ENTHALPY BALANCES WITH CHEMICAL REACTION

Calculation of the amount and temperature of combustion products

Methane is burnt in 50 % excess of air. Considering that the process is adiabatic and all methane burns, determine the temperature of the combustion products. The temperature of the air and methane fed into the reactor is 25 °C. What is the consumption of the air per 1 kmol of methane and what is the composition of the combustion products? Solve the problem by means of fictitious streams and without. The values of specific heat capacities are given below.

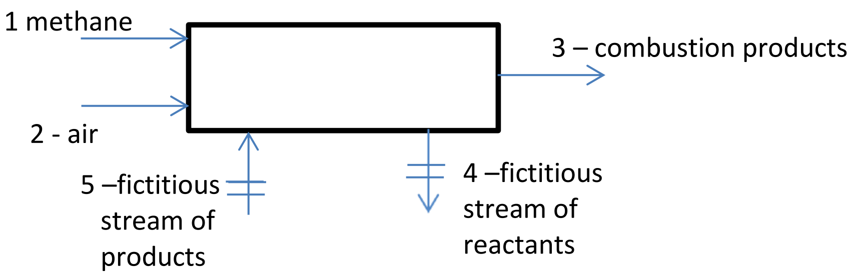
$c_p(O_2)$ = 36 kJ kmol^{-1} K^{-1}; $c_p(CO_2)$ = 36 kJ kmol^{-1} K^{-1}; $c_p(H_2O)$ = 45.5 kJ kmol^{-1} K^{-1}; $c_p(N_2)$ = 45.5 kJ kmol^{-1} K^{-1};

Data: M – CH_4; K – O_2; U – CO_2; V – H_2O; D – N_2; $CH_4 + 2O_2 = CO_2 + 2H_2O$;

$x_{M1} = 1$; $x_{K2} = 0.21$; $x_{D2} = 0.79$; $t_1 = t_2 = 25$ DC; $n_1 = 1$ kmol; 50 % excess of K, complete oxidation of M; $c_{p,i}$ given above

Solution:

1. Using the fictitious streams: Schematics



Matrix of the problem:

j	1	2	3	4	5
A_j	+1	+1	-1	-1	+1
n_j / kmol	1	n_2	n_3	n_4	n_5
x_M	1	0	0	x_{M4}	0
x_K	0	0,21	x_{K3}	x_{K4}	0
x_D	0	0,79	x_{D3}	0	0
x_U	0	0	x_{U3}	0	x_{U5}
x_V	0	0	x_{V3}	0	x_{V5}
t_j / °C	25	25	t_3	-	-
h_j / kJ kmol^{-1}	h_1	h_2	h_3	h_4	h_5

2. **Balance equations:**

total balance: $1 + n_2 + n_5 = n_3 + n_4$

molar balance of component M: $1 = x_{M4}n_4$

molar balance of component K: $0.21n_2 = x_{K3}n_3 + x_{K4}n_4$

molar balance of component D: $0.79n_2 = x_{D3}n_3$

molar balance of component U: $x_{U5}n_5 = x_{U3}n_3$

The excess of air defines the real consumption of oxygen for burning:

$$P_{O_2} = \frac{n_{K2} - n_{K2,theoretical}}{n_{K2,theoretical}}$$

where the theoretical consumption of air can be found from the extent of reaction.

For a completely burnt CH_4: $0 = n_{CH_4,0} + \nu_{CH_4}\xi$

For theoretical consumption of O_2: $0 = n_{O_2,0} + \nu_{O_2}\xi$ ----> $n_{O_2,0} = \frac{\nu_{O_2}}{\nu_{CH_4}} n_{CH_4,0}$

By combining the equations describing the excess of air and theoretical consumption of air one arrives at an expression for the actual consumption of air:

$$n_{O_2} = \left(1 + P_{O_2}\right)\left(\frac{\nu_{O_2}}{\nu_{CH_4}}\right) n_{CH_4,0} = (1 + 0.5)\left(\frac{-2}{-1}\right) 1 = 3kmol$$

By knowing the composition of air one can calculate the total amount of air required:

$$n_2 = \frac{n_{O_2}}{x_{O_2,2}} = \frac{3}{0.21} = 14.3\ kmol$$

The composition of the fictitious streams is: $x_{CH_4} = \frac{1}{3};\ x_{O_2} = \frac{2}{3};\ x_{CO_2} = \frac{1}{3};\ x_{H_2O} = \frac{2}{3};$

