

Closed Carbon Balance

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Red is measured
Green is known

Assuming a closed carbon-balance leads to:

$$\dot{n}_{in,CO_2} = \dot{n}_{out,CO_2} + \sum \dot{n}_{out,i}$$

$$\Delta \dot{n}_{CO_2} = \dot{n}_{in,CO_2} - \dot{n}_{out,CO_2} = \sum \dot{n}_{out,i}$$

GC measurements give volumetric fractions. Assuming an ideal gas mixture, volumetric fractions are identical to mole fractions. Therefore outgoing quantities are replaced with molar fractions according to:

$$x_{out,i} = \frac{\dot{n}_{out,i}}{\sum \dot{n}_{out,i} + \dot{n}_{out,CO_2} + \dot{n}_{out,H_2} + \dot{n}_{out,CO} + \dot{n}_{out,H_2O}}$$

Two simplifying assumptions are taken, as both water and hydrogen cannot be analysed. Firstly it is assumed that all oxygen from converted carbon dioxide is reacted to water (i.e. no oxygenated hydrocarbon products) then the water molar flowrate can be replaced with:

$$\dot{n}_{out,H_2O} = 2\Delta \dot{n}_{CO_2}$$

Secondly the outgoing hydrogen flow is replaced by a second balance. Herein the converted hydrogen is calculated via stoichiometric reactions and product selectivity:

$$\dot{n}_{out,H_2} = \dot{n}_{in,H_2} - (3 \cdot S_{CH_4} \Delta \dot{n}_{CO_2} + 2 \cdot S_{C_2+} \Delta \dot{n}_{CO_2})$$

$$\dot{n}_{out,H_2} = \dot{n}_{in,H_2} - \Delta \dot{n}_{CO_2} (3 \cdot S_{CH_4} + 2 \cdot S_{C_2+})$$

This again assumes no formation of alcohols and negligible olefins. This leads to:

$$\dot{n}_{out,i} = x_{out,i} (\Delta \dot{n}_{CO_2} + \dot{n}_{in,CO_2} - \Delta \dot{n}_{CO_2} + \dot{n}_{in,H_2} - \Delta \dot{n}_{CO_2} (3 \cdot S_{CH_4} + 2 \cdot S_{C_2+}) + 2\Delta \dot{n}_{CO_2})$$

$$\dot{n}_{out,i} = x_{out,i} (\Delta \dot{n}_{CO_2} (2 - (3 \cdot S_{CH_4} + 2 \cdot S_{C_2+})) + \dot{n}_{in,CO_2} + \dot{n}_{in,H_2})$$

The boundary case of differential conditions $\Delta \dot{n}_{CO_2} \approx 0$ yields :

$$\dot{n}_{out,i} = x_{out,i} \cdot \dot{n}_{in,tot}$$

The calculation of the selectivity requires a conversion (i.e. $\Delta \dot{n}_{CO_2}$), therefore an iterative approach is necessary. Herein a starting value of $\Delta \dot{n}_{CO_2}$ is taken by calculating with assuming differential conditions. With the resulting outgoing molar flows, a new $\Delta \dot{n}_{CO_2}$ is calculated and the loop is repeated until a sufficiently small difference is achieved.

Selectivity is calculated with

$$S_i = \frac{\dot{n}_{out,i}}{\sum \dot{n}_{out,j}} = \frac{\dot{n}_{out,i}}{\Delta \dot{n}_{CO_2}}$$

Both Selectivity and molar fractions must adhere to the closing condition:

$$S_{CH_4} + S_{C_2+} + S_{CO} = 1$$

$$x_{CH_4} + x_{C_2+} + x_{CO} = 1$$

From experience no CO is detected and therefore both molar fraction of CO and selectivity towards it are zero.

The inlet molar flowrate is known from the set volumetric flowrates at norm conditions. Bronkhorst norm conditions are 0°C and 1.013 bar.

$$\dot{n}_{in,i} = \frac{p_N \dot{V}_{in,i}}{RT_N}$$