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UPGRADING PLANT CAPACITY BY INTEGRATION AND PRODUCTIVE UTILISATION OF WASTE STREAMS

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L'industrie des engrais traverse une phase cruciale de changement de politique qui peut fortement affecter la rentabilité d'une unité. Il y a une pression sur l'industrie en vue de moderniser les unités et d'apporter des changements innovants de façon à augmenter la productivité et la rentabilité.

GNFC possède la plus grande unité au monde à un seul flux d'ammoniac/urée basée sur l'oxydation partielle de fuel oil. L'exposé décrit l'approche adoptée pour l'utilisation productive de flux résiduaire ou secondaire qui a contribué à la rentabilité par addition de produits chimiques à la ligne de production entraînant une augmentation de production et une grande économie de catalyseur et d'utilités. Les efforts dans le domaine du retraitement, réemploi/recyclage et réduction on été résumés.

SUMMARY

The fertilizer industry is passing through a crucial phase of changes in the policy, which can greatly affect the profitability of a unit. There is a pressure on the industry to modernise the plants and make innovative changes so as to improve productivity and profitability.

GNFC has the world's largest single stream ammonia/urea complex based on partial oxidation of fuel oil. The paper describes approach adopted for productive utilisation of waste or secondary streams, which has contributed to the profitability by adding chemicals to product line, enhancing ammonia production and a large saving in catalyst and utilities. The efforts in areas of reprocessing, reuse/recycle and reduction have been summarised.

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INTRODUCTION

GNFC has the world's largest single stream ammonia/urea complex based on partial oxidation of fuel oil. Continuous improvement in productivity and innovations have been the key to success. Various innovative measures used for utilisation of waste/secondary streams which contributed to the profitability by adding chemicals like formic acid, aniline, etc., to the product line, enhancing ammonia production and large saving in catalyst, oil, DM water, boiler feed water and other utilities have been dealt with in the paper.

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Although the plants are designed with in-built provisions to minimise material and energy losses and pollution, a systematic approach was adopted to identify further scope of improvement by listing out various streams. Apart from the operating group, other groups such as technical services, projects, and performance monitoring were involved in the exercise to evolve more productive and profitable methods, processes and products. In the process major breakthroughs were achieved in the areas of reprocessing, reuse and recycle and reduction.

Integration and Reprocessing of Secondary Streams :

1. **Reprocessing of tail gas for formic acid and TDI :** After partial oxidation of fuel oil, the raw gas is processed through CO shift converter. In the downstream rectisol wash unit, CO2 and H2S removal is carried out. The remaining impurities such as CO, CH4 and argon are removed in the nitrogen wash unit. These impurities are washed out with liquid nitrogen and taken out as tail gas stream. The tail gas stream of 5000 Nm3/hr contains 45% CO and has heating value of 5000 Kcal/Nm3 and hence it is burnt in furnace for superheating HP steam as per design.
   However, CO being a basic compound, an alternate use of the stream was thought of. In the process the stream was found to be compatible for manufacture of formic acid. Also market survey was found to be encouraging. Ultimately a 5000 MTPA formic acid plant was set up at a cost of Rs.14 crores (USD 3.5 m). Presently this plant is operating above 150% load and expansion of the unit is under consideration. Only part of the CO of tail gas stream is used in formic acid production. In order to make full use of the component, CO enhancement unit has been set up to produce 10,000 MTPA of toluene di isocynate, the production of which is already started (Fig.1).

