

MATERIAL BALANCE

Let 100 kg/hr of feed from the chloronitrobenzene production contains:

p-Nitrochlorobenzene = 65 kg

o-Nitrochlorobenzene = 35 kg

50% of the p – Nitrochlorobenzene is been recovered from 1st crystallizer.

$$\begin{aligned}\therefore \text{Weight of P- Nitrochlorobenzene Crystallizes out} &= (65 \times 0.5) \\ &= 32.5 \text{ kg.}\end{aligned}$$

\therefore The mother liquor will contain,

32.5 kg of P – Nitrochlorobenzene (48.1%)

35 kg of Nitrochlorobenzene (51.9%)

Now, from overall balance, since the system operates at steady state, and there will be no loss of P-Nitrochlorobenzene with any other stream.

Therefore p-nitrochlorobenzene that crystallizes in the second crystallizer = 32.5 kg.

Now assuming that the crystallization is been taken at 18⁰C

The composition of the mother liquor should must be over 35% of p – Nitrochlorobenzene.

Let it be, 38% of P-Nitrochlorobenzene

And 62% of O-Nitrochlorobenzene

Let 'R' be the recycled mother liquor to the still per kg of mother liquor from the crystallizer.

$$\begin{aligned}\therefore \text{The Recycle stream} &= (32.5 + 35) R \text{ kg} \\ &= 67.5 R \text{ Kg.}\end{aligned}$$

$$\begin{aligned}\therefore \text{p-Nitrochlorobenzene coming in to the still} &= (67.5 R \times 0.38 + 32.5) \\ &= (25.65 R + 32.5) \text{ kg.}\end{aligned}$$

$$\begin{aligned}\text{And O-Nitrochlorobenzene feed in} &= (67.5R \times 0.62 + 35) \\ &= (42.85 R + 35) \text{ kg.}\end{aligned}$$

Since operated at steady state,

Incoming feed = out going stream.

Let the weight fraction of p- Nitrochlorobenzene is recovered is 70% pure.

And the entire p-nitrochlorobenzene is recovered in the stream.

$$\begin{aligned}\text{Therefore the flow of the stream II} &= \left(\frac{25.65R + 32.5}{0.7} \right) \\ &= (36.64 R + 46.43) \text{ kg.}\end{aligned}$$

∴ The para composition of 70% is dropped to 38%.

Therefore for ortho nitrochlorobenzene basis (Inert, since it doesn't crystallizes out)

$$= 70/30 = 7/3 \text{ and}$$

In the Mother liquor = $38 / 1-38 = 38 / 62$.

And o-Nitrochlorobenzene present in the fraction II

$$\begin{aligned}&= (36.6 R + 46.43) - (25.65 R + 32.5) \\ &= (10.99R + 13.93) \text{ kg.}\end{aligned}$$

Therefore

$$(10.99R + 13.93) \times [7/3 - 38/62] = 323.5 \text{ kg.}$$

$$10.99 R + 13.93 = 18.89$$

$$R = 0.451$$

∴ Ortho nitrochlorobenzene in the second fraction

$$\begin{aligned}&= (41.85 \times 0.451 + 35) - (10.99 \times 0.451 + 13.93) \\ &= 35 \text{ kg.}\end{aligned}$$

100% of nitrochlorobenzene will produce 65% p – Nitrochlorobenzene.

∴ Chlorobenzene needed to produce 10,000 tpd (416.66 kg / hr) of p – nitrochlorobenzene

$$\begin{aligned}&= \frac{416.66 \times 100}{65} \\ &= 641.01 \text{ kg / hr.}\end{aligned}$$

Therefore feed to produce 10,000 tpd (416.66 kg/hr) of p – nitrochlorobenzene , = 641.01 kg/hr

Weight of p – nitrochlorobenzene that crystallizes in 1st crystallizer

641.01

$$= 0.65 \times 0.5 \times$$

$$= 208.33 \text{ kg/hr.}$$

Now from overall balance, since the system operates at steady state, and there is no loss of p – nitrochlorobenzene in any of the stream.