The total balance reduces to $1 + n_2 = n_3$, since $n_4 = n_5$. n_3 is then equal to 15.3 kmol.

n_4 can be calculated from $n_4 = n_{CH_4} + n_{O_{2,theoretical}} = 1 + 2 = 3\ kmol$

and finally the composition of the combustion products can be calculated from the particular component molar balances:

for oxygen: $x_{O_2,3} = \frac{n_2 x_{O_2,2} - n_4 x_{O_2,4}}{n_3} = \frac{14.3 \cdot 0.21 - 3 \cdot 2/3}{15.4} = 0.065$

for nitrogen: $x_{N_2,3} = \frac{n_2 x_{N_2,2}}{n_3} = \frac{14.3 \cdot 0.79}{15.4} = 0.733$

for carbon dioxide: $x_{CO_2,3} = \frac{n_5 x_{N_2,5}}{n_3} = \frac{3 \cdot 1/3}{15.4} = 0.065$

for water: $x_{H_2O,3} = \frac{n_5 x_{H_2O,5}}{n_3} = \frac{3 \cdot 2/3}{15.4} = 0.13$

3. Enthalpy balance

a) solution using the fictitious streams

The first thing to do is to find the standard enthalpy of formation usually given at 25 °C. This table can be found on departmental website: (http://uchi.vscht.cz/index.php/en/studium/uplatneni-absolventu/e-tabulky/formation_enthalpy)

standard enthalpy of formation for carbon dioxide: $\Delta h_{F,CO_2}(25^{\circ}C) = -393800\,J/mol$

standard enthalpy of formation for water (in the state of ideal gas): $\Delta h_{F,H_2O}(25^{\circ}C) = -242000\,J/mol$

standard enthalpy of formation for methane (in the state of ideal gas): $\Delta h_{F,CH_4}(25^{\circ}C) = -74900\,J/mol$

The standard enthalpy of formation for oxygen and nitrogen is equal to zero.

The total enthalpy balance including fictitious streams reads:

$$n_1 h_1 + n_2 h_2 + n_5 h_5 = n_3 h_3 + n_4 h_4$$

By choosing 25 °C and all components in the state of ideal gas as a reference state we can simplify the above expression to

$$n_5 h_5 = n_3 h_3 + n_4 h_4$$

where $h_3 = \sum_{i=1}^{I} x_{i,3} \langle c_{pi} \rangle (t_3 - t^{ref}) = \left(x_{O_2,3}\langle c_{pO_2}\rangle + x_{N_2,3}\langle c_{pN_2}\rangle + x_{H_2O,3}\langle c_{pH_2O}\rangle + x_{CO_2,3}\langle c_{pCO_2}\rangle\right)(t_3 - t^{ref}) = (0.065 \cdot 36 + 0.733 \cdot 34 + 0.065 \cdot 56 + 0.13 \cdot 45.5) = 36.493\ kJ\ kmol^{-1} K^{-1}$;

$h_4 = -x_{CH_4} \Delta h_{F,CH_4}$; and $h_5 = -\left(x_{CO_2}\Delta h_{F,CO_2} + x_{H_20}\Delta h_{F,H_2O}\right)$

By putting all equations together and rearranging we can arrive at the expression for the temperature of the output stream:

$$t_3 = \frac{n_4 x_{CH_4} \Delta h_{F,CH_4} - n_5\left(x_{CO_2}\Delta h_{F,CO_2} + x_{H_20}\Delta h_{F,H_2O}\right)}{\sum_{i=1}^{I} x_{i,3}\langle c_{pi}\rangle} + 25$$

$$= \frac{3000 \cdot \frac{1}{3} \cdot (-74900) - 3000\left(\frac{1}{3}(-393800) + \frac{2}{3}(-242000)\right)}{15400 \cdot 36.493} + 25 = 1456^{\circ}C$$

b) solution without the use of fictitious streams

In this case the total enthalpy balance reduces to $H_1 + H_2 = H_3$ which requires a definition of a new reference state. This new reference state is given by the temp. 25 °C and elements in their most stable state. The expressions for the enthalpies are:

$H_1 = n_1 \Delta h_{F,CH_4}$; $H_2 = 0$; $H_3 = n_3 \left[\sum_{i=1}^{I} x_{i,3} \langle c_{pi} \rangle \left(t_3 - t^{ref} \right) + x_{CO_2} \Delta h_{F,CO_2} + x_{H_2 0} \Delta h_{F,H_2O} \right]$

By rearranging one obtains an expression for t_3:

$$t_3 = \frac{\left[\left(\frac{n_1}{n_3} \Delta h_{F,CH_4} \right) - \left(x_{CO_2} \Delta h_{F,CO_2} + x_{H_2 0} \Delta h_{F,H_2O} \right) \right]}{\sum_{i=1}^{I} x_{i,3} \langle c_{pi} \rangle (t_3 - t^{ref})} + 25$$

$$= \frac{\left[\left(\frac{1000}{15300} (-74900) \right) - \left(0.065(-393800) + 0.13(-242000) \Delta h_{F,H_2O} \right) \right]}{36.493} + 25 = 1454°\text{C}$$

FLUIDIZATION

Calculation of the voidage in a fluidized bed from the pressure drop

What is the voidage of the fluidized bed and the total mass of K_2SO_4 crystals in a fluidized bed when the pressure drop across the fluidized bed is 125 mbar, its height 1 m and the diameter of the device is 0.9 m. The fluid used for creating the fluidized bed is air with temperature of 25 DC and normal pressure.

Solution:

1. The total mass of crystals can be calculated from the known pressure drop.
$$m_c = \frac{\pi D^2 \Delta p_{DIS}}{4g(\rho_s - \rho_f)}\rho_s = \frac{\pi 0.9^2 \cdot 12500}{4 \cdot 9.81 \cdot (2660 - 1.185)} 2660 = 811\ kg$$
2. One can determine the voidage from its definition and the knowledge of the device geometry and the amount of crystals.
$$\varepsilon = 1 - \frac{V_s}{V} = 1 - \frac{4m_s}{\pi D^2 h \rho_s} = \frac{4 \cdot 811}{\pi 0.9^2 \cdot 1 \cdot 2660} = 0.52$$

Calculation of the minimum fluidization velocity for spherical particles

Calculate the minimum fluidization velocity of aluminium spheres with diameter of 0.95 mm. The fluid used is methanol at 10 DC.

Solution:

1. Calculation of the Ar number
$$Ar = \frac{g d_s^3 (\rho_s - \rho_f)}{\eta_f^2}\rho_f = \frac{9.81 \cdot 0.00095^3 (2700 - 801)}{0.00071^2} \cdot 801 = 25379$$
2. Calculation of the corresponding Re number from $Ar = 150 \frac{1-\epsilon_0}{\varepsilon_0^3} Re_0 + \frac{1.75}{\varepsilon_0^3} Re_0^2$, where ε_0 is 0.4 (typical value for a fixed bed of spherical particles).
$$25379 = 150 \frac{1-0.4}{0.4^3} Re_0 + \frac{1.75}{0.4^3} Re_0^2$$ ---------> $Re_0 = 14.15$
3. Calculation of v_0 from the definition of Reynolds number for fluidization:
$$Re_0 = \frac{d_s v_0 \rho_f}{\eta_f} \quad \text{------->} \quad v_0 = \frac{Re_0 \eta_f}{d_s \rho_f} = \frac{14.15 \cdot 0.00071}{0.00095 \cdot 801} = 0.0132\ ms^{-1}$$

Results: The minimum fluidization velocity is 0.0132 ms^{-1}.

CHARACTER OF FLUID FLOW

Calculation of volume of a flow-through device in using residence time distribution function

A continuous flow of a tracer was suddenly introduced into a flow-through device of unknown volume. The ratio of outlet and inlet concentrations as a function of time is given in the table below.

τ (hours)	c_{outlet} / c_{inlet}	τ (hours)	c_{outlet} / c_{inlet}
0.0	0.000	0.8	0.860
0.1	0.023	0.9	0.900
0.2	0.120	1.0	0.940
0.3	0.270	1.2	0.970
0.4	0.430	1.4	0.990
0.5	0.580	1.6	0.996
0.6	0.700	1.8	0.999
0.7	0.790		

Determine the residence time distribution function, differential residence time distribution function, mean residence time, and the volume of the device for the volumetric flow rate 4 m^3h^{-1}.

