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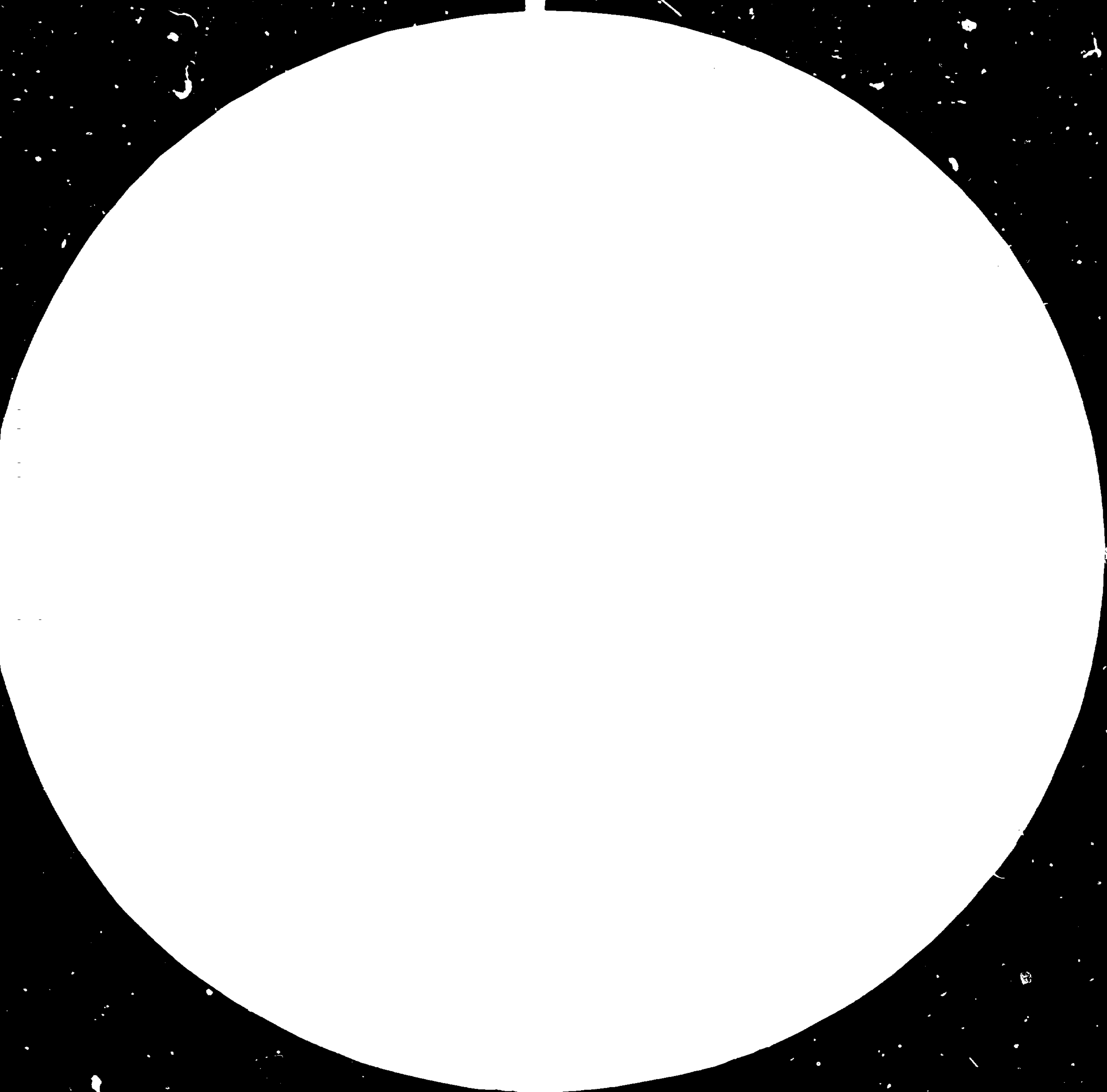

