrigeration	=	600
TOTAL	=	930

A. For air compression:

Power required for air compressor is 200 Kwh/T for compressing 1012.5 kg moles/hr of air.

- Power consumption in air compressors for base plant =
  600 x 200 = 120000 Kwh/day for 1012.5 kg moles/hr.

- Power consumption with purge gaz recycle for air compressors

for 1019.16 kg moles/ hr air = $\dfrac{600 \times 200 \times 1019.16}{1012.5}$ = 120789 Kwh/day

- Excess power consumption in air compressors = 789 Kwh/day.

B. For processing gas from HDS to synthesis:

Power required for processing gas from HDS to synthesis in base plant is about 130 Kwh/ton for processing 3217 kg moles/hr of synthesis gas.

With purge gas recycle, gas to be processed= 3278.7 kg moles/hr.

Excess power consumption in processing gas = $\dfrac{600 \times 130 \times 3278.7 - 600 \times 130}{3217}$ = 1496 Kwh/day.

C. For ammonia synthesis:

Power consumption for synthesis compressors and refrigeration is about 600 Kwh/ton. Out of this about 400 Kwh/ton is used for compressing make-up gas and rest 200 Kwh is used for recirculation converter loop gas and refrigeration compressors. This can be assumed that recirculating and refrigeration power will remain same and there will be no extra consumption on account of purge gas recycle. Power consumption for compressing make up gas will increase by recycling purge gas.

Power consumption in base plant= 600x400 Kwh/day for 3124 kg moles/hr make-up gas.

. Excess power consumption with purge gas recycle for 3184.3 kg moles/hr =
$\dfrac{600 \times 400 \times 3184.3}{3124}$ - 600 x 400 = 4632.5 Kwh/day.

D. Total:

Total additional power consumption for purge gas recycle =
789 + 1496 + 4632.5 = 6917.5 Kwh/day.

Power consumption per ton of ammonia = $\dfrac{6917.5}{7.99}$ = 866 Kwh/t NH_3

BASE AMMONIA PLANT - MASS BALANCE (DRY BASIS)   TABLE III

Flow sheet figures for 600 TPD ammonia (Table III-A)   Unit: kg moles/hr

Component	Primary Reformer Outlet	Air Addition (1012.5 kg moles/h) and hydrogen combustion	Methane Reforming	Secondary Reformer Outlet
H_2	1672	- 425	+ 238x3	1961
CO	266	-	+ 238	504
CO_2	425	-	-	425
CH_4	249	-	249-238	11
N_2	6	+ 790	-	796
A	-	+ 10	-	10
TOTAL	2618	+ 375	+ 714	3707

Component	Methanator Inlet	Methanator Oulet	Make-up gas	Recycle gas to FSRU and losses
H_2	$1961-10^*+(504-14)=2141$	$2441-14\times3-3\times4=2387$	2318.28	68.72
CO	14	-	-	-
CO_2	3	-	-	-
CH_4	11	$11+14+3 = 28$	27.19	0.81
N_2	$796 - 4^* = 792$	792	769.20	22.8
A	10	10	9.71	0.29
TOTAL	3271	3217	3124.38	92.62

*10 kg moles of H_2 and 4 kg moles of nitrogen get dissolved in HPC solution in CO_2 absorber.

- To remove inerts (methane and argon) entering the synthesis loop, 176.38 kg moles/hr or gas are continuously purged from the loop.

Composition of purge gas is given below:

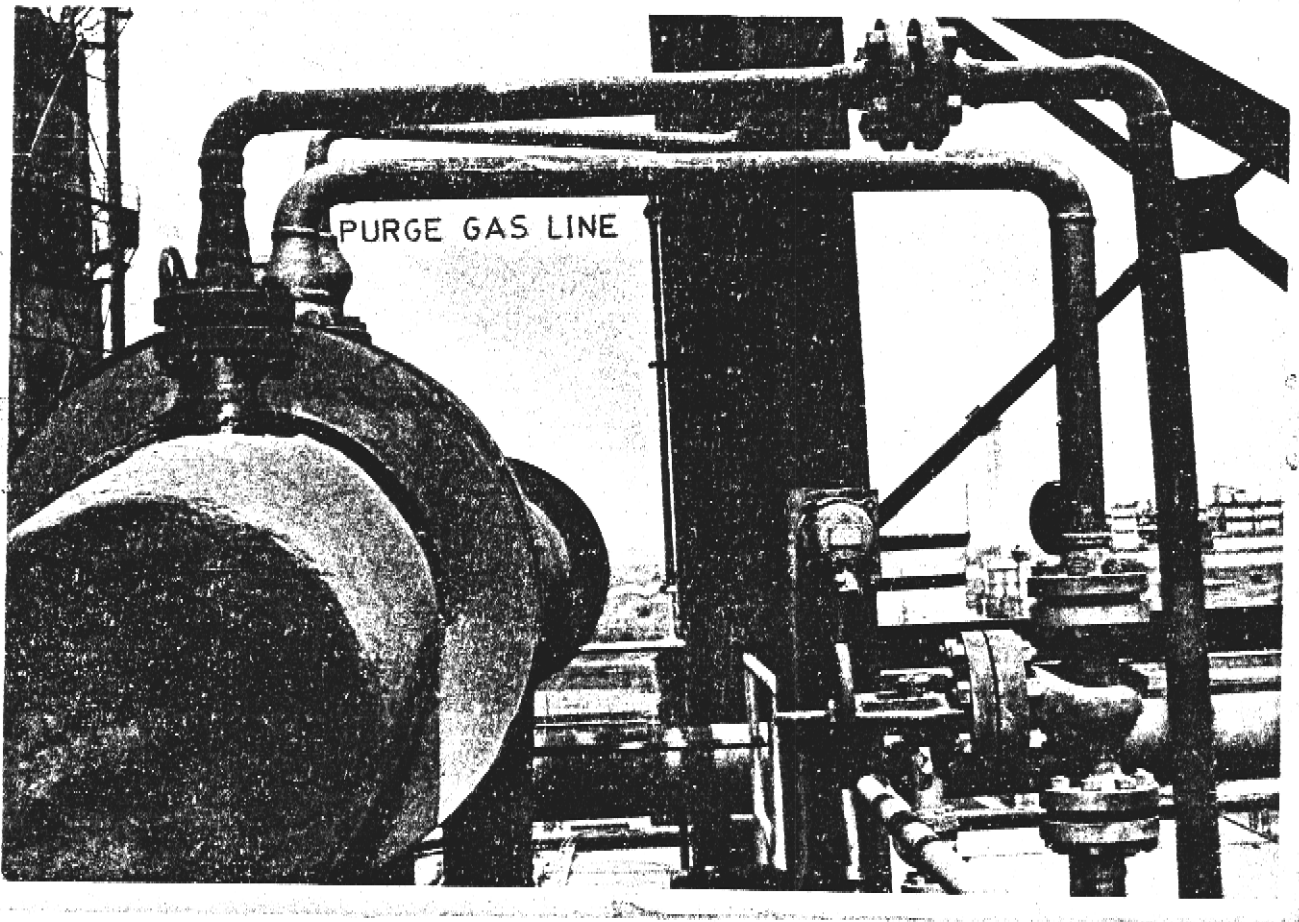| Component	kg moles/hr	%
H_2	105.12	59.6
N_2	36.16	20.5
CH_4	26.10	14.8
A	9.0	5.1
TOTAL	176.38	100

Nitrogen consumption = 769.20 - 36.16 = 733.04 kg moles/hr.

Hydrogen consumption = 2318.28 - 105.12 = 2213.16 kg moles/hr.

BASE AMMONIA PLANT-MASS BALANCE

TABLE III-A

PRIMARY REFORMER

RECYCLE GAS TO F.S.R.U & LOSSES

PROCESS AIR

Kg.Moles/Hr
N₂ = 790.0
O₂ = 212.5
A = 10.0

	Kg.Moles/Hr	Mole %
H₂	1672.0	63.86
CO	266.0	10.16
CO₂	425.0	16.23
N₂	6.0	0.24
CH₄	249.0	9.51
TOTAL	2618.0	100.00

	Kg.Moles/Hr	Mole %
H₂	2441.0	74.63
CO	14.0	0.43
CO₂	3.0	0.09
CH₄	11.0	0.34
N₂	792.0	24.21
A	10.0	0.30
TOTAL	3271.0	100.00

	Kg.Moles/Hr	Mole %
H₂	68.72	74.2
N₂	22.80	24.62
CH₄	0.81	0.87
A	0.29	0.31
TOTAL	92.62	100.00

	Kg.Moles/Hr	Mole %
H₂	2318.28	74.20
N₂	769.20	24.62
CH₄	27.19	0.87
A	9.71	0.31
TOTAL	3124.38	100.00

