

WORKSHOP ON ENERGY CALCULATION IN THE GLASS INDUSTRY

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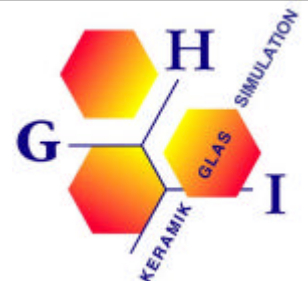
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&

Department of Science Service

Bangkok 8th September 2009

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the heat balance

$$Q_{12} = \Delta H = H_2 - H_1$$

two types of heat:

$$Q_r = H_{\text{products}}^{\circ} - H_{\text{educts}}^{\circ} | T = 25^{\circ}\text{C}$$

$$Q_T = H_{\text{products}}(T_2) - H_{\text{products}}(T_1)$$

$$Q_r + Q_T = H_{\text{ex}}$$

heat exchanger

melting tank

balance valid for:

H [kWh/t]

Q' = $H \cdot m'$ [kW]

q = $H \cdot r$ [kW/m²]

m' [t/h]

A [m²]

r = m'/A [t/(m²·h)]

recovered (re)

wall losses,
heat exchanger (wx)

exchanged in the
heat exchanger (exch)

stack losses (stack)

heat input
(in)

offgas
(off)

set free (sf)

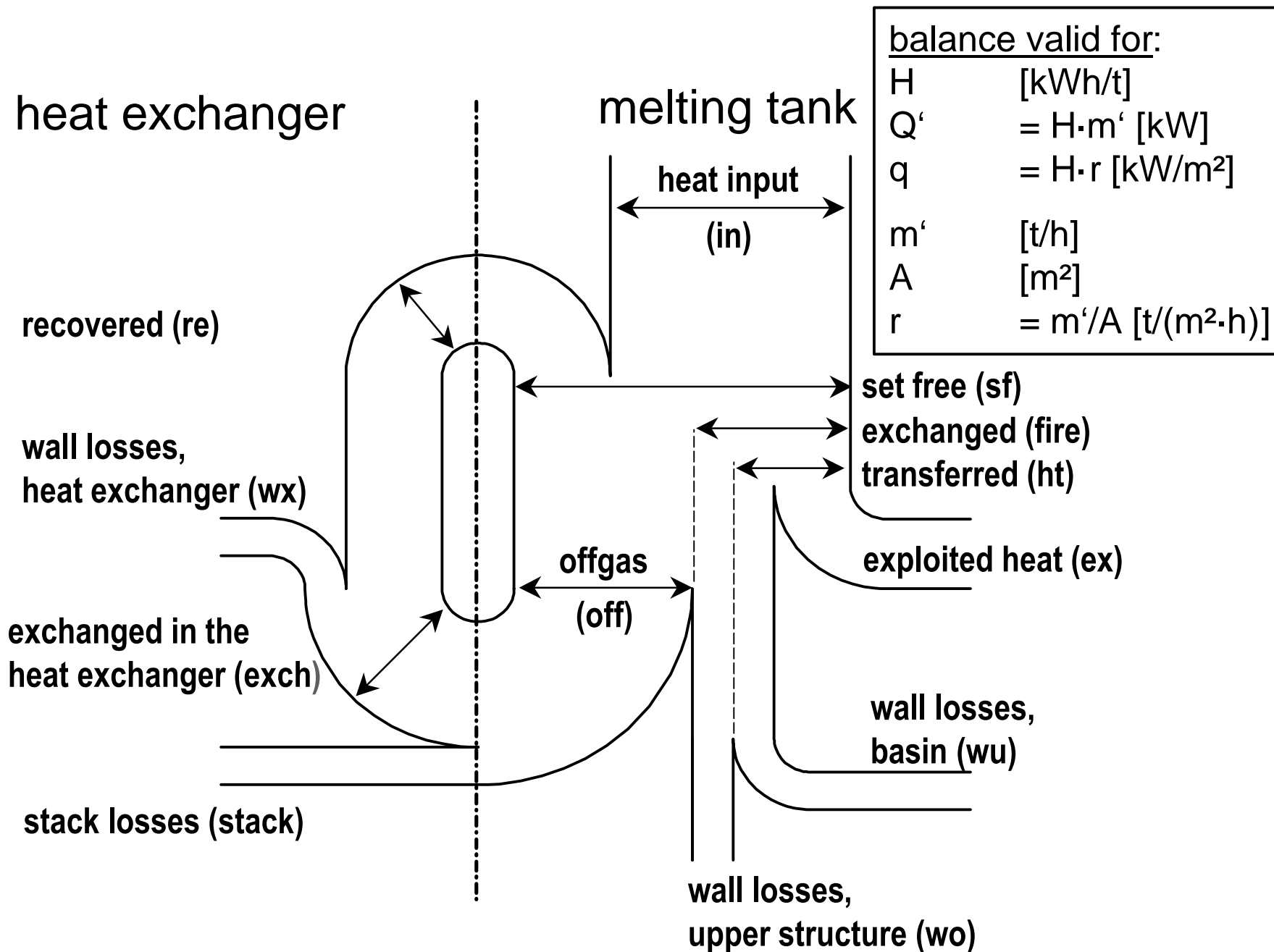
exchanged (fire)

transferred (ht)

exploited heat (ex)

wall losses,
basin (wu)

wall losses,
upper structure (wo)



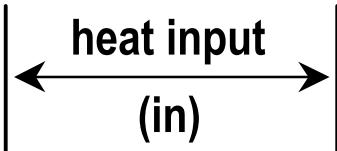
heat exchanger

melting tank

balance valid for:

H	[kWh/t]
Q'	= H·m' [kW]
q	= H·r [kW/m ²]
m'	[t/h]
A	[m ²]
r	= m'/A [t/(m ² ·h)]

recovered (re)



wall losses

set free (sf)

heat

exchanged (fire)

$$1 \text{ kWh} = 3.6 \text{ MJ} = 860.4 \text{ kcal}$$

excha

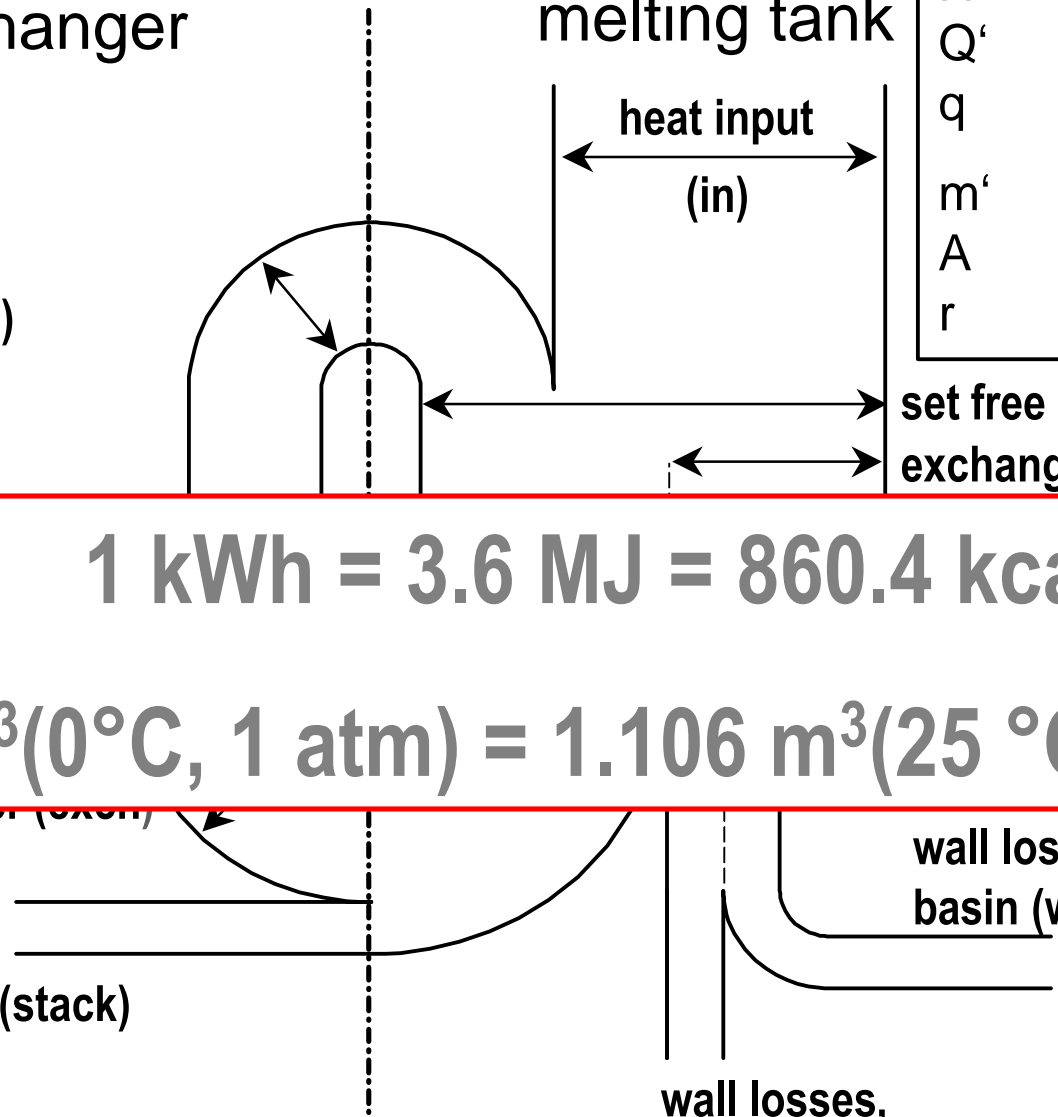
$$1 \text{ m}^3(0^\circ\text{C}, 1 \text{ atm}) = 1.106 \text{ m}^3(25^\circ\text{C}, 1 \text{ bar})$$

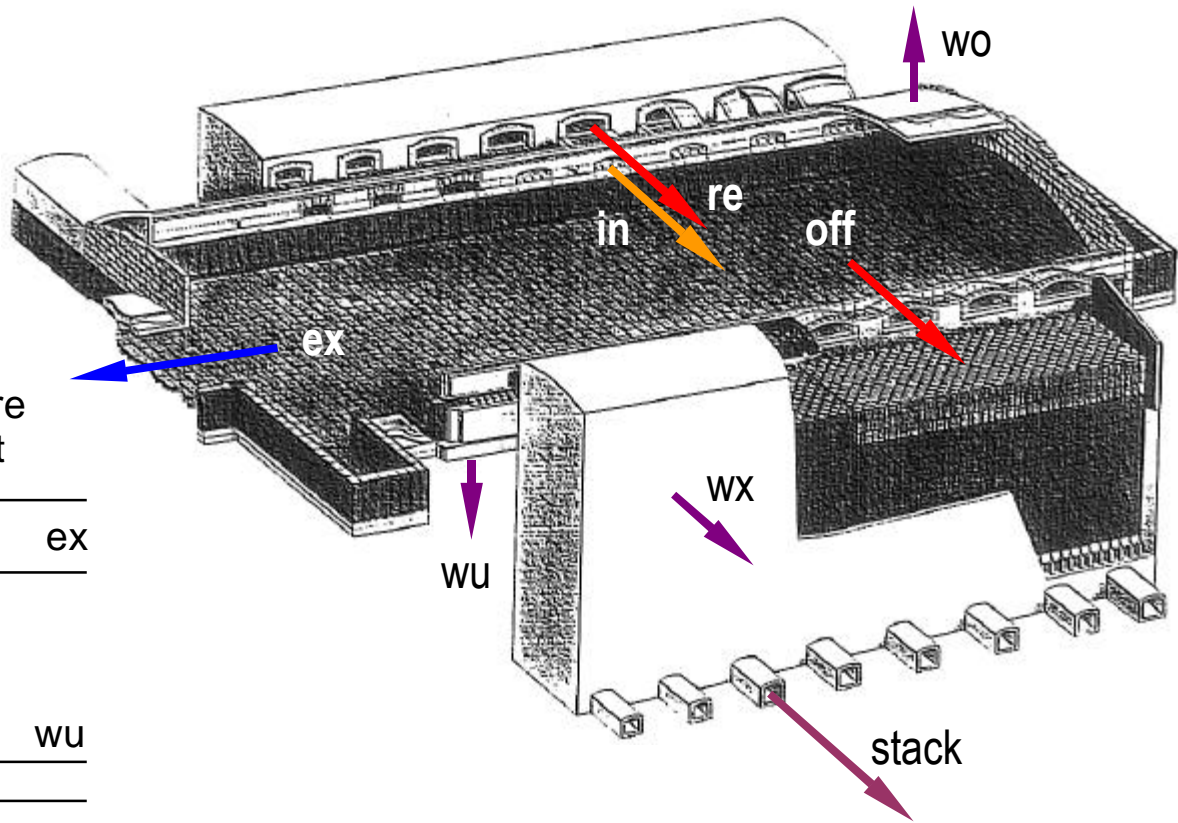
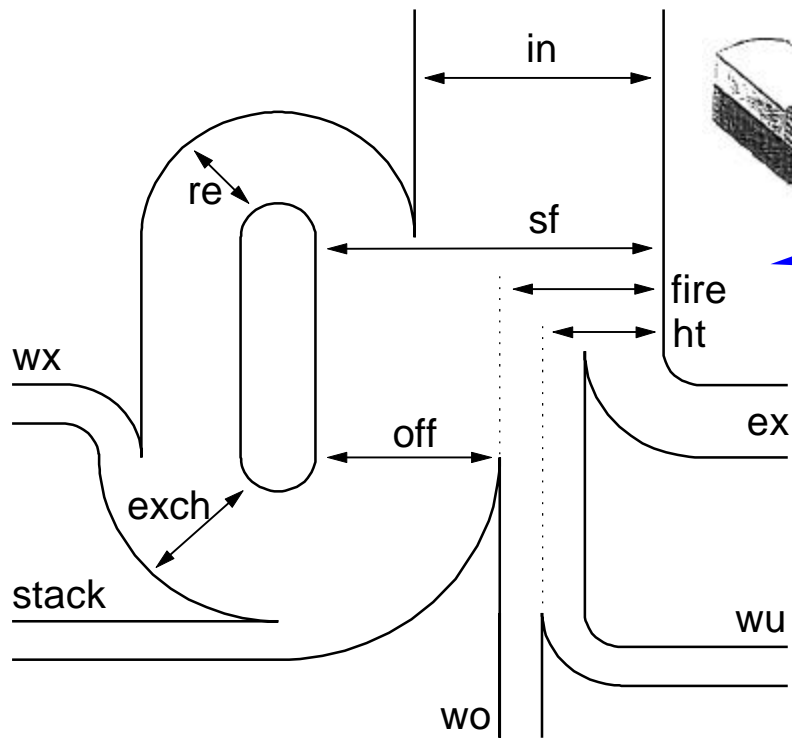
heat exchanger (exch)

stack losses (stack)

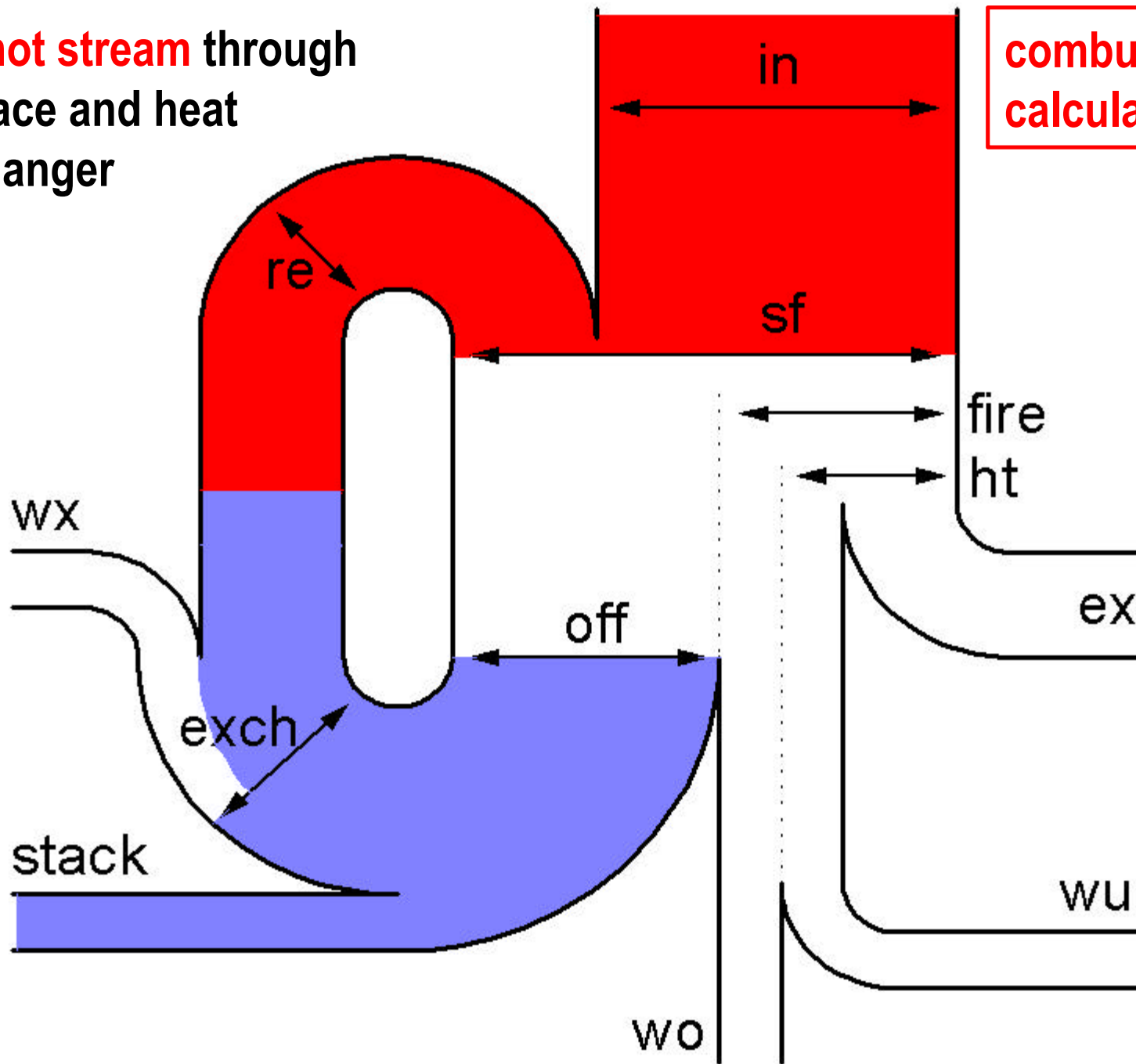
wall losses, basin (wu)

wall losses, upper structure (wo)



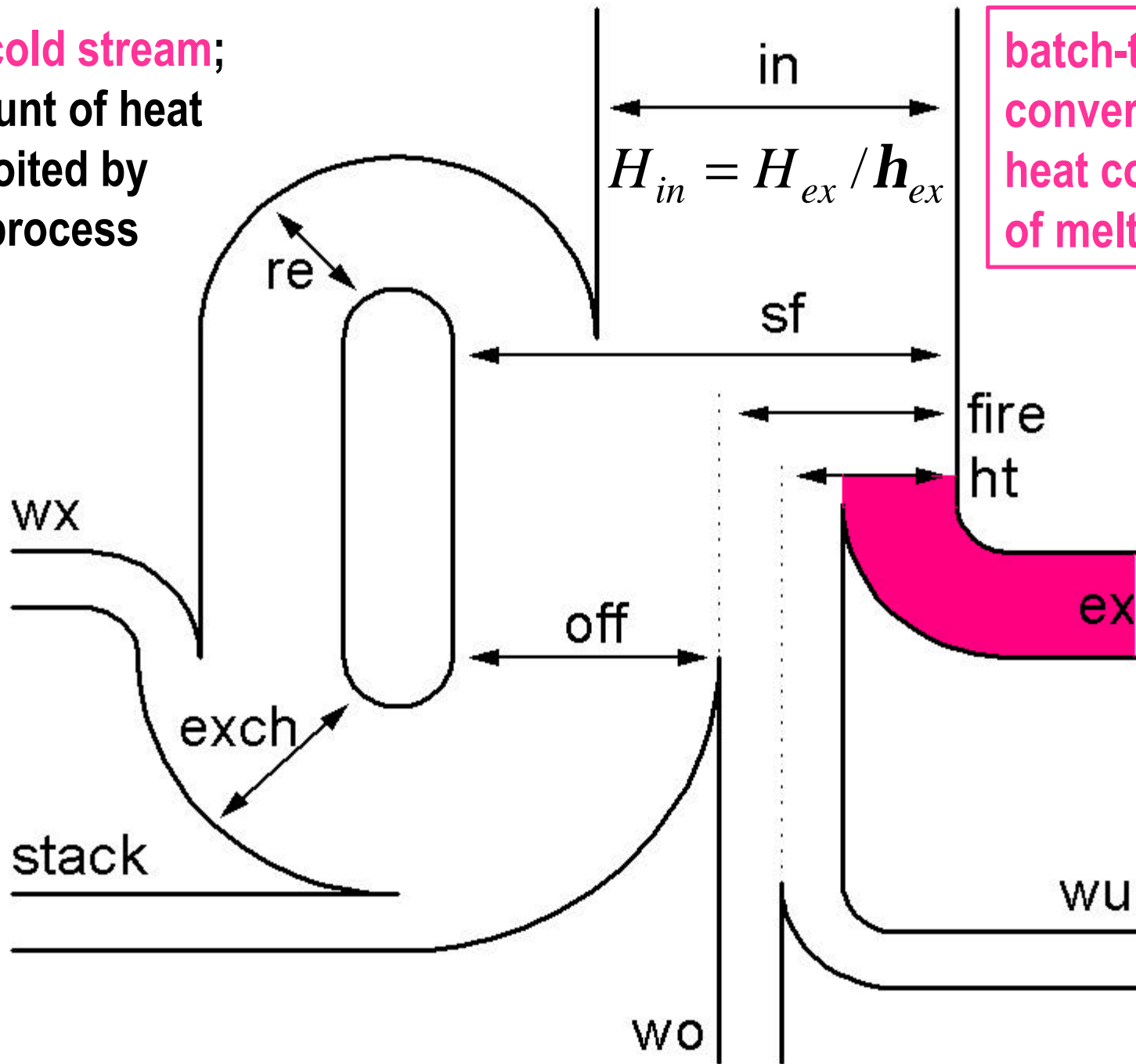


the **hot stream** through furnace and heat exchanger



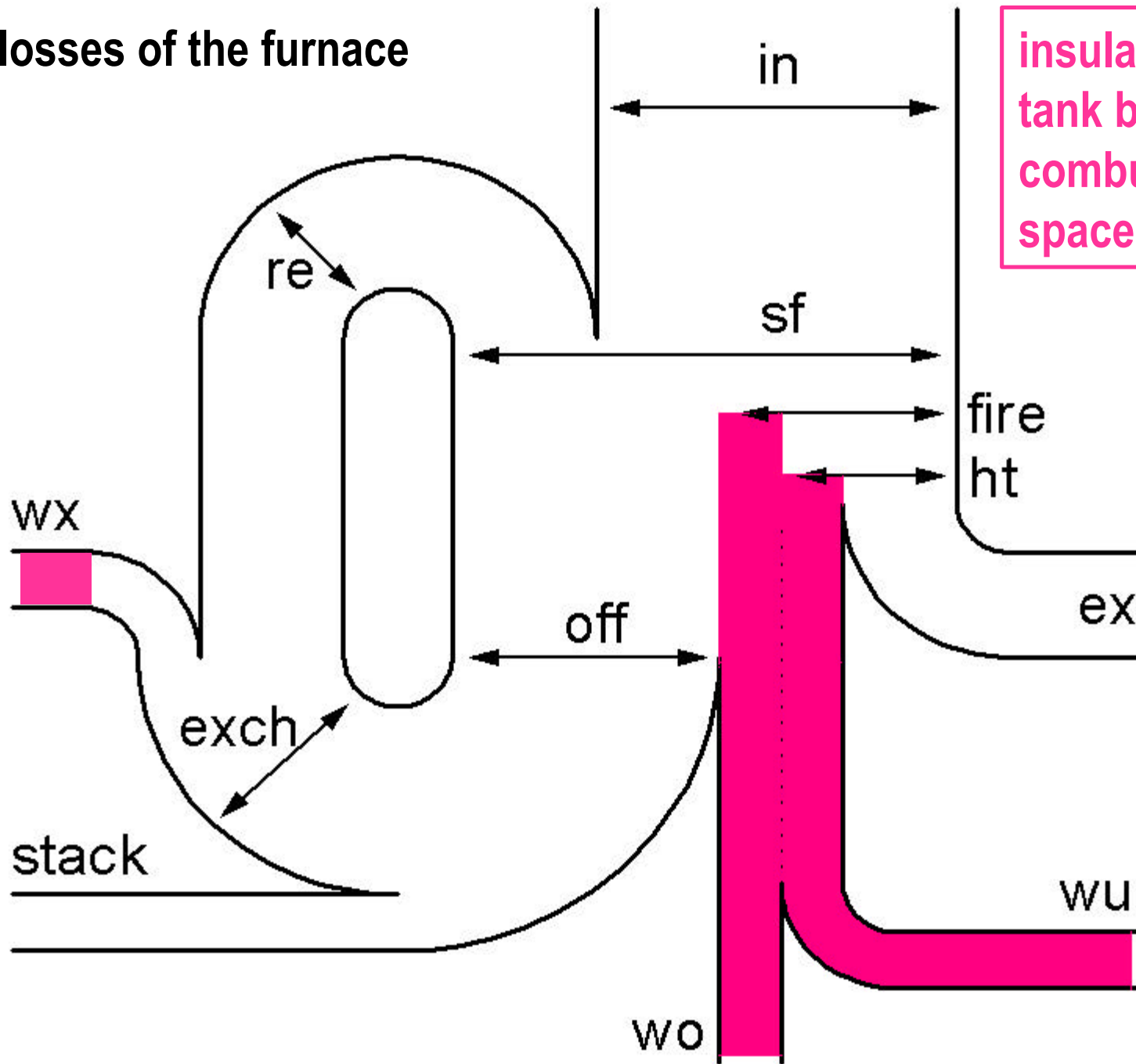
combustion calculations

the **cold stream**;
amount of heat
exploited by
the process



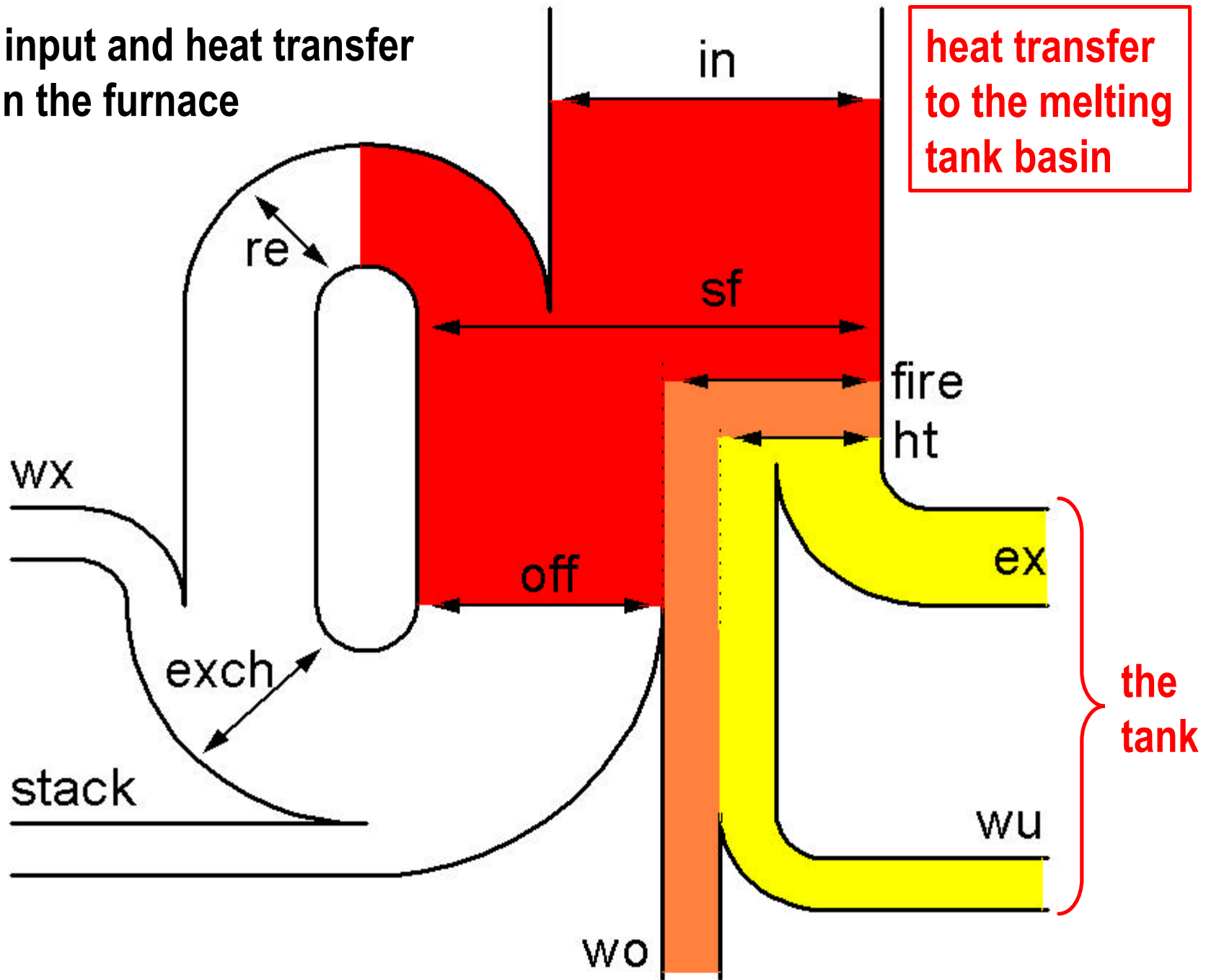
batch-to-melt
conversion;
heat content
of melt

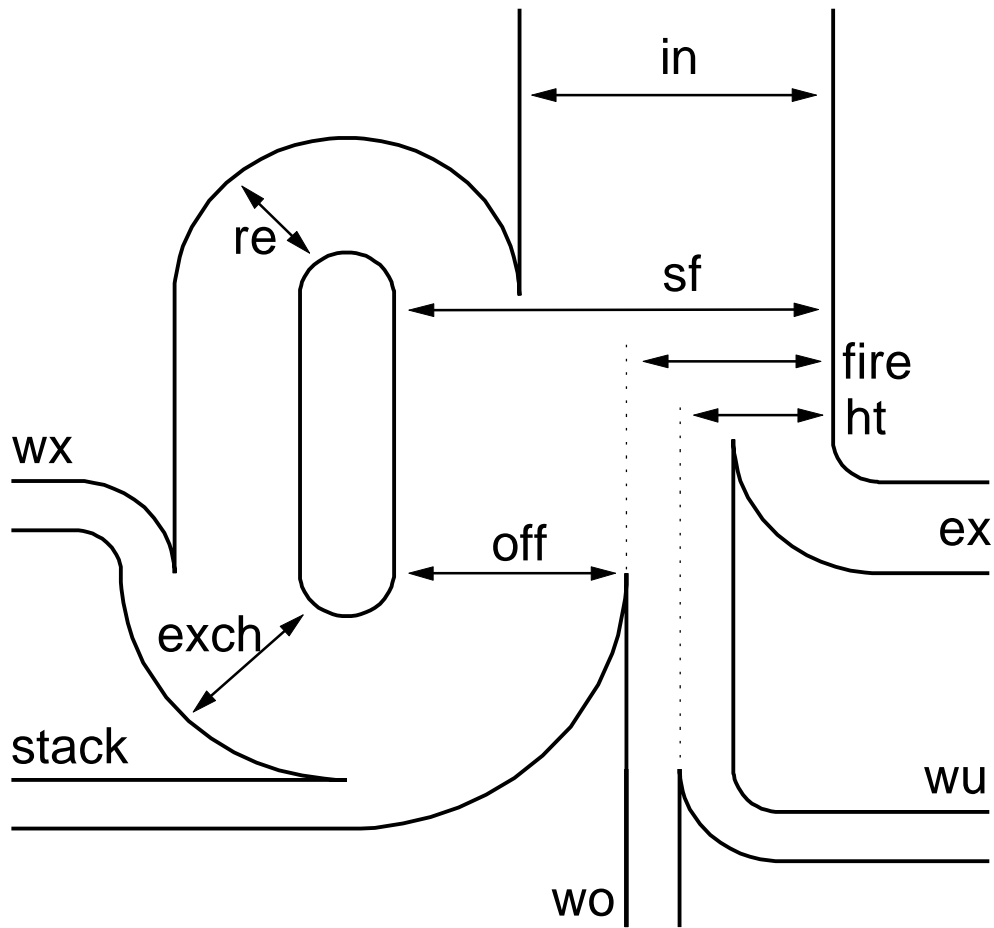
wall losses of the furnace



insulation of tank basin and combustion space lining

heat input and heat transfer within the furnace





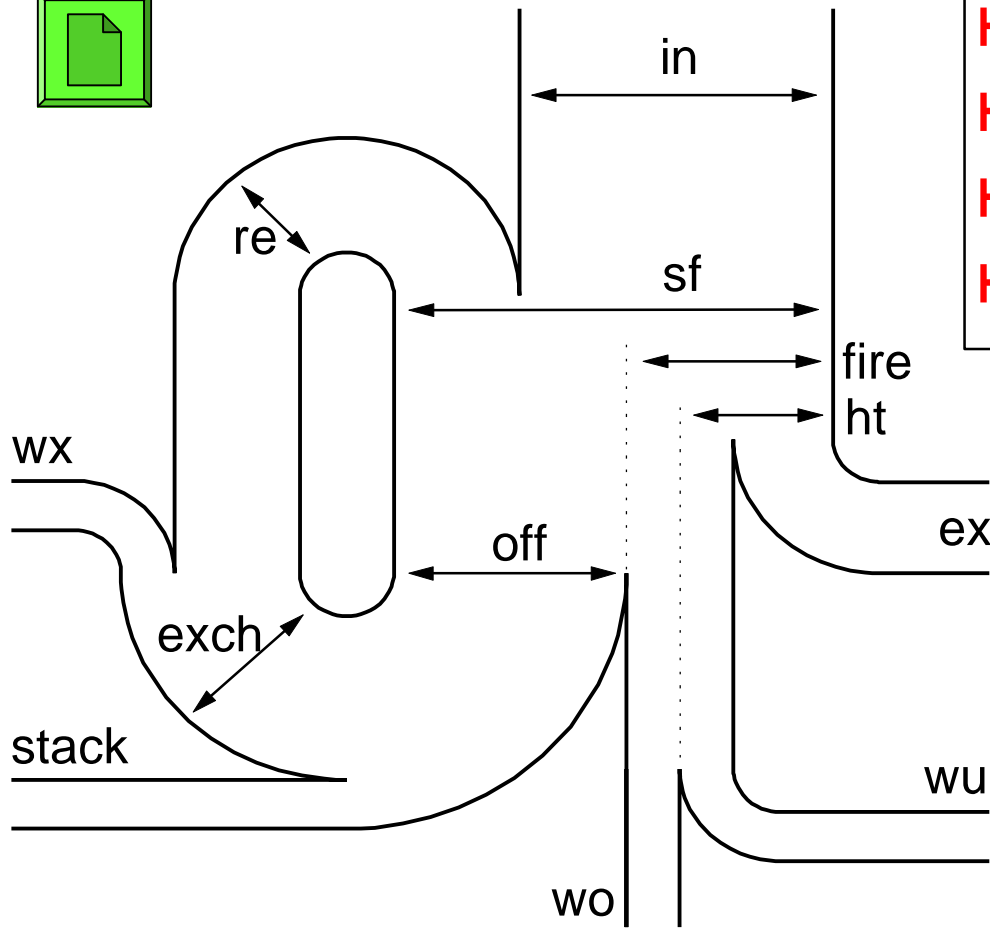
$$H_{sf} = H_{in} + H_{re} = H_{off} + H_{ex} + H_{wo} + H_{wu}$$

$$H_{fire} = H_{sf} - H_{off} = H_{ex} + H_{wo} + H_{wu}$$

$$H_{ht} = H_{ex} + H_{wu}$$

$$H_{off} = H_{stack} + H_{re} + H_{wx}$$

$$H_{exch} = H_{off} - H_{stack} = H_{re} + H_{wx}$$



$$H_{in} = V(\text{fuel}) \cdot H_{NCV}$$

$$H_{re} = C_p(\text{air}) \cdot V(\text{air}) \cdot (T_{re} - 25 \text{ }^\circ\text{C})$$

$$H_{off} = C_p(\text{off}) \cdot V(\text{off}) \cdot (T_{off} - 25 \text{ }^\circ\text{C})$$

$$H_{stack} = C_p(\text{off}) \cdot V(\text{off}) \cdot (T_{stack} - 25 \text{ }^\circ\text{C})$$

$$H_{sf} = H_{in} + H_{re} = H_{off} + H_{ex} + H_{wo} + H_{wu}$$

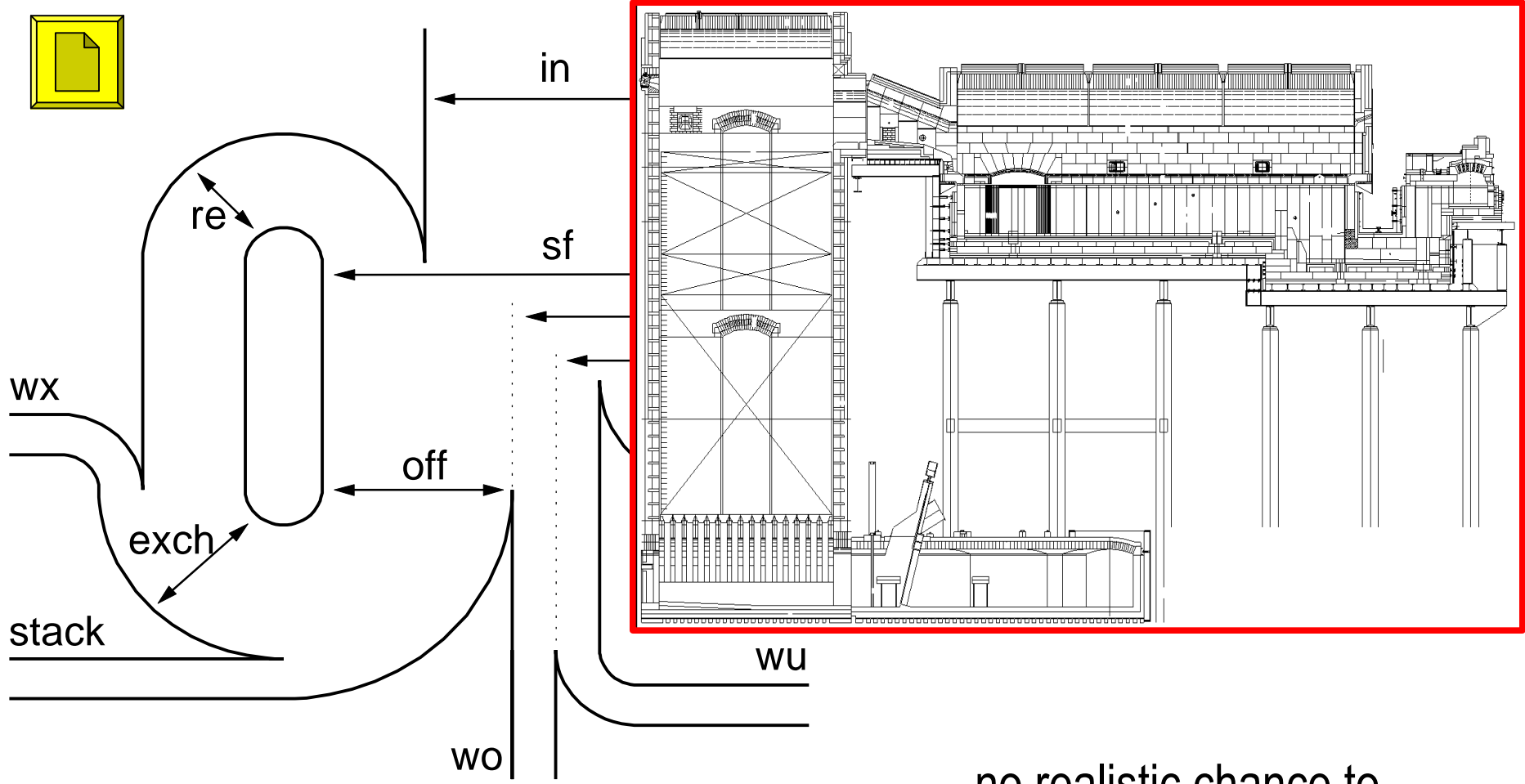
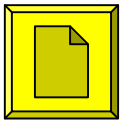
$$H_{fire} = H_{sf} - H_{off} = H_{ex} + H_{wo} + H_{wu}$$

$$H_{ht} = H_{ex} + H_{wu}$$

$$H_{off} = H_{stack} + H_{re} + H_{wx}$$

$$H_{exch} = H_{off} - H_{stack} = H_{re} + H_{wx}$$

good chance to determine H_{in} , H_{re} , H_{off} , H_{stack} via combustion calculations, and H_{sf} , H_{fire} , H_{wx} , H_{exch} by difference



$$H_{sf} = H_{in} + H_{re} = H_{off} + H_{ex} + H_{wo} + H_{wu}$$

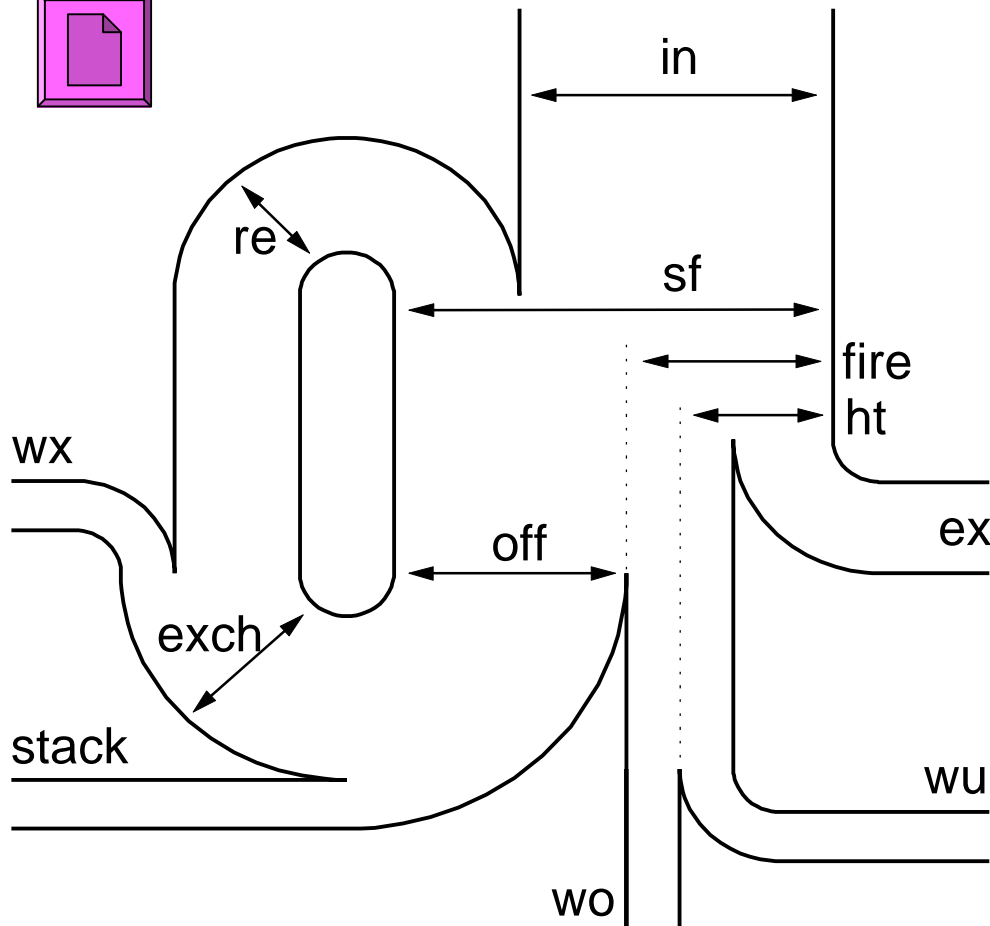
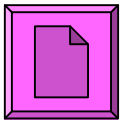
$$H_{fire} = H_{sf} - H_{off} = H_{ex} + H_{wo} + H_{wu}$$

$$H_{ht} = H_{ex} + H_{wu}$$

$$H_{off} = H_{stack} + H_{re} + H_{wx}$$

$$H_{exch} = H_{off} - H_{stack} = H_{re} + H_{wx}$$

no realistic chance to determine H_{wo} , H_{wu}



H_{ex}

let us focus on the determination of H_{ex}

$$H_{sf} = H_{in} + H_{re} = H_{off} + H_{ex} + H_{wo} + H_{wu}$$

$$H_{fire} = H_{sf} - H_{off} = H_{ex} + H_{wo} + H_{wu}$$

$$H_{ht} = H_{ex} + H_{wu} \quad \leftarrow \text{for the 2}^{nd} \text{ part, remember this line!}$$

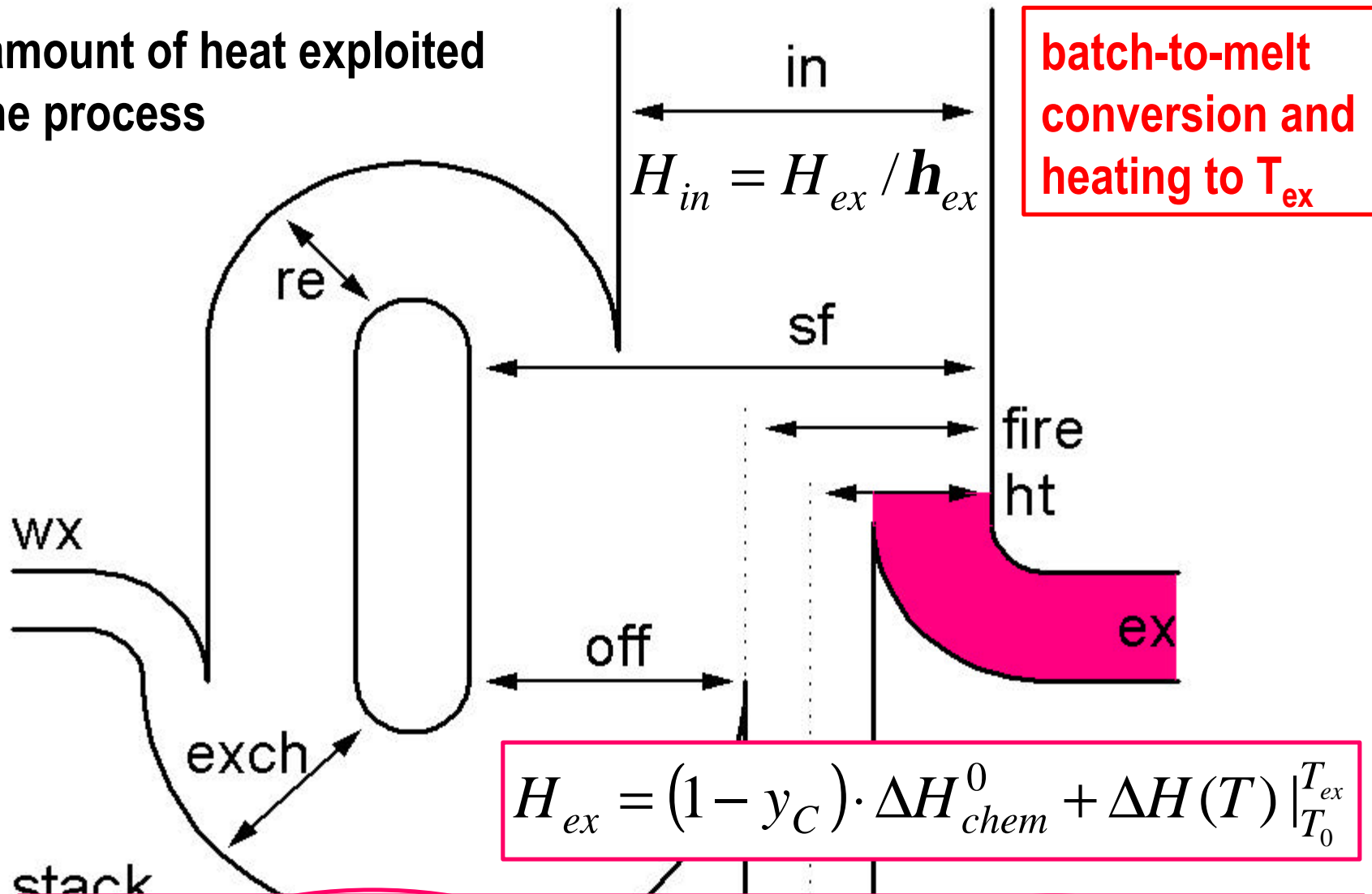
$$H_{off} = H_{stack} + H_{re} + H_{wx}$$

$$H_{exch} = H_{off} - H_{stack} = H_{re} + H_{wx}$$

excursion H_{ex}

**the glass
&
the melt**

the amount of heat exploited by the process



$$H_{ex} = (1 - y_C) \cdot \Delta H_{chem}^0 + \Delta H(T) \Big|_{T_0}^{T_{ex}}$$

ΔH_{chem}^0 : raw materials (25 °C) @ glass + batch gases (25 °C)

$\Delta H(T)$: glass (25 °C) @ glass melt(T)

$$H_{glass}^{\circ} = \sum_k n_k \cdot (H_k^{\circ} + H_k^{vit})$$

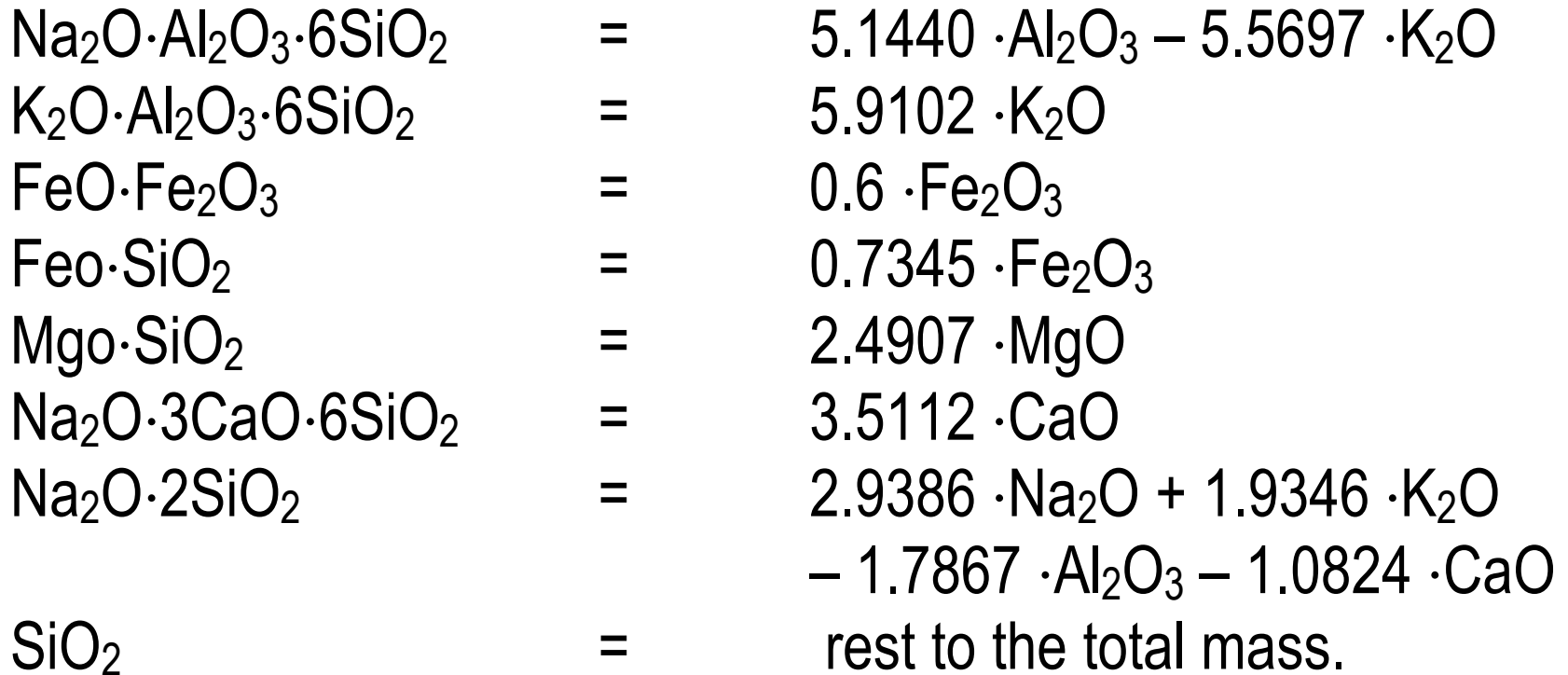
$$H_{1673,liq}^{\circ} = \sum_k n_k \cdot H_{1673,liq,k}^{\circ}$$

$$C_{P,liq} = \sum_k n_k \cdot C_{P,liq,k}$$

$$H_{T,liq} = H_{1673,liq}^{\circ} + C_{P,liq} \cdot (T - 1673)$$

$$\Delta H_{T,liq} = H_{T,liq} - H_{glass}^{\circ}$$

k for the soda-lime based mass glasses



oxide amounts in wt. %

Table 1. Thermodynamic data of compounds *k* employed to represent the crystalline reference systems (c.r.s.) of industrial glasses; enthalpies *H* in kJ/mol, entropies *S* and heat capacities *c_P* in J/(mol·K); superscripts: ° = standard state at 298.15 K, 1 bar; ^{vit} = vitrification; subscripts: _{liq} = liquid state; ₁₆₇₃ = 1673.15 K

<i>k</i>	- <i>H</i> [°]	<i>S</i> [°]	<i>H</i> ^{vit}	<i>S</i> ^{vit}	- <i>H</i> _{1673,liq}	<i>S</i> _{1673,liq}	<i>c_P</i> _{liq}
P ₂ O ₅ ·3CaO	4117.1	236.0	135.1	51.5	3417.1	898.7	324.3
P ₂ O ₅	1504.9	114.4	18.2	9.5	1151.5	586.6	181.6
Fe ₂ O ₃	823.4	87.4	45.2	17.2	550.2	370.3	142.3
FeO·Fe ₂ O ₃	1108.8	151.0	82.8	31.4	677.8	579.9	213.4
FeO·SiO ₂	1196.2	92.8	36.7	13.8	962.3	342.7	139.7
2FeO·SiO ₂	1471.1	145.2	55.2	20.5	1118.8	512.1	240.6
MnO·SiO ₂	1320.9	102.5	40.2	15.1	1085.3	345.2	151.5
2ZnO·SiO ₂	1643.1	131.4	82.4	31.4	1261.1	494.5	174.5
ZrO ₂ ·SiO ₂	2034.7	84.5	86.6	32.6	1686.2	381.2	149.4
CaO·TiO ₂	1660.6	93.7	67.4	25.5	1365.7	360.2	124.7
TiO ₂	938.7	49.9	44.8	10.5	766.0	200.7	87.9

k	$-H^\circ$	S°	H^{vit}	S^{vit}	$-H_{1673.\text{liq}}$	$S_{1673.\text{liq}}$	$C_{\text{P.liq}}$
$\text{BaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$	4222.1	236.8	130.5	95.4	3454.3	1198.3	473.2
$\text{BaO}\cdot 2\text{SiO}_2$	2553.1	154.0	81.6	26.8	2171.1	533.5	241.4
$\text{BaO}\cdot\text{SiO}_2$	1618.0	104.6	56.5	41.0	1349.8	361.1	146.4
$\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$	6036.7	308.8	184.1	12.1	5235.4	1173.2	498.7
$\text{Li}_2\text{O}\cdot\text{SiO}_2$	1648.5	79.9	16.7	6.3	1416.7	339.7	167.4
$\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$	7914.0	439.3	106.3	29.3	6924.9	1559.4	765.7
$\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$	4217.1	266.1	80.4	22.1	3903.7	666.5	517.6
$\text{K}_2\text{O}\cdot 4\text{SiO}_2$	4315.8	265.7	26.4	21.3	3697.8	983.7	410.0
$\text{K}_2\text{O}\cdot 2\text{SiO}_2$	2508.7	190.6	12.6	23.9	2153.1	595.4	275.3
$\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$	7841.2	420.1	125.0	28.4	6870.1	1512.5	648.1
$\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$	4163.5	248.5	92.0	27.9	3614.1	856.9	423.8
B_2O_3	1273.5	54.0	18.2	11.3	1088.7	271.1	129.7
$\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3\cdot 4\text{SiO}_2$	5710.9	270.0	42.7	21.1	4988.0	1090.2	637.6
$\text{Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3$	5902.8	276.1	58.3	40.1	4986.7	1275.5	704.2
$\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$	3284.9	189.5	48.8	26.6	2735.9	780.3	444.8
$\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3$	1958.1	147.1	43.6	19.5	1585.7	538.7	292.9

k	$-H^\circ$	S°	H^{vit}	S^{vit}	$-H_{1673.\text{liq}}$	$S_{1673.\text{liq}}$	$C_{P,\text{liq}}$
$2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$	9113.2	407.1	135.8	41.4	7994.8	1606.2	1031.8
$\text{MgO}\cdot \text{SiO}_2$	1548.5	67.8	46.6	13.6	1318.0	296.2	146.4
$2\text{MgO}\cdot \text{SiO}_2$	2176.9	95.4	61.4	11.0	1876.1	402.9	205.0
$\text{CaO}\cdot \text{MgO}\cdot 2\text{SiO}_2$	3202.4	143.1	92.3	25.7	2733.4	621.7	355.6
$2\text{CaO}\cdot \text{MgO}\cdot 2\text{SiO}_2$	3876.9	209.2	106.7	32.0	3319.2	775.3	426.8
$\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$	4223.7	202.5	103.0	37.7	3628.8	791.2	380.7
$2\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot \text{SiO}_2$	3989.4	198.3	129.9	49.4	3374.0	787.8	299.2
$3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$	6820.8	274.9	188.3	71.5	5816.2	1231.8	523.4
$\text{CaO}\cdot \text{SiO}_2$	1635.1	83.1	49.8	18.8	1382.0	329.7	146.4
$2\text{CaO}\cdot \text{SiO}_2$	2328.4	120.5	101.3	38.5	1868.2	509.2	174.5
$\text{Na}_2\text{O}\cdot 2\text{SiO}_2$	2473.6	164.4	29.3	13.2	2102.5	588.7	261.1
$\text{Na}_2\text{O}\cdot \text{SiO}_2$	1563.1	113.8	37.7	9.8	1288.3	415.1	179.1
$\text{Na}_2\text{O}\cdot 3\text{CaO}\cdot 6\text{SiO}_2$	8363.8	461.9	77.3	20.5	7372.6	1555.6	786.6
$\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$	4883.6	277.8	57.7	13.4	4240.9	990.4	470.3
$2\text{Na}_2\text{O}\cdot \text{CaO}\cdot 3\text{SiO}_2$	4763.0	309.6	87.0	22.6	4029.6	1107.9	501.2
SiO_2	908.3	43.5	6.9	4.0	809.6	157.3	86.2

- (1) Take the glass composition in wt. %..
- (2) Calculate the glass composition in $n(j) = \text{mol per 1 kg of glass}$:
$$n(j) = 10 \times \text{wt. \% (j)} \times M(j)$$
- (3) Find the compounds k.
- (4) Calculate the mass of k.
- (5) Sum up to get $H^\circ(\text{glass})$ and $H_T(\text{melt})$.

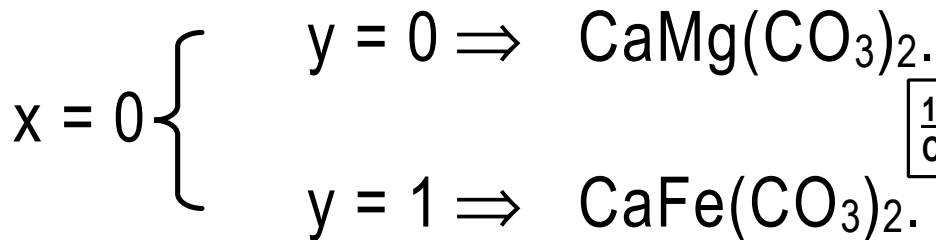
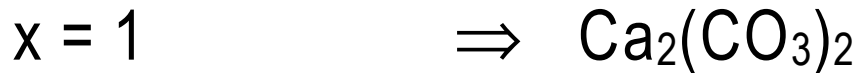
the raw materials

sand and feldspar at 25° C

H° in MJ/kg; oxide amounts in wt. %

$$\begin{aligned} - H^\circ &= 15.174 \cdot \text{SiO}_2 + 17.100 \cdot \text{Al}_2\text{O}_3 + 4.633 \cdot \text{Fe}_2\text{O}_3 \\ &+ 15.030 \cdot \text{MgO} \\ &+ 12.035 \cdot \text{CaO} \\ &+ 10.52 \cdot \text{Na}_2\text{O} + 7.639 \cdot \text{K}_2\text{O} \end{aligned}$$

dolomite and limestone

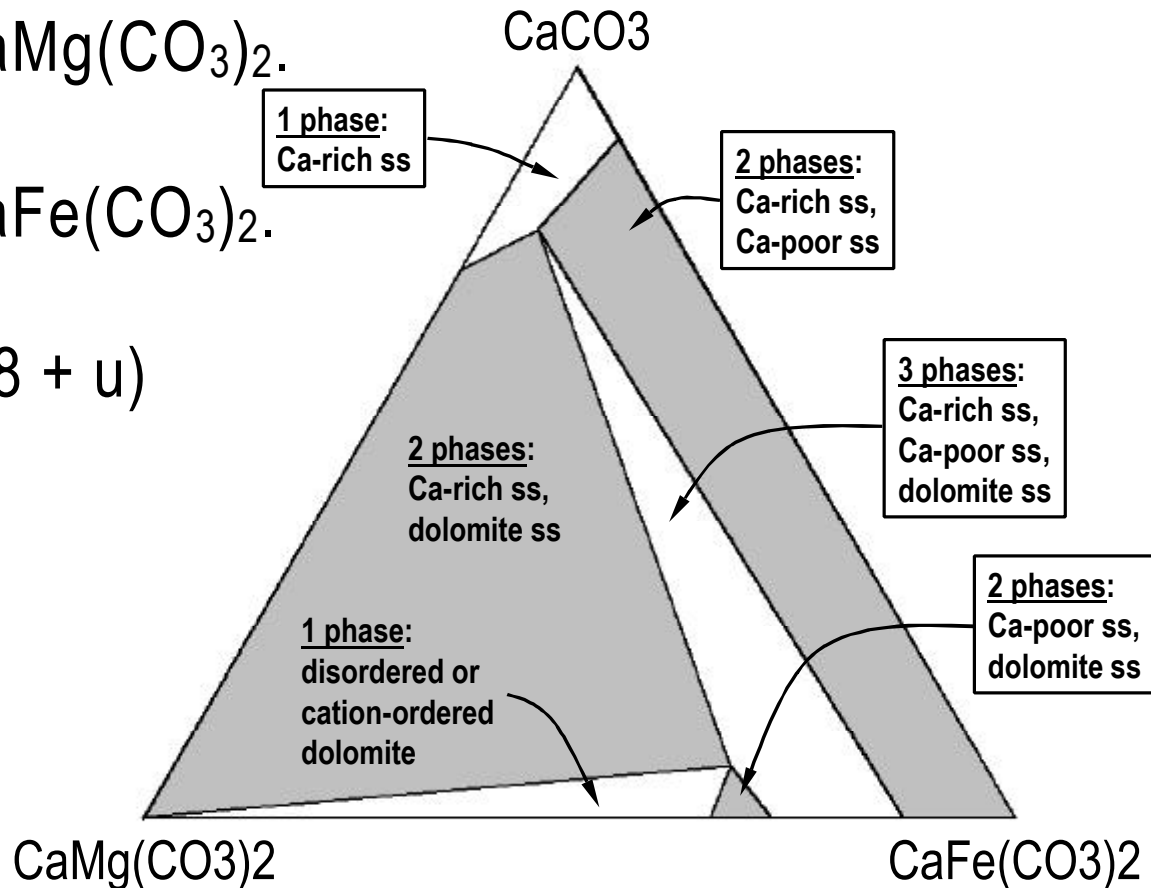


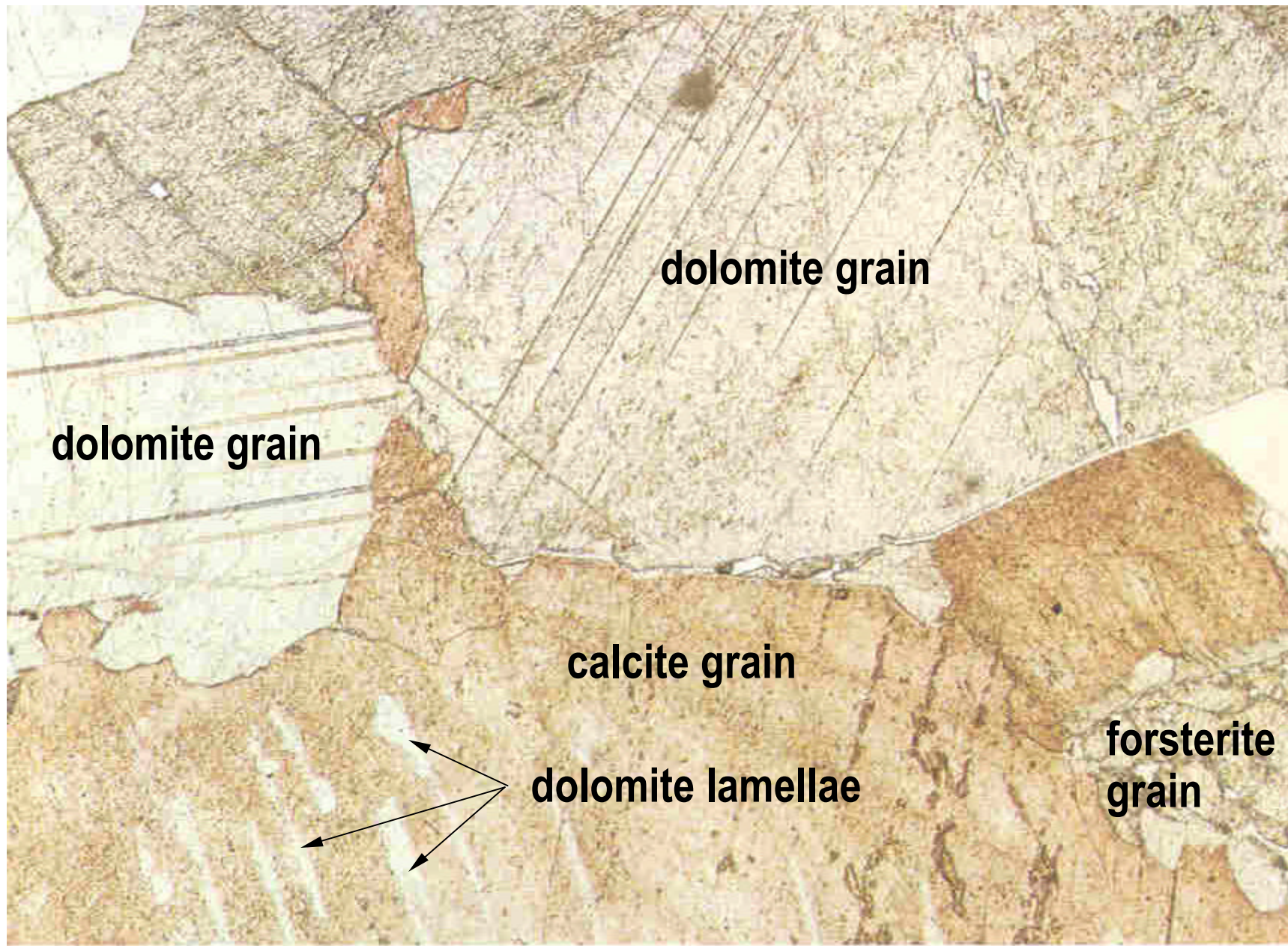
$$x = (0.7188 - u)/(0.7188 + u)$$

$$u = \text{Fe} / \text{Mg}$$

$$y = v/(1.7832 + v)$$

$$v = \text{Mg} / \text{Ca}$$





dolomite grain

dolomite grain

calcite grain

dolomite lamellae

forsterite grain

dolomite and limestone at 25° C

$$H_{\text{dolomite}}^{\circ} = \frac{-2413.8 - 9.97 \cdot (1 - x)}{184.411 + 15.768 \cdot x + 31.535 \cdot y \cdot (1 - x)}$$

$$H_{\text{limestone}}^{\circ} = \frac{-2314.2 + 129.4 \cdot x + 74.0 \cdot y}{184.411 + 15.768 \cdot x + 31.535 \cdot y \cdot (1 - x)}$$

H° in MJ/kg; x, y, as calculated before

chemical grade raw materials at 25° C

		– H° in MJ/kg
sulfate	Na_2SO_4	9.783
Chili saltpeter	NaNO_3	5.509
coal	C	0.000
soda ash	Na_2CO_3	10.659
potash	K_2CO_3	8.343
	BaCO_3	6.169
	PbO	0.983
	Pb_3O_4	1.048

the batch gases

batch gases at 25° C

	$-H^\circ$ in MJ/kg
CO ₂	2.482
H ₂ O	3.728
O ₂	0.000
N ₂	0.000
SO ₂	1.287

$$DH_T(\text{gl}) = C_P(\text{gl}) (T_{\text{ex}} - 25 \text{ }^\circ\text{C})$$

$$C_P(\text{gl}) \text{ in kWh}/(\text{t}\cdot\text{K}) = 1.163 \cdot (T \cdot S A_j \cdot y_j + S C_j y_j) / (1 + 1.46 \cdot T)$$

oxide j	A _j	C _j		oxide j	A _j	C _j
SiO ₂	0.468	0.1657		MnO	0.294	0.1498
Al ₂ O ₃	0.453	0.1765		ZnO	0.486	0.2020
B ₂ O ₃	0.598	0.1935		PbO	0.013	0.0490
Fe ₂ O ₃	0.380	0.1449		Li ₂ O	1.183	0.2665
MgO	0.514	0.2142		Na ₂ O	0.829	0.2992
CaO	0.410	0.1707		K ₂ O	0.455	0.1756
BaO	0.300	0.1251		SO ₃	0.830	0.1890

practice

#GLASS.xls

#SAND & FELDSPAR.xls

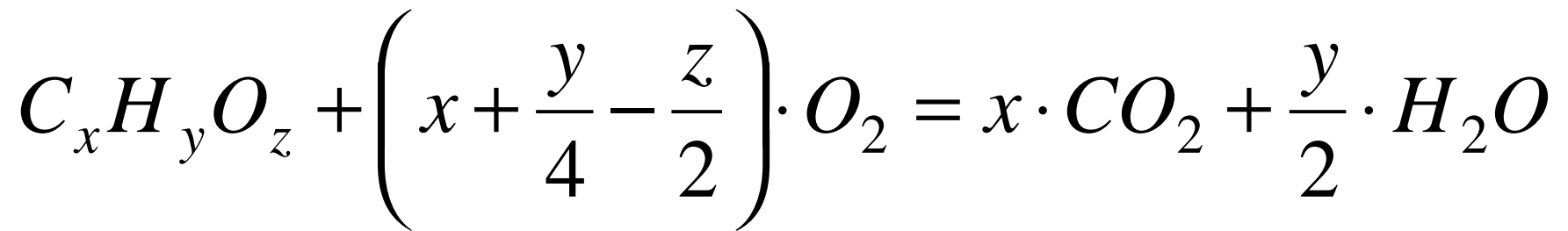
#DOLOMITE & LIMESTONE.xls

#SODA & BORATES & KAOLIN.xls

#BATCH-TO-MELT CONVERSION.xls

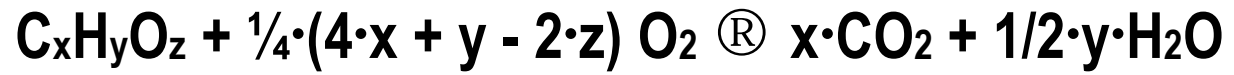
excursion
combustion

**fuels, air demand,
offgas volume**

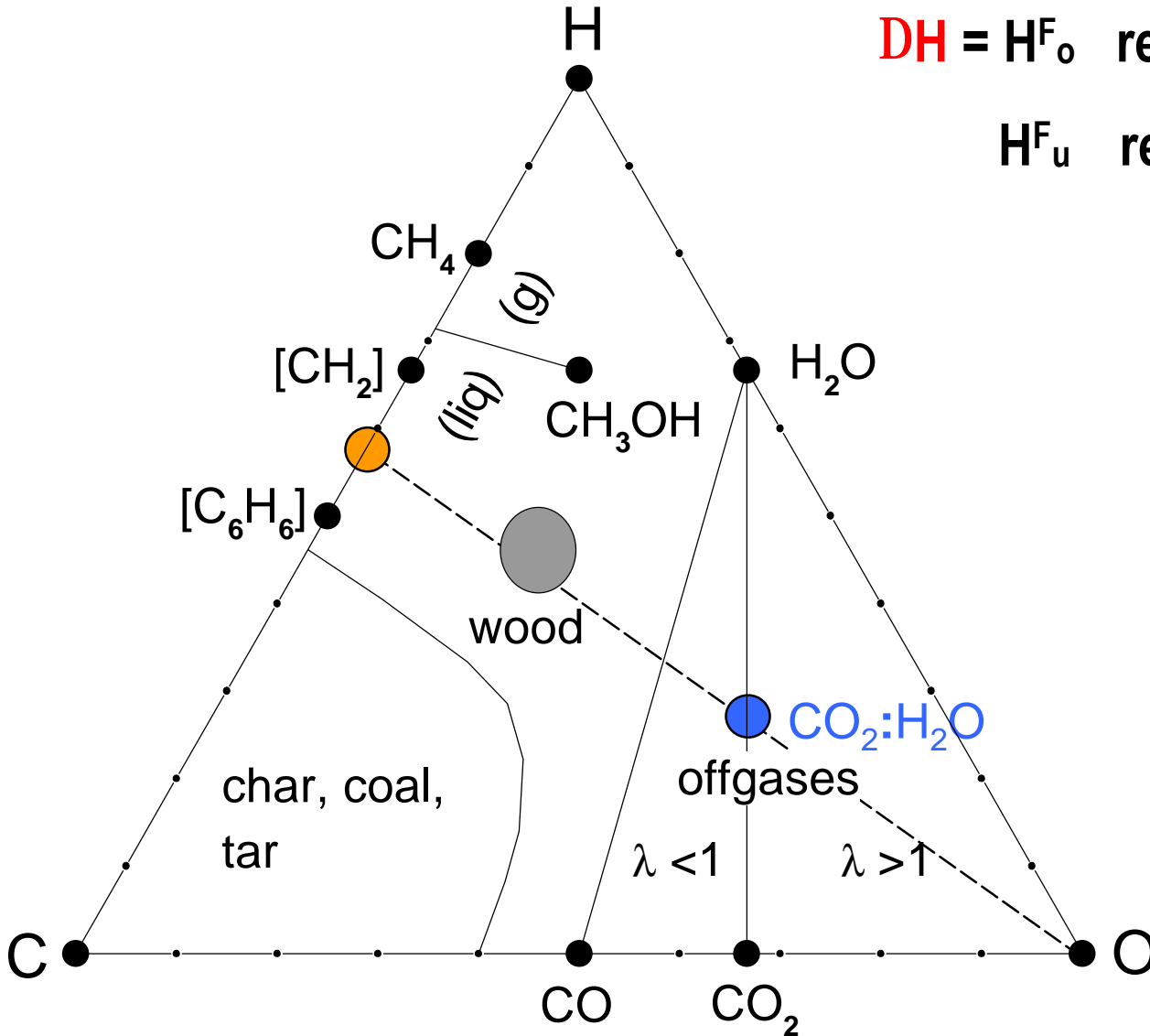


fuels

DH

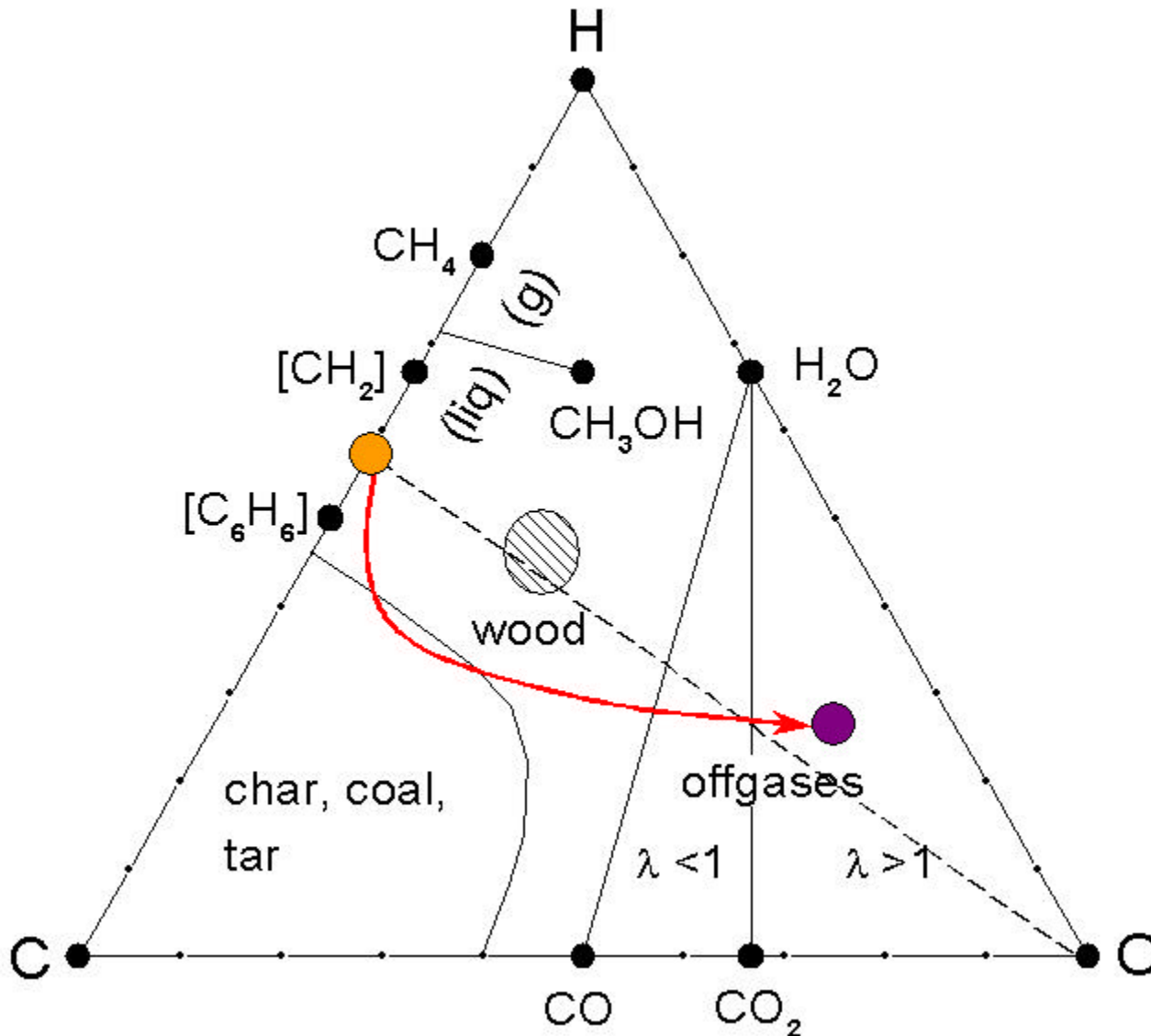
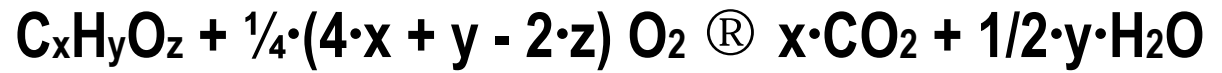


DH = H^F_o referred to $\text{H}_2\text{O}(\text{liq})$,
 H^F_u referred to $\text{H}_2\text{O}(\text{gas})$

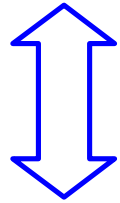


fuels

DH

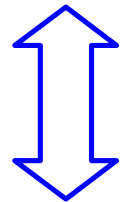


$V^F(\text{air}), V^F(\text{off})$ in m^3_{NTP} **per m^3 fuel**



density d in kg/m^3

$V^F(\text{air}), V^F(\text{off})$ in m^3_{NTP} **per kg fuel**



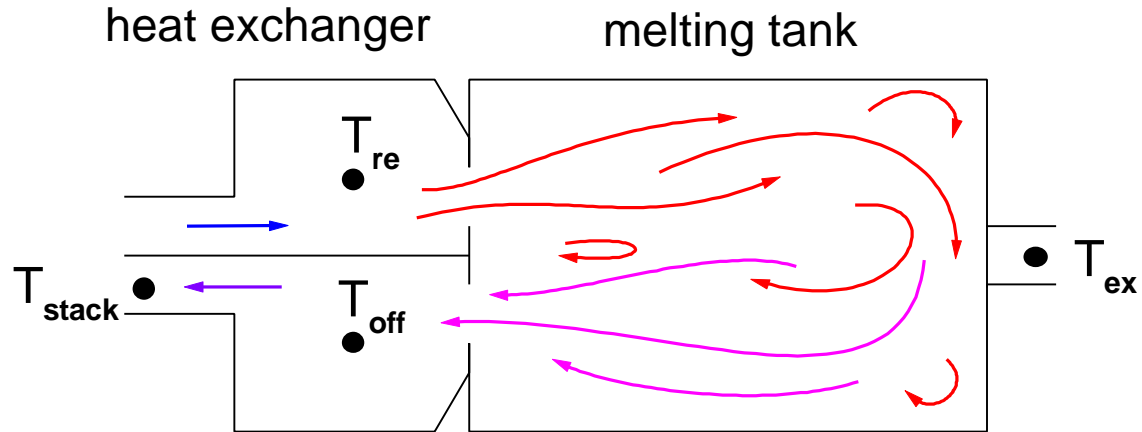
$m_F =$ fuel demand in kg per t glass

$V(\text{air}), V(\text{off})$ in m^3_{NTP} **per t glass**

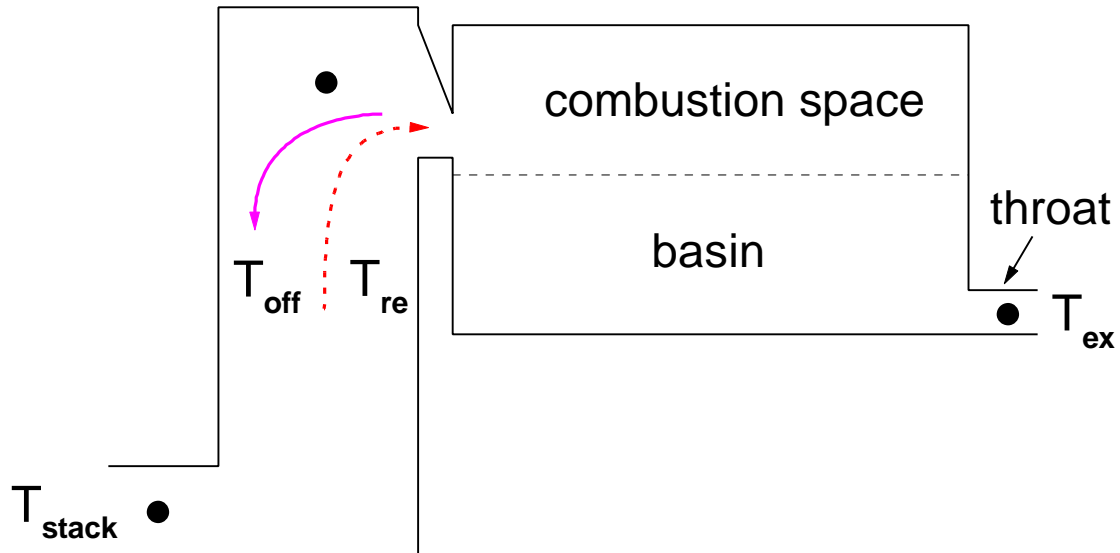
$$V(\text{air}) = m_F \cdot V^F(\text{air})$$

$$V(\text{off}) = m_F \cdot V^F(\text{off})$$

horizontal projection



vertical projection (longitudinal axis)



composition of different fuels:

gas:

volume fractions of all species C_xH_y and CO_2 , N_2 are provided by the supplier

$$\Rightarrow \text{Vol. \% } C_xH_y$$

oil:

wt. fractions of elements C, H, O, S are provided by the supplier; conversion to $[CH_2]$ and C_6H_6 required:

$$\begin{aligned} \Rightarrow m_{CH_2} &= -1.1678 \cdot m_C + 13.916 \cdot m_H \\ m_{C_6H_6} &= 2.1678 \cdot m_C - 12.916 \cdot m_H \end{aligned}$$

coal:

wt. fractions of elements C, H, O, S
and humidity are provided by the supplier

heat capacities of air and offgas:

$$C_P \text{ in Wh}/(\text{m}^3_{\text{NTP}}\cdot\text{K}) = S X_k \cdot v_k + (S Y_k \cdot v_k) T + (S Z_k \cdot v_k)/T^2$$

calculation according to the actual gas composition				fast calculation			
k	X _k	Y _k	Z _k	k	X _k	Y _k	Z _k
O ₂	0.3357	0.0468	-0.00187	air	0.3398	0.0323	-0.00249
N ₂	0.3409	0.0285	-0.00266	gas-off	0.3546	0.0528	-0.00274
CO ₂	0.4946	0.1013	-0.00957	oil-EL-off	0.3606	0.0499	-0.00318
H ₂ O	0.3362	0.1199	0.00037	oil-S-off	0.3609	0.0497	-0.00320

example: air at 1200 °C (1473 K) :

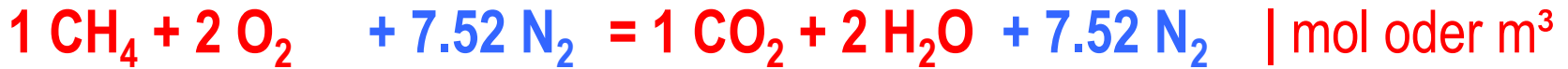
$$\begin{aligned}
 C_P &= 0.3398 + 0.0323 \cdot 1.473 - 0.00249 \cdot 1.473^{-2} \\
 &= 0.382 \text{ Wh}/(\text{m}^3_{\text{NTP}}\cdot\text{K})
 \end{aligned}$$

C_P ✓

example CH₄

V^F

air: 0.21 O₂ + 0.79 N₂ resp. 1 O₂ + 3.76 N₂



9.52 m³ air

10.52 m³ offgas
wet

8.52 m³ offgas
dry

9.5 % CO₂
19.0 % H₂O
71.5 % N₂

air: $0.21 \text{ O}_2 + 0.79 \text{ N}_2$ resp. $1 \text{ O}_2 + 3.76 \text{ N}_2$

VF

air excess $\lambda = 1.08$



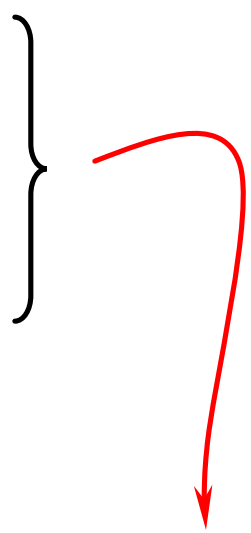
$7.52 \text{ N}_2 + (1 - 1) \text{ air}$

$$1 \cdot 9.52 = 10.28 \text{ m}^3 \text{ air}$$

$$10.52 \text{ m}^3 + (1 - 1) \text{ air} = 11.28 \text{ m}^3 \text{ offgas wet}$$

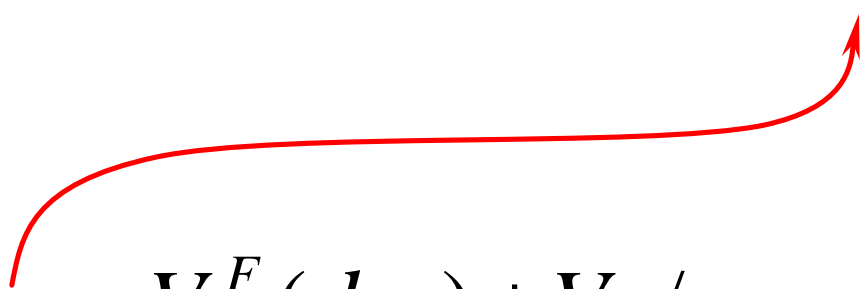
8.9 % CO_2
17.7 % H_2O
72.0 % N_2
0.14 % O_2

batch gases V_b [m^3/t glass]:

$$\begin{aligned} V_b &\gg 0.269 \cdot \text{dolo} + 0.248 \cdot \text{lime} \\ &\quad + 0.234 \cdot \text{soda} \quad [\text{kg}/t \text{ glass}] \\ &\gg 0.6 \cdot (m_{\text{batch}} - 1000) \end{aligned}$$


$$V(\text{air}) = m_F \cdot \mathbf{I} \cdot V^F(\text{air})$$

$$V(\text{off}) = m_F \cdot (V^F(\text{off}) + (\mathbf{I} - 1) V^\circ(\text{air})) + V_b$$

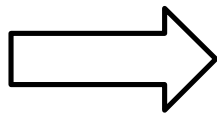

$$\mathbf{I} = \frac{V^F(\text{dry}) + V_b / m_F}{V^F(\text{air})} \cdot \frac{P_{O_2}}{0.21 - P_{O_2}}$$

density d_k at 298 K, partial NCV h_k and volumes of oxygen, air, and offgas components for fuel species from the system C-H-O-S

species k	d_k kg/m ³	h_k kWh/kg	volumes V^F in m ³ NTP per kg species						
			air	off	dry	O ₂	N ₂	CO ₂	H ₂ O
CO gas	1.130	2.81	2.11	2.55	2.55	0.44	1.66	0.88	0.00
H ₂ gas	0.081	33.32	29.26	35.42	23.10	6.15	23.13	0.00	12.30
CH ₄ gas	0.647	13.89	14.71	16.26	13.17	3.09	11.63	1.55	3.09
C ₂ H ₆ gas	1.213	13.19	13.74	14.97	12.50	2.89	10.85	1.65	2.47
C ₃ H ₈ gas	1.779	12.88	13.38	14.51	12.26	2.81	10.57	1.69	2.25
C ₄ H ₁₀ gas	2.345	12.70	13.20	14.26	12.13	2.77	10.43	1.71	2.13
C ₅ H ₁₂ gas	2.911	12.60	13.09	14.12	12.06	2.75	10.34	1.72	2.06
C ₆ H ₁₄ gas	3.477	12.53	13.01	14.02	12.00	2.73	10.28	1.73	2.01
C ₅ H ₁₂ liq	626.2	12.49	13.09	14.12	12.06	2.75	10.34	1.72	2.06
C ₆ H ₁₄ liq	659.4	12.43	13.01	14.02	12.00	2.73	10.28	1.73	2.01
[CH ₂] liq	780.0	12.14	12.62	13.51	11.74	2.65	9.97	1.77	1.77
C ₆ H ₆ liq	873.7	11.15	11.33	11.81	10.86	2.38	8.95	1.90	0.95
S ¹⁾ diss.	≈1920	2.57	3.68	3.68	3.68	0.77	2.91	0.00	0.00
C solid	≈1800	9.10	9.83	9.83	9.83	2.06	7.76	2.06	0.00

¹⁾ dissolved sulfur generates 0.77 m³ SO₂ per kg S

species k	d _k kg/m ³	h _k kWh/kg	volumes V ^F in m ³ NTP per kg of species						
			air	off	dry	O ₂	N ₂	CO ₂	H ₂ O
generator gases									
CO gas	1.130	2.81	2.11	2.55	2.55	0.44	1.66	0.88	0.00
H ₂ gas	0.081	33.32	29.26	35.42	23.10	6.15	23.13	0.00	12.30
mineral gases									
CH ₄ gas	0.647	13.89	14.71	16.26	13.17	3.09	11.63	1.55	3.09
:	:	:	:	:	:	:	:	:	:
C ₆ H ₁₄ gas	3.477	12.53	13.01	14.02	12.00	2.73	10.28	1.73	2.01
mineral oils									
[CH ₂] liq	780.0	12.14	12.62	13.51	11.74	2.65	9.97	1.77	1.77
C ₆ H ₆ liq	873.7	11.15	11.33	11.81	10.86	2.38	8.95	1.90	0.95



$$H_{F_u} = S \sum_k x_k h_k \cdot d_k$$

$$V^F(\text{air}) = S \sum_k x_k d_k \cdot V_k(\text{air})$$

$$V^F(\text{off}) = S \sum_k x_k d_k \cdot V_k(\text{off})$$

$$V^F(\text{dry}) = S \sum_k x_k d_k \cdot V_k(\text{dry})$$

species	v_j %	d_j kg/m ³	H_{uj} kWh/kg	H_{oj} kWh/kg	O_2 m ³ /kg	air m ³ /kg	off m ³ /kg	dry m ³ /kg
CH ₄	86.33	0.647	13.89	15.42	3.09	14.72	16.26	13.17
C ₂ H ₆	5.73	1.213	13.19	14.41	2.89	13.74	14.98	12.50
C ₃ H ₈	1.05	1.779	12.88	13.98	2.81	13.38	14.51	12.26
C ₄ H ₁₀	0.43	2.345	12.70	13.75	2.77	13.20	14.27	12.13
C ₅ H ₁₂	0.10	2.911	12.60	13.61	2.75	13.09	14.12	12.06
C ₆ H ₁₄	0.07	3.477	12.53	13.52	2.73	13.01	14.02	12.01
N ₂	1.72	1.130	0	0	0	0	0.88	0.88
CO ₂	4.57	1.775	0	0	0	0	0.56	0.56

	v_j	d_j kg · m ³	$v_j d_j$ kWh/m ³	$v_j d_j z_j$ kWh/m ³	v_j m ³ /m ³	d_j m ³ /m ³	z_j m ³ /m ³	$v_j d_j z_j$ m ³ /m ³
CH ₄	86.33	0.559	7.76	8.61	1.73	8.22	9.09	7.36
C ₂ H ₆	5.73	0.070	0.92	1.00	0.20	0.95	1.04	0.87
C ₃ H ₈	1.05	0.019	0.24	0.26	0.05	0.25	0.27	0.23
C ₄ H ₁₀	0.43	0.010	0.13	0.14	0.03	0.13	0.14	0.12
C ₅ H ₁₂	0.10	0.003	0.04	0.04	0.01	0.04	0.04	0.04
C ₆ H ₁₄	0.07	0.002	0.03	0.03	0.01	0.03	0.03	0.03
N ₂	1.72	0.019	0.00	0.00	0.00	0.00	0.02	0.02
CO ₂	4.57	0.081	0.00	0.00	0.00	0.00	0.05	0.05
S1	100.00	0.763	9.11	10.09	2.02	9.63	10.68	8.71
S2	93.71			10.76				

**heat transfer,
adiabatic flame temperature**

$$\frac{Q_{12}}{T} = \Delta S = S_2 - S_1$$

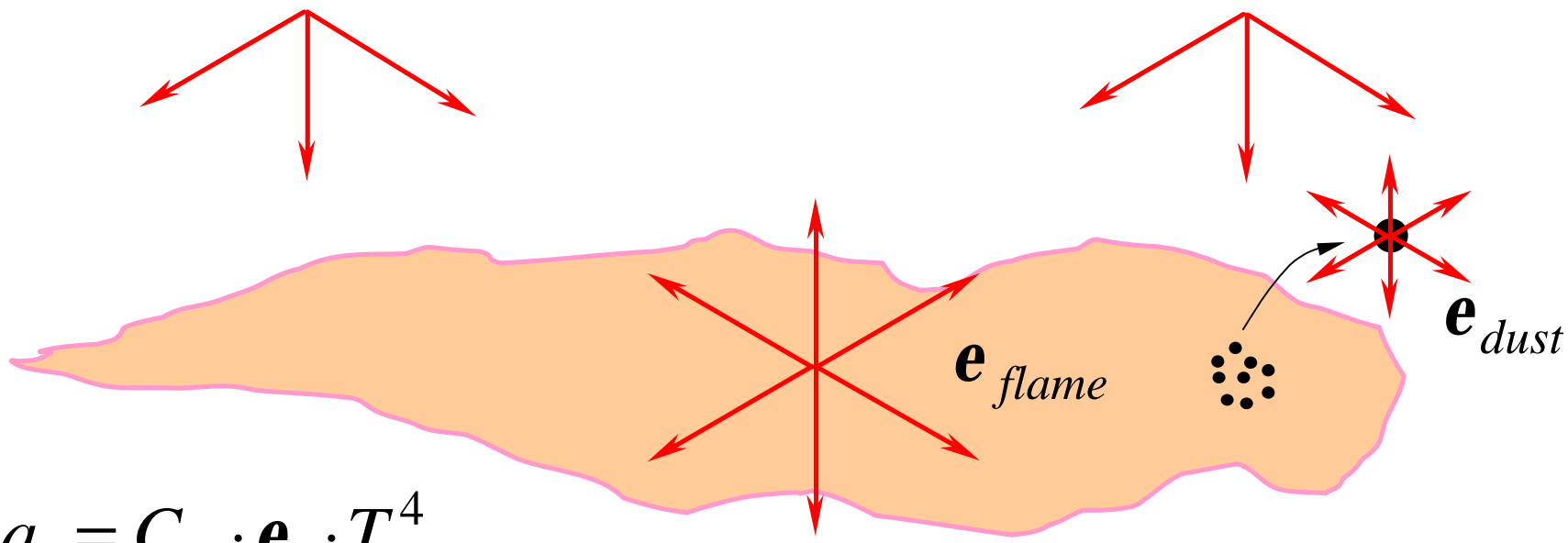
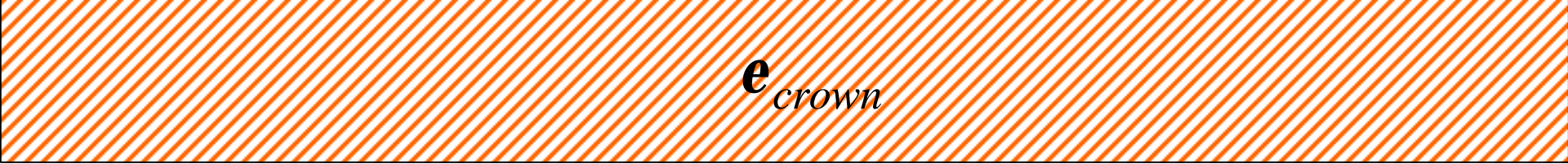
Heat Q is not „consumed“.

*When transferred from T_H to T_L ,
it is devaluated.*

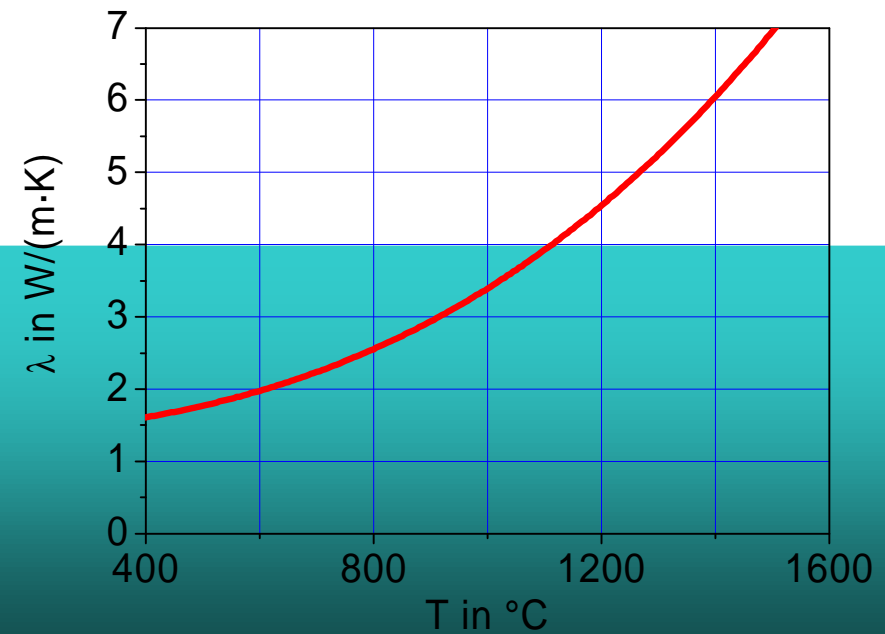
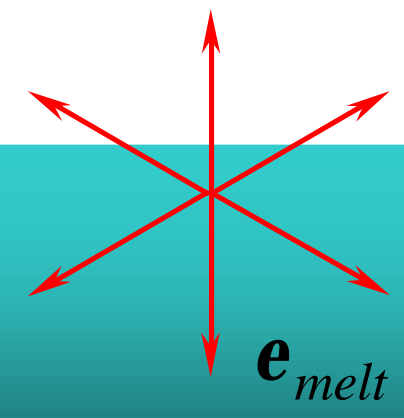
- *Heat can be transferred over any infinitesimally small temperature difference $T_H - T_L$.*
- *The problem is the **transfer rate** achieved:*

$$\dot{Q} = A \cdot \mathbf{a}_{ht} \cdot (T_H - T_L), \dot{Q} \text{ in kW}$$

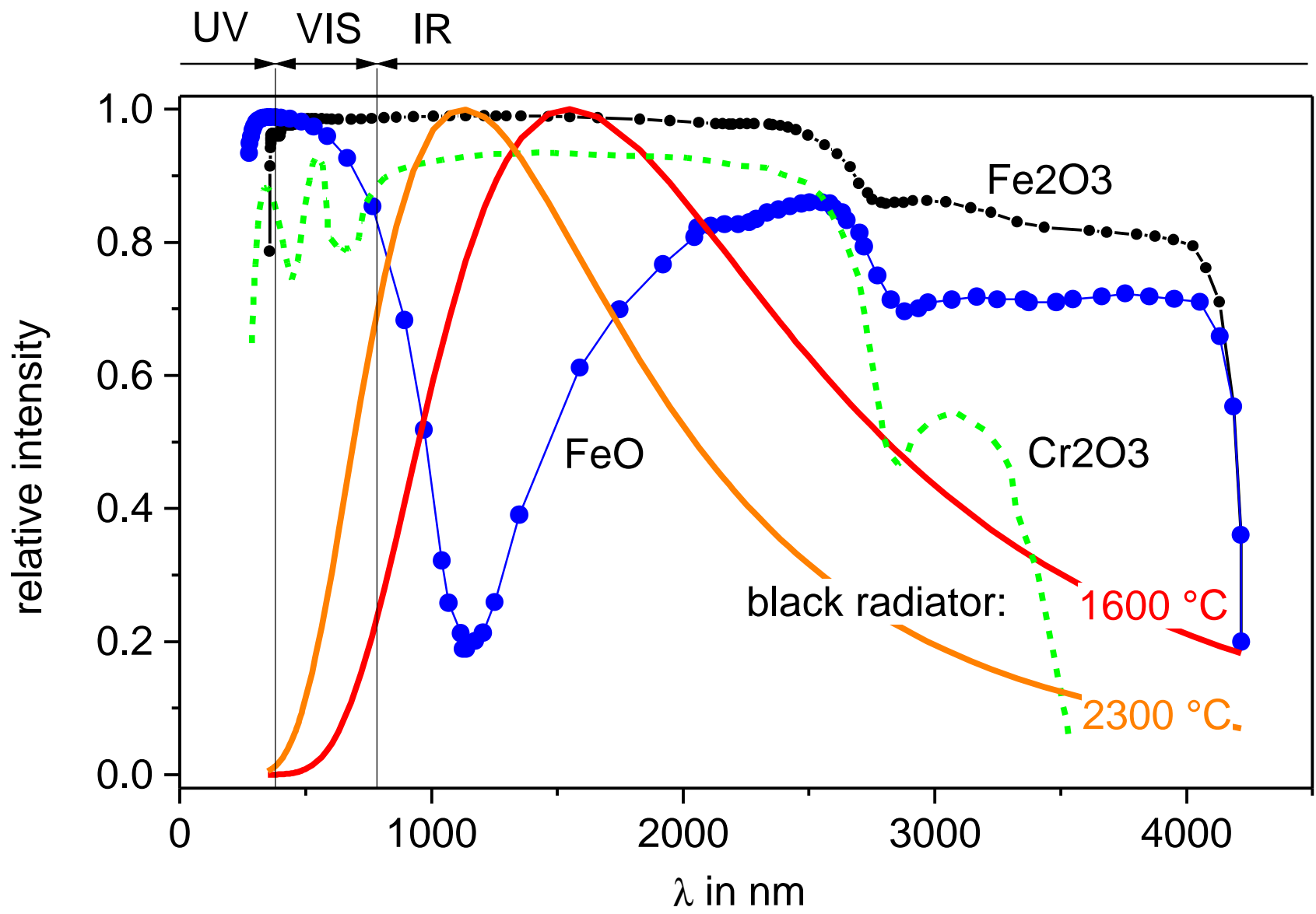
With a given transfer coeff. \mathbf{a}_{ht} and area A , $T_H - T_L$ is fixed by the required power \dot{Q} .



$$q_i = C_S \cdot \mathbf{e}_i \cdot T_i^4$$

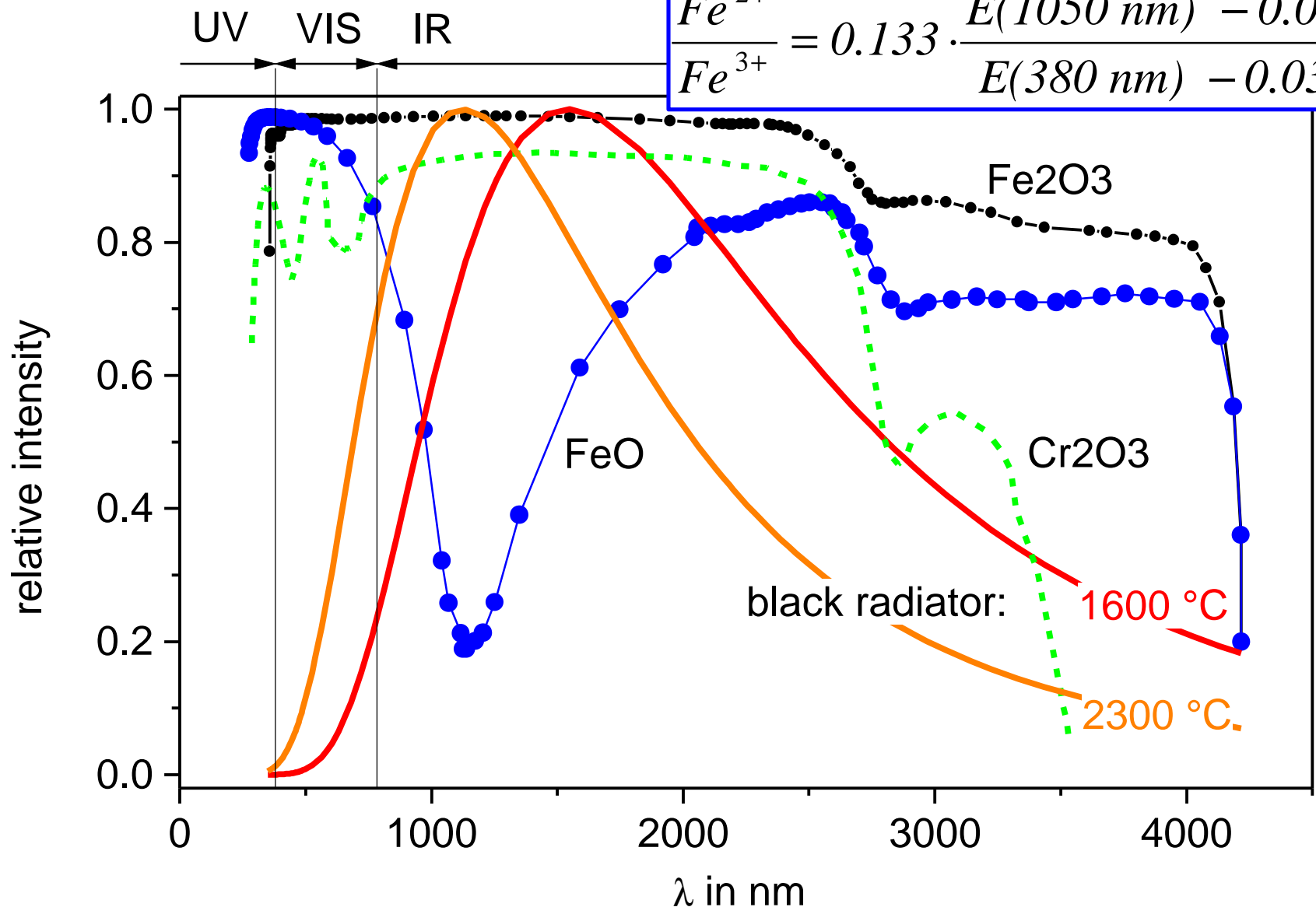


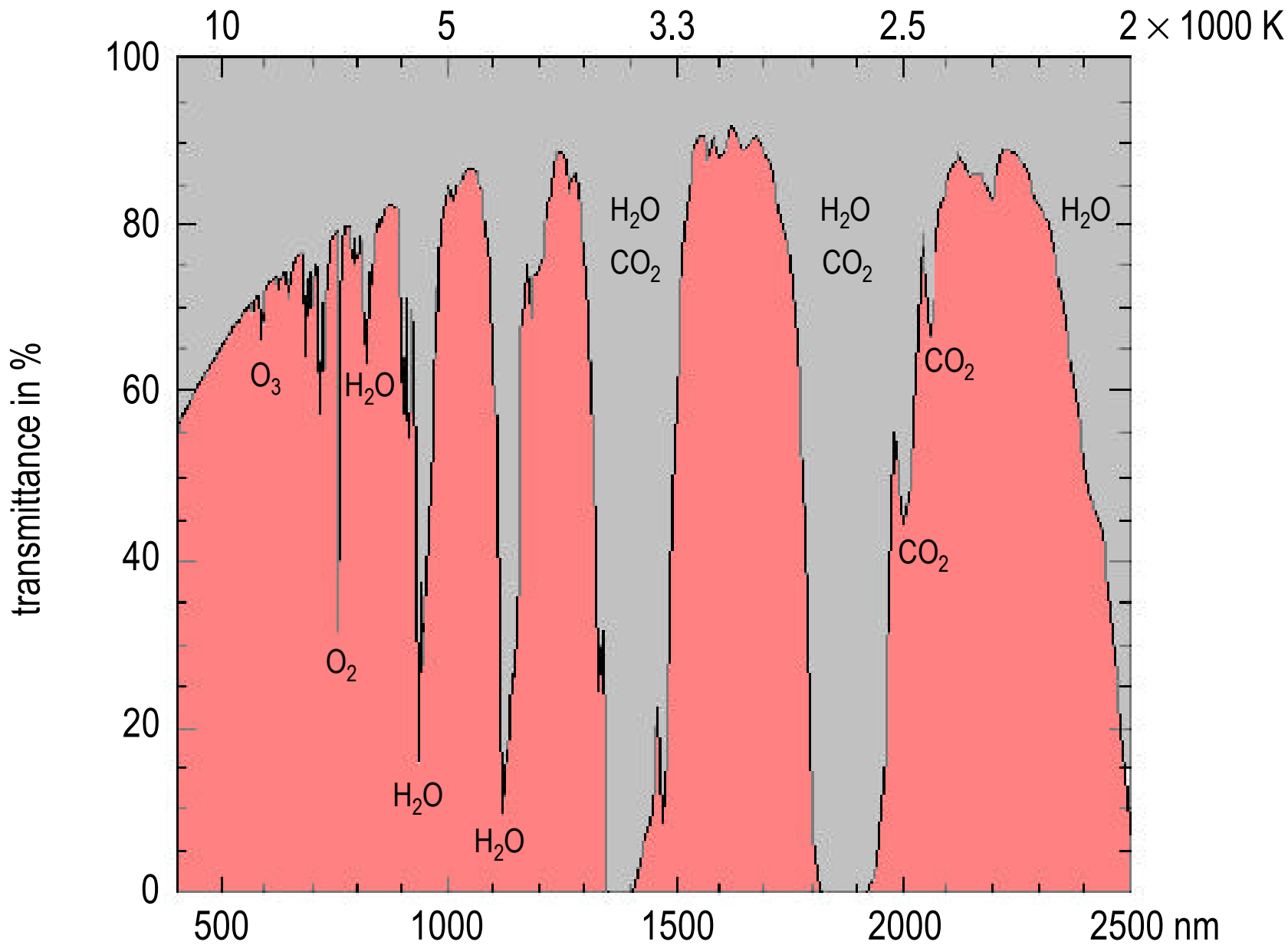
black radiator : I_{\max} in nm $\approx \frac{5000 \text{ nm}}{T / K}$



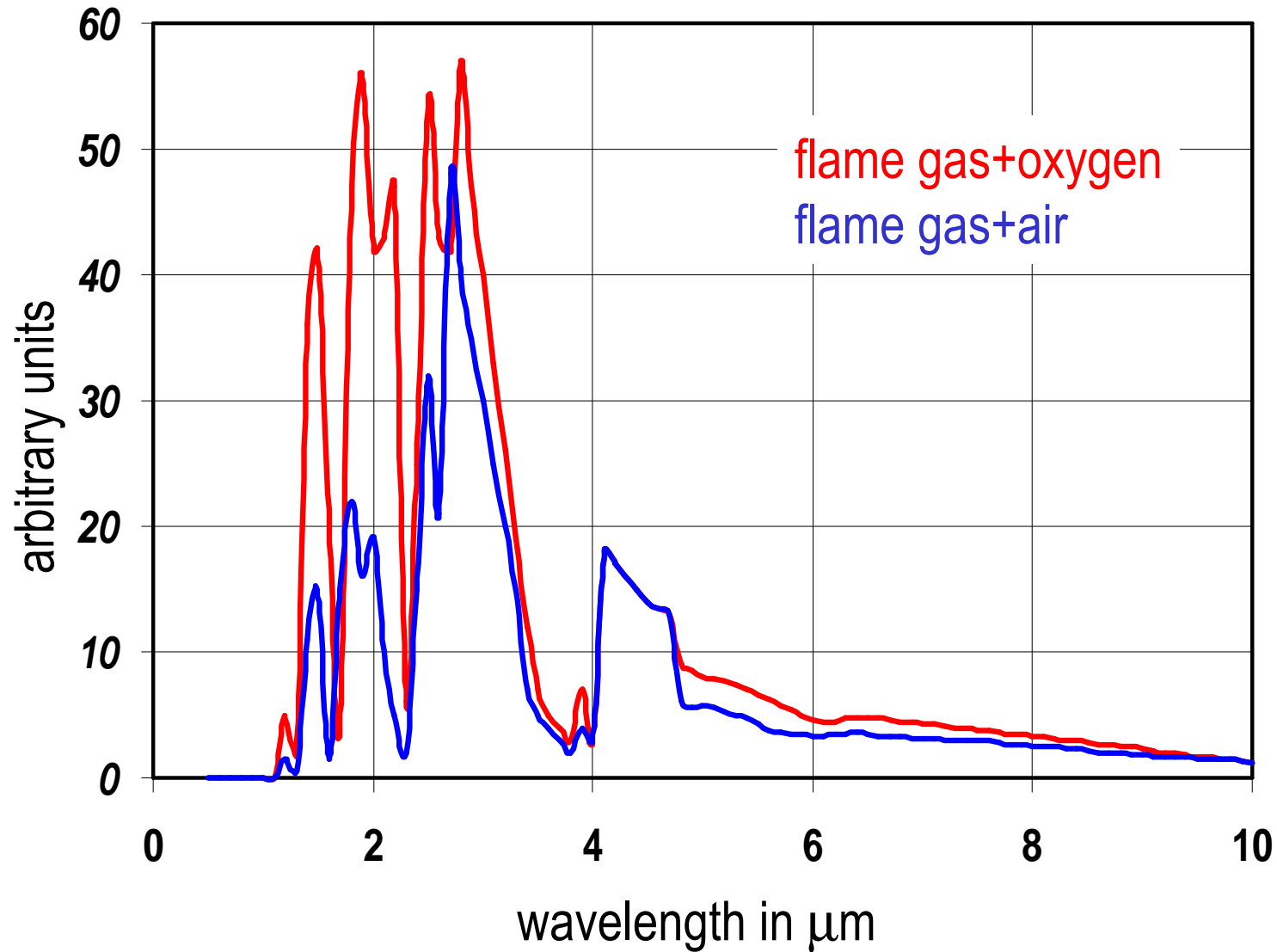
black radiator: I_{max} in nm $\approx \frac{5000 \text{ nm}}{T / K}$

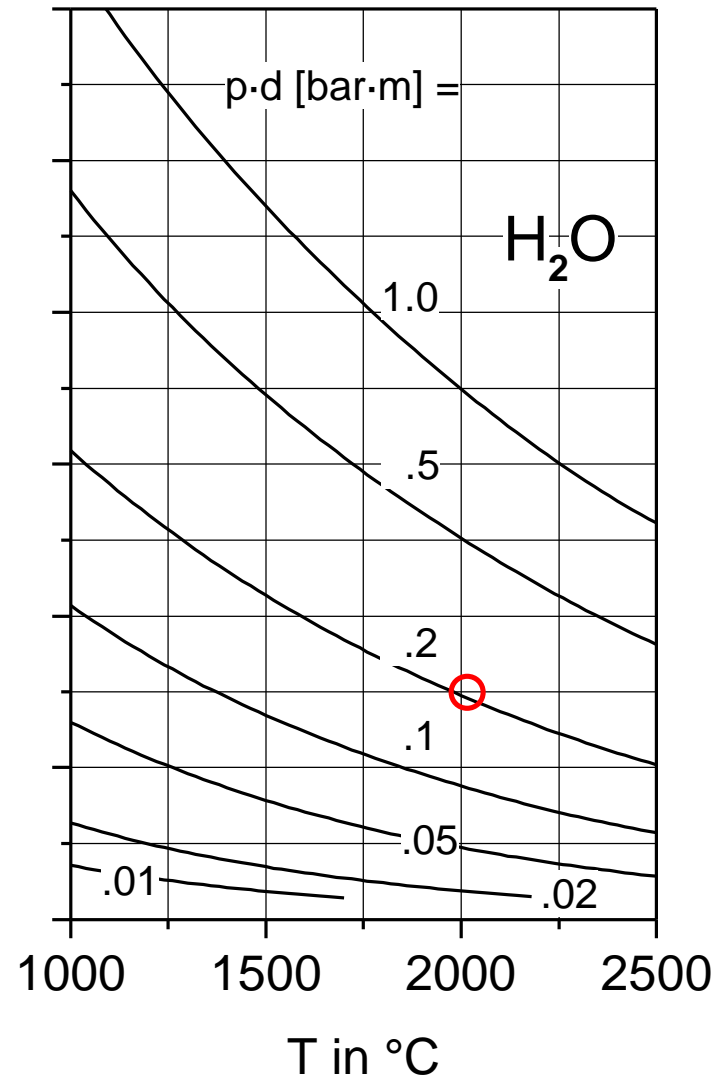
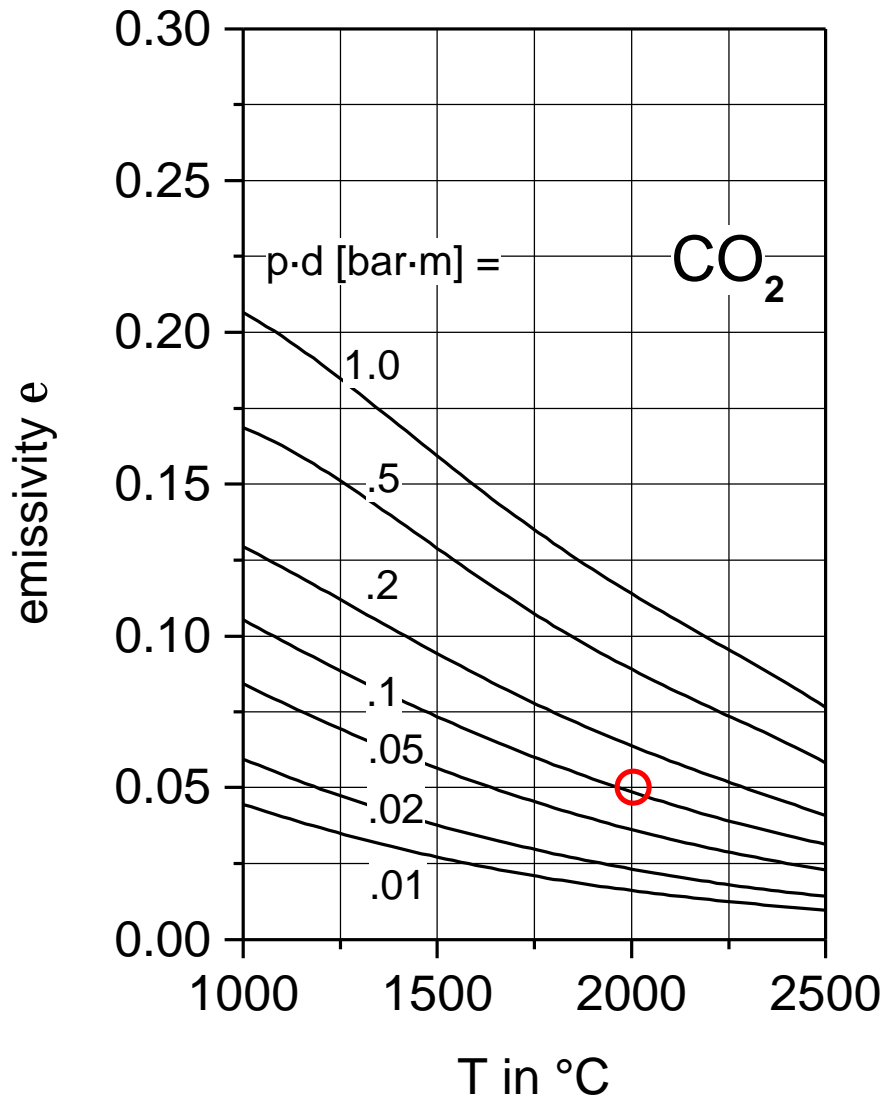
$\frac{Fe^{2+}}{Fe^{3+}} = 0.133 \cdot \frac{E(1050 \text{ nm}) - 0.036}{E(380 \text{ nm}) - 0.036}$





flame radiation \Leftrightarrow oscillation and rotation of molecules with dipoles
(i.e., H_2O , CO_2 ; rest is athermic; no black radiation!)



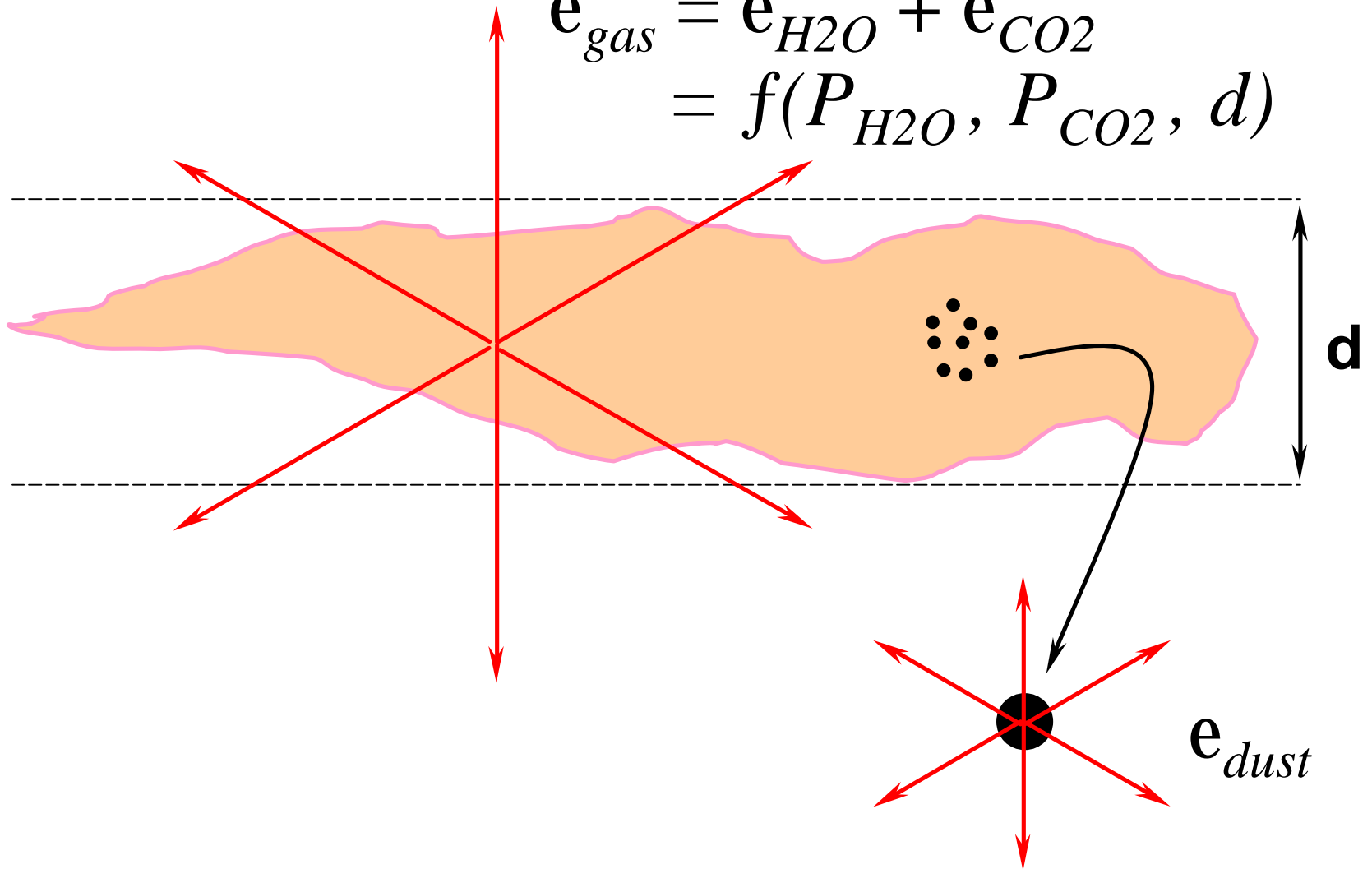


mineral gas flame, $d = 1.0$ m, $P_{\text{CO}_2} \approx 0.1$ bar, $P_{\text{H}_2\text{O}} \approx 0.2$ bar

$$\varepsilon = \varepsilon_{\text{CO}_2} + \varepsilon_{\text{H}_2\text{O}} = 0.05 + 0.075 = 0.125$$

$$e_{total} = e_{gas} + e_{dust} - e_{gas} \cdot e_{dust}$$

$$e_{gas} = e_{H2O} + e_{CO2}$$
$$= f(P_{H2O}, P_{CO2}, d)$$

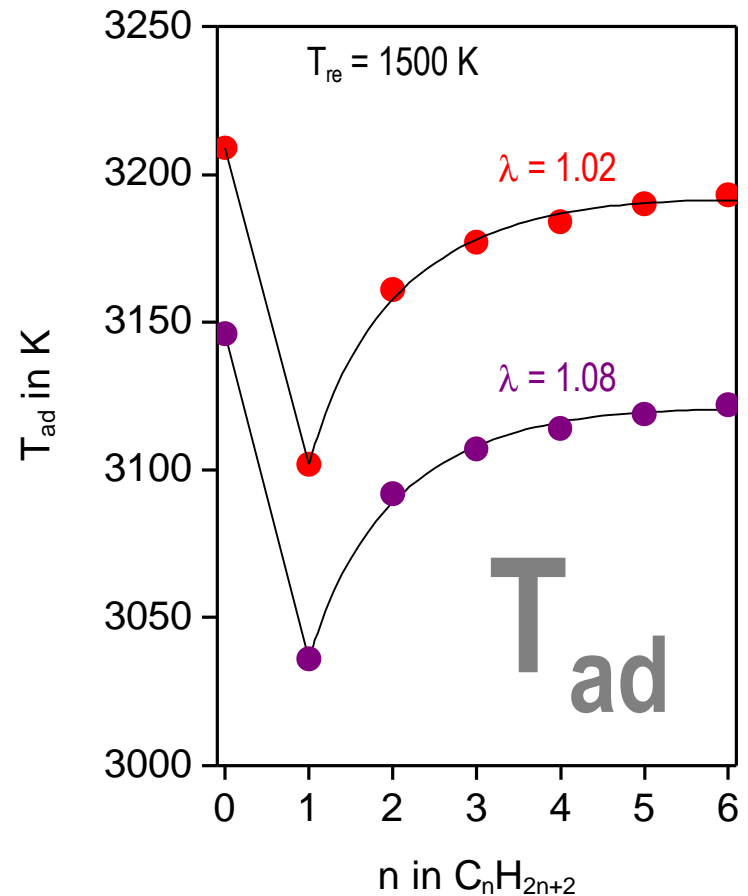


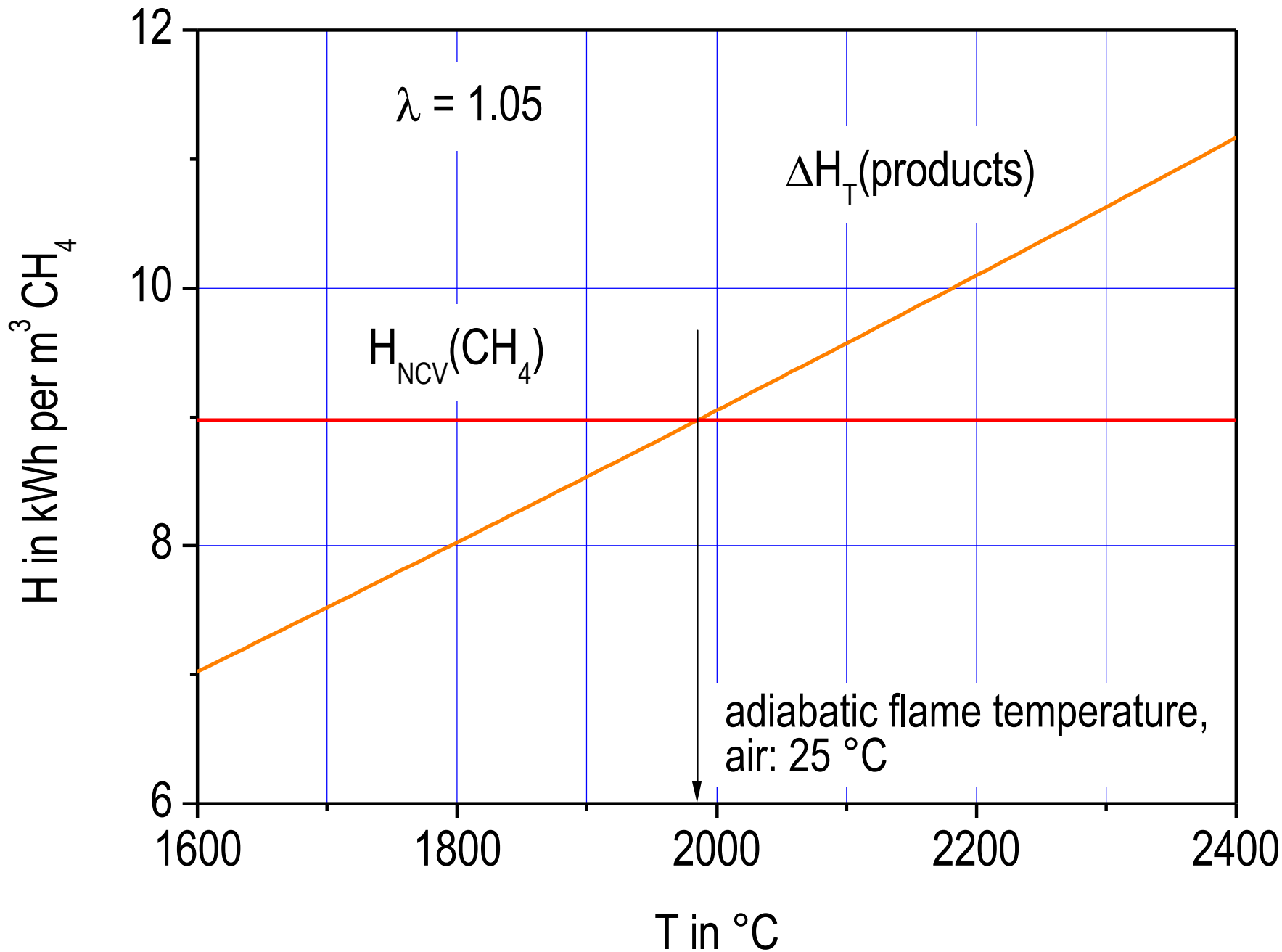
$$\Delta H_{ad} = H_{NCV} + I \cdot n_{O_2} \cdot (H_{O_2}(T) + 3.76 \cdot H_{N_2}(T_0)) \quad \left| \begin{array}{l} T = T_{re} \\ T = T_0 \end{array} \right.$$

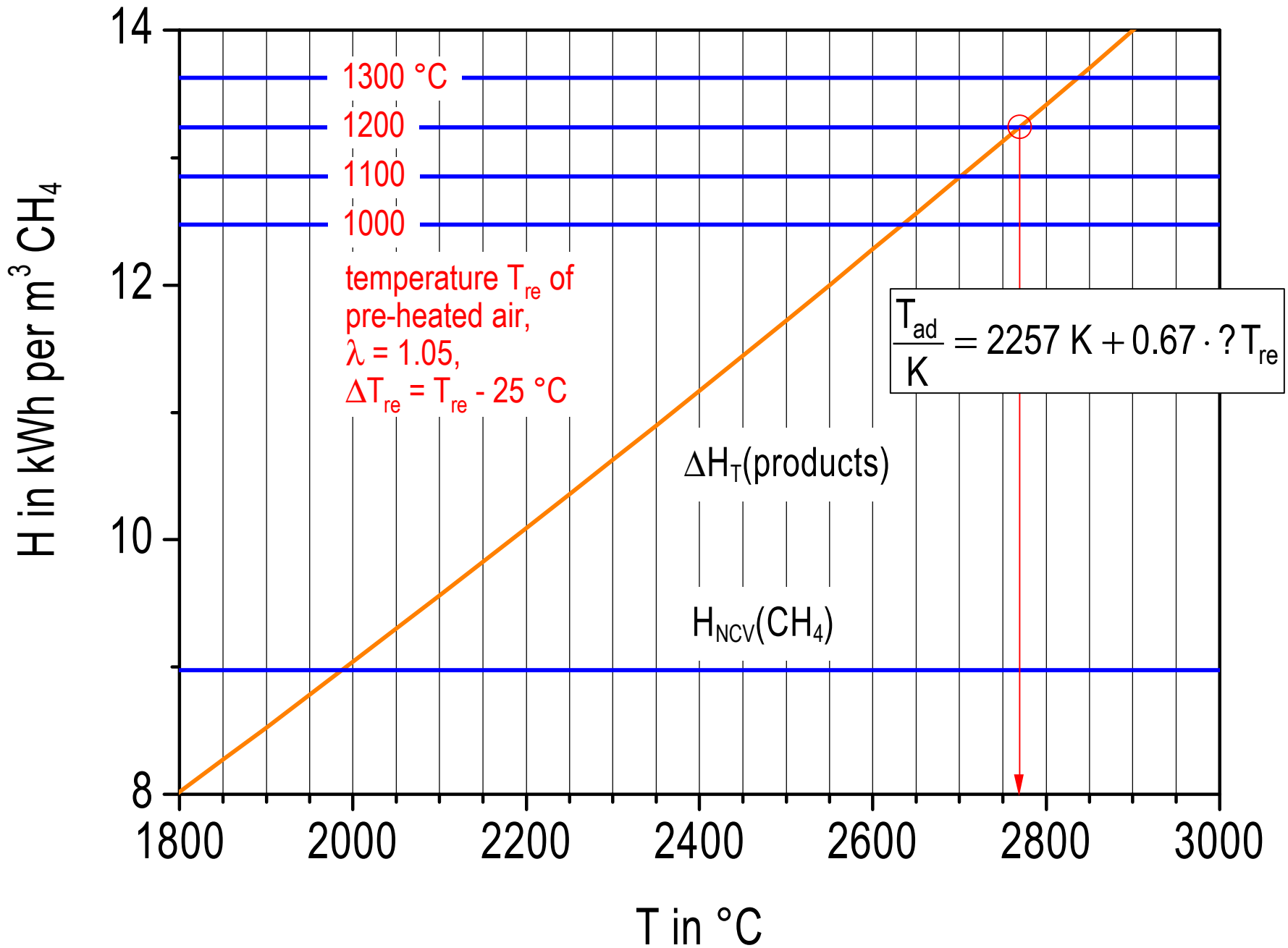
$$\Delta H_{ad} = (n_{CO_2} \cdot H_{CO_2}(T) + n_{H_2O} \cdot H_{H_2O}(T)) + n_{O_2} \cdot ((I - 1) \cdot H_{O_2}(T) + I \cdot 3.76 \cdot H_{N_2}(T)) \quad \left| \begin{array}{l} T = T_{ad} \\ T = T_0 \end{array} \right.$$

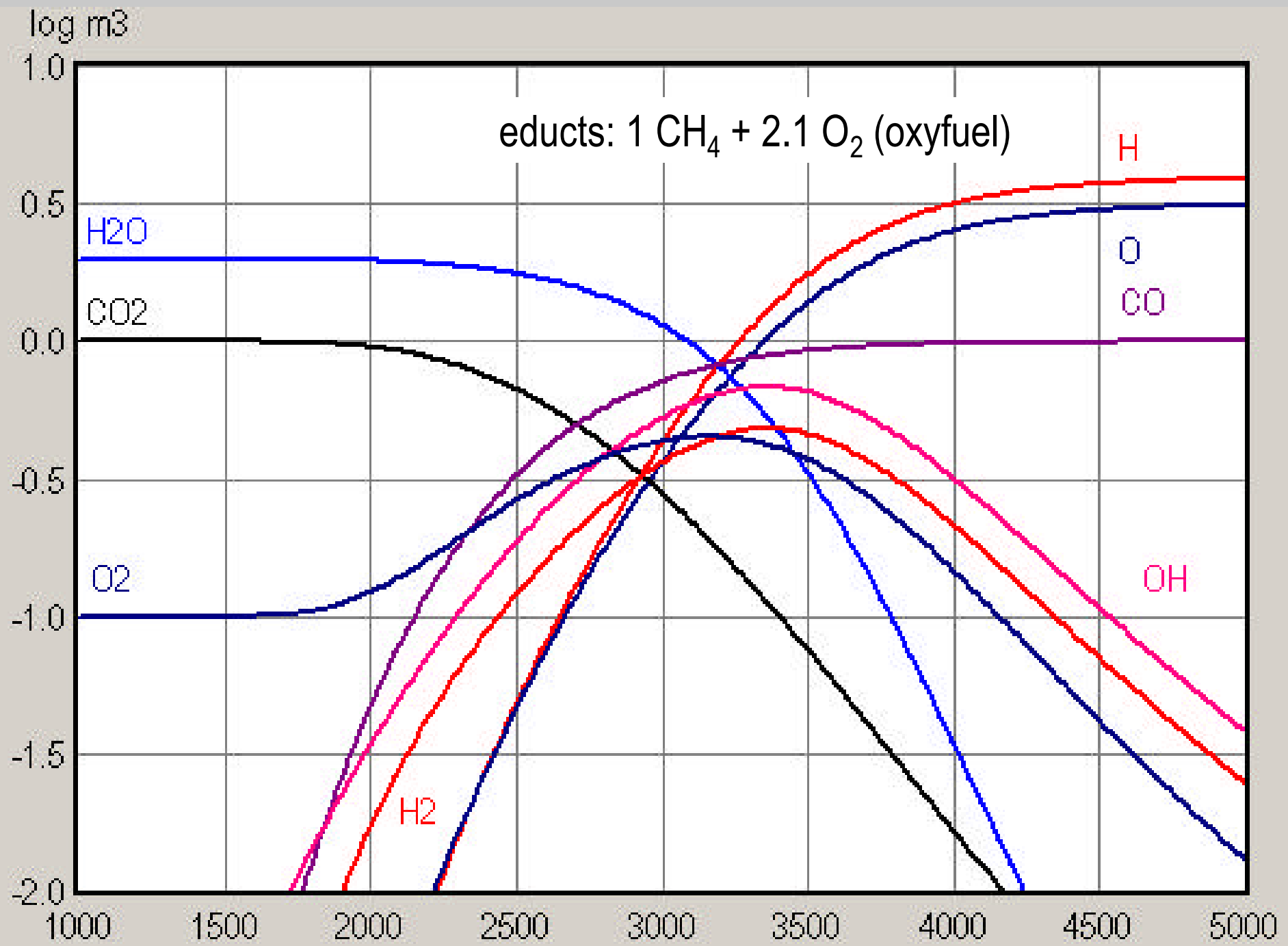
Vary T in the second line until the ΔH_{ad} value matches with the ΔH_{ad} value of the first line. Due to the complicated $c_p(T)$ functions, a straight-forward calculation is not possible.

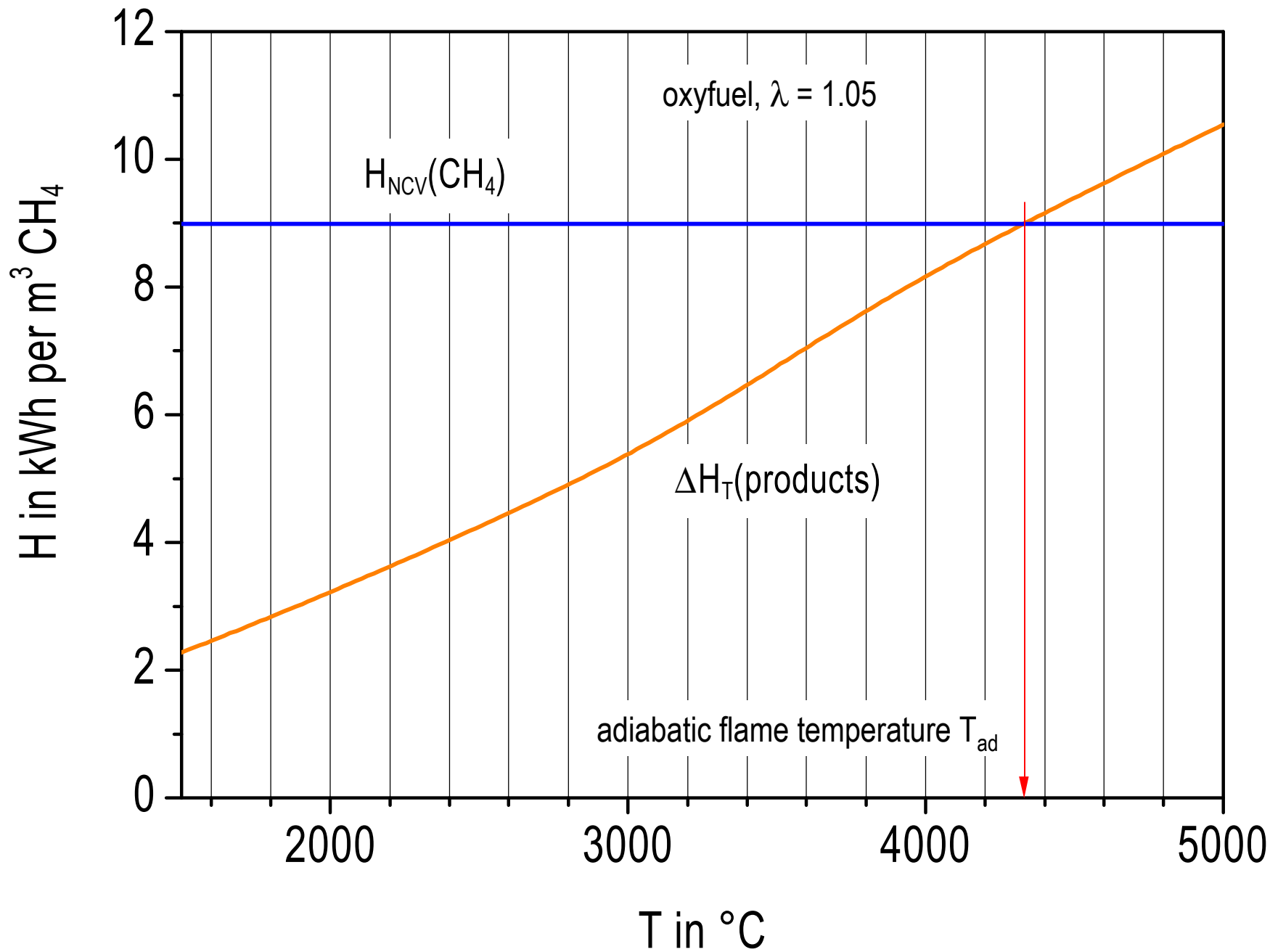
	air-fuel, 298 K	air-fuel, 1500 K	oxy-fuel
$\lambda = 1.02$	2303	3102	4718
$\lambda = 1.08$	2221	3036	4634











practice

#FUELTAB-1.xls

#FUELTAB-2.xls

#FUELTAB-3.xls

#THDYN-GAS.xls

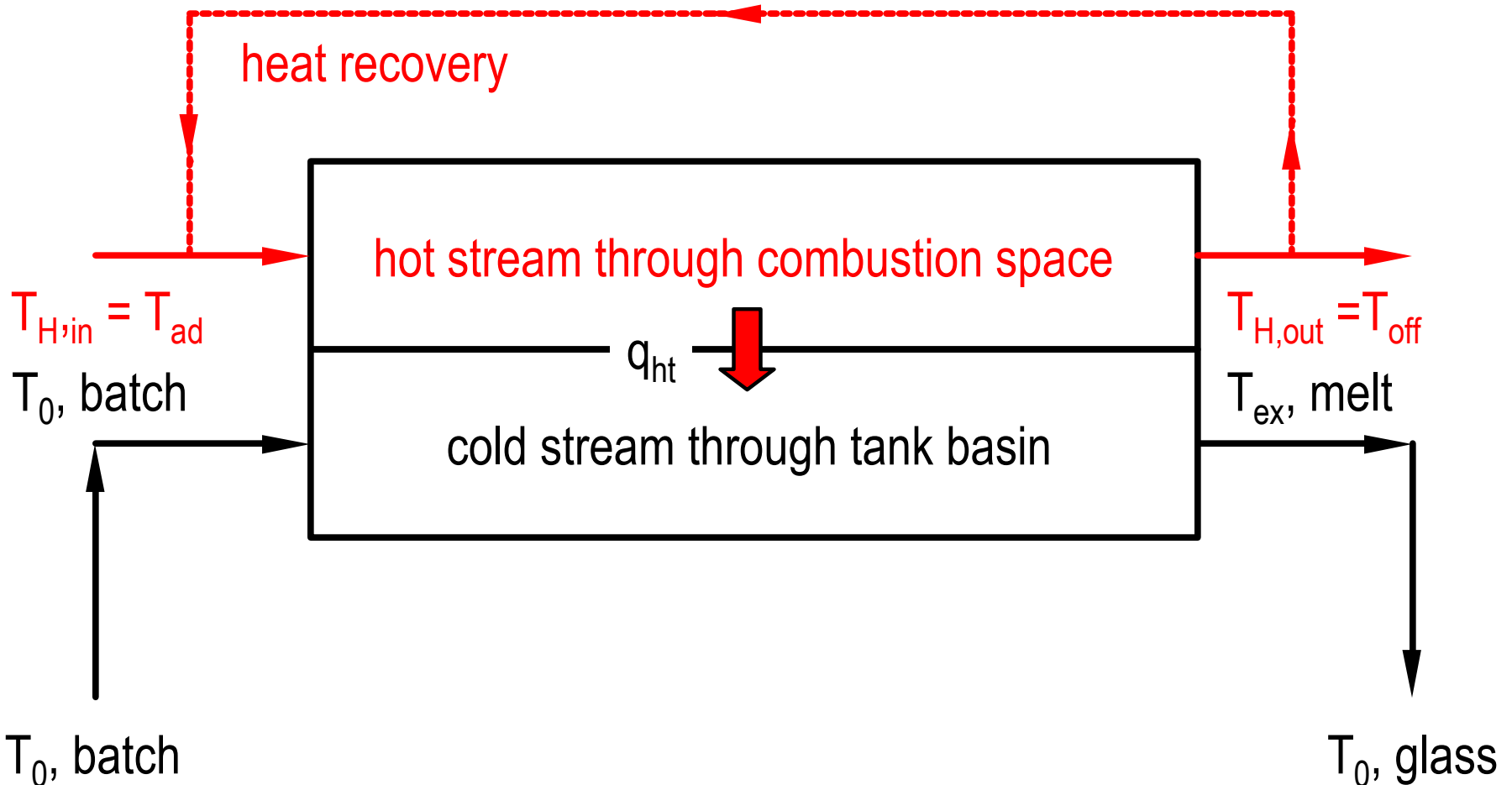
#COMBUSTION.xls

#HEAT IN GASES.xls

**the glass furnace -
a thermochemical reactor**

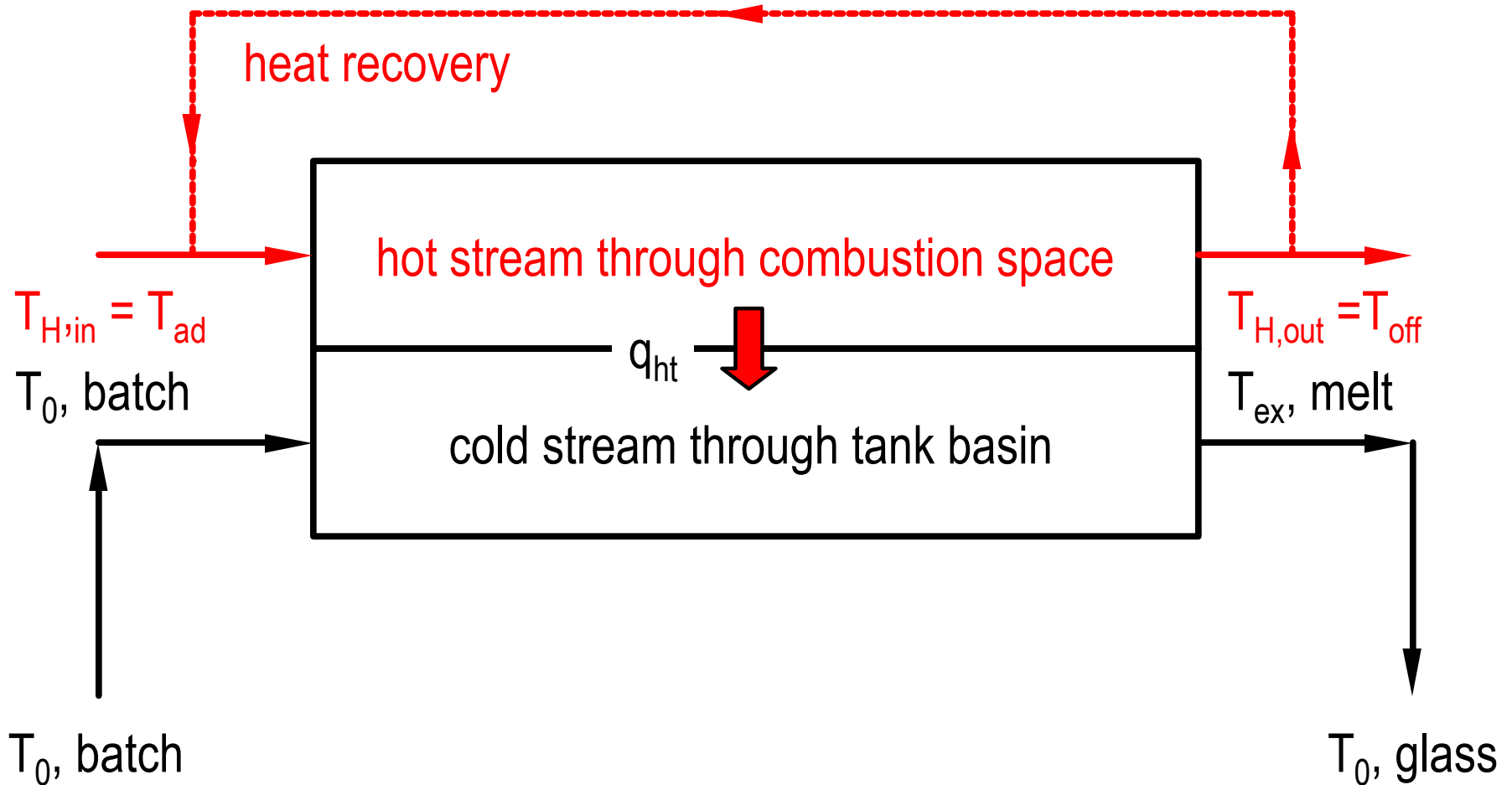
heat transfer problem:

$$\frac{q_{ht}}{q_{in}} = \frac{\dot{m} \cdot c_p \cdot (T_{H,in} - T_{H,out})}{\dot{m} \cdot c_p \cdot (T_{H,in} - T_L)} = \frac{\text{heat extracted from hot stream}}{\text{heat made available by hot stream}}$$

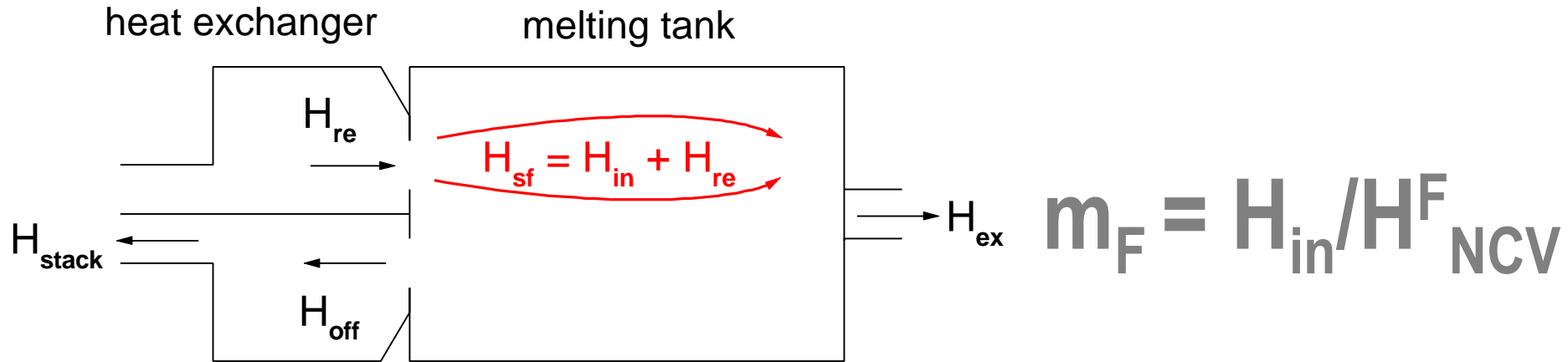


heat transfer problem:

$$\frac{q_{ht}}{q_{in}} = \frac{\Delta T_{ad} - \Delta T_{off}}{\Delta T_{ad} - h_{re} \cdot \Delta T_{off}} \Rightarrow H_{in} = H_{ht} \cdot \frac{1 - h_{re} \cdot h_{ht}}{1 - h_{ht}}; \quad h_{ht} = 1 - \frac{\Delta T_{off}}{\Delta T_{ad}}$$



fuel input: H_{in} [kWh/t], H_{NCV}^F [kWh/m³], m_F [m³/t]

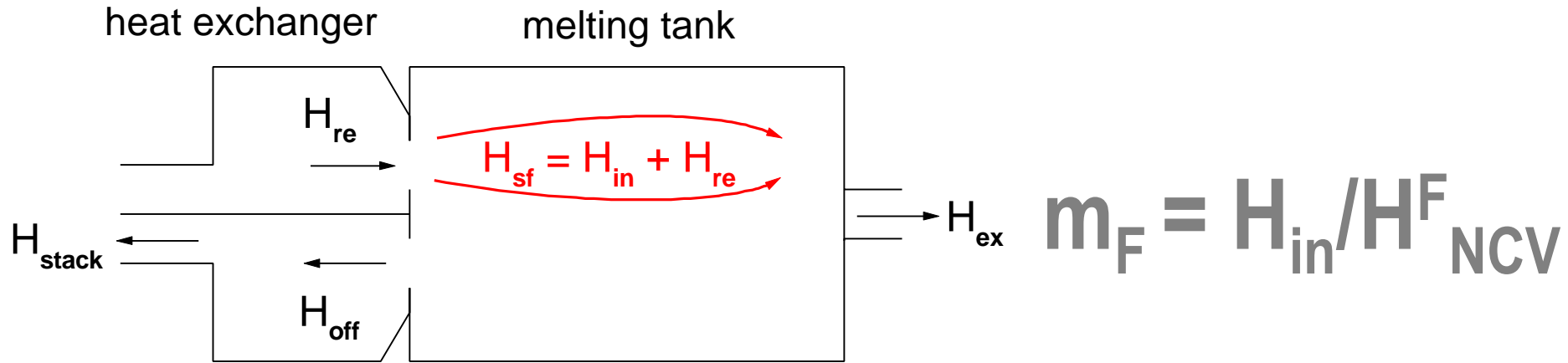


$$H_{in} - (H_{off} - H_{re}) = m_F \cdot H_{NCV}^F - (1 - h_{re}) \cdot H_{off} = H_{wu+wo} + H_{ex}$$

$$\left(V^F(off) \cdot c_{P,off} + (1 - 1) \cdot V^F(air) \cdot c_{P,air} \right) \cdot \Delta T_{off}$$

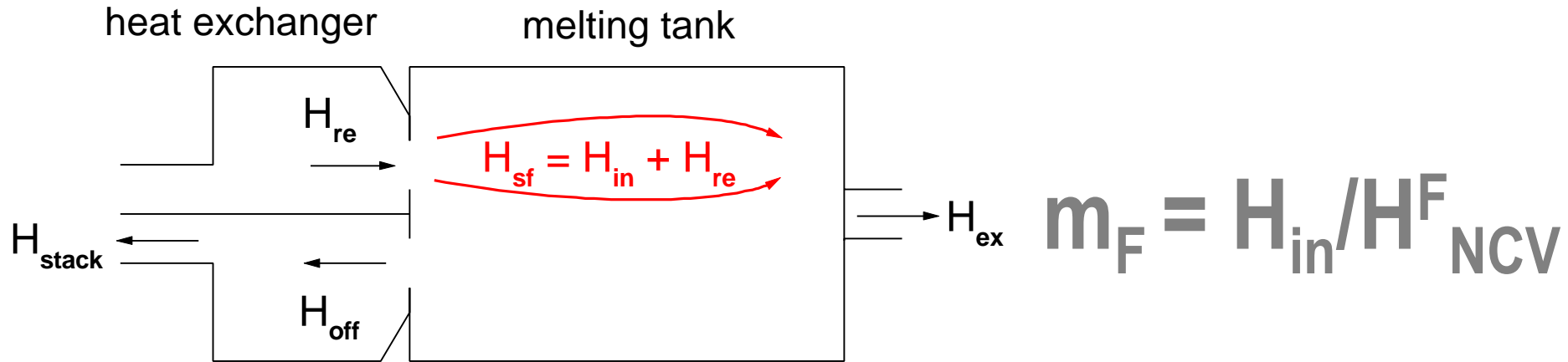
resolve for m_F

fuel input: H_{in} [kWh/t], H_{NCV}^F [kWh/m³], m_F [m³/t]



$$m_F = \frac{H_{wu+wo} + H_{ex}}{H_{NCV}^F - (1 - h_{re}) \cdot (V^F(off) \cdot c_{P,off} + (1 - 1) \cdot V^F(air) \cdot c_{P,air}) \cdot \Delta T_{off}}$$

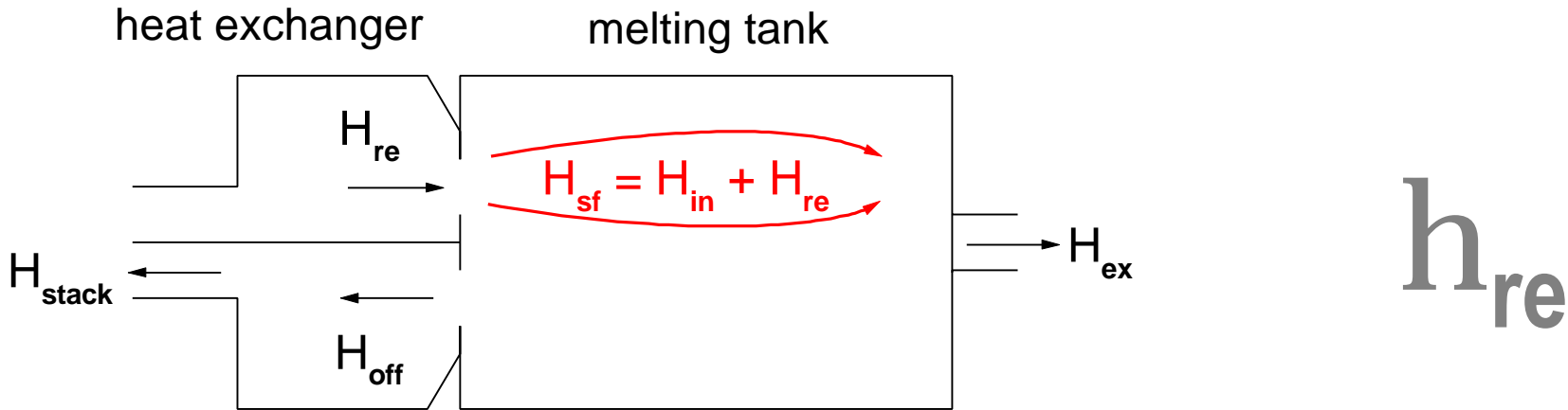
fuel input: H_{in} [kWh/t], H_{NCV}^F [kWh/m³], m_F [m³/t]



$$m_F = \frac{H_{wu+wo} + H_{ex}}{H_{NCV}^F - (1 - h_{re}) \cdot (V^F(off) \cdot c_{P,off} + (I - 1) \cdot V^F(air) \cdot c_{P,air}) \cdot \Delta T_{off}}$$

$\downarrow \Delta H_{chem}^0, y_C, T_{ex}$
 \uparrow \uparrow \uparrow

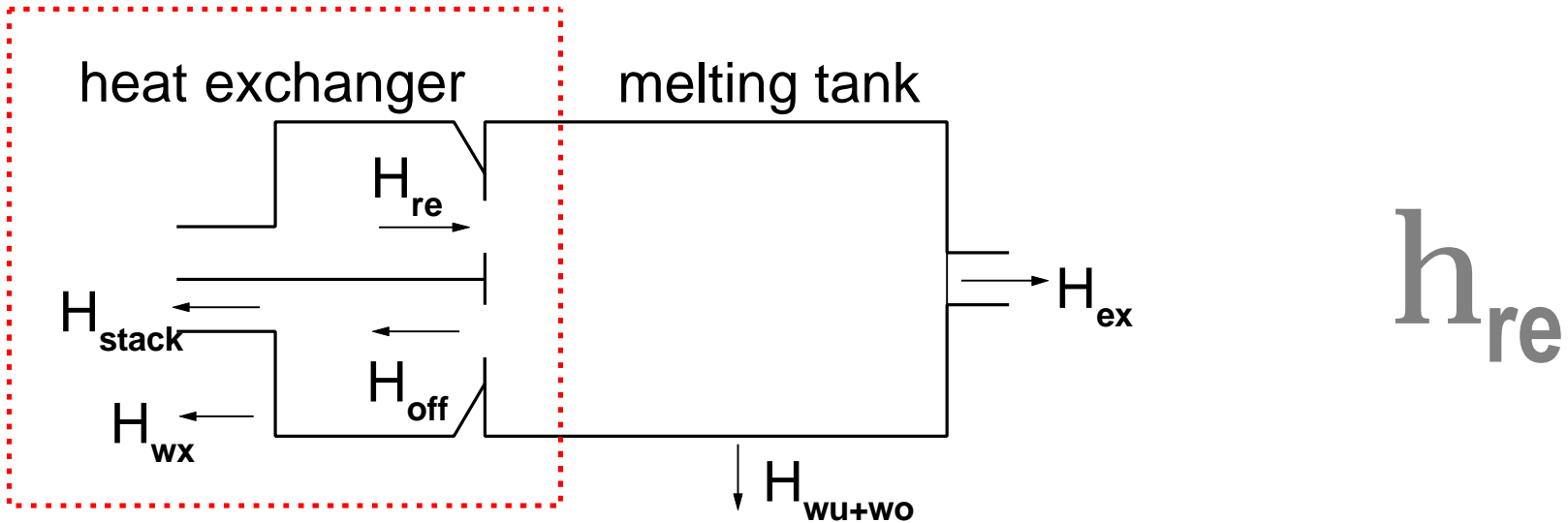
fuel input: H_{in} [kWh/t], H_{NCV}^F [kWh/m³], m_F [m³/t]



$$m_F = \frac{H_{wu+wo} + H_{ex}}{H_{NCV}^F - (1 - h_{re}) \cdot (V^F(off) \cdot c_{P,off} + (I - 1) \cdot V^F(air) \cdot c_{P,air}) \cdot \Delta T_{off}}$$

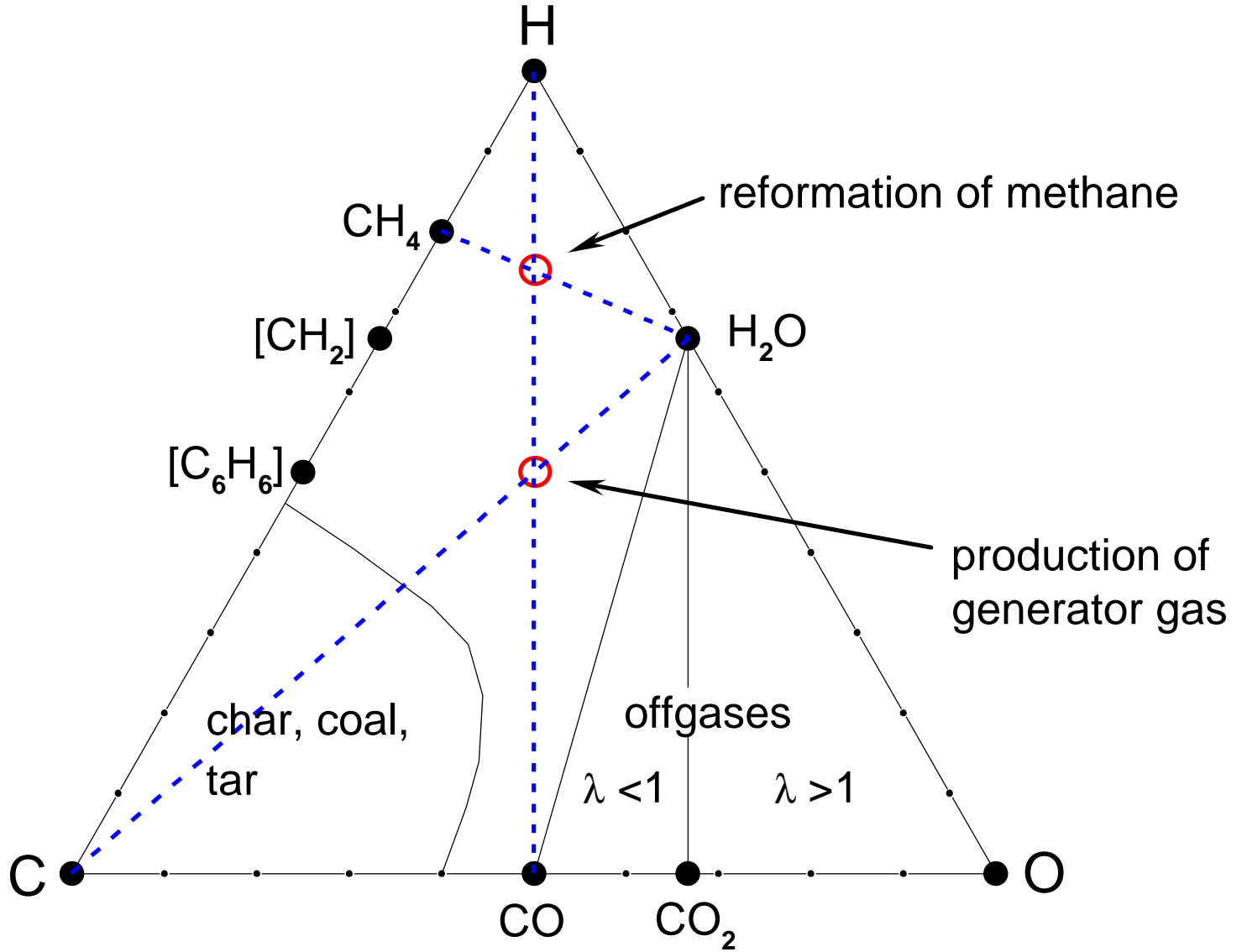
resolve for h_{re}

$$\eta_{re} = H_{re} / H_{off}$$

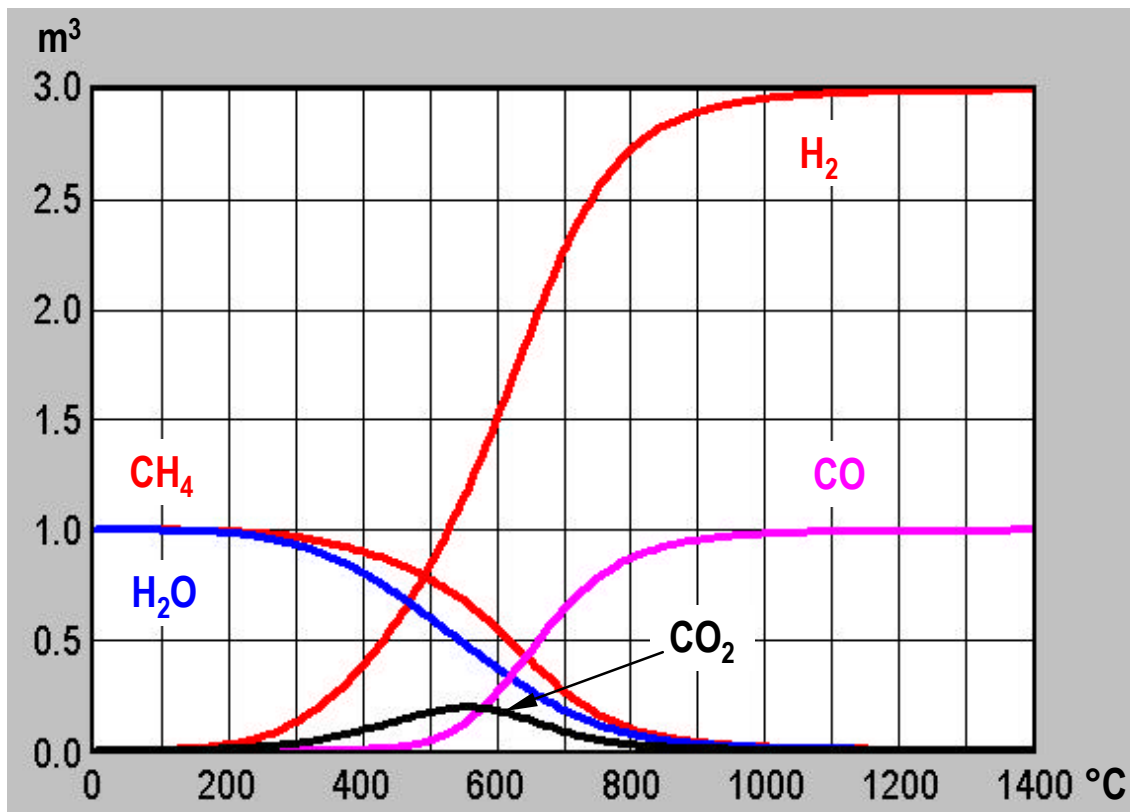
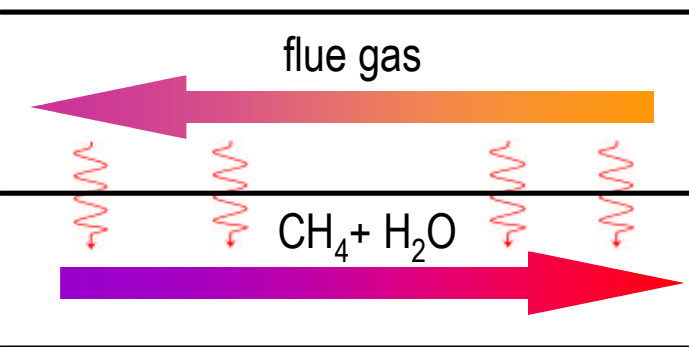


$$h_{re} = \left(\frac{V^F (air)}{V^F (off)} \right) \cdot \left(\frac{c_{P,air}}{c_{P,off}} \right) \cdot \frac{\Delta T_{re}}{\Delta T_{off}} \cdot \frac{1}{1+B} \leq 0.8 \cdot \Delta T_{re} / \Delta T_{off}$$

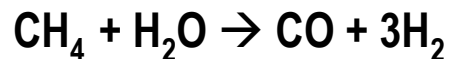
$$h_{re} \approx 60 - 65\%$$



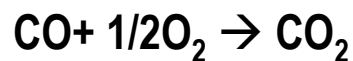
thermochemical recuperator



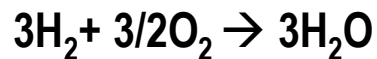
- 8.99 kWh/m³



+2.31 kWh/m³



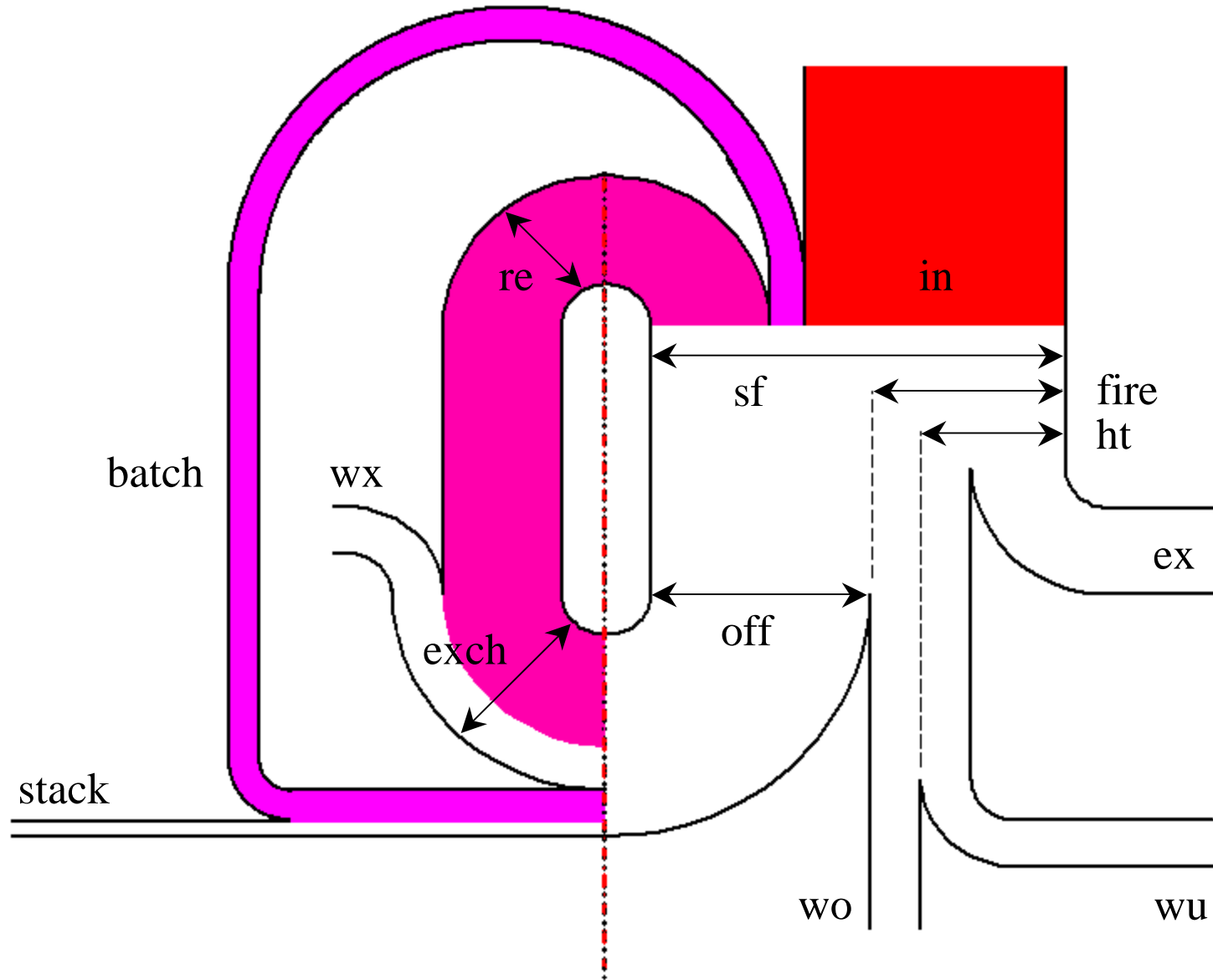
- 3.17 kWh/m³

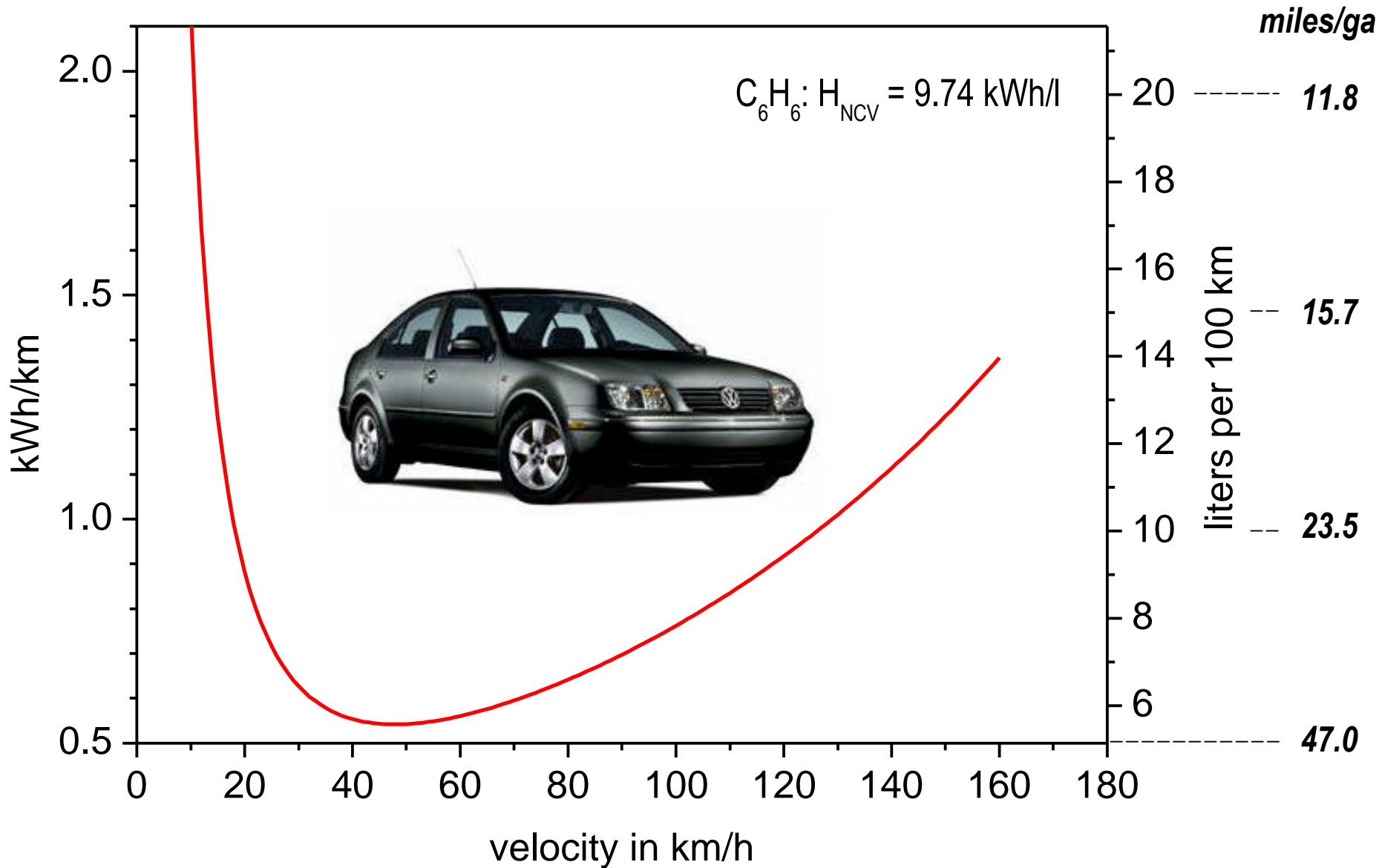


- 8.13 kWh/m³

} - 11.30 kWh/m³

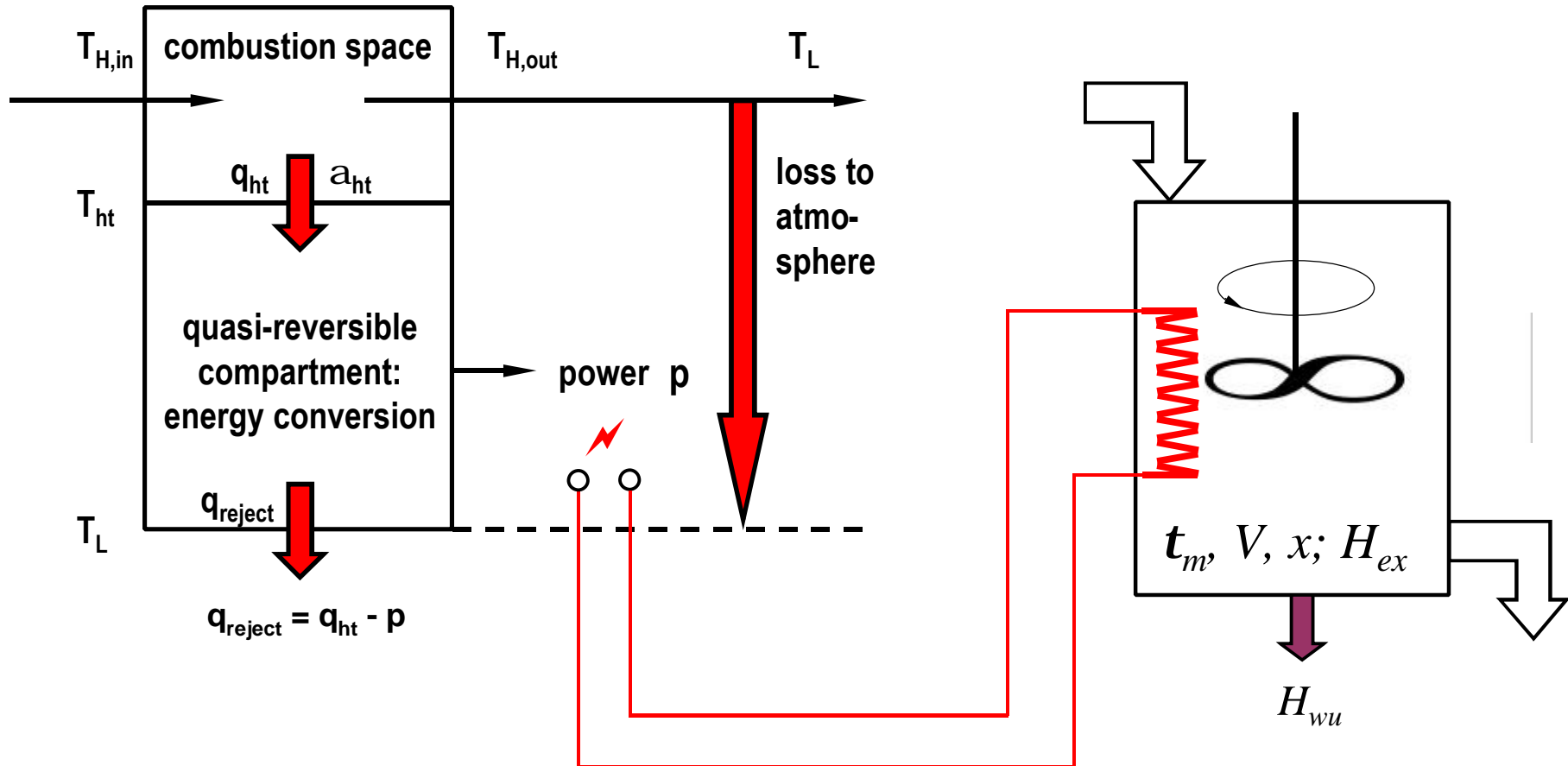
BATCH PREHEATER





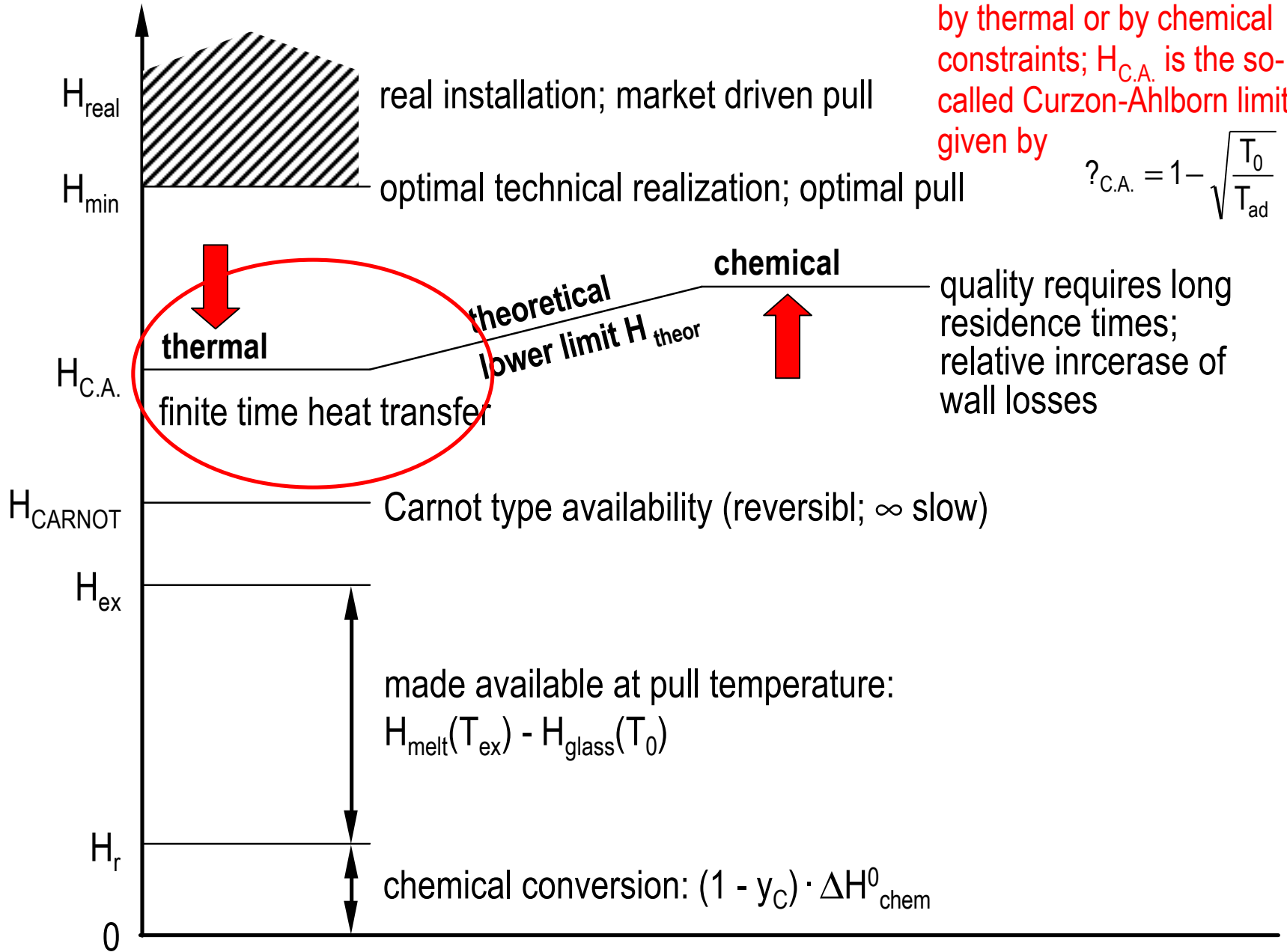
- 100 km/h = 62 mph
- z liters per 100 km correspond to $235.2 / z$ miles per US gallon

2nd theorem treatment, „finite-time heat thermodynamics“

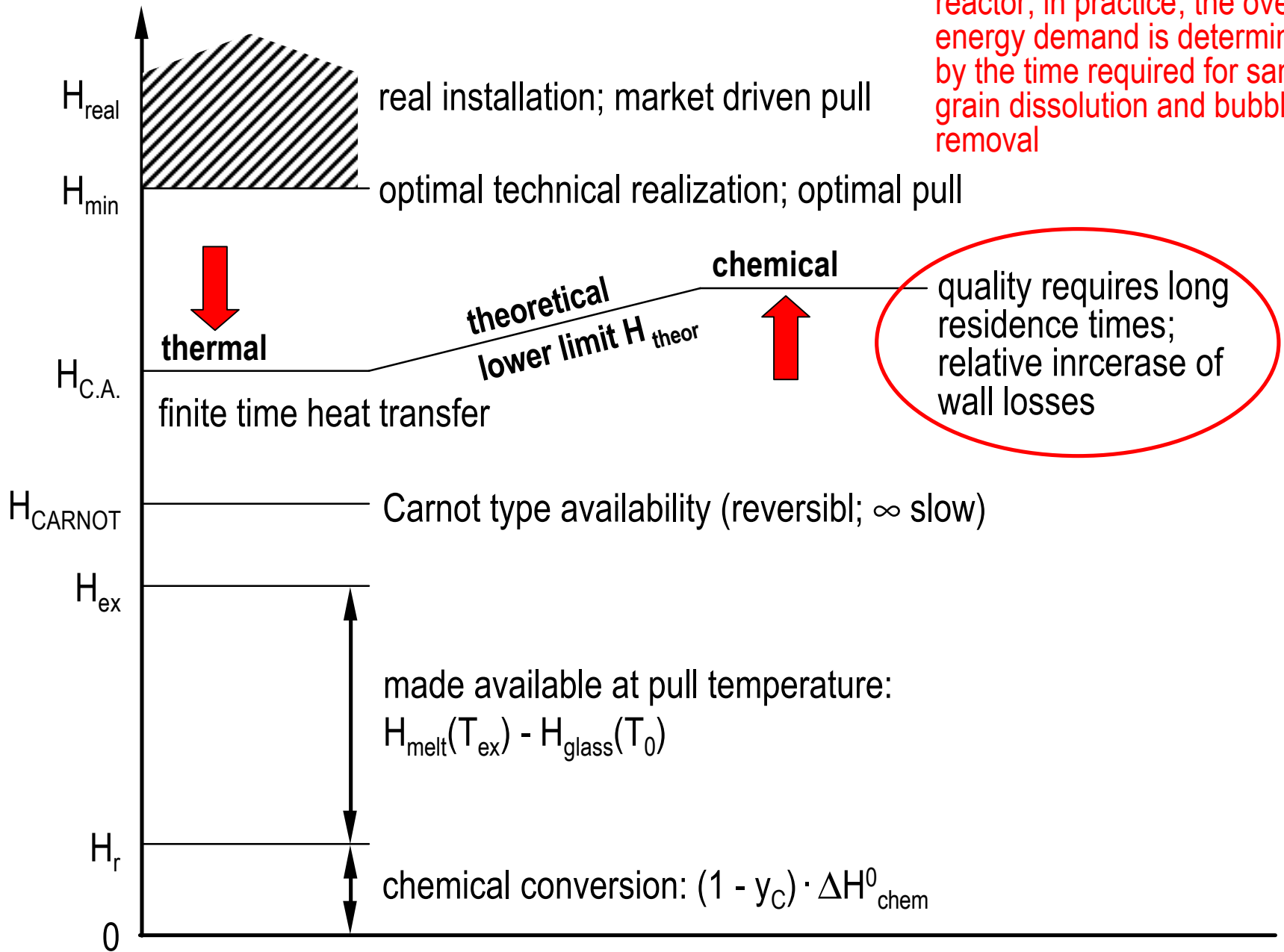


the energy demand of a glass furnace is determined either by thermal or by chemical constraints; $H_{C.A.}$ is the so-called Curzon-Ahlborn limit given by

$$\eta_{C.A.} = 1 - \sqrt{\frac{T_0}{T_{ad}}}$$



a glass furnace is not only a thermal, but also a chemical reactor; in practice, the overall energy demand is determined by the time required for sand grain dissolution and bubble removal



Main influences:

The compiled influences may be attributed to three areas:

physics & chemistry (basics):

nos. 1 - 3, no. 4

product & market:

nos. 5 - 6

technical realization:

nos. 7 - 8

$$1. H_{\text{BATCH + CULLET}} = (1 - y_C) \cdot \Delta H_{chem}^0$$

$$2. H_{\text{HEAT CAPACITY}} = \Delta H_T, \text{ at } T = T_{ex}$$

$$3. H_{\text{EXPLOITATION}} = H_{ex}$$

$$4. H_{\text{HEAT TRANSFER}} \propto \frac{1}{1 - \sqrt{\frac{T_0}{T_H}}}$$

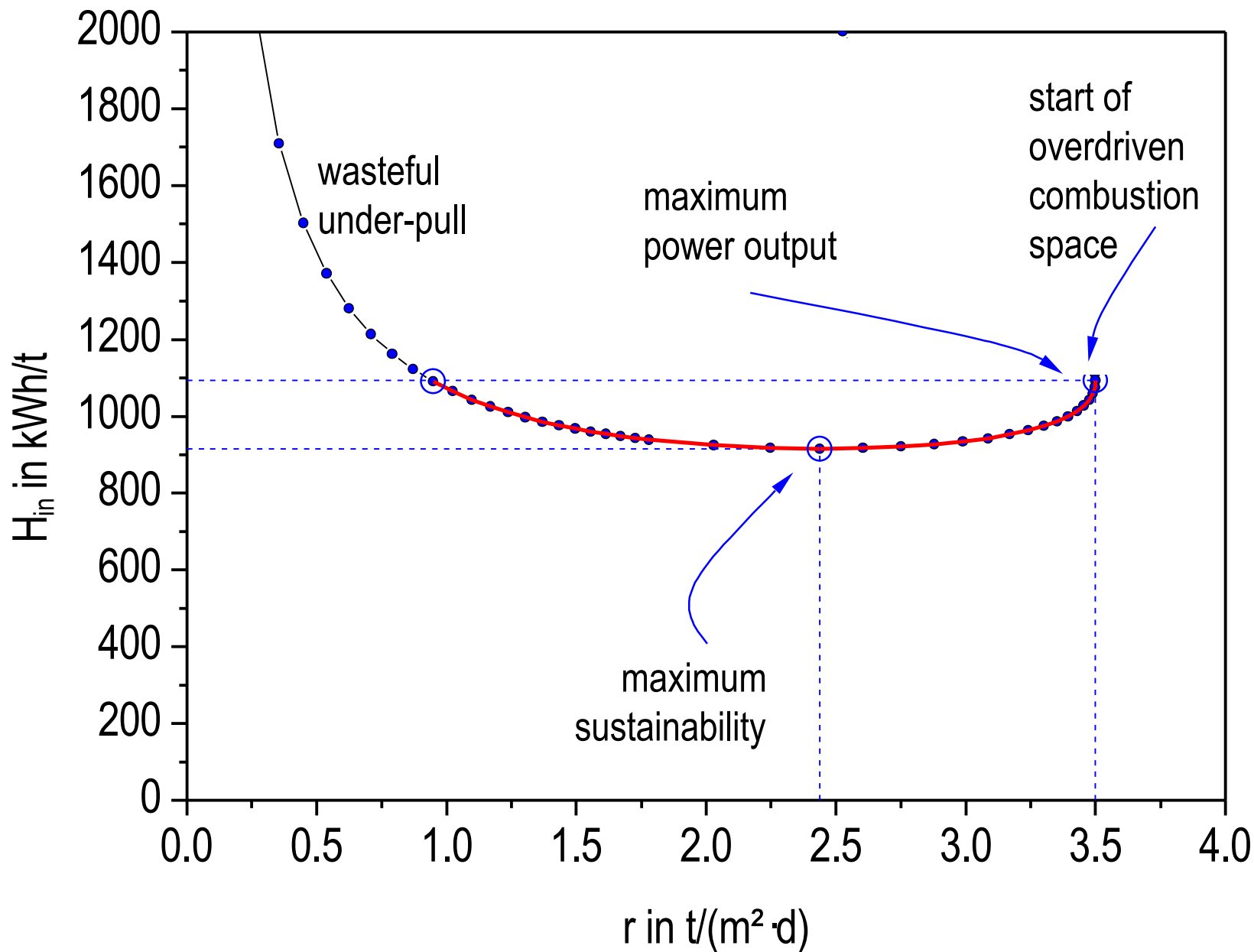
$$5. H_{\text{GLASS QUALITY}} \propto K_Q, \quad 1 \leq K_Q \propto \frac{1}{1 - x}$$

$$6. H_{\text{UTILIZATION OF CAPACITY}} \propto \frac{q}{r}, \quad q \text{ in } kW/m^2, \quad r \text{ in } t/(m^2 \cdot h)$$

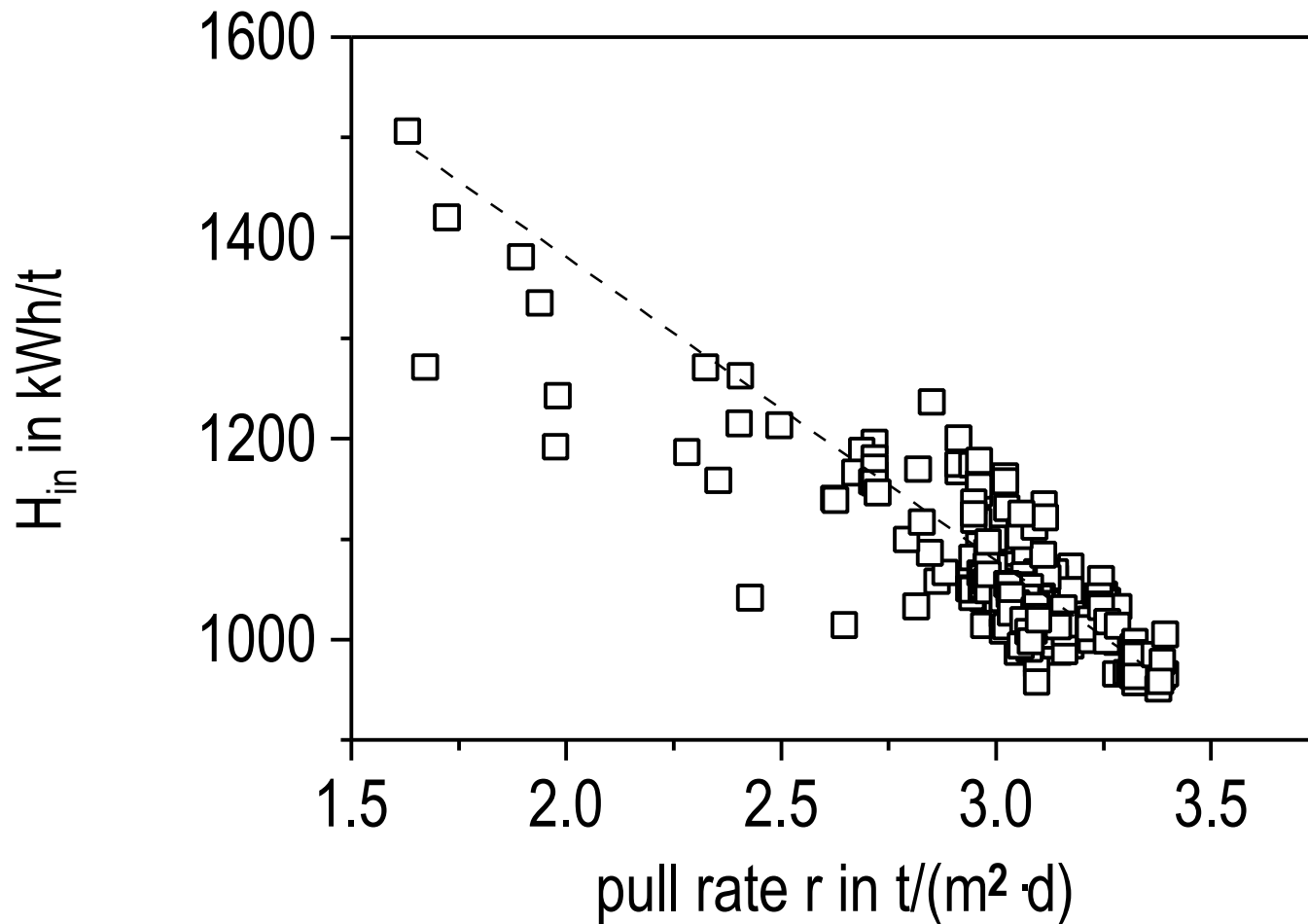
$$7. H_{\text{AGE OF AGGREGATE}} \propto (1 + a \cdot t)$$

$$8. H_{\text{TECHNICAL CONSTRAINTS}}$$

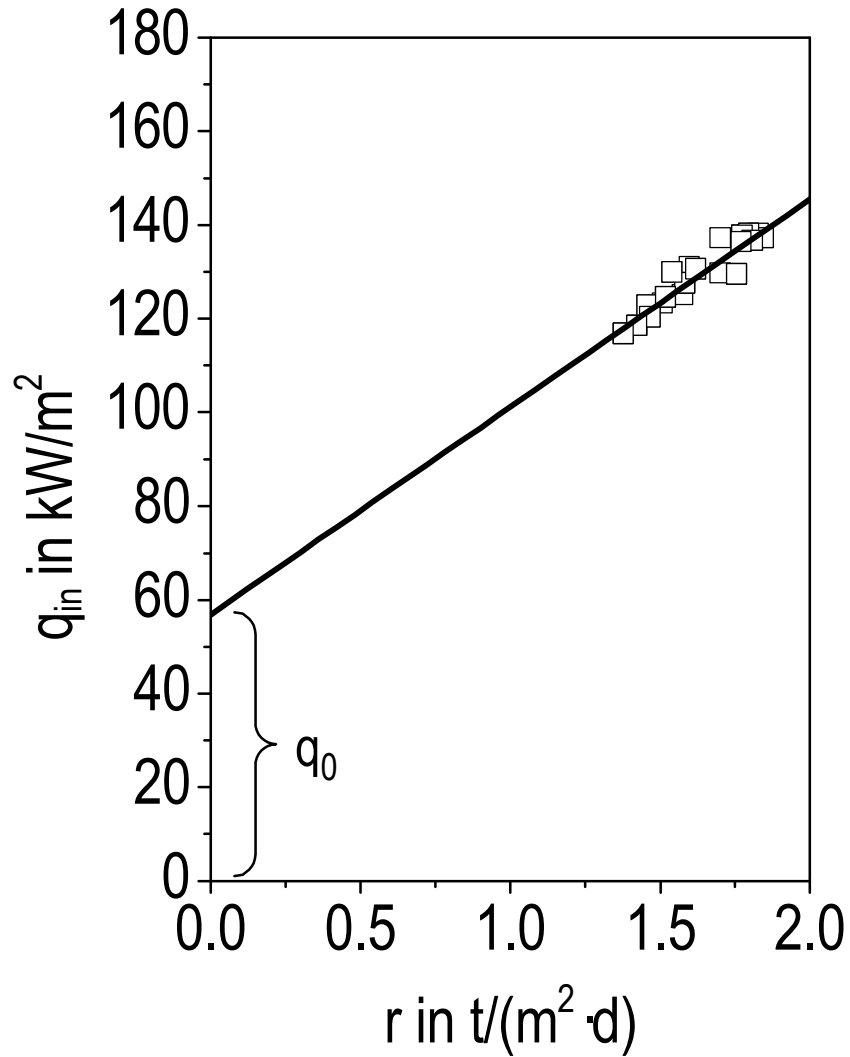
large furnaces with small heat leak show a point of minimum heat demand per t of produced glass



for a small furnace with high heat leak, the minimum is not observed



a plot of $H_{in} \cdot r$ versus r yields a straight line:



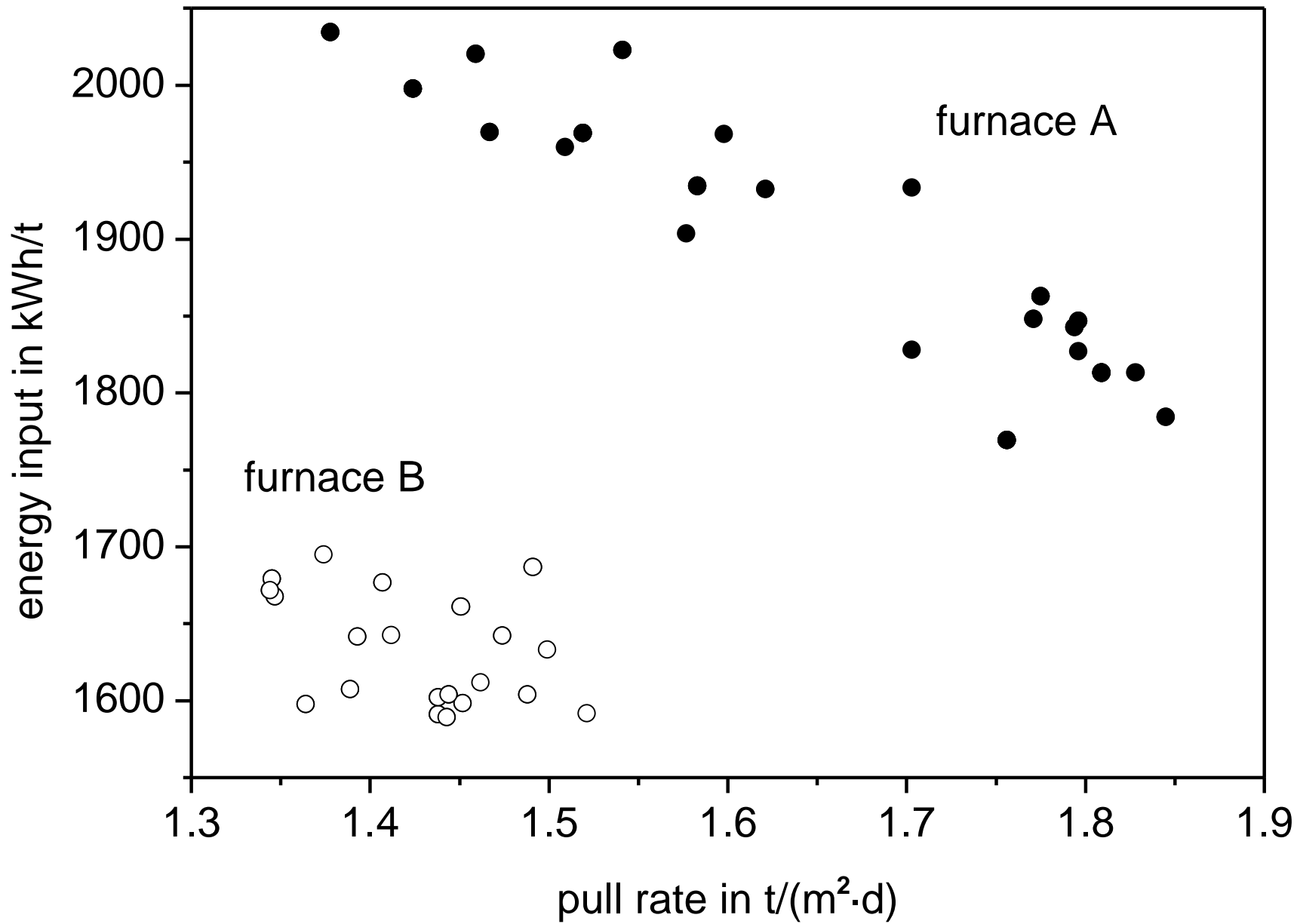
$$q_{in} = q_0 + H_0 \cdot r$$

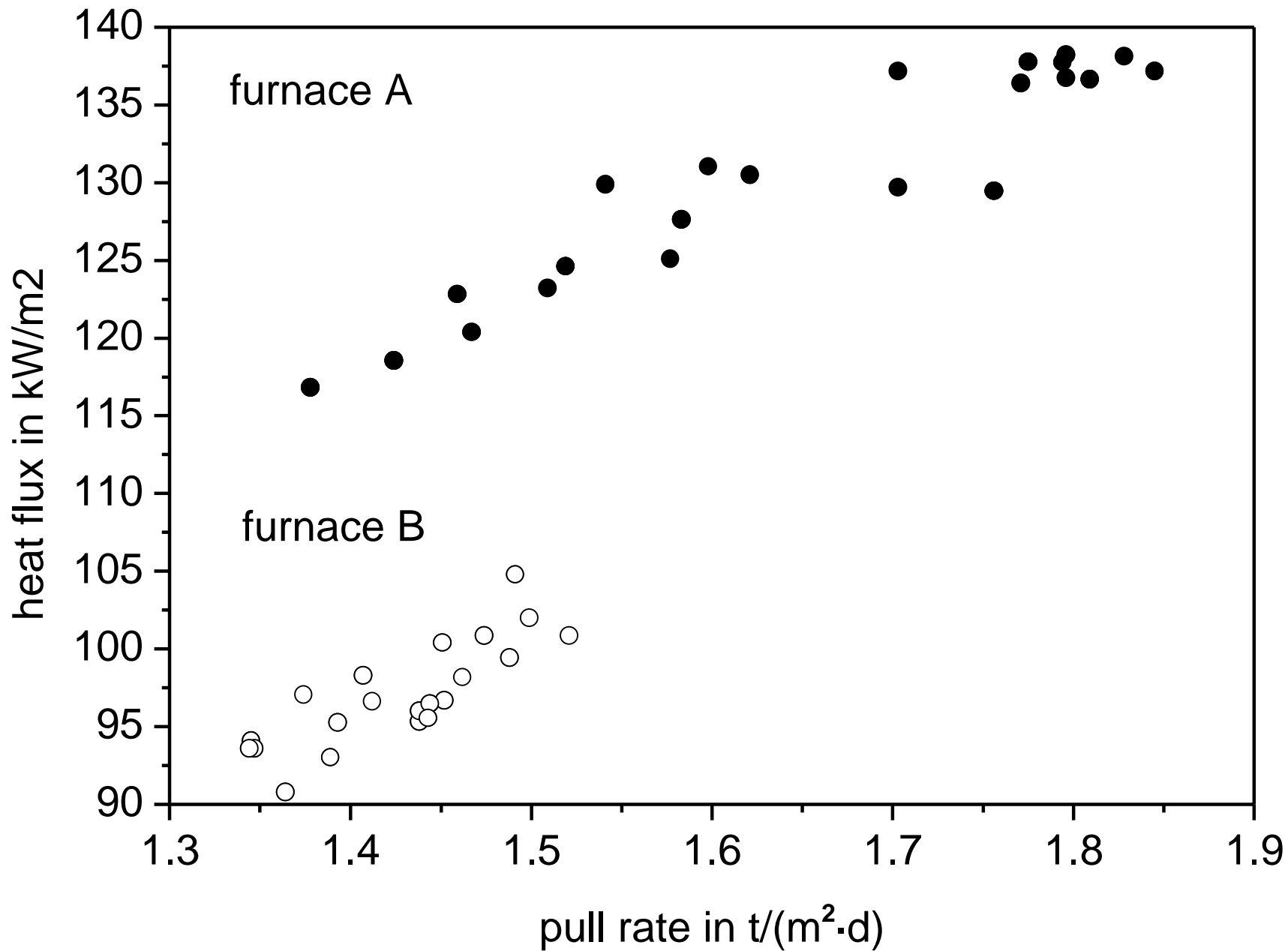
and

$$q_{in} = H_{in} \cdot r$$

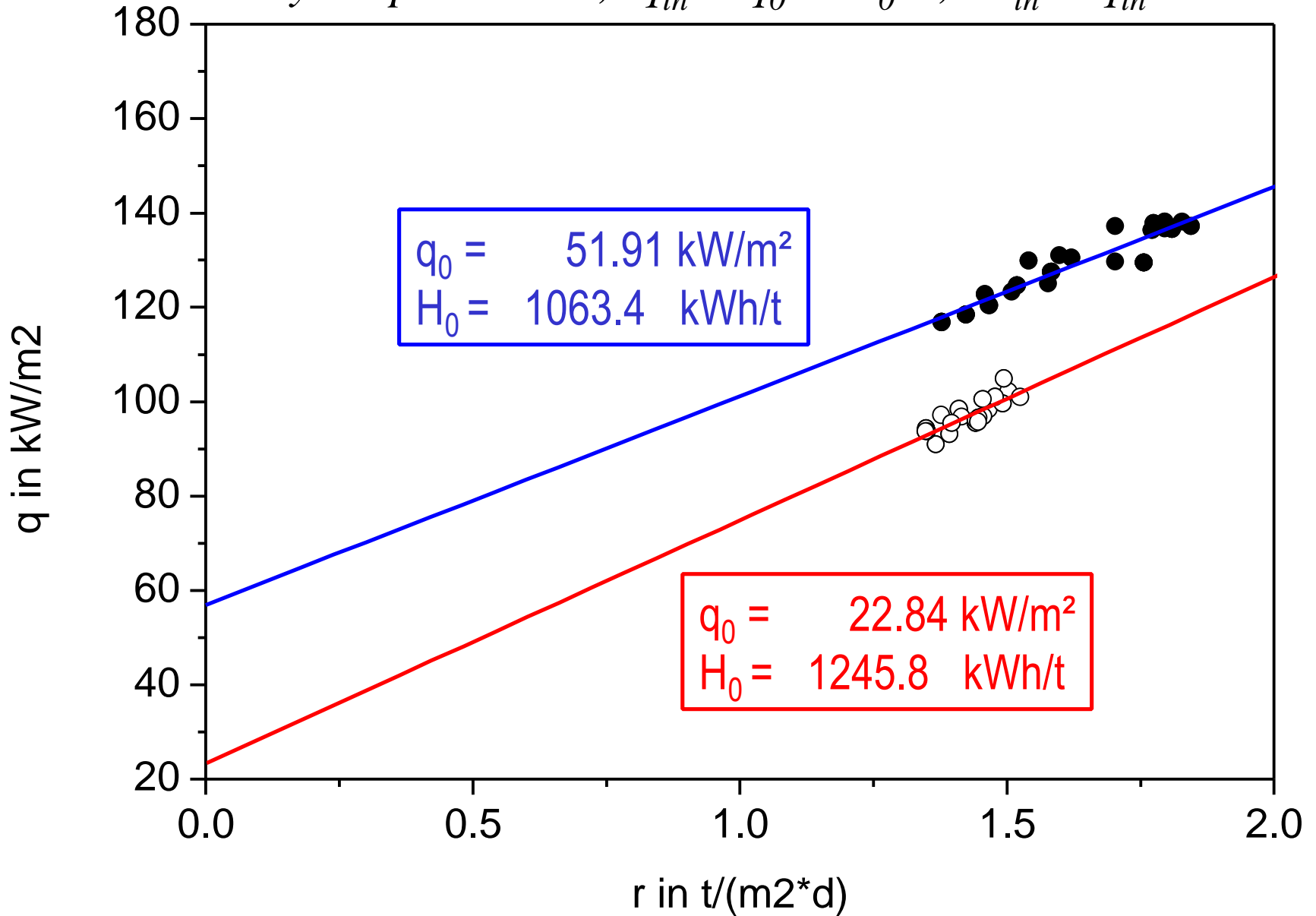
\Rightarrow

$$H_{in} = H_0 + \frac{q_0}{r} \propto \frac{1}{r}$$

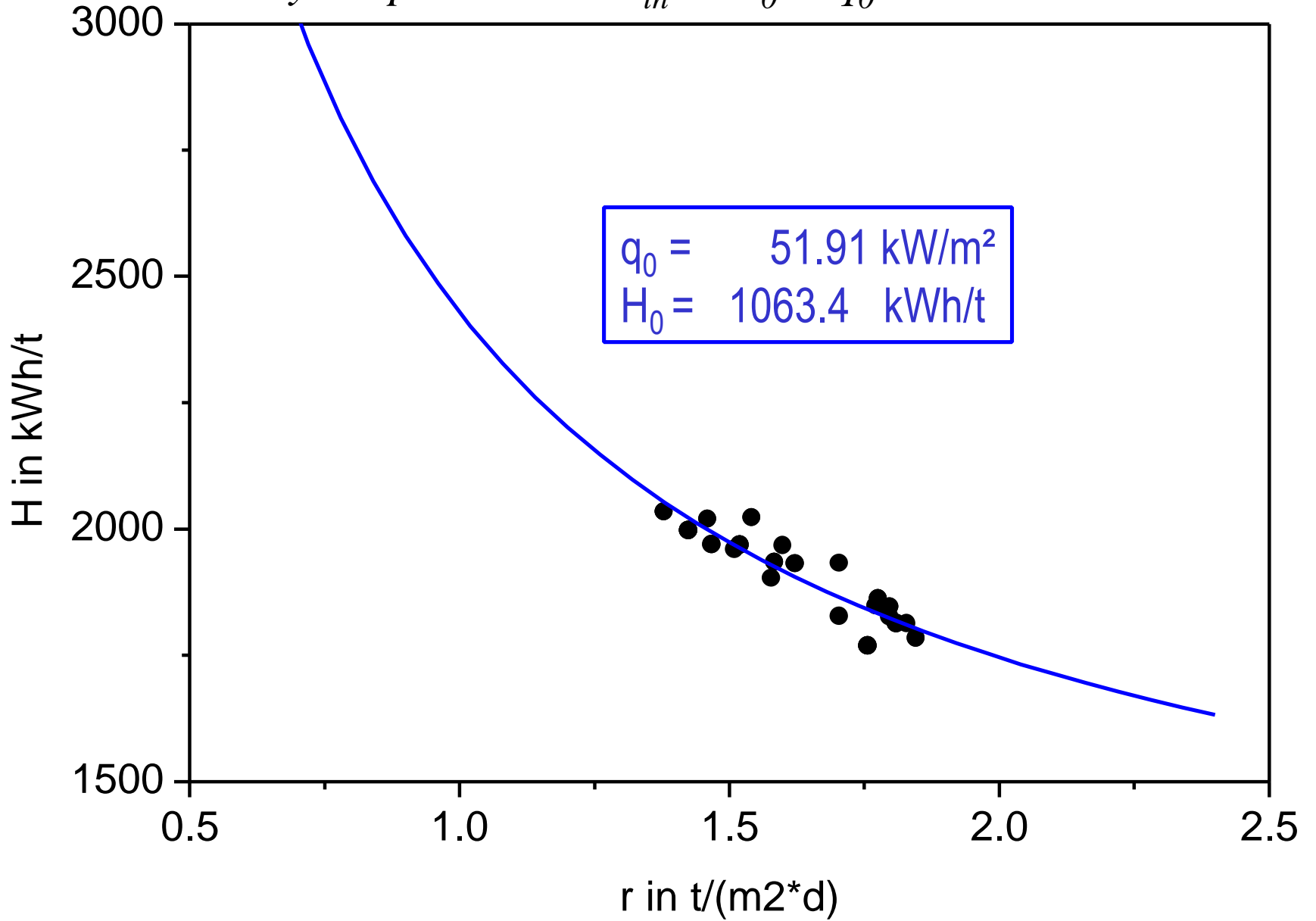


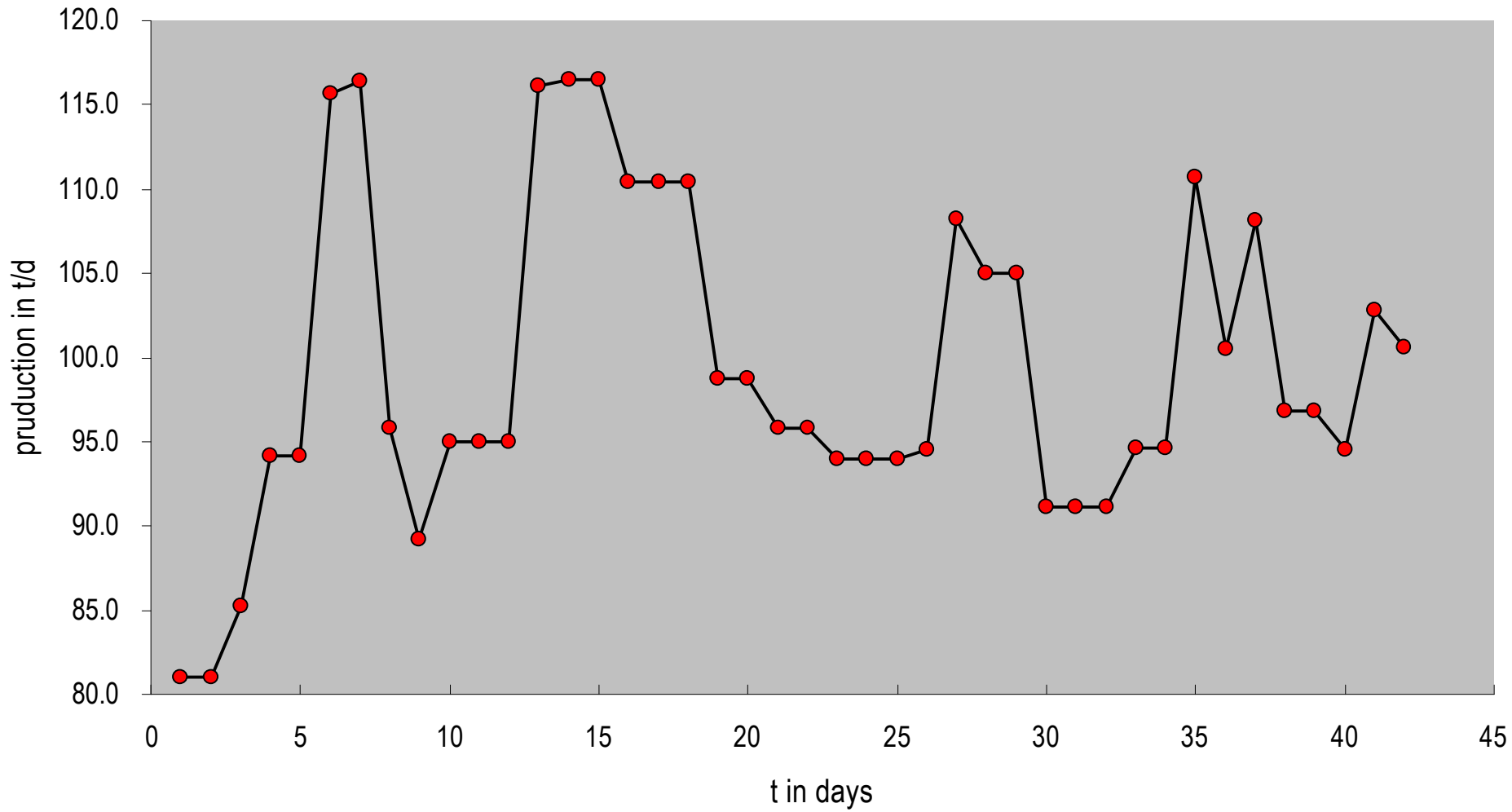


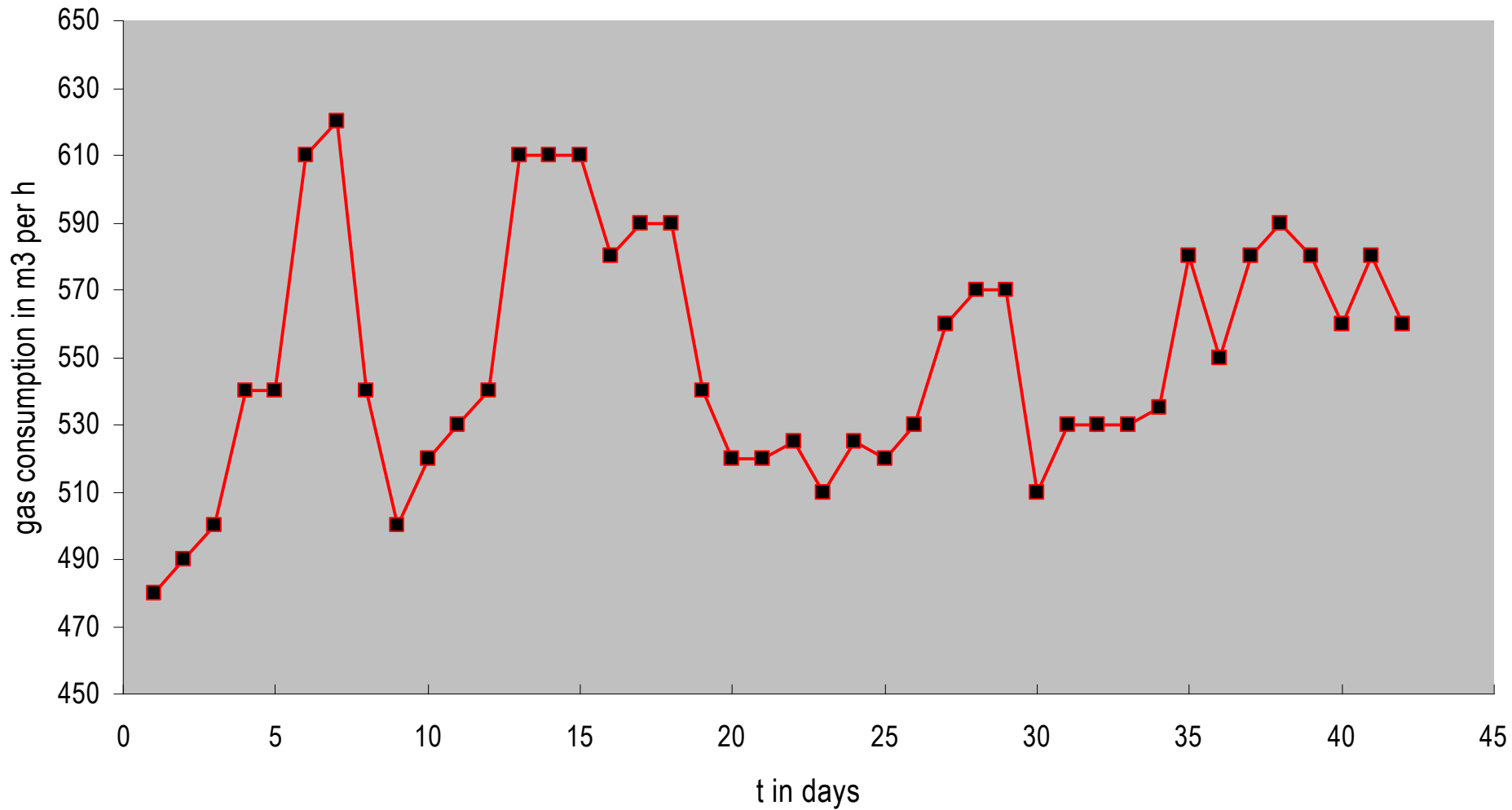
very simple model:: $q_{in} = q_0 + H_0 \cdot r$; $H_{in} = q_{in} / r$

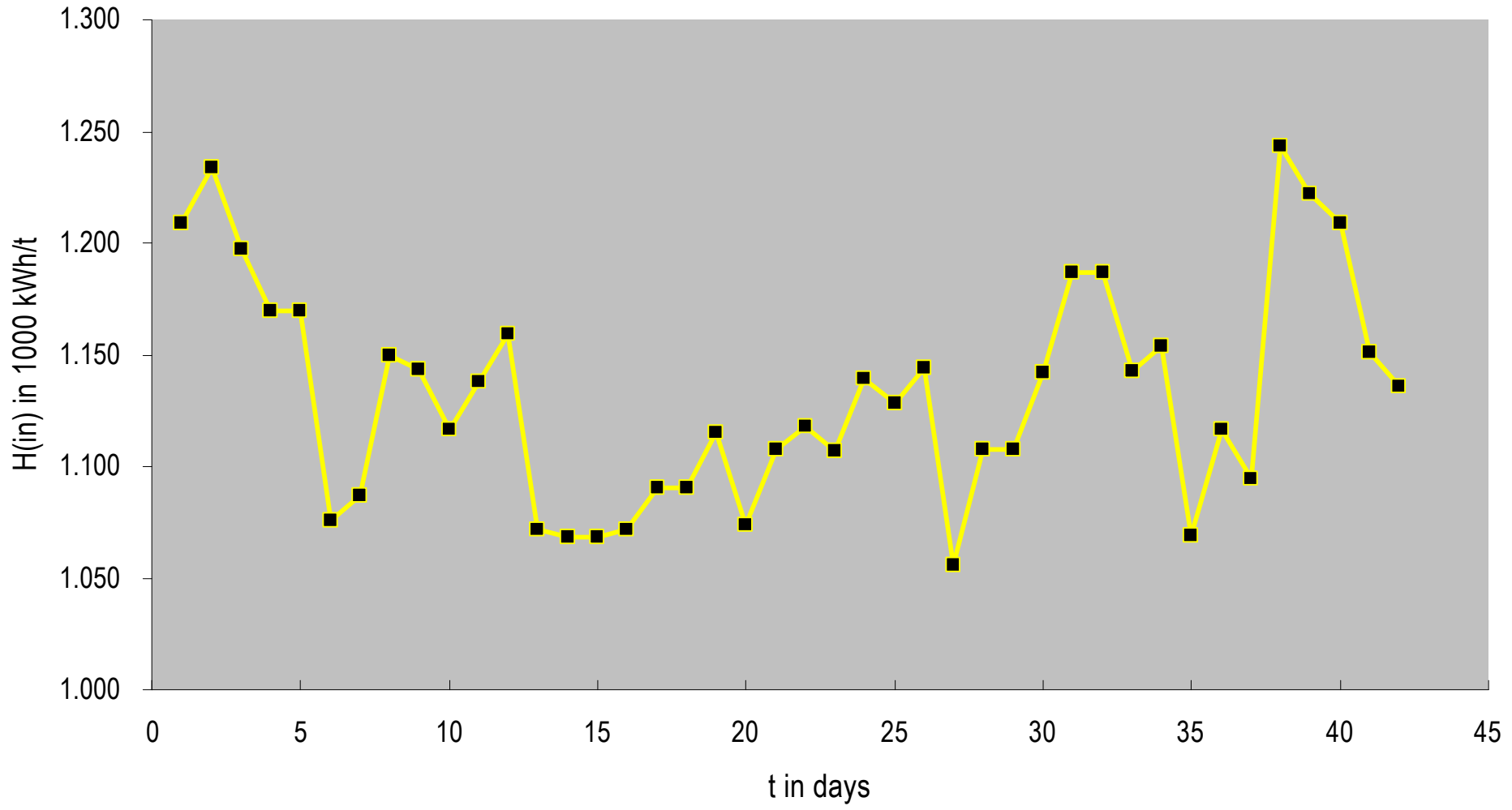


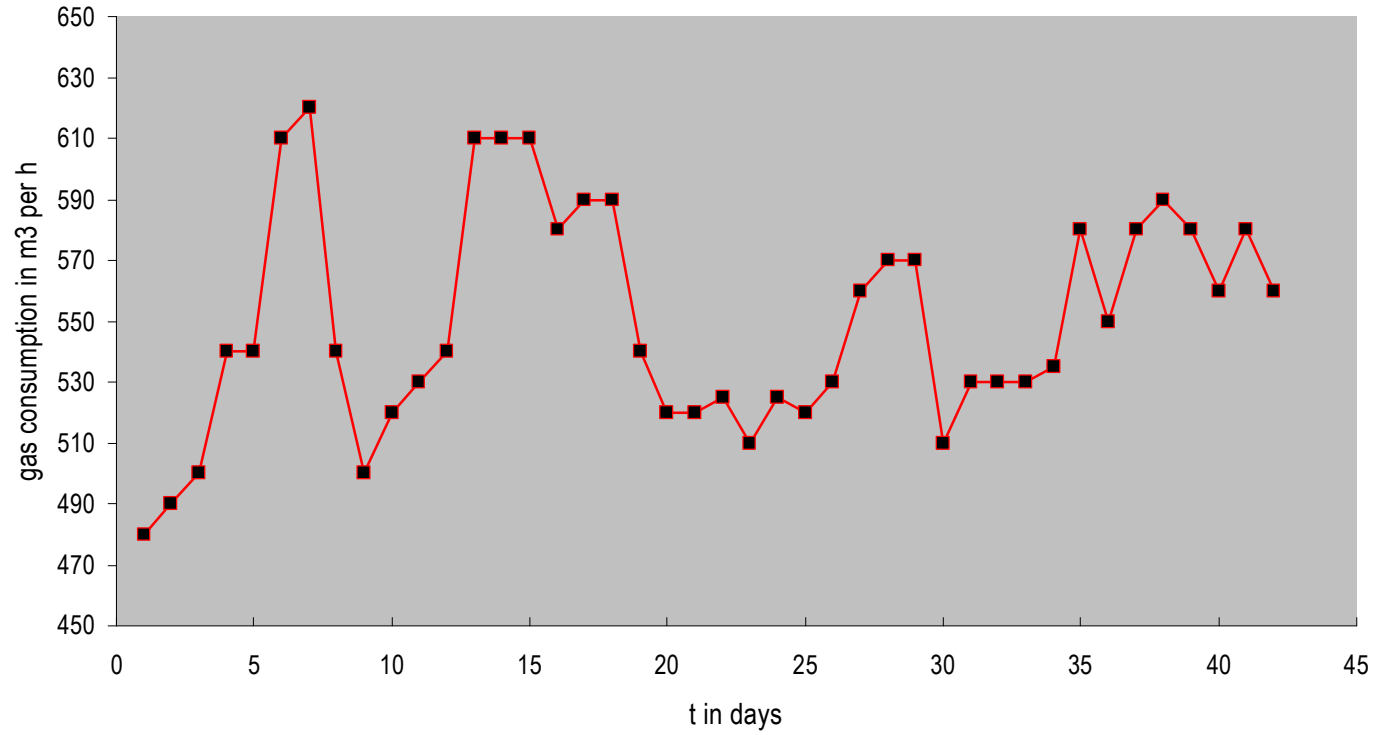
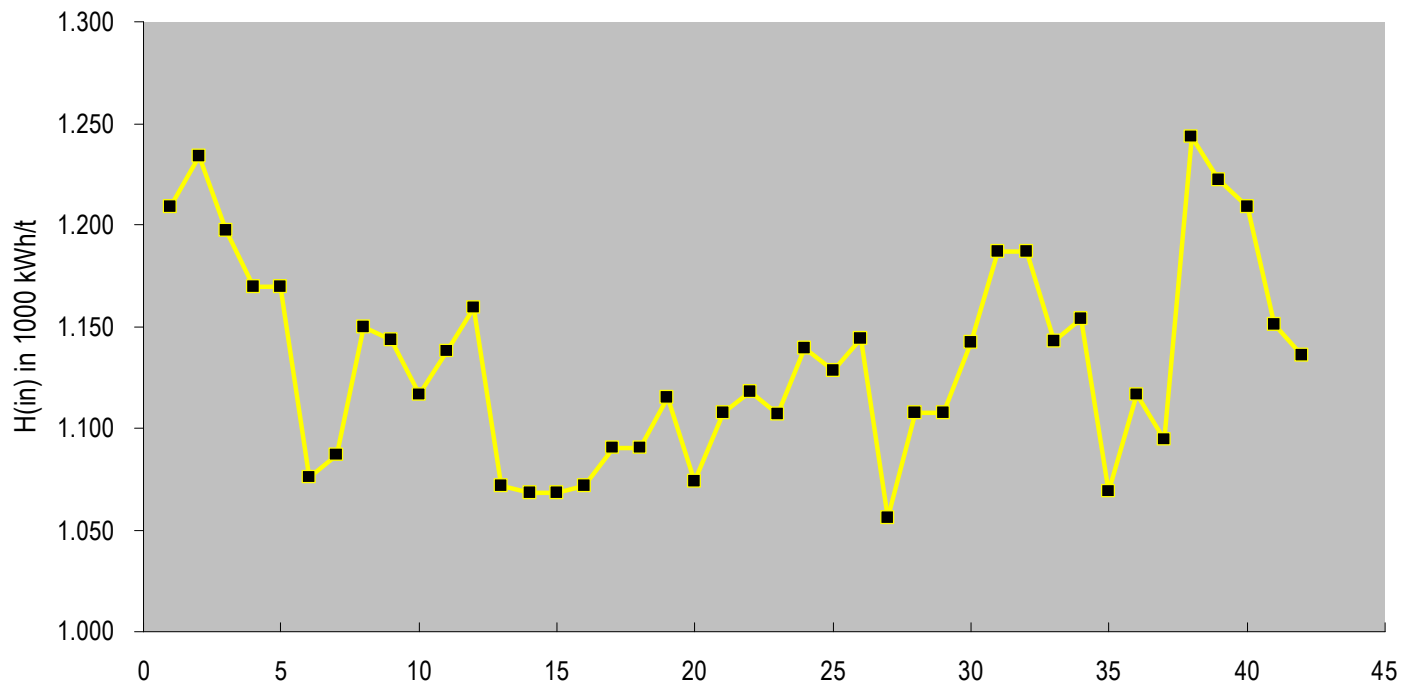
very simple model: $H_{in} = H_0 + q_0 / r$

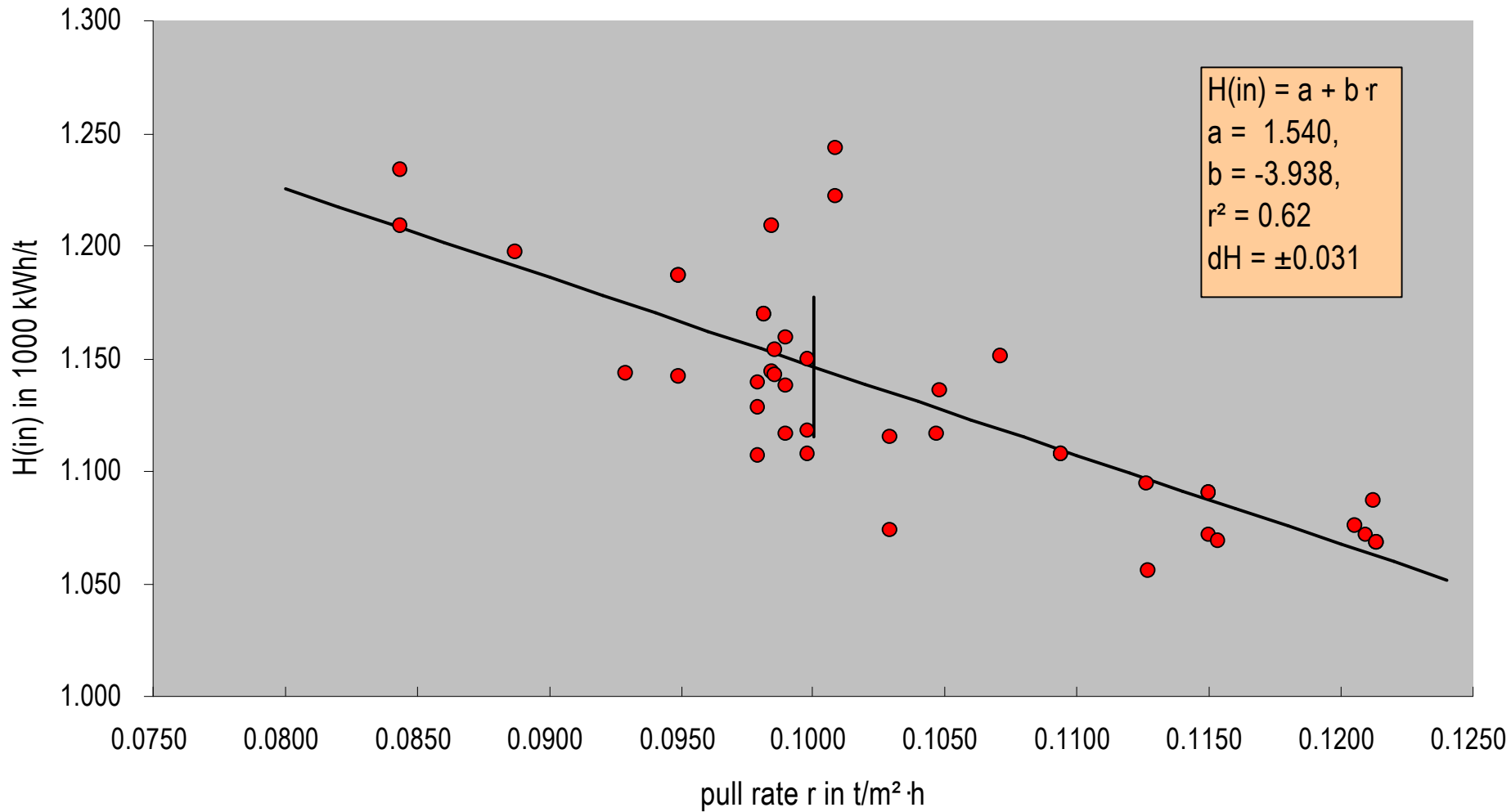


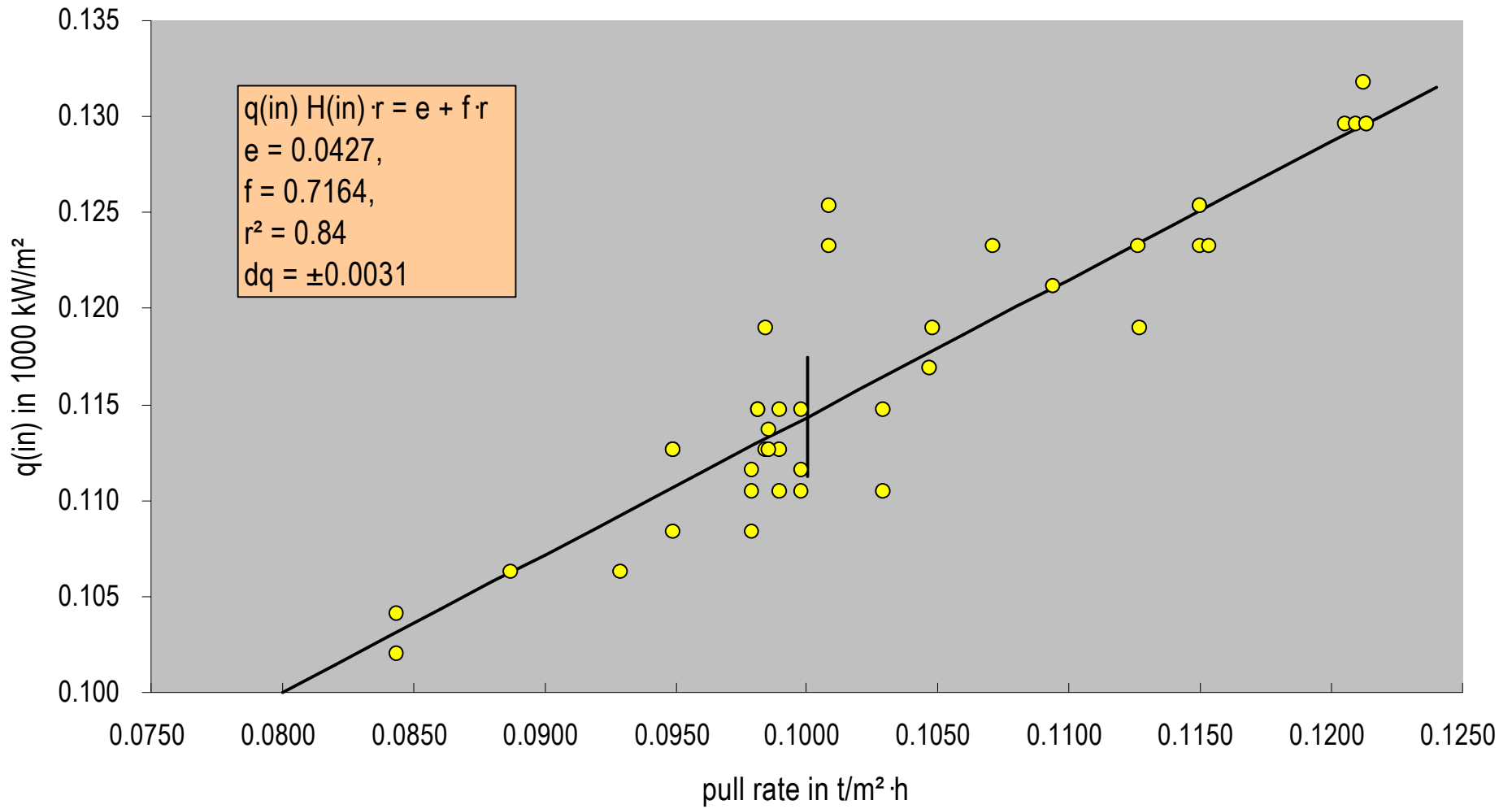