Solution:

1. The residence time distribution function is given by $F(\tau) = \frac{c(\tau)-c_0}{c_\infty - c_0}$. In our problem c_0 = 0 (no tracer in the device at c_0), and $c_\infty = c_{inlet}$ since the type of perturbation is permanent switch.
   Then $F(\tau) = \frac{c(\tau)-c_0}{c_\infty - c_0} = \frac{c(\tau)}{c_{inlet}} = \frac{c_{outlet}}{c_{inlet}}$ and the RTD function is thus equal to the ratio of c_{outlet}/c_{inlet} given in the table.
2. The differential residence time distribution function can be obtained by numerical differentiation of F(τ): $E(\tau_i) = \frac{F(\tau_{i+1})-F(\tau_{i-1})}{\tau_{i+1}-\tau_{i-1}}$; $E(\tau_{end}) = \frac{F(\tau_{end-2})-4F(\tau_{end-1})+34F(\tau_{end})}{2(\tau_{end}-\tau_{end-2})}$

   For τ_i=0.1 h the equation above reads: $E(0.1) = \frac{0.120-0.000}{0.2} = 0.6;$

$$E(1.8) = \frac{0.990-4\cdot 0.996+3\cdot 0.999}{2\cdot 0.2} = 0.008;$$

τ (hours)	c_{outlet} / c_{inlet}	E(τ)/h^{-1}	τ (hours)	c_{outlet} / c_{inlet}	E(τ)/h^{-1}
0.0	0.000	0.000	0.8	0.860	0.550
0.1	0.023	0.600	0.9	0.900	0.400
0.2	0.120	1.235	1.0	0.940	0.230
0.3	0.270	1.550	1.2	0.970	0.125
0.4	0.430	1.550	1.4	0.990	0.065
0.5	0.580	1.350	1.6	0.996	0.023
0.6	0.700	1.050	1.8	0.999	0.008
0.7	0.790	0.800			

3. The mean residence time is calculated by numerical integration of: $\bar{\tau} = \int_0^\infty \tau E(\tau) \mathrm{d}\tau$

   e. g. by using Simpson method: $\int_a^b f(x)\mathrm{d}x \approx \frac{\Delta x}{3}(y_0 + 4(y_1 + y_3 + y_5 + y_7 + \cdots) + 2(y_2 + y_4 + y_6 + y_8 + \cdots) + y_n)$

   The mean residence time will be calculated for two intervals τ: 0 to 1 and 1 to 1.8.

$$\bar{\tau} = \frac{0.1}{3}(0.230 + 4 \cdot 2.12 + 2 \cdot 1.937) + \frac{0.2}{3}(0.2436 + 2 \cdot 0.091 + 4 \cdot 0.1860) = 0.497h$$

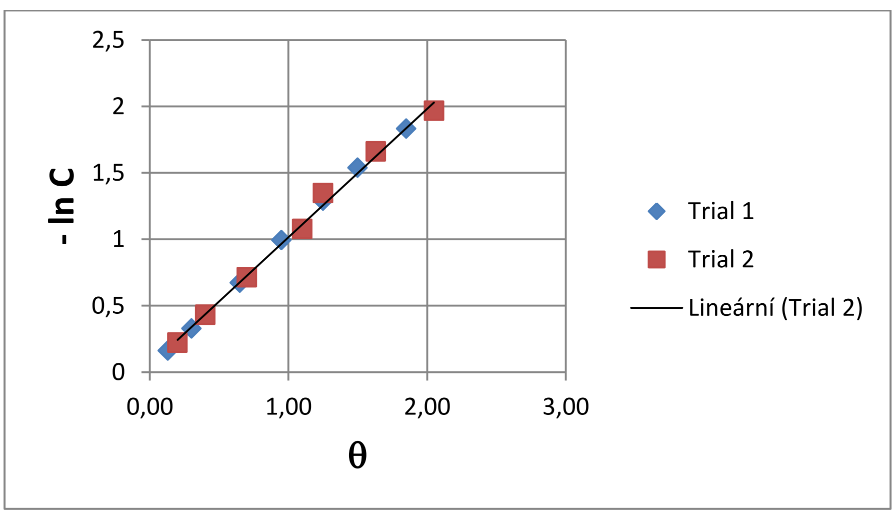
4. The flow volume of the device is then $V_d = \dot{V}\bar{\tau} = 4 \cdot 0.497 = 1.99\ m^3$

Verification of the assumption of ideal mixing

Mixing in a reactor was characterized in a set of experiments in which a pulse of helium was added to air of constant flow rate. Based on the measured data in the table below, decide, whether the reactor can be considered as ideal mixer. C is the dimensionless concentration of helium ($C = \frac{c-c_K}{c_0-c_K}$), θ is the dimensionless time.