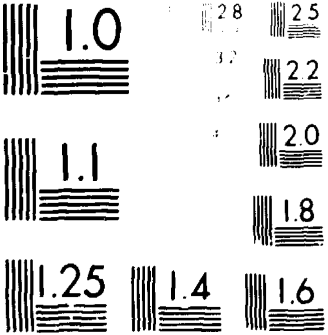
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200 MT/D AMMONIA PLANT WITH HEAVY OIL AS FEEDSTOCK*

by

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ABSTRACT

With heavy oil as feedstock, the process currently used in China for ammonia production is described in this article. The main leatures of this process are: Partial oxidation of heavy oil at 34 kg/cm^2 (A) and direct quenching of the high temperature crude gas are used in gasification. High/low temperature CO shift, A.D.A. (Anthraquinone Disulphonic Acid) desulfurization, modified hot carbonate CO_2 removal and mathanation are employed in gas purification. The features in ammonia synthesis and the utilization of heat energy are also described. It is considered that in the ammonia production scheme. It is advisable to use the direct quenching to recover the sensible heat in the crude gas and heavy oil to extract the carbon black in soot water and recycle the slurry back to gasifier as feedstock. Although there is a very small amount of water in the slurry it is still economical. The medium or small sized ammoria plants have advantages of low investment cost, short construction period, easily putting into operation and short R01 time.

INTRODUCTION

The partail oxidation of heavy oil to manufacture synthesis gas ammonia production has been practiced in China since 1964. From then on, a number of such plants have been built and put into operation in China. Their total capacity is about 25% of the total output by all the medium-sized plants in China.

Among the plants now operating in China, the output of water-gas per unit for the pressure gasifier is 360,000 NM^3/D. The gasifier is designed with a capacity for the average ammonia output of 200 tons per day. Currently the plants are steady in operation and their on-stream factor is over 90%.

In the past according to sulfur content in the feedstock there were two alternative schemes used to cool the high temperature crude gas from gasifier in our country --- W.H.B. and direct quenching. Recently, as a sulfur-resistent CO shift catalyst has been developed in China direct quenching scheme can also be used for the high sulfur feedstock. The 220 T/D ammonia plant using direct quenching scheme shall be presented in the following.

FEATURES OF THE PROCESS

1. Gasification

The partial oxidation process is adopted. According to the design conditions, as long as the oxygen oil and steam ratios are controlled strictly, steady operation can be acheived and the satisfactory composition of "effecient" gas can be obtained. On the aspect of recovering the sensible heat in the crude gas the direct quenching scheme gives a better recovery. Figure 1 shows the outline of a gasifying unit.

For the recovery of carbon black in soot-water the heavy oil extraction process with R.D.C. (Rotating Disc Contactor) is employed. The feature of this method is that the feedstock heavy oil is used as extractant instead of expensive naphtha. Since the oil-carbon black slurry can be recycled back to the gasifier as feedstock the feedstock consumption will be reduced. Figure 2 shows a heavy oil-extracting unit in a plant of the Lanzhou Chemical Industry Corporation.

2. Purification of the Crude Gas

The purification of the crude gas adopts the following scheme:

High/low temperature CO shift followed by desulfurization and CO_2 removal, and final removal the small amount of $CO.CO_2$ by methanation. For the crude oil in China, the sulfur Content in heavy oil is generally lower than 0.3% (wt), the high is more than 1% (wt). In China, a low temperature sulfur-resistent CO shift catalyst has been developed recently which has the good adaptability and low activity temperature. If the heavy oil contains more than 500 mg/NM^3 of sulfur, it can be used both in the high/low temperature conversions. With the application of this new catalyst the utilization of heat will become more reasonable, and much energy can be saved.

The A.D.A. method is adopted for desulfurization. Since more than 95% of organic sulfur has been already converted into inorganic sulfur during high/low temperature conversions, the efficiency of the A.D.A. desulfurisation method can reach ideal result.

The modified hot carbonate method is used for CO_2 removal. In comparison with other chemical absorption methods of similar type, this method possesses such advantages as non-toxic, lower consumption of steam, higher degree of purification, higher purity of CO_2, completely meeting the requirements of urea production.