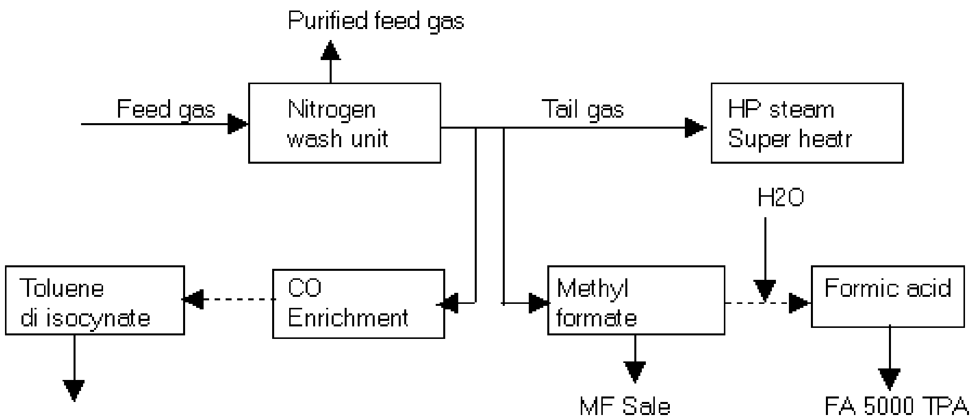


Figure 1 : Formic Acid and TDI from Tail Gas

2. **Reprocessing of Purge Gas for Ammonia and Aniline :** 100,000 MTPA methanol plant based on natural gas reforming is designed with a purge of 5000 Nm3/hr from methanol synthesis section, which is used as fuel in reformer. The purge stream has 70% of hydrogen and of low heating value. Productive use of this stream containing about 3500 Nm3/hr hydrogen was thought of to produce ammonia. The compatibility of the stream was established in ammonia plant upstream of rectisol unit after boosting the pressure from 54 bar g to 75 bar g by using recycle compressor. After implementing the scheme, ammonia production has increased to 40 MT per day on consistent basis (Fig.2).

   After installing pressure swing adsorption unit a part of purge gas is being reprocessed to pure hydrogen. This hydrogen is used for producing aniline (20,000 MTPA).

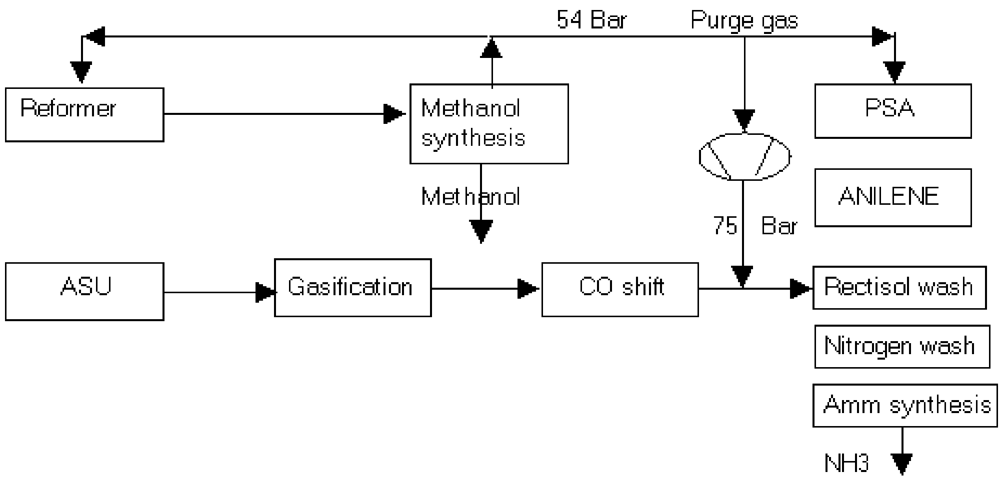


Figure 2 : Ammonia and H2 /Aniline from Methanol Plant Purge Gas

3. **Processing of Waste CO2 for ANP / Methanol and Pure CO2 Enhancement :** The CO2 and H2S removal from the feed gas of ammonia plant is done by rectisol wash process. In the process a waste stream containing 85% CO2 and rest nitrogen is generated and vented to atmospheric stack.

   The availability of all such streams was kept in mind while selecting new project and its technology, to improve feasibility. Between 3500 and 1800 Nm3/hr waste CO2 stream was diverted to ammonium nitrophsophate and methanol plant respectively after minor modification in the system. This has helped greatly in reducing project cost of these products. 40,000 Nm3/hr of this stream is still left for further use (Fig.3).

