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Techno-economic feasibility of flue gases recirculation in heat recovery for urea plants

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ABSTRACT

Energy efficiency and its conservation is one of the ways to bridge the gap between demand and supply, and to mitigate the environmental impacts of rapid development. The climatic condition of earth is largely affected by greenhouse emission and global warming. However, a planned energy cycle of production, conversion and utilization of these gases can solve global environmental problems. In fertilizer plant energy conservation aims in reduction of specific energy consumption. Urea is one of the important and widely produced chemicals in the world. This paper describes some of the modification in urea/ammonia plants understanding the flammability diagrams through actual experimentation through inline monitoring would mix the inerts, fuel and oxygen escape safely from explosive range.

Key words: Ammonia, Urea, Flue gases, Waste heat recovery, CO, capture



Graphical Abstract: Ammonia and Urea production

Introduction

In the industrial manufacturing of fertilizers, urea being nitrogen rich is used as a raw material for many important plastic, acts as reduction agent for transforming graphene from graphite. As a nontoxic, stable and easyto transport and store has also medical applications and is used asan ingredient in hair removers, skin creams, moisturizers and hair conditioners. Other applications for urea are melamine production,feed supplement and manufacturing of adhesives (Springer, 2003). The indus-

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trial urea production is initiated through ammonia and carbon dioxide from natural gas. $CH_4 + H_2O$ $CO + 3H_2$. The flue gas leaving has temperature in excess of 900°C. About 50-60% of fuel's heat value is directly used in the process. The waste heat is recovered in the reformer convection section. The flue gas leaving the convection section at 100-200°C is one of the main source of emissions from the fertilizer plants (Giddey et al., 2013). These emissions are mainly CO₂ NOx, with small amounts of SO₂ and CO. In Urea processes it is necessary to introduce continuously into the synthesis loop a small quantity of oxygen in order to protect the stainless steel surfaces against corrosion. This operation is normally performed by injecting air to the CO₂ feed to the urea reactor. Part of the oxygen reforms the oxide layer where it was damaged by solution action and the excess oxygen has to be vented along with the nitrogen introduced with the air. At the same time the CO₂ and NH₃ fed to the urea plant contain some "inerts". The inerts are a mixture of H_2 , CH_4 , Ar, N₂ etc. and are so called because they do not affect the urea formation process; therefore they have to be vented together with the excess air. The process gas from the low temperature shift converter contains mainly H₂ N₂ CO₂ and excess process steam. The gas is cooled and most of the excess steam is condensed before it enters the CO₂ removal section. This condensate usually contains 1500-2000 ppm of ammonia, 800-1200 ppm of methanol and minor concentration of other chemicals. All these are stripped and in the best practices the condensate is recycled (Chakma, 1995). The havoc in global warming is contributed by increasing level of carbon dioxide (CO₂) due waste heat dumped into the

environment by direct burning of flue gases, even though it could still be reused for some useful and economic purpose. The essential quality of heat is not the amount but rather its "value". The strategy of how to recover this heat depends in part on the temperature of the waste heat gases and the economics involved leaked into the atmosphere through flue gases. A nearly 14% reduction in CO₂ can be strategically possible by its capture and storage (CCS) technology.However along CO₂ emissions in flue gases, nitrogen oxides (NOx) and sulfur oxides (SOx) pollutants are emitted into the atmosphere.

Materials and Methods

In Urea plant these off gases are discharged to the atmosphere through vent from washing tower. Maintained at medium pressure of 15.5 kg/cm²g with the flow of gases in the range of 500 to 800 Nm³/hr in each stream depending on the plant load. As stated above these gases are a mixture of H_{2} , CH_{4} , Ar, N_{2} , CO and NH_{2} etc. Venting of these gases causes a problem in terms of air pollution as well as **loss of ammonia**, since a substantial amount of gaseous ammonia will be discharged to the atmosphere if a washing step for recovery such ammonia is not foreseen. Hence in Snamprogetti plants, the ammonia in the off gases is scrubbed with condensate in washing tower (Yan and Zhang, 2019). For study of heat recovery potential from vent off gases the process flow initiatives of two Urea plants are taken into consideration at National Fertilizer Limited, India shown in Figure 1