3. Synthesis of ammonia

For the systhesis of ammonia, we use a process developed ourselves during 60's in China. The ammonia convertor comprises a medium pressure WHB for the recovery of reaction heat. According to the requirments of enduses, steam can be generated within the pressure range of 15-50 kg/cm^2(A).

In recent years the newly developed Chinese Type A-110 catalyst has been used in the synthesis of ammonia. It has such advantages as low active temperature, high ammonia convertion rate and high toxic-resistence.

4. The Steam System

The steam system was designed in accordence with a plant of the capacity of 220 MT/D, and employing steam turbines wherever feasible to fully utilize the residual heat.

According to the steam pressure required for the heavy oil atomization in the burner of the gasifier and considering the factors of boiler material, the steam parameters of auxiliary boiler was chosen to be 50kg/cm^2(G) and 425 ^oC superheat so that the inlet conditions of steam turbine and various steam parameters required in process can be met. For the sake of utilising the exhaust steam from steam turbine for heating in the urea unit, the total steam output of auxiliary boiler is enlarged to include the amount of steam consume for the manufacture of urea. Therefore, in this plant a set of steam turbine driven air compressor of 3600 KW and a set of 3650 KW generator are installed, in order to improve the energy cycle. Figure 3 shows the steam balance system of this plant.

PROCESS DESCRIPTION

The feedstock heavy oil, steam and oxygen are atomized through the burner into the gasifier, in which the reaction takes place.

The high temperature crude gas produced is quenched with hot water to saturate the gas with water vaper and to remove soot from it and then enters the high and low temperature CO shift unit. The soot water is sent to the R.D.C. carbon black extraction unit. The treated oil/soot slurry is sent back to the gasifier as a feedstock. The settled water is recycled to the gasification unit as carbon scrubbing agent. After the low temperature shift reaction, the CO content in crude gas is reduced to about 0.3 % (V). The effluent gas passing through the heat recovery system enters the A.D.A. sulfur removal unit, in which H_2S is reduced to about 3 ppm. The gas after going through heat exchanger to be heated up again enters the modified hot potassium carbonate CO_2 removal unit, in which the CO_2 content is reduced to 0.1%, and then passes through the ZnO desulphurization unit to make the total sulphur content in the gas reduced reduced to 1 ppm or less, finally enters the methanation unit to carry out the final purification so that CO and CO_2 in the synthesis gas is controlled within 10 ppm or less. The purified synthesis gas is compressed to 320kg/cm^2 (G) than sent to the ammonia synthesis unit to produce ammonia.

The process flow diagram is shown in figure 4. Summary of the main techno-economil figure. The composition and physical properties of the feedstock heavy oil are shown in Table 1.

Table 1. Composition and physiscal properties of the Feedstock

Composition (W%)		Physiscal Properties	
C	85.7	Specific gravity Y_4^{20}	0.9574
H	11.58	Viscosity (100°C)	9.1°E
O	0.85	Solidify Point	37°C
N	0.77	Flash Point	180°C
S	1.00	Carbon Residum	12%(wt)
Ash	0.1	HHV	10071 kcal/kg

Table 2 shows the typical operation conditions, under which a steady operation can be achived in the plant.

Table 2 Typical operation data:

1. Pressures	kg/cm^2
Gasifier	33
Ammonia Synthesis	320
Oxygen Compressor (reciprocating type) discharge	44
Steam in the auxiliary boiler	50

-Continued

Steam turbine inlet	45
L.P. boiler	3
NH_3 Product	22

2. Temperatures

	°C
Oil preheating	200
Oxygen pre-heating	100
Steam for gasification	400
Gasifier	1200-1500

The following table shows the anticipated techno-economic figures for the 220 MT/D ammonia plant

Table 3 Techno-Economic Figures

Item	Unit	Quantity
Anticipated consumption figures		
Per Ton NH_3		
Heavy oil:		
As feedstock	kg	778
As fuel	kg	500
Cooling water	M^3	452
Electric power	KWH	611
Steam out-put	Ton	-2.90
Sulphur product	kg	-7.64
Consumption total energy per ton NH_3	kcal	12.45×10^6

DISCUSSION ON MAJOR TECHNICAL QUESTIONS

1. Operating Experiences

The burner is one of the key devices in oil gasification. Nowadays, there are mainly two types of burners in operation : the combination type and air-current type. Their atomizing efficiency can perfectly meet the requirements of the condition for optimum operation.