p-nitrochlorobenzene crystallizing in second crystallizer

$$= 416.66 - 208.33$$

$$= 208.33 \text{ kg}$$

$$\text{Kg's of solution in the recycle stream} = (208.33 + 0.35 \times 641.01)R]$$

$$= (208.33 + 0.35 \times 641.01) 0.451$$

$$= 195.14 \text{ kg/ hr.}$$

P – Nitrochlorobenzene coming to the still

$$= (195.14 \times 0.38 + 208.33)$$

$$= 282 \text{ kg / hr.}$$

And O – Nitrochlorobenzene feed in to the still

$$= (195.14 \times 0.62 + 224.35)$$

$$= 345.53 \text{ kg.}$$

Since operated at steady state. Incoming stream = outgoing stream.

Let the weight fraction of p – nitrochlorobenzene stream recovered is 70% pure.

i.e. 70% p – nitrochlorobenzene and 30% o-Nitrochlorobenzene.

And the entire feed is recovered in the stream.

$$\text{Flow of the stream} = 282 / 0.7$$

$$= 402.85 \text{ kg}$$

And in the mother liquor we have 38 parts of p – Nitrochlorobenzene to 62 parts of o – Nitrochlorobenzene

And o-Nitrochlorobenzene in fraction 2

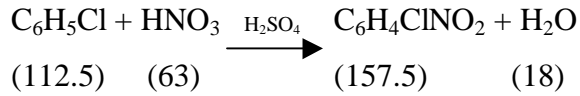
$$= 402.85 - 282$$

$$= 120.85 \text{ kg.}$$

∴ O-Nitrochlorobenzene recovered from fraction 2

$$= 345.33 - 120.85$$

$$= 224.32 \text{ kg.}$$



Assuming from literature (Groggin's unit processes in organic synthesis) conversion of 98% of chlorobenzene to Nitrochlorobenzene.

Basis: 1 hr operation.

Theoretical amount of chlorobenzene required

$$\begin{aligned} &= (641.01) \times \frac{112.5}{157.5} \\ &= 457.867 \text{ kg.} \end{aligned}$$

Using 2% excess,

$$\begin{aligned} \text{Therefore chlorobenzene required} &= 457.867 \times 1.02 \\ &= 467.62 \text{ kg.} \end{aligned}$$

Using 96% H₂SO₄ and 90% HNO₃. For nitration acid mixture of following composition.

HNO₃ 35.5% (By weight)

H₂SO₄ 52.5% (By weight)

H₂O 12.0 % (By weight)

(Taken from Kirk and Othmer volume – 15)

Theoretical amount of Nitric acid (100%) Needed

$$\begin{aligned} &= 0.98 \times 63 \times 641.01 / 157.5 \\ &= 251.27 \text{ kg/hr.} \end{aligned}$$

Therefore amount of (90%) Nitric acid needed = 251.27/0.9

$$= 279.18 \text{ kg/ hr.}$$

providing 2% excess.

Therefore total amount of 90%

$$\begin{aligned}\text{Nitric acid needed} &= 279.18 \times 1.02 \\ &= 284.8 \text{ kg/hr}\end{aligned}$$

$$\begin{aligned}\text{Amount of Nitrating acid mixture required} &= 279.18 / 0.355 \\ &= 707.8 \text{ kg / hr.}\end{aligned}$$

$$\begin{aligned}\text{Amount of sulphuric acid required} &= \frac{707.8 \times 0.525}{0.96} \\ &= 387 \text{ kg/hr}\end{aligned}$$

$$\begin{aligned}\text{Providing 2\% excess} &= 1.02 \times 387 \\ &= 395 \text{ kg / hr.}\end{aligned}$$