   The shortage of pure CO2 was a limiting factor for increasing urea production. The CO2 used for injection in waste CO2 for ammonium nitrophosphate of 2000-3000 Nm3/hr was required at low pressure. A scheme was developed and implemented inhouse to produce 3000 Nm3/hr low pressure (0.3 bar g) pure CO2 from rectisol wash unit. This CO2 is direct reduction of CO2 in waste gas being vented. The urea plant load could be raised to this extent.

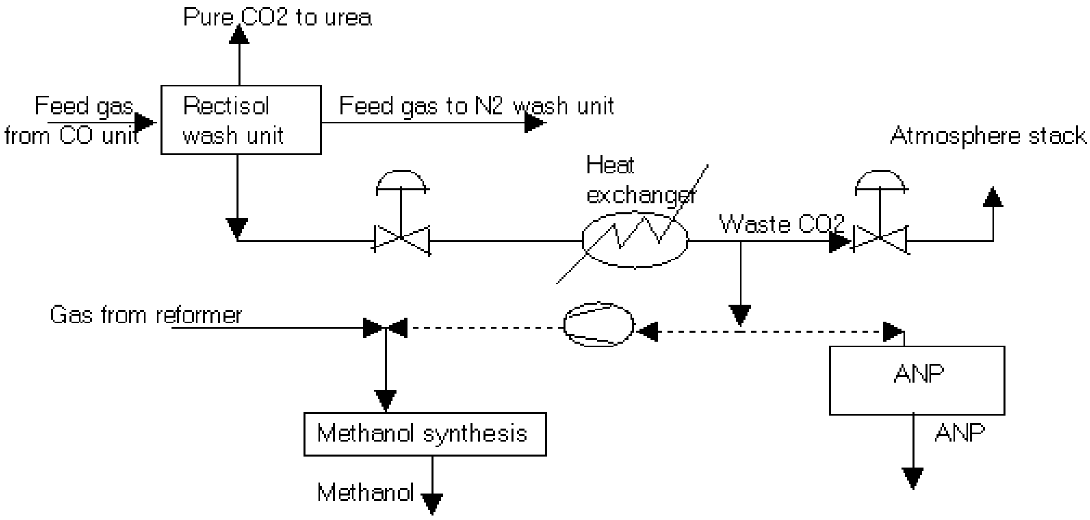


Figure 3 - Use of Waste CO2 for ANP and Methanol

4. **Reprocessing of CO Waste Gas for Ammonia/Methanol :** A stream of gas generated in gasification unit contains mainly CO+H2. This gas stream is purified to remove impurities of CO2 and H2S followed by CO enrichment. 99.5% pure CO is used for the production of acetic acid. In the process of CO enrichment, a waste CO+H2 stream is generated. The hydrogen of this stream is reprocessed in nitrogen wash unit for enhancing ammonia production as in built feature where CO content of the stream is lost in tail gas stream of nitrogen was unit. A scheme to use this stream in methanol plant or upstream of CO shift section has been made which will spare hydrogen for increasing methanol / ammonia production.

5. **Processing of Fuel Oil for Naphtha :** The ammonia plant at GNFC is based on partial oxidation of fuel oil in a gasification unit. The unburnt carbon is recovered by extraction with naphtha followed by mixing with fuel oil and distillation. Thus naphtha is recovered for recycling. However, about 60 MT per month of naphtha is required as make-up in the system due to losses.

   It was observed that taking more fuel oil through carbon extraction unit generates some naphtha on distillation. Hence the practice of processing maximum quantity of fuel oil through this route was undertaken to minimise naphtha consumption.

6. **Development of Catalyst for Sulphur from Clause Gas :** The ammonia plant was designed for furnace oil containing 3.5 to 4% sulphur and the clause gas generated in rectisol wash unit was expected to contain 45% H2S. However, higher hydrogen yield is obtained by using residual fuel oil containing low sulphur content of 0.5 to 1%. Also fuel oil sulphur content has reduced over a period of time. With these changes, clause gas contains only 12% H2S which cannot be processed in the clause unit and requires flaring. Concentrated research efforts were made to evolve a liquid catalyst which can

yield sulphur from low H2S concentration gases. This new catalyst has been patented by GNFC and is available to others as "Narmada Catsol".