Alloy Cr25Ni20 was usually used to make the burner tip in our country. It could be operated for more than 6 months. Recently a new kind ofmaterial containing elemenys of W and Mo is being experimented. With this new material to fabricate the burner tip the operating life of burner is expected to be further prolonged.

In recent years, as the result of the research work the quality of refractory bricks has been improved in our country, At present our country can produce Al_2O_3 corundum brick with high purity. And the types of special-shaped bricks have been greatly simplified, and standardized. It has been proven in actual plant operation that the life of these bricks can reach two years or more.

For heavy oil extraction of carbon black in soot-water there is the R.D.C. method. The R.D.C. method has the advantages of steady operation, higher-flexible loading ability and wider-adaptability to the viscosity of heavy oil. Our experiments showed that almost all kinds of heavy oil with the specific gravity of less than0.96 could be used as extraction agent.

2. Comparison of energy consumption between the

schemes of direct quenching and W.H.B. under different pressures of gasification when ammonia synthesism is at the pressure of 320 kg/cm^2 (G).

A comparison has been made on the energy consumptions, for three different pressures 22,34 & 50 kg/cm^2(A) for gasification respectively using direct quenching and W.H.B. (only 34kg/cm^2(A)) schemes to recover the sensible heat in the high temperature crude gas, and all are under the same pressure of 320 kg/cm^2(G) for ammonia synthesis. The results are as follows:

The consumption rates and energy consumptions per each metric ton of ammonia for both the direct quenfhing and W.H.B. Schemes.

The above calculation results show: when the gasification pressure is 34 kg/cm^2(A), the energy consumptions for both the direct qunching and W.H.B. schemes for each ton of ammonia are approximately the same. The reason is that the steam output at the pressure of 50 kg/cm^2(G) produced in the W.H.B. is rather small, moreover the steam pressure is so low that it can not be used secondarily, where as for the direct quenching scheme, with the raising of the gasification pressure, the sum of the consumption of heavy oil. both as feedstock and as fuel will come down corespondingly, and so does the power consumption.

The comparison results in the Table 4, also shows that difference between energy consumptions corresponding to the gasification pressures P=34 kg/cm^2(A) and P=50 kg/cm^2(A) is not so large, at the same time, the practical operating experiences on heavy oil gasification under the pressure of 34 kg/cm^2 in our country is successful and reliable, and the complete set of equipment used for ammonia production with heavy oil as feedstock has already been serialized, so the spare parts of the equipment can be easily supplied. Hence we recommend the direct quenching scheme is to be used with heavy oil under prossure of 34 kg/cm^2(A).

3. The Influence of Refeeding the Carbon-Black into the Gasifier on the Gasification of Heavy Oil.

Under the gasification conditions of 34 kg/cm^2(A) and 1350 ^oC, the calculation results of refeeding and non-refeeding carbon-black into gasifier are listed in Table 5.