SECONDARY REFORMER → **SHIFT CONVERSION & CO₂ ABSORPTION** → **METHANATOR** → **SYNTHESIS**

Kg.Moles/Hr
H₂ CONSUM. = 2213.16
N₂ CONSUM. = 733.04

	Kg.Moles/Hr	Mole %
H₂	1961.0	52.90
CO	504.0	13.60
CO₂	425.0	11.46
CH₄	11.0	0.29
N₂	796.0	21.47
A	10.0	0.28
TOTAL	3707.0	100.00

	Kg.Moles/Hr	Mole %
H₂	2387.0	74.20
N₂	792.0	24.62
CH₄	28.0	0.87
A	10.0	0.31
TOTAL	3217.0	100.00

PURGE GAS TO H.D.S & FUEL

WATER WASH

AMMONIA PRODUCT

	Kg.Moles/Hr	Mole %
H₂	105.12	59.6
N₂	36.16	20.5
CH₄	26.10	14.8
A	9.0	5.1
TOTAL	176.38	100.00

PHOTOGRAPH I

It shows the purge gas line coming out of purge gas heat exchanger in ammonia synthesis loop and going to ammonia wash tower.
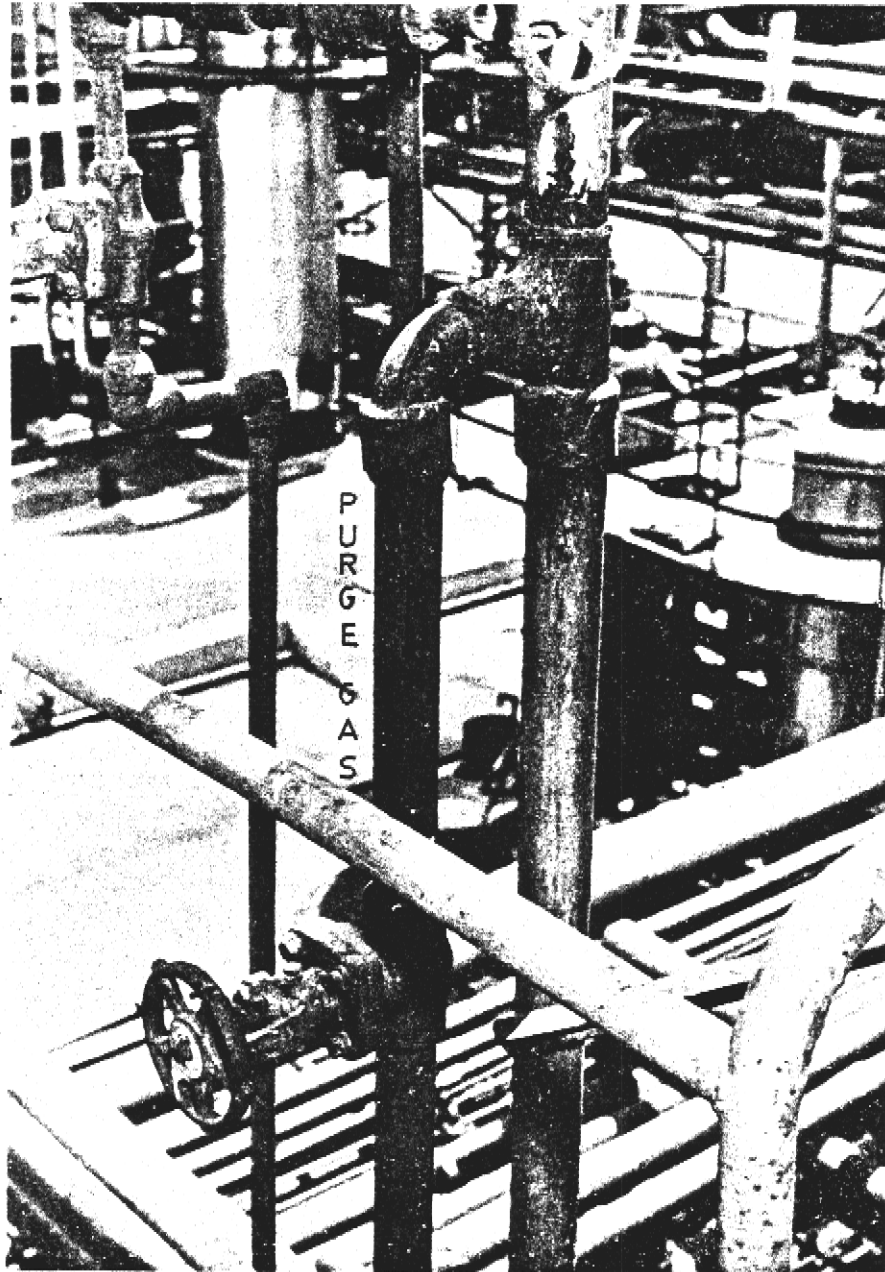
PURGE GAS