7. **Integration of Reformer Gas with Two Methanol Plants and Ammonia Plant:** Based on availability of the natural gas, a reformer with 250 MT/day equivalent ammonia capacity was installed. The integration of the unit is done to supply reformed gas to small methanol plant (Methanol-I) to produce 110 MTPD methanol and rest gas can be supllied to existing ammonia plant after CO-shift producing 140 MTPD ammonia. A provision is also made to take reformed gas to Methanol-II plant increasing its capacity from 300 to 340 - 380 MTPD, and producing about 60 - 100 MTPD ammonia by supplying purge gas to ammonia plant.

Reuse and Recycling of Streams

1. Reuse of CO shift catalyst : The CO shift unit downstream of gasification is based on BASF technology and its cobalt molybdenum catalyst is active in presence of H2S. The unit consists of three reactors in series. Over a period of 3-6 months first CO shift reactor, catalyst bed experienced fouling with fine carbon dust carried over with gas. Decomposition of nickel carbonyl to nickel and attrition of catalyst took place. This resulted in rise of pressure drop of this reactor from 0.8 to 2.5-3.0 bar g. A plant shutdown of 3-4 days was required to replace fouled catalyst upto affected depth.

   The fouled catalyst was required to be discarded inspite of having high activity. The cost of the catalyst being very high, a part of the catalyst was recycled after screening as a trial. A marginal decrease in life was observed with the saving of catalyst was very high. This idea was exploited to install efficient system for dust removal and recycling of catalyst. A vibrating screen was designed to suit the requirement and installed on the top floor of the reactor in Sept.94. This system has given very good results in terms of dust removal and quantity of catalyst recycled. With this catalyst consumption has been reduced from 45 M3 to 15 M3 per year.

   Other packings used in ammonia plant are pearl gel for acetylene removal in ASU and 5A molecular sieves for CO2 /methanol removal in the nitrogen unit. Although the indicated life of these packing is 5 years, more than 10 years life could be extracted. This was made possible by continuous monitoring of the performance of packings, physical and chemical analysis at regular interval and screening of the packings during by-annual shutdown for removal of dust and undersized packings. After the use of 1/8” mol.sieve (5A) in ammonia plant service is used after 10 years in acetic acid plant since they can be tolerate lower size (i.e. 1/16”).

2. Reuse of condensate streams from different locations : In the CO shift reaction 50 MT/hr of water is consumed from the saturated gas generated by gasification. This water is supplied by grey water circuit of carbon extraction unit. Also about 20 MT/hr of water is required to be blown down from the grey water drum to maintain chloride and TDS in the system. 70 MT/hr of water requirement is met through make up of BFW or condensate to grey water drum as per design.

This consumption of BFW being very high, use of waste streams available was thought of and the following streams were identified and connected with grey water circuit.

- From urea plant 30 MT/hr hydrolyser effluent is recycled to grey water drum through a control valve. The contaminant limits for ammonia and urea are fixed at 100 ppm and 50 ppm respectively.

- From formic acid plant 10 MT/hr condensate of steam is taken to condensate recovery drum by pump.

- From methanol plant 20 MT/hr condensate containing about 5 ppm methanol is diverted to grey water drum.

Thus, load on DM water and BFW system is reduced by about 60 MT/hr giving considerable savings.

3. Recovery of drain and leaking oil : The fuel oil is fed to gasification unit by 2 reciprocating pumps at 90 bar g pressure. The packing leakage of these pumps and other leakages were going to storm water sewer. Earlier this oil was removed at effluent treatment plant.

   A slop oil system has been developed to recover this oil in ammonia plant itself. Underground tank and pump has been installed and oil from all leakage and drain points is diverted to this tank by underground header. This system has helped greatly in recovering and recycling the leakage oil to main system, thus reducing pollution and increasing continuity of the plant. Still a small quantity of oil slips to store water sewer due to washings. To restrict it from going to main sewer, a API type separator has been installed in the sewer followed by a belt type oil skimmer which removes even traces of oil from stream.

4. Recycling of DM water during preheating : The gasifiers being refractory lined reactors, require preheating and cooling during shutdown. During preheating or cooling about 60 M3/hr of DM water used to pass through quench ring for its protection which was drained to sewer.