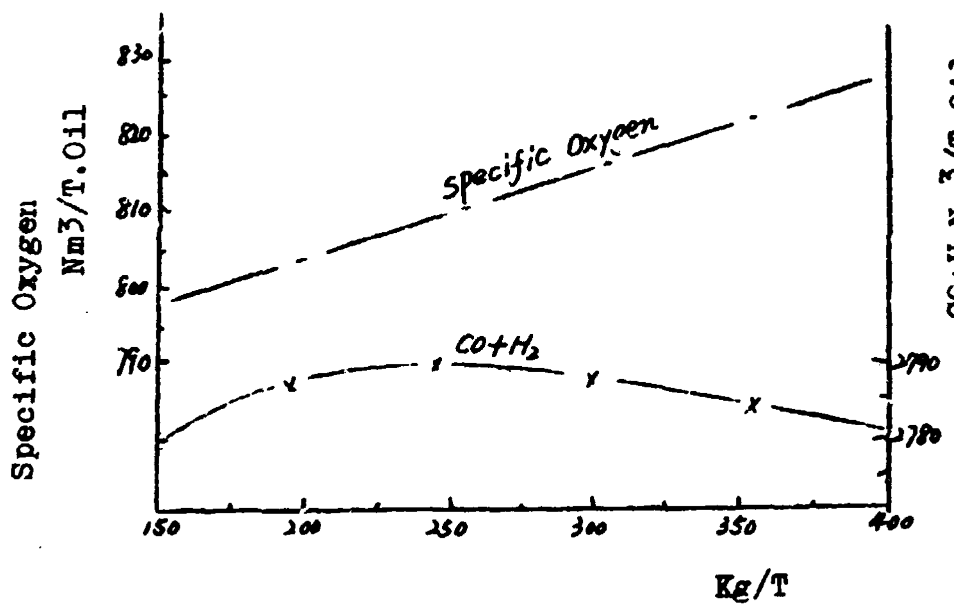

Fig 5. Effects of various steam/oil Ratio On Gasification

Table 4

Name	Direct Quenching $P=22kg/cm^2(A)$		Direct Quenching $P=34kg/cm^2(A)$		Direct Quenching $P=50kg/cm^2(A)$		WHB $P=34kg/cm^2(A)$	
	Consumption rates	Energy consumption $\times 10^6$ kcal	Consumption rates	Energy consumption $\times 10^6$ kcal	Consumption rates	Energy consumption $\times 10^6$ kcal	Consumption rates	Energy consumption $\times 10^6$ kcal
Heavy oil: as feedstock kg	765	7.65	778	7.78	790	7.90	778	7.78
As fuel kg	515	5.15	500	5.00	478	4.78	514	5.14
Electrical power kWH	694	2.08	597	1.79	523	1.57	623	1.87
Steam output kg	2934	-2.49	2934	-2.49	2934	-2.49	2934	-2.49
Cooling water M^3	429	0.32	452	0.34	487	0.37	485	0.36
Total		12.71		12.42		12.13		12.66

Notes: The calculation data of energy consumption are as follows:

Heavy oil: 10000 kcal/kg — Eletrical power: 3000 kcal/KWH

Steam: 850 " — Cooling water: 0.25 KWN/M^3

Table 5 Influence of Carbon Black Refeeding on Heavy Oil Gasification

Item	Refeeding Carbon Black x 1			
	Oil-carbon slurry with water	Oil-carbon slurry with water	Oil-carbon slurry with water	Non-refeeding
The preheating temperature of heavy oil	200 °C	200 °C	200 °C	200 °C
Steam	$P=46kg/cm^2(A)$ $t=400^\circ C$	$P=46kg/cm^2$ (A) $t=400^\circ C$	$P=46kg/cm^2(A)$ $t=400^\circ C$	$P=46kg/cm^2(A)$ $t=400^\circ C$
Ratio of steam/oil	400	400x2	250	400
Oxygen purity(V%)	O_2 99.5;Ar 0.5	O_2 99.5; Ar 0.5	O_2 99.5; Ar 0.5	O_2 99.5; Ar 0.5
	$P=43kg/cm^2(A)$ $t=95^\circ C$	$P=43kg/cm^2(A)$ --	$P=43kg/cm^2(A)$ --	$P=43kh/cm^2(A)$ --
Oxygen consumption NM^3/T of heavy oil	814	827	810	797
The output of dry gas NM^3/T of heavy oil	2987	2993	2954	2928

- to be continued

The output of CC+H_2 NM^3/T of heavy oil	2798	2781	2789	2738
H_2 +CO Concentration V%	93.65	92.90	94.34	93.52
The water contents In crude gas	11.50	13.36	9.28	12.06

Notes:

X 1. The recovery amount of carbon-black from each ton of oil is 2.14 kg-mol. the amount isn't included in the total weight of oil.

X 2. The water contents brought in by oil-carbon black slurry isn't included into this figure.