Unfortunately, scrubbing these vapors can create

Fig. 1. Process flow diagram of the case study of Urea I and II plants at National Fertilizer Limited, India

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a serious problem in terms of safety since the absorption of ammonia can lead to the formation of an explosive mixture, because of the contemporary presence in the mixture of flammable compounds (H_2 , CH_4) and oxygen (Cuéllar-Franca, 2015; EN 1839:2017 (E), 2017). To escape safely from explosive range in such cases, outlet gases are largely diluted by Low pressure steam (LS) introduced in downstream. In such plants steam is generated at high pressure in reformers and synthesis boilers. Medium pressure steam is utilized mainly in the reformer feed along with natural gas to produce reformed gas for ammonia production. A typical steam balance diagram in ammonia / urea complex is shown in figure highlights that high pressure steam at 10^{5} kg/cm² heads into medium pressure steam at 40 kg/cm². The steam balance has been calculated and labeled in Figure 2.

The material and energy balance is also evaluated and depicted in Figure 3.

Results and Discussion

Average Composition of off gases

The proximate analysis of gas at the radiator vent was online monitored regularly for a period 2 months with its % composition and latent heat value



Fig. 2. Steam balance of the plant



Fig. 3. Material and energy balance



as shown in Table 1. Out of two urea plats the component of methane was higher in plant 2 as shown in Figure

Composition of off gases and NG Analysis

Scrubbing these vapors can create a serious problem in terms of safety since the absorption of ammonia can lead to the formation of an explosive mixture, because of the contemporary presence in the mix-

 Table 1. %composition and latent heat value of vent off gases

Component	H_2	O ₂	N ₂	CH_4	NH_3
% Composition	28.34	9.685	46.23	12.885	2.86
LHV (kcal/Nm ³)	2579	0	0	8555	3375

ture of flammable compounds (H_2, CH_4) and oxygen. Hence explosive limits (Valencia *et al.*, 2019; Arvanitoyannis, 2008) can be checked before and after mixing of NG to ensure safety limits through the ternary plots as shown in Figures 5 and 6. In the first case The upper and lower flammability limits



Fig. 5. Before NG mixing: The calculated Point (C) lies close to the explosive limit



Fig. 6. After NG mixing: The calculated Point (C) lies outside the explosive limit

Table 2. Proximate analysis of fuel feed

Natural Gas Component	CH_4	C_2H_6	C ₃ H ₈	I-C ₄ H ₁₀	$N-C_4H_{10}$	I-C ₅ H ₁₂	N-C ₅ H ₁₂	$I-C_6H_{14}$	CO ₂	O ₂	N ₂	H ₂	S
Percentage	92.09	2.93	2.19	0.41	0.59	0.13	0.13	0.25	1.15	0.00	0.14	0.00	0.00

of fuel that is methane in oxygen are located on the axis very close to the explosive limit, whereas after mixing NG, the calculated point lies away from the explosive limits.

Techno economic feasibility of utilizing waste heat

Using the fuel analysis data,

Weighted average LHV of fluegas mixture = (0.2854 x 2579) + (0.12885 x 8555) + (0.0286 x 3375) = 1929.72 kcal/ Nm³

Volumetric flow of off gas= 2000 Nm³/ hr@500Nm³/ hr for each stream. LHV of NG = 8597.43 kcal/ Nm³ Equivalent quantity of NG = (1929.72 x 2000)/ 8597.43

= 448.90 Nm³/ hr

= 473.54 Sm³/ hr

Assuming cost of NG = Rs.10/ Sm³ Annual energy saving taking 330 on stream days = $473.54 \times 10 \times 24 \times 330$ = Rs.375.04lakhs per year.

