Process Stages Energy Efficiency Increasing In High Capacityammonia Production Plants (1360 – 1420 T NH_3/Day)

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There are presented the results of low temperature CO to CO₂ conversion investigations for decreased steam consumption and deeper conversion of CO in nitrogen-hydrogen mixture. The results of monoethanolamine purification stage retrofit are presented too.

Key words: ammonia plant, nitrogen-hydrogen mixture, conversion, carbon oxide, reaction, equilibrium, reaction rate, energy efficiency, steam.

Introduction

In Ukraine synthetic ammonia is produced by 18 plants with total capacity 6.2 million tons per annum. Total energy consumption is $10 Gcal/tNH_3$ that is 25 % more than energy consumption of similar plants abroad.

Main energy consumer of ammonia plant is the stage of nitrogen-hydrogen mixture preparation from natural gas – methane (CH_4).

The natural gas and energy resources consumption decreasing is actual goal today.

According to ammonia production processing rules in high capacity ammonia plant AM-76 ($1420 tNH_3/day$) steam consumption for ratio $n = V^{CO}_{H_2O}:V^{CO}_{\text{СГ}} = 0{,}44:1$ is significantly more than necessary according to stoichiometric reaction of carbon oxide (II) conversion:

$$CO + H_2O \rightleftarrows CO_2 + H_2 + 41{,}13\,J \qquad (1)$$

Carbon oxide conversion in mixture for decreased steam consumption

To estimate the possibilities of surplus steam decreasing the investigation of kinetic and thermodynamic of CO conversion in nitrogen-hydrogen mixture stream close to industrial was carried out with use of copper contained catalyst K-CO and CHK-2 with particles of catalyst size (0.25-0.5) and (0.1-1.5) mm.

According to the investigation plan the parameters of CO to CO_2 conversion process were varied: temperature, $t°C$, pressure P, MPa, volumetric flow rate $W, 1/hour$. Their influence on equilibrium level of carbon oxide conversion χ^*_{CO} was investigated as well as steam, CO, CO_2 and H_2 containing in the mixture.

The investigations had shown that process temperature t increasing resulted the decreasing of equilibrium level of conversion χ^*_{CO} according to constant of rate K ($molCO/molNH_3$) increasing and from another side in return reaction (1) the equilibrium was removed to initial substances side and χ^*_{CO} was decreased.

Gas mixture pressure $P(MPa)$ increasing from 0.1 to 4.0 MPa causes only small increasing of χ^*_{CO} because of higher inlet concentrations of CO and H_2O in gas mixture.

The most influence to CO conversion process had different ratios «steam-water» $n = V^{CO}_{H_2O}:V^{CO}_{\text{СГ}}$ from (0.1:1) to (0.3:1). For these rates χ^*_{CO} was increased from 0 to $\chi^*_{CO} = 80 - 85\%$. Further increasing $n > (0.3:1)$ not led to significant increasing of equilibrium rate of carbon oxide conversion χ^*_{CO}.

The results obtained show that chemical reaction of carbon oxide (II) conversion has forced mechanism on CO and relates to reducing-oxidizing chemical reaction.

It was proved that kinetic orders of reaction (1) are as follows: hydrogen H_2 not influences on reaction rate r_{CO} ($m_{CO} = 0$); carbon dioxide (IV) decreases the rate of direct reaction ($m_{CO_2} < 0$); carbon oxide proportionally increases reaction rate and has the first order ($m_{CO} = 1$); relating to water the reaction order depends on rate $n = [V_{H_2O}^{CO}]:[V_{CO}]$ and m_{CO} changes from 1 to 0.

It is necessary to notice that increasing of «steam-gas» ratio above $n = V_{H_2O}^{CO}:V_{\text{СГ}}^{CO} > 0.3:1$ has not significant influence on the rate of CO conversion process.

According to obtained results of low temperature CO conversion investigations it is possible to conclude that existing ratio «steam-gas» according to adapted process regulations is equal $n = 0.44:1$ and shows on significant steam surplus in nitrogen-hydrogen mixture.

Kinetic and thermodynamic calculations of low temperature CO conversion with decreased ratio $n = V_{H_2O}^{CO}:V_{\text{СГ}}^{CO} > 0.38:1$ shows on steam consumption saving $G_{\text{П}} = 157.5\, kg/tNH_3$ or energy saving $0.104\ G\ cal/tNH_3$ for ammonia plant AM-76 ($1420tNH_3/day$).

Investigations of deeper carbon dioxide conversion for III-d stage

For final CO removal the metanation process is carrying out according to reaction:

$$CO + 3H_2 = CH_4 + H_2O \qquad (2),$$

where the hydrogen necessary for ammonia synthesis is spent. Methane obtained according to reaction (2) is the ballast in nitrogen-hydrogen mixture and is periodically removed with another ballast gases.

To decrease the hydrogen losses according reaction (2) the investigations of deeper conversion of CO to CO_2 were carried out for virtual III-d stage of conversion with input content of CO equal to 0.49 % vol.

The results show on thermodynamic and kinetic possibility of CO conversion on III-d stage at different «steam-gas» ratios $n = V_{H_2O}^{CO}:V_{\text{СГ}}^{CO} = (0.1:1)-(0.5:1)$ at temperature range $t = (180 - 220)°C$ and similarity of process mechanism with low temperature conversion of CO to CO_2 at initial equilibrium concentration $2.9\ \%$ of hydrogen.

Thermodynamic and economical calculations had shown the efficiency of III-d stage unit of deeper conversion for ammonia plant AM-76 ($1420tNH_3/day$) that saves $4\ \%$ of hydrogen consumption that led to increase plant capacity on 60tNH_3/day, and 57 % decreasing of purge gases and therefore connected ammonia losses.

Enhancement of efficiency of monoethanolamine purification stage

The use in ammonia plant the III-d stage of CO conversion increases the content of carbon dioxide (IV) in nitrogen-hydrogen mixture more than normative so it is to be removed with monoethanolamine (MEA) capture stage.

To enhance the efficiency of MEA capture stage the number of scientific investigations and design works were carried out to retrofit this stage at two ammonia plants AM-70 ($1360tNH_3/day$). Existing shell-and tube heat exchangers at position 310 were changed on system with six high effective plate heat exchangers and desorbers as heat recuperators from hot lean solution to cold MEA-solution rich with carbon dioxide (IV) and as partial desorbers of CO_2 before regenerator.

High efficiency of plate heat exchange system let to decrease the temperature difference at hot and cold ends of heat exchange position on $10°C$ and to decrease steam consumption of regenerator reboilers on $7t/hour$. Simultaneously the heat losses through air coolers of lean MEA-solution before absorber inlet and through vapor mixture condenser were decreased on $8.35\ MW/hour$.

Conclusion

The indicators mentioned above may significantly increase the efficiency of existing high capacity ammonia plants and decrease the natural gas consumption.