Having compared the above calculation results, we have learned that, when carbon-black is refeed into the gasifier as feedstock and the ratio of steam to oil is 400, as carbon-black consumes 17 NM^3 more of oxygen, producing 60 NM^3 more of $CO+H_2$, meanwhile, as the water brought in by the oil-carbon slurry consumes 13 NM^3 more of oxygen, decresing the H_2+CO production by 17 NM^3. The overall result is that increasing the oxygen consumption by 30 NM^3 results in a net increase of $CO+H_2$ production by 43 NM^3 . Thus when oil-carbon black slurry is refeed into gasifier as feedstock, no doubt the feedstock consumption can be reduced and the production cost can be lowered to a certain degree.

In the comparison table it can be shown that if the ratio of steam to oil is properly lowered the oxygen consumption will decrease and the quantity of $CO+H_2$ will increse. Provided that the heavy oil-carbon black slurry contains a certain amount of water, the relationship between the ratio of steam to oil and oxygen consumption as well as $CO+H_2$ production varies along the following curves: (Please see Fig.5, page 10)

Summing up all the above mentioned, this paper has discussed some aspects on the application of partial oxidation for heavy oil gasification and direct quenching scheme as well as the refeeding of carbon black into the gasifier as feedstock, and also the chemical absorption process used to purify the crude gas for ammonia synthesis. We consider that it is economically feasible to build an ammonia plant with the output of 220 MT per day.

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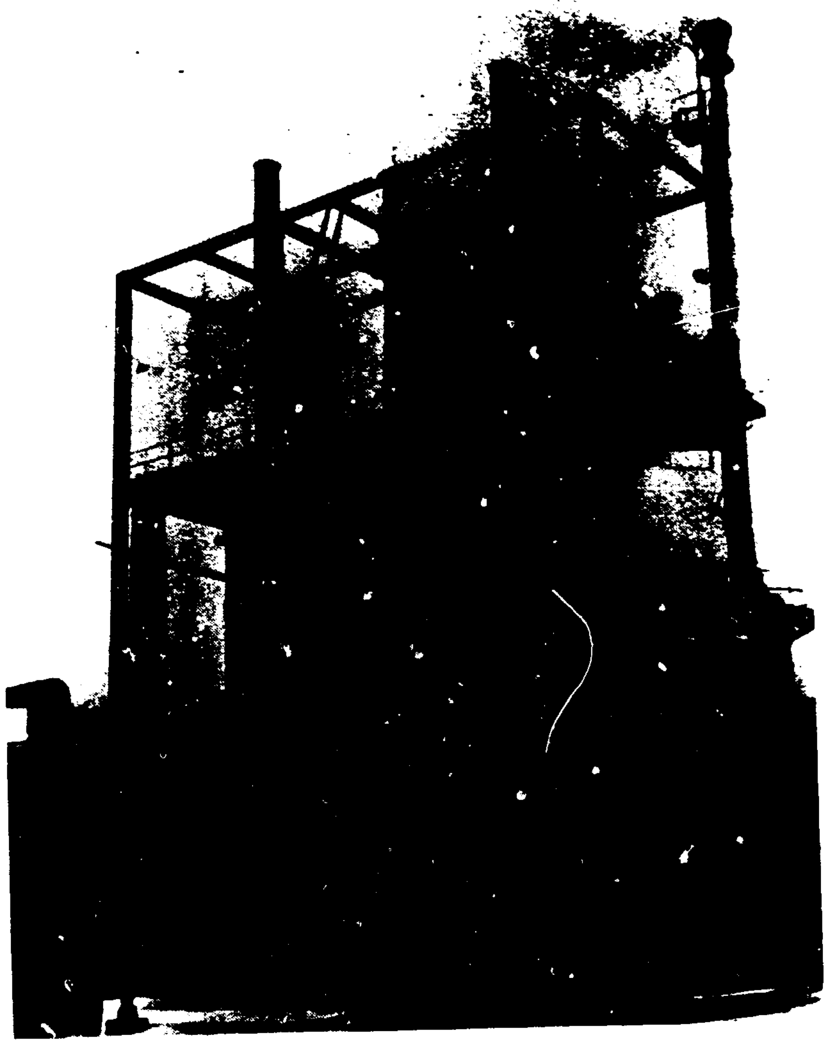

Fig. 1 The outline of a gasifying unit.