   About 50,000 M3/yr. of DM water was lost in the process. A scheme has been drawn for recycling the DM water in close circulation. Once this scheme is put on line the loss of DM water will be avoided.

5. Recycle of cooling water to conserve water and chemicals : Ammonia plant has cooling water system consisting of 12 cells with 35000 M3/hr cooling water circulation. During operation of the plant 200 M3/hr of CW is blown down from bearing housing coolers, LO coolers, blow down drums, etc., and cycle of concentration of 3.5 - 4 was achieved. However, some scope for increasing cycle of concentration did seem to exist. Hence a scheme has been prepared for recycling the CW being drained to sewer, to the basin. This will save water as well as chemicals by raising cycle of concentration to 5-6.

6. Reuse of waste methanol stream from methanol plant (Fusal oil) as micro-nutrient in effluent treatment plant (DNR) and use of methanol to be removed from formic acid plant in the acetic acid plant.

Reduction of Waste

1. Check list for monitoring any steam venting/leakages or energy loss and on-line maintenance.

2. Eliminating the pumping and treatment costs of turbine condensate routing these directly to deaerator with quality control.

3. Avoiding draining of pure condensate from oxygen preheater by taking back to condensate system after due precautions.

4. Reduction of plant air header pressure to minimise consumption of plant air and utilising in ASU for additional ammonia production.

5. About 400 MT of ammonia dead stock required disposal after water dilution during decommissioning of the two atmospheric ammonia storage tanks (10,000 MT). This has been avoided by processing ammonical water in waste water section of urea plant.

6. Recovery of ammonia and condensate from effluent of CO shift unit after H2S stripping.

7. Sewer water after filtration and chlorination will be recycled as cooling water make up.

Future Focus : Recovery of Valuables

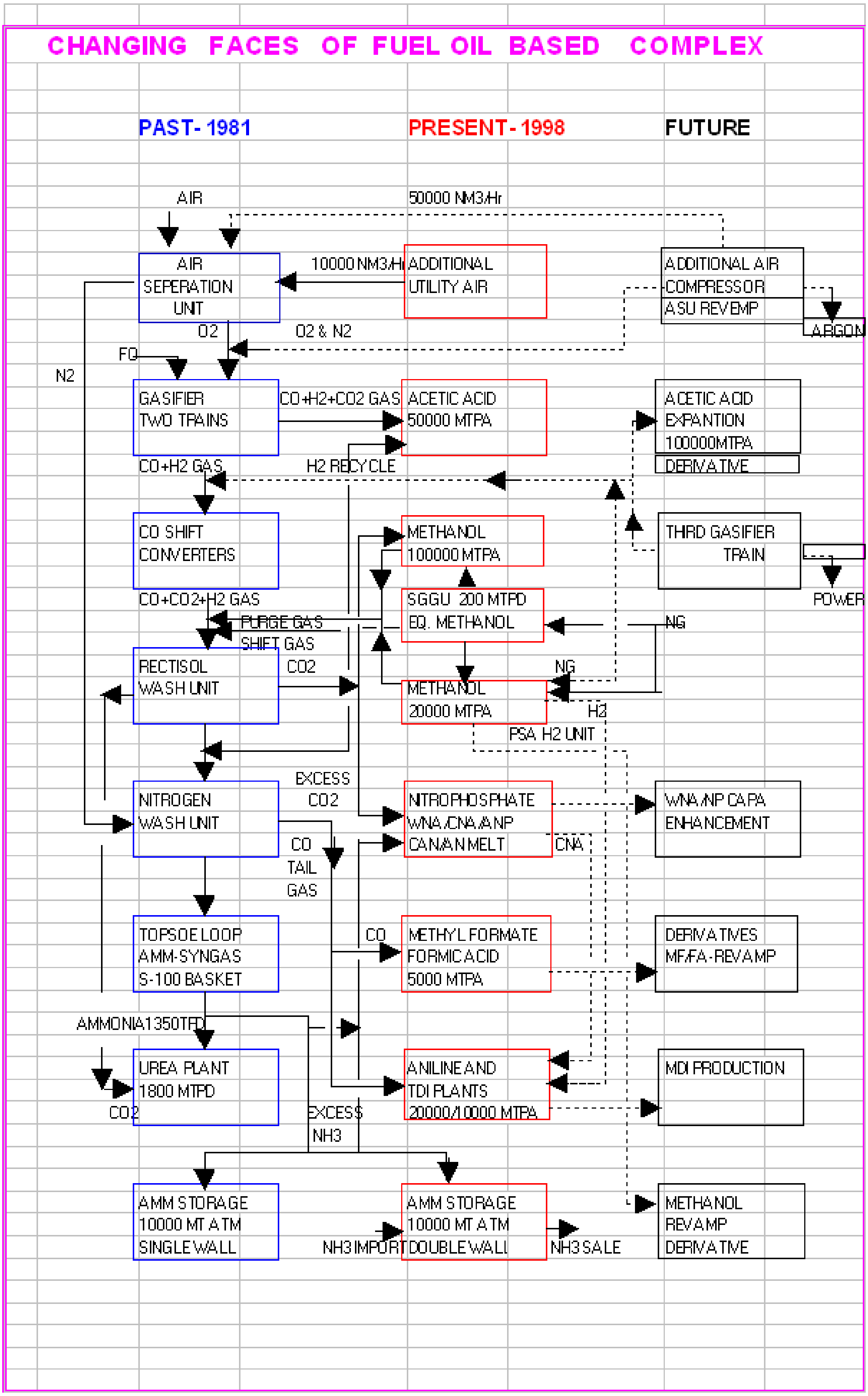
Efforts are being continued to find better solutions to some of the waste stream identified. It is intended to solve these through interaction with various institutes.