Trial 1		Trial 2	
Volumetric flow rate: 6.25 cm^3/s		Volumetric flow rate: 10.6 cm^3/s	
Revolutions of the stirrer: 1290 min^{-1}		Revolutions of the stirrer: 630 min^{-1}	
θ	C	θ	C
0.13	0.85	0.20	0.80
0.30	0.72	0.40	0.65
0.65	0.51	0.70	0.49
0.95	0.37	1.10	0.34
1.25	0.275	1.25	0.26
1.5	0.215	1.63	0.19
1.85	0.16	2.05	0.14

1. Using the unsteady mass balance for an ideal mixer and solving it, one can derive the expression for the relation between C and θ: $C = \exp(-\theta)$, or $-\ln C = \theta$. By plotting the measured data in a graph of –ln*C* as a function of θ we should get a line.



Results: The assumption of the reactor working as an ideal mixer is correct.

SETTLING

Calculation of the settling velocity of a spherical particle

What shall the diameter of a dryer in the upper part be so that the air velocity was 5 % lower than the settling velocity of spherical particles with diameter of 0.2mm and density of 1770 kgm^{-3}? The volumetric flow rate of air measured at 20°C and normal pressure (atmospheric pressure) is 2700 m^3h^{-1}. The conditions in the dryer are: 70 DC and 735 torr. What is the settling velocity of given particles at the conditions in the dryer.

Solution:

1. Calculation of the Ar number: $Ar = \frac{g d_p^3(\rho_p - \rho)}{\rho\, \nu^2} = \frac{9.81\left(0.2\times10^{-3}\right)^3(1770-0.996)}{0.996(20.5\times10^{-6})^2} = 357$
2. Calculation of the Ly number from the corresponding equation for the transient region

$$Ar = 138.6Ly^{0.875} \quad \text{------->} Ly = \left(\frac{Ar}{138.6}\right)^{\frac{1}{0.875}} = \left(\frac{357}{138.6}\right)^{\frac{1}{0.875}} = 2.949$$

3. Calculation of the settling velocity from the known value of Ly:

$$Ly = \frac{Re^3}{Ar} = \frac{v_s^3\rho}{g\,\nu(\rho_p - \rho)} \quad \text{------->} \quad v_s = \left(\frac{Ly g\,\nu(\rho_p - \rho)}{\rho}\right)^{\frac{1}{3}} = (2.949 \cdot 9.81 \cdot 20.510^{-6}(1770 - 0.996)/0.996)^{\frac{1}{3}} = 1.12\, ms^{-1}$$

4. Calculation of the air velocity:

$$v_{air} = 0.95 v_s = 0.95 \cdot 1.12 = 1.06\, ms^{-1}$$

5. Calculation of the actual air volumetric flow rate in the dryer using ideal gas state equation:

$$Q_{air,d} = \frac{p_1 T_1 Q_{air,m}}{p_2 T_2} = \frac{101325 \cdot 343.16}{735 \cdot 133.32 \cdot 293.16}\frac{2700}{3600} = 0.908\, ms^{-1}$$

6. Calculateion of the extended diameter of the dryer:

$$D = \left(\frac{4Q_{air,d}}{\pi v_{air}}\right)^{1/2} = \left(\frac{4 \cdot 0.908}{\pi 1.06}\right)^{1/2} = 1.04\, m$$

Results: The diameter of the extended part of the dryer is 1.04 m. The settling velocity of the particle is 1.12 ms^{-1}.

Calculation of the diameter of a spherical particle from known settling velocity

The diameters of two samples of a material with a density of 2650 kgm^{-3} were determined form the settling velocities. The experiments were carried out in water with temperature of 20 DC. The distance the particle of the first sample traveled in 5 min 23 s was 15 cm. The particle of the second sample travelled 90 cm in 30 s. Calculate the diameter of particles.