Fig. 2 A heavy oil-extracting unit in a plant of the Lanzhou Chemical Industry Corporation

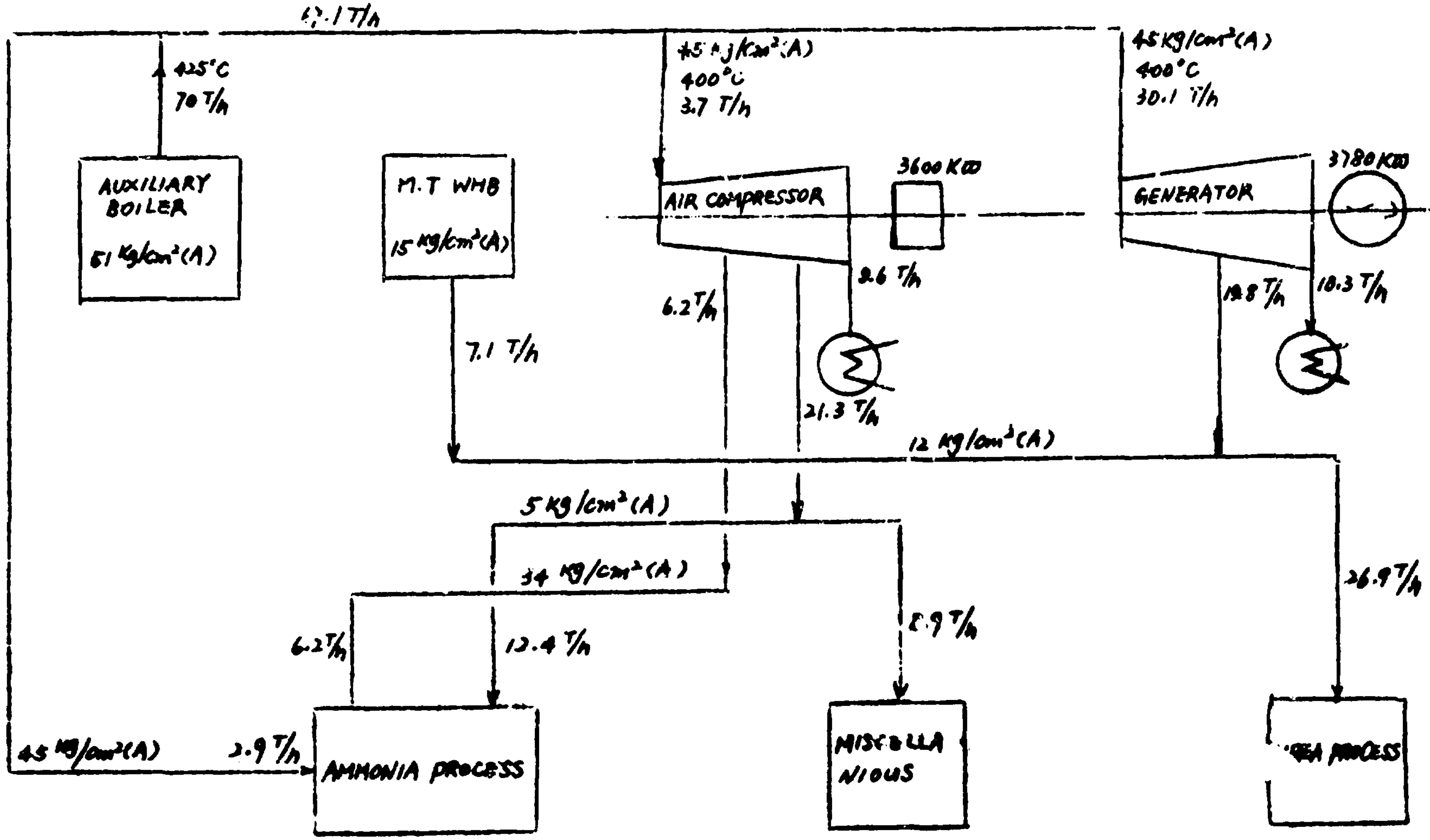