Products from Nitrator:

$$\text{Nitrochlorobenzene} = 641.01 \text{ kg/hr.}$$

$$\begin{aligned}\text{Water formed during reaction} &= 457 \times \frac{18}{112.5} \\ &= 73.12 \text{ kg/hr.}\end{aligned}$$

$$\begin{aligned}\text{Unreacted chlorobenzene} &= 467.02 - 457.86 \\ &= 9.16 \text{ kg/hr.}\end{aligned}$$

$$\begin{aligned}\text{Water present in nitric acid} &= 0.1 \times 284.8 \\ &= 28.48 \text{ kg/hr.}\end{aligned}$$

$$\begin{aligned}\text{Water present in sulphuric acid} &= 0.04 \times 395 \\ &= 15.8 \text{ kg/hr}\end{aligned}$$

$$\begin{aligned}\therefore \text{Total water present in nitric acid and sulphuric acid} &= 28.48 + 15.8 \\ &= 44.28 \text{ kg/hr}\end{aligned}$$

$$\text{Unreacted sulphuric acid} = 379.2 \text{ kg/ hr.}$$

$$\begin{aligned}\text{Unreacted nitric acid} &= 284.8 - 279.8 \\ &= 5 \text{ kg/hr}\end{aligned}$$

Separation of nitration product:

Separation is done by gravity separator. We assume a sulphuric acid concentration of 0.8% in nitration product.

Component	Acid layer (kg/hr)	Nitration product (kg/hr)
Nitrochlorobenzene	-	641.01
Chlorobenzene	-	9.16
Nitric acid	5	-
Sulphuric acid	376.167	3.023
Water	117.4	-
	= 498.56 kg/hr	= 651.4 kg/hr

Concentration of sulphuric acid in acid layer = 75.4%

Concentration of nitric acid in acid layer = 1%

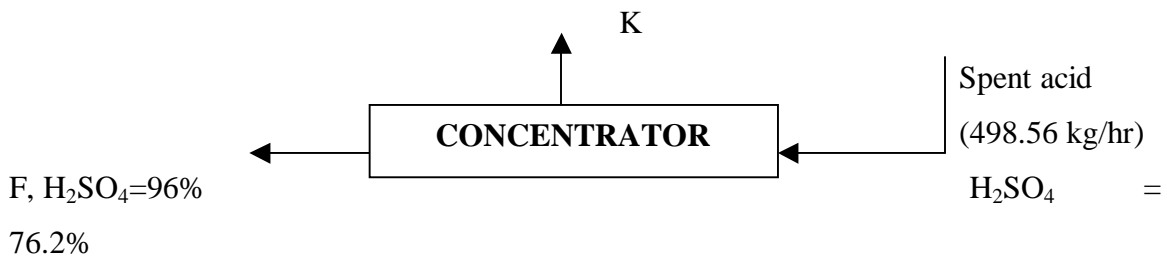
Since the concentration of nitric acid in acid layer is low, hence it can be neglected.

Concentration of water in Acid = 23.6%.

Concentrator:

% of sulphuric acid in nitric acid free basis = 76.21%

% of water in nitric acid free basis = 23.79%



Where 'K' is the kg's of water to be evaporated per hour.

Sulphuric acid balance

$$F \times 0.96 = 498.56 \times 0.7621$$

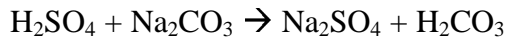
$$\therefore F = 395.74 \text{ kg/hr.}$$

Water balance

$$395.74 \times 0.04 + K = 498.56 \times 0.2379$$

$$K = 103.32 \text{ kg/hr}$$

∴ Water to be evaporated = 103.32 kg/hr

Washing of nitration products:**a) Washing with sodium carbonate:**

$$(98) \quad (106)$$

Quantity of sodium carbonate required to neutralize sulphuric acid present in Nitration product

$$= 3.033 \times \frac{106}{98}$$

$$= 3.280 \text{ kg/hr}$$

b) Washing with water:

Wash water is used in the ratio of 1:2 on weight bases.

i.e., 2 parts of water for 1 part of nitrated product.

Therefore quantity of wash water required

$$= 650.23 \times 2$$

$$= 1300.46 \text{ kg/hr}$$