Solution:

1. Calculation of the settling velocity from the measured data:

$$v_{s,1} = \frac{L_1}{t_1} = \frac{0.15}{323} = 2.408 \times 10^{-4} ms^{-1}$$

$$v_{s,2} = \frac{L_2}{t_2} = \frac{0.9}{30} = 0.03 ms^{-1}$$

2. Calculation of the corresponding Ly numbers:

$$Ly_1 = \frac{v_{s1}^3 \rho}{g\, \nu(\rho_p - \rho)} = \frac{2.408 \times 10^{-4^3} \cdot 998.2^2}{9.81 \cdot 1.005 \times 10^{-3}(2650 - 998.2)} = 6.13 \times 10^{-6}$$

$$Ly_2 = \frac{v_{s2}^3 \rho}{g\, \nu(\rho_p - \rho)} = \frac{0.03^3 \cdot 998.2^2}{9.81 \cdot 1.005 \times 10^{-3}(2650 - 998.2)} = 1.653$$

3. Calculation of the Ar from the corresponding equation:

particle 1: $Ar_1 = 5832 {Ly_1}^{0.5} = 5832 \cdot (6.13 \times 10^{-6})^{0.5} = 0.189$

particle 2: $Ar_1 = 138.6 {Ly_2}^{0.875} = 138.6 \cdot (1.653)^{0.5} = 216$

4. Calculation of the particle diameter from the Ar

particle 1: $Ar = \frac{g d_p^3 (\rho_p - \rho)}{\rho\, \nu^2}$ --------> $d_{p,1} = \left(\frac{Ar_1 \rho\, \nu^2}{g(\rho_p - \rho)}\right)^{1/3} = \left(\frac{0.189 \cdot (1.005 \times 10^{-6})^2}{9.81(2650 - 998.2)2}\right)^{1/3} =$ $0.228 \times 10^{-4} m$

particle 2: $d_{p,2} = \left(\frac{Ar_2 \rho\, \nu^2}{g(\rho_p - \rho)}\right)^{1/3} = \left(\frac{216 \cdot (1.005 \times 10^{-6})^2}{9.81(2650 - 998.2)2}\right)^{1/3} = 0.2388 \times 10^{-3} m$

Results: The diameters of the first and the second sample are 22.8 µm and 239 µm.

Design of a gravitational settler

Calculate the performance (tons/hour) of a settler whose shape is a cylinder with inner diameter of 3 m. The processed suspension having temperature of 15 DC contains 15 wt. % of solid phase. The solid phase is spherical particles with diameter of 50 μm and density of 3000 kgm^{-3}. The sludge contains 60 wt. % of the solid phase. Consider the settling particles do not affect each other.

Data:

Solution:

1. Calculation of the settling velocity o particles

   1.1 Ar from the known particle diameters: $Ar = \frac{g d_p^3(\rho_p - \rho)}{\rho \nu^2} = \frac{9.81(50\times10^{-6})^3(3000-998.2)}{998.2(1.007\times10^{-6})^2} = 2.425$

   1.2 Ly calculated from the corresponding equation: $Ly = \frac{Ar^2}{5832} = \frac{2.425^2}{5832} = 1.008 \times 10^{-3}$

   1.3 v$_s$ from the Ly: $Ly = \frac{Re^3}{Ar} = \frac{v_s^3 \rho}{g \nu(\rho_p - \rho)}$ ------->

$$v_s = \left(\frac{Ly g \nu(\rho_p - \rho)}{\rho}\right)^{\frac{1}{3}} = (1.008 \times 10^{-3} \cdot 9.81 \cdot 1.007 \times 10^{-6}(3000 - 998.2)/998.2)^{\frac{1}{3}} = 2.713 \times 10^{-3} ms^{-1}$$

2. Calculation of the settler performance:

   By combining of: $\dot{m}_s = \dot{m}_F + \dot{m}_K; \dot{m}_S w_S = \dot{m}_K w_K; A = \frac{\dot{Q}_F}{v_s}; \dot{m}_F = \dot{Q}_F \rho_F$ we arrive at

$$\dot{m}_F = \frac{v_S A \rho_F w_K}{w_K - w_S} = \frac{2.713\times10^{-3}\cdot\pi/4\cdot3^2\cdot998.2\cdot0.6}{0.6-0.15} = 25.53\ kg\ s^{-1} = 91.9 \text{ tons/hour}$$

Results: The performance of the settler is 91.9 tons per hour.