Fig. 3 220 MT/D NH_3 plant steam balance diagram

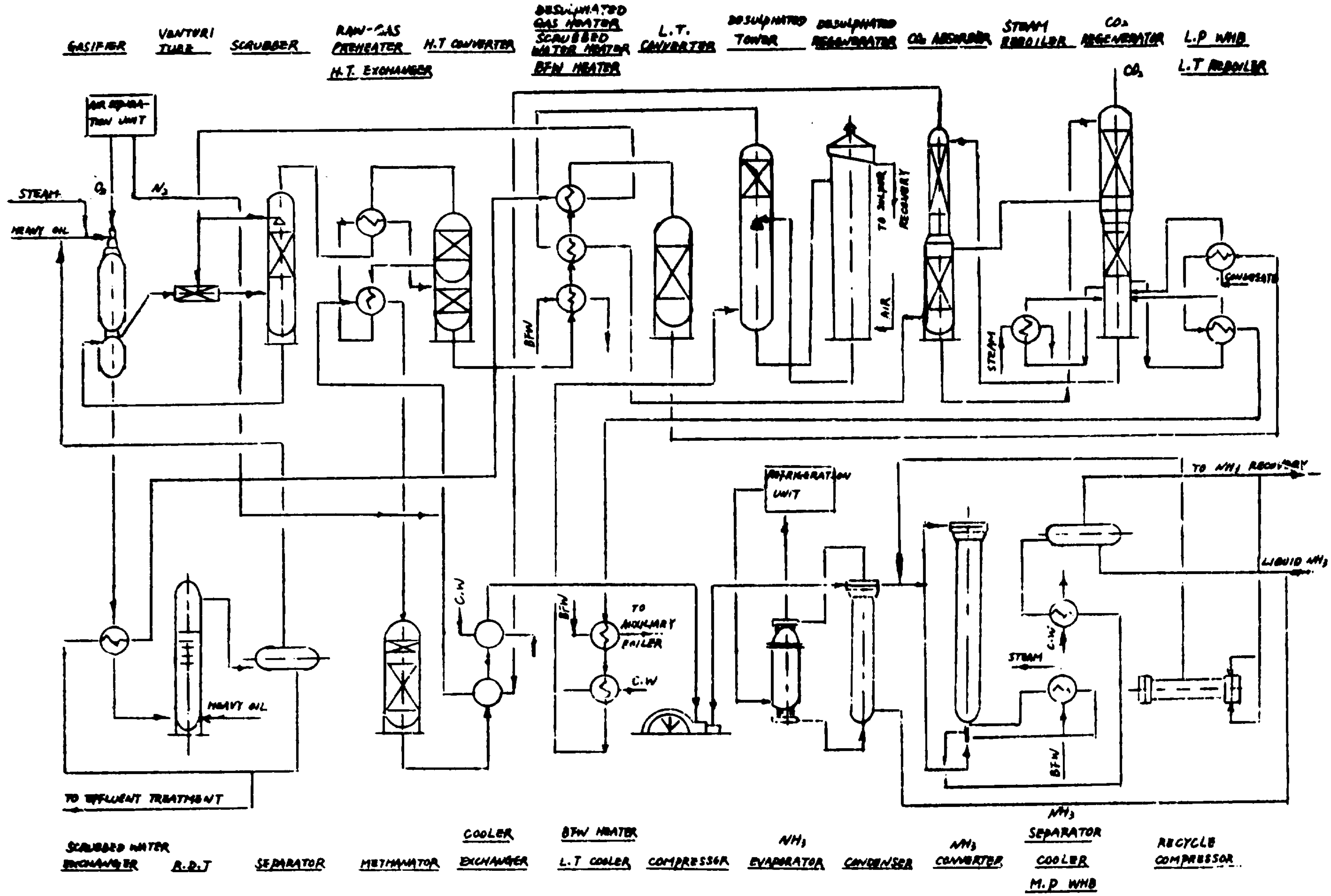

FIG.4 — $220^{MT}/D$ NH_3 PLANT FLOW SHEET