PHOTOGRAPH II

It shows the purge gas coming out of the ammonia wash tower and going to primary reformer exit.
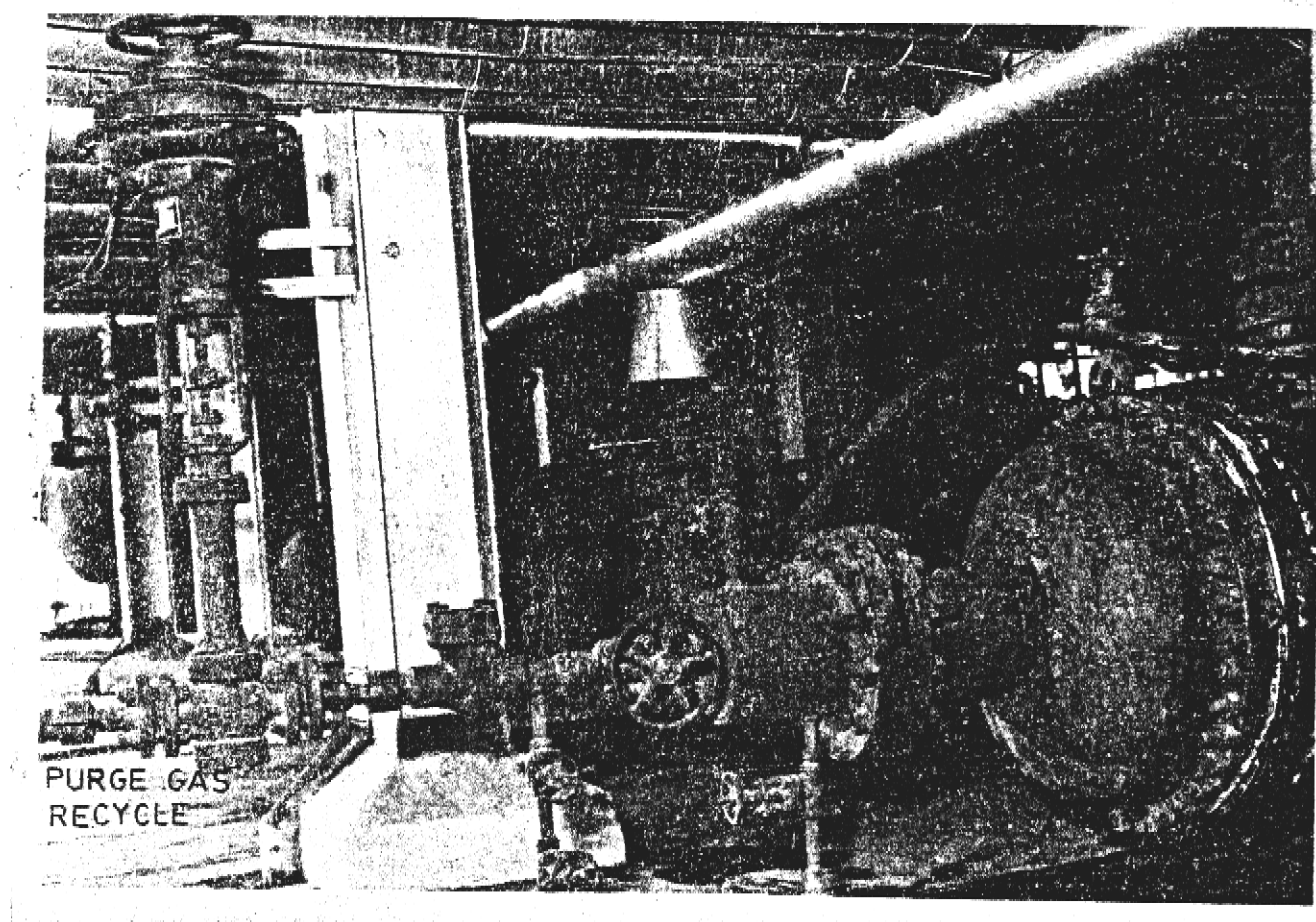
PHOTOGRAPH III

It shows the purge gas coming from ammonia wash tower and entering into one of the branch transfer lines exit the primary reformer through a control valve, non-return valve and isolation valve.