1. Use of tail gas containing 80% CO2 from rectisol wash unit. PRAX AIR is in touch with GNFC to try and process this stream further.

2. Recovery of Ni, V, Ti from slag of gasifier and scales of heat exchangers.

CONCLUSION

Simple devices and plain thoughts applied for waste streams and thoughful integration to improve upon operating efficiency, energy saving and conversion to useful value added products can enhance greatly the prosperity of the company. The search in this direction is being continued for further improvement to uphold its position in a competitive environment.


CHANGING FACES OF FUEL OIL BASED COMPLEX
PAST- 1981
PRESENT- 1998
FUTURE
AIR
50000 NM3/Hr
AIR SEPERATION UNIT
10000 NM3/Hr
ADDITIONAL UTILITY AIR
ADDITIONAL AIR COMPRESSOR ASU REVEMP
ARGON
O2
O2 & N2
FO
N2
GASIFIER TWO TRAINS
CO+H2+CO2 GAS
ACETIC ACID 50000 MTPA
ACETIC ACID EXPANTION 100000MTPA
DERIVATIVE
CO+H2 GAS
H2 RECYCLE
CO SHIFT CONVERTERS
METHANOL 100000 MTPA
THIRD GASIFIER TRAIN
POWER
CO+CO2+H2 GAS
SGGU 200 MTPD EQ. METHANOL
PURGE GAS
SHIFT GAS
NG
RECTISOL WASH UNIT
CO2
METHANOL 20000 MTPA
NG
H2
PSA H2 UNIT
EXCESS CO2
NITROGEN WASH UNIT
NITROPHOSPHATE WNA/CNA/ANP CAN/AN MELT
CNA
WNA/NP CAPA ENHANCEMENT
CO TAIL GAS
TOPSOE LOOP AMM-SYNGAS S-100 BASKET
CO
METHYL FORMATE FORMIC ACID 5000 MTPA
DERIVATIVES MF/FA-REVAMP
AMMONIA1350TPD
UREA PLANT 1800 MTPD
CO2
ANILINE AND TDI PLANTS 20000/10000 MTPA
MDI PRODUCTION
EXCESS NH3
AMM STORAGE 10000 MT ATM SINGLE WALL
AMM STORAGE 10000 MT ATM DOUBLE WALL
NH3 IMPORT
NH3 SALE
METHANOL REVAMP DERIVATIVE