Estimation of GHG emission can be calculated from off gas combusted in primary reformer (Nm³/ hr) generated in urea plant (Fpr) = 488.90(Nm³/ hr)

Vent valve opening (X) = 0%

Quantity of C-3 off gas vented out to atmosphere (Fv) is calculated from vent valve opening%

Quantity of C-3 off gas combusted in primary reformer (Fg) = Fpr – Fv = 488.90-0 = 488.90 (Nm³/ hr)

Estimate quantity of methane burnt (kg/hr):

$$Q_m = F_g x C H_4 x \frac{16}{22.414} = 44.968 \text{ kg/hr}$$

Where

Fg = Quantity of C-3 off gas combusted in primary reformer (Nm^3 / hr) = 488.90(Nm^3 / hr)

% $CH_4 = 12.885$ % (as in the table above)

Molecular weight of $CH_4 = 16$

Avogadro's Constant = 22.414

Total project emissions (tons/hr):

 $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

16 kg 64 kg 44kg 36kg

Stoichiometric Carbon Dioxide (CO_2) release from complete combustion of CH_4

16 kg of $CH_4 = 44$ kg of CO_2 1 kg of $CH_4 = 44/16$ of $CO_2S = 2.75$ kg of CH_4

Complete combustion of 1 kg methane (CH_4) releases 2.75 kg of carbon dioxide (CO_2) [5]

1000

E project =
$$\frac{Qm \times 2.75 \times 24 \times 330}{2}$$

$$= \frac{44.968 \times 2.75 \times 24 \times 330}{1000}$$
$$= 979.403 \text{ tonnes/yr}$$

Total project emissions = 979.403 tones /yr Total Baseline Emission (tons / yr):

Ebaseline =
$$\frac{Fm \times 21 \times 24 \times 330}{1000}$$

Where

Ebaseline = Total baseline emission (tons/yr) Fm = Flow of Methane (kg/hr)

Global warming potential of $CH_4 = 21$

On stream days = 330 days

Ebaseline =
$$\frac{44.968 \times 21 \times 24 \times 330}{1000}$$

= 7479.07 Tones / year

Total emission reduction (Cc) = total baseline emissions (Ebaseline) – total project emission (Eproject)

Cc = Ebaseline – Eproject = 7479.07 – 979.403 = 6499.67 tons/yr

Investment and Particulars for reduction in Boiler steam pressure

Steam is generated at pressures normally dictated at high side which does not work well with the boiler efficiency and life span. Techno economic study for the effective design of boilers would help in the sustainable gain. An Auxiliary Boiler bottom supported, 2 drum, natural circulation water tube boiler with burner specifications Volcano make, SFVX- 600 Oil/Gas Combination burner, 4 Sets, turndown ratio: 6:1 (for LSHS) and 10:1 (for Natural Gas) can be planted at Urea plant, battery limit around 35 to 45

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Table 3. Expected expenditure for revamp of	f	boi	lers
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Expected Expenditure	Cost(Rs. In lakh)		
3" pipe of CS (As per snam specification, 1000m long at a rate of Rs. 1000 per meter)	20		
Control Valve / HIC and Accessories (2 nos PIC) in Urea plant	4		
Miscellaneous fittings	8		
Fabrication and Erection	0.60		
Burner modification (if required)(2 no.s)	20		
Instrumentation (CPP instrumentation+Urea-1+UreaII)	32		
Expenditure for Four streams (Line 1 & 2)	84.60		
Total Expenditure	84.60		

Pay Back

Simple Payback

^oC, under peak load 48 to 50 ^oC. Material of construction of the off gas line at Boiler end is SNAN Spec: 61B, CS material, API Spec 5L grade B ERW.

Conclusion

Accordingly utilization of off gases will avoid methane venting and will reduce the use of natural gas fuel which leads to GHG emission reduction or the plant would have vented 448.90 Nm³/hr of off gases with methane quantity of 44.968 kg/hr to atmosphere. The project of utilizing the off gases as a fuel contributes to sustainable development in environmental, social and technological aspects by GHG reduction. This would decline the consumption of non-renewable fuel like NG conserving natural resources. Avoiding venting of gasreduces air pollution and designing of new technology for off gas and combustion contribute to technological wellbeing.

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= (84.60/.375.04) * 12 = (2.7) months.

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