Determination the phase contact surface size of nitric acid with ammonia neutralization process for the ammonium nitrate production

I U Sakharov, A F Makhotkin, U N Sakharov* and I A Makhotkin

Equipment Chemical Plants Department, Kazan National Research Technological University, 68 K. Marx str., Kazan 420015, Russia

*usacharas@mail.ru

Abstract. Neutralization process of 64% nitric solution with 90% gaseous ammonia has been investigated. Kinetics of nitric acid solutions neutralization process with ammonia investigation was carried out on batch apparatus model. The contact surface minimum area value for the process at adjusted productivity has been determined. The process ways of intensify have been formulated.

The neutralization process was carried out in cylindrical reactor filled with gaseous ammonia. At the beginning of the process, a nitric acid solution was fed into the reactor from the bottom with the formation of a liquid layer having a geometric phase contact surface of gas-liquid. The process was carried out at constant pressure, the value of which is achieved by automatic movement of movable piston inside the reactor. The description of the experimental installation and research technique are given in works [1, 2]. In the course of the process, time and position of movable piston on the measuring scale of reactor was fixed. The volume of reacted ammonia was determined by volume of gas change in the reactor during the process. The process was carried out at solution temperature: $T_1 = 20^\circ C$, $T_2 = 40^\circ C$, $T_3 = 60^\circ C$, $T_4 = 80^\circ C$. Based on the results of neutralization process investigation, the equation of reacted ammonia volume dependence on the time, elapsed since the beginning of the process, were obtained (figure 1).

The numerical value of ammonia volume in the reactor is determined by changing of gas volume from the beginning to the end of the process by the formula (1):

$$\Delta V = (V_\text{f} - V_\text{i})$$

where $V_\text{i}$ – initial volume of the gas phase, ml;
$V_\text{f}$ – final volume of the gas phase, ml.

In experimental conditions, this volume was:

$$\Delta V = (140 - 14) = 126 \text{ ml}$$

where 14 ml – final volume of the gas phase (air);
140 ml – the volume of gas in the reactor before the process start.

The initial concentration of ammonia in gas phase is determined by the formula (2):

$$C_{\text{NH}_3} = \frac{\Delta V}{V_\text{f}} \cdot 100\% = \frac{126}{140} \cdot 100\% = 90\%$$

At the initial stage of the process, according to the amount of gas participating in the process per unit of time, we calculate the rate of the mass transfer process according to the formula (3):
where \( M_T \) – mass transfer process volume rate at temperature \( T \), ml/s;
\[
\Delta V_T = \frac{\Delta V}{\Delta \tau} = \frac{V_T - V_i}{\Delta \tau} - \text{gas volume change in gas-liquid system from gas volume value at the beginning of mass transfer process } V_a \text{ to the current value } V_i \text{, at temperature } T, \text{ ml};
\]
\( \Delta \tau \) – time interval from beginning of mass transfer process to the current value, s.

The process rate value at initial stage of the process at different temperatures (figure 1) was:

1) \( \text{M}_{20^\circ C} = \frac{\Delta V}{\Delta \tau} \bigg|_{20^\circ C} = \frac{30}{5} = 6,0 \text{ ml/s} \)
2) \( \text{M}_{40^\circ C} = \frac{\Delta V}{\Delta \tau} \bigg|_{40^\circ C} = \frac{56}{3} = 7,2 \text{ ml/s} \)
3) \( \text{M}_{60^\circ C} = \frac{\Delta V}{\Delta \tau} \bigg|_{60^\circ C} = \frac{48}{3} = 9,6 \text{ ml/s} \)
4) \( \text{M}_{80^\circ C} = \frac{\Delta V}{\Delta \tau} \bigg|_{80^\circ C} = \frac{60}{5} = 12,0 \text{ ml/s} \).

We convert the volumetric rate value into the molar rate according to the formula (4):

\[
M_{nT} = \frac{M_T}{V_m},
\]

where \( M_{nT} \) – molar rate of mass transfer process at temperature \( T \), mol/s;
\( M_T \) – volumetric rate of mass transfer process at temperature \( T \), ml/s;
\( V_m \) – molar volume of ideal gas 22400, ml/mol.

\[
M_{n(20^\circ C)} = \frac{60}{95} \times \frac{2,678 \times 10^{-4} \text{ mol}}{1 \text{ s}} = 2,678 \times 10^{-4} \text{ mol/s},
\]

\[
M_{n(40^\circ C)} = \frac{72}{95} \times \frac{3,214 \times 10^{-4} \text{ mol}}{1 \text{ s}} = 3,214 \times 10^{-4} \text{ mol/s},
\]

\[
M_{n(60^\circ C)} = \frac{48}{95} \times \frac{4,285 \times 10^{-4} \text{ mol}}{1 \text{ s}} = 4,285 \times 10^{-4} \text{ mol/s},
\]

\[
M_{n(80^\circ C)} = \frac{60}{95} \times \frac{5,357 \times 10^{-4} \text{ mol}}{1 \text{ s}} = 5,357 \times 10^{-4} \text{ mol/s}.
\]

The activation energy value determined by graphical method (figure 2). To do this, we build the graph in coordinates \( \ln k \) vs. \( 1/T \).

\[
\ln k(20^\circ C) = \ln 2,678 \times 10^{-4} = -8,225 \text{ mol/s};
\]

\[
\ln k(40^\circ C) = \ln 3,214 \times 10^{-4} = -8,042 \text{ mol/s};
\]

\[
\ln k(60^\circ C) = \ln 4,285 \times 10^{-4} = -7,755 \text{ mol/s};
\]

\[
\ln k(80^\circ C) = \ln 5,357 \times 10^{-4} = -7,532 \text{ mol/s}.
\]

Figure 1. Relation of the volume of reacted ammonia per the process time in the reactor 1 – 20°C, 2 – 40°C, 3 – 60°C, 4 – 80°C.

Figure 2. Relation of the neutralization process rate constant per 1/T

The calculated value of the activation energy will be. \( T_1, T_4 \) values is given in Kelvin degrees:

\[
E_a = \frac{\ln \frac{k_{T_4}}{k_{T_1}} \cdot R}{\frac{1}{T_1} - \frac{1}{T_4}} = \frac{\ln 5,357 \times 10^{-4}}{\frac{1}{2,678 \times 10^{-4}} - \frac{1}{4,285 \times 10^{-4}}} = \frac{0,744 \times 8,314}{0,00058} = 10668 \text{ J/mol}.
\]
the-clock operation mode, productivity relative to ammonia at the consumption rate 214 kgNH₃/1t NH₄NO₃: B_{NH₃} = 566,47 t/day = 6,556 kg/s use the formula (6):

\[ F_{aT} = \frac{B}{(K_yT \Delta Y_{cp})}, \]  

where \( F_{aT} \) – phase contact surface area at temperature T, m²; \( B \) – specified productivity relative to ammonia, kg/s; \( K_y \) – process mass transfer coefficient at temperature T, kg/s·m²; \( \Delta Y_{cp} \) – average driving force of the mass transfer process.

Mass transfer coefficient \( K_y \), per contact surface unit area at temperature T, calculated by the expression (7):

\[ K_yT = \frac{M_{mT}}{F}, \]  

where \( M_{mT} \) – process rate, kg/s; \( F \) – the phase contact surface area in the system gas-liquid, m².

Convert the value of mass transfer process volumetric rate at temperature T into the dimension kg/s according to the formula (8):

\[ M_{mT} = M_T \rho_{NH_3}, \]  

where \( M_T \) – mass transfer process volumetric rate value at temperature T, m³/s; \( \rho_{NH_3} = 0,73 \text{ kg/m}^3 \) – accepted value the density ammonia gas.

The process rate value was:

\[
\begin{align*}
M_{m20^\circ C} &= 6,0 \cdot 10^{-6} \cdot 0,73 = 4,380 \cdot 10^{-6} \text{ kg/s} \\
M_{m40^\circ C} &= 7,2 \cdot 10^{-6} \cdot 0,73 = 5,256 \cdot 10^{-6} \text{ kg/s} \\
M_{m60^\circ C} &= 9,6 \cdot 10^{-6} \cdot 0,73 = 7,008 \cdot 10^{-6} \text{ kg/s} \\
M_{m80^\circ C} &= 1,20 \cdot 10^{-5} \cdot 0,73 = 8,760 \cdot 10^{-6} \text{ kg/s}
\end{align*}
\]

Phases contact surface geometric area of the cylindrical reactor in the system gas-liquid is determined by the formula (9):

\[ F = \frac{(\pi \cdot D^2)}{4}, \]  

where \( D = 0,039 \text{ m} \) – inner diameter of a cylindrical reactor.

The effective phases contact surface area is calculated by the formula (10):

\[ F_{ef} = F \cdot Z_{NH_3}, \]  

where \( Z_{NH_3} = 0,5 \) – molar fraction of ammonia in gas phase at the beginning of the process.

\( F_{ef} = 1,194 \cdot 10^{-3} \cdot 0,9 = 1,075 \cdot 10^{-3} \text{ m}^2 \)

In this case, the mass transfer coefficient referred to the phases contact surface will be

\[
\begin{align*}
K_{y20^\circ C} &= \frac{M_{m20^\circ C}}{F_{ef}} = 4,074 \cdot 10^{-3} \text{ kg/s·m}^2 \\
K_{y40^\circ C} &= \frac{M_{m40^\circ C}}{F_{ef}} = 4,889 \cdot 10^{-3} \text{ kg/s·m}^2 \\
K_{y60^\circ C} &= \frac{M_{m60^\circ C}}{F_{ef}} = 6,519 \cdot 10^{-3} \text{ kg/s·m}^2 \\
K_{y80^\circ C} &= \frac{M_{m80^\circ C}}{F_{ef}} = 8,148 \cdot 10^{-3} \text{ kg/s·m}^2
\end{align*}
\]

Absorption process driving force value is defined as a difference between ammonia concentration value in gas phase and the value of ammonia equilibrium concentration over the liquid phase [3]. For simplification we take: ammonia concentration value in the gas at the initial stage of the process is equal to the initial concentration, ammonia equilibrium concentration value over the liquid phase is equal to zero.

\[ \Delta Y_{mid} = \frac{C_{NH_3} - Q_{NH_3 \text{ liquid}}}{100\%} = \frac{90\% - 0\%}{100\%} = 0,9, \]  

(11)

To ensure the specified productivity relative to ammonia, phases contact surface area at the corresponding process temperature will be:

\[
\begin{align*}
F_{a20^\circ C} &= \frac{6,556}{4,074 \cdot 10^{-3} \cdot 0,9} = 1778,03 \text{ m}^2 \\
F_{a40^\circ C} &= \frac{6,556}{4,889 \cdot 10^{-3} \cdot 0,9} = 1489,96 \text{ m}^2 \\
F_{a60^\circ C} &= \frac{6,556}{6,519 \cdot 10^{-3} \cdot 0,9} = 1117,41 \text{ m}^2 \\
F_{a80^\circ C} &= \frac{6,556}{8,148 \cdot 10^{-3} \cdot 0,9} = 894,01 \text{ m}^2
\end{align*}
\]
With temperature increasing, the required phases contact surface area of nitric acid with ammonia neutralization process, which provides specified production capacity of ammonium nitrate, is decreasing.

Process rate constant relation per temperature is described by the Arrhenius formula (12):

$$K = A \cdot e^{\frac{E_a}{RT}}.$$  \hspace{1cm} (12)

From here \( \ln[k(160^\circ \text{C})] = -6,860 \text{ mol/s} \), in this case, the molar rate at the process temperature in an industrial reactor is 160°C (92% solution NH₄NO₃) will be \( M_n(160^\circ \text{C}) = 10,489 \cdot 10^{-4} \text{ mol/s} \).

Process rate relation per temperature is approximately described by the empirical Van’t Hoff law (13):

$$M_t = M_0 \cdot \gamma^n,$$  \hspace{1cm} (13)

where \( M_0 \) – process rate at the temperature \( t_o \); 
\( M_t \) – process rate at the temperature \( t_i \); 
\( \gamma \) – process rate temperature coefficient in the range 20°C; 
\( n = \frac{t - t_o}{20} \) – number of temperature change intervals; 
\( M_{m \text{ } 80^\circ \text{C}} = 8,760 \cdot 10^{-6} \text{ kg/s} \), 
\( M_{m \text{ } 60^\circ \text{C}} = 7,008 \cdot 10^{-6} \text{ kg/s} \), 
\( \gamma_{20} = \frac{8,760 \cdot 10^{-6}}{7,008 \cdot 10^{-6}} = 1,25. \)

Calculate the process rate value in the reactor at the neutralization process temperature equal to 160 °C

\( M_{m \text{ } 160^\circ \text{C}} = M_{m \text{ } 80^\circ \text{C}} \cdot 1,25^4 = 8,760 \cdot 10^{-6} \cdot 1,25^4 = 13,076 \cdot 10^{-6} \text{ kg/s}. \)

The molar fraction of ammonia in the gas phase that enter to the neutralization stage of ammonium nitrate production technology is equal to 1, while the mass transfer coefficient referred to the phases contact surface will be

$$K_{\gamma \text{ } 160^\circ \text{C}} = \frac{M_{m \text{ } 160^\circ \text{C}}}{F} = \frac{13,076 \cdot 10^{-6}}{1,194 \cdot 10^{-3}} = 10,951 \cdot 10^{-3} \text{ kg/s} \cdot \text{m}^2.$$

Phases contact surface area value to ensure the specified ammonium nitrate production capacity that carried out in industrial conditions will be:

$$F_{\theta \text{ } 160^\circ \text{C}} = \frac{6,556}{10,951 \cdot 10^{-3} \cdot 1,0} = 596,67 \text{ m}^2.$$

Ways of intensifying the nitric acid with ammonia neutralizing process in the ammonium nitrate production technology should be directed to reducing spray loses in the reactor and increasing the throughput of the reactor in the gas phase. The formulated ways of intensification are optimally provided by using the vortex contact devices of the reactor [4]. In some technological processes, vortex devices made it possible not only to intensify the processes, but also to reduce capital expenditures and energy costs practically to zero. The last is achieved by combining different processes within one vortex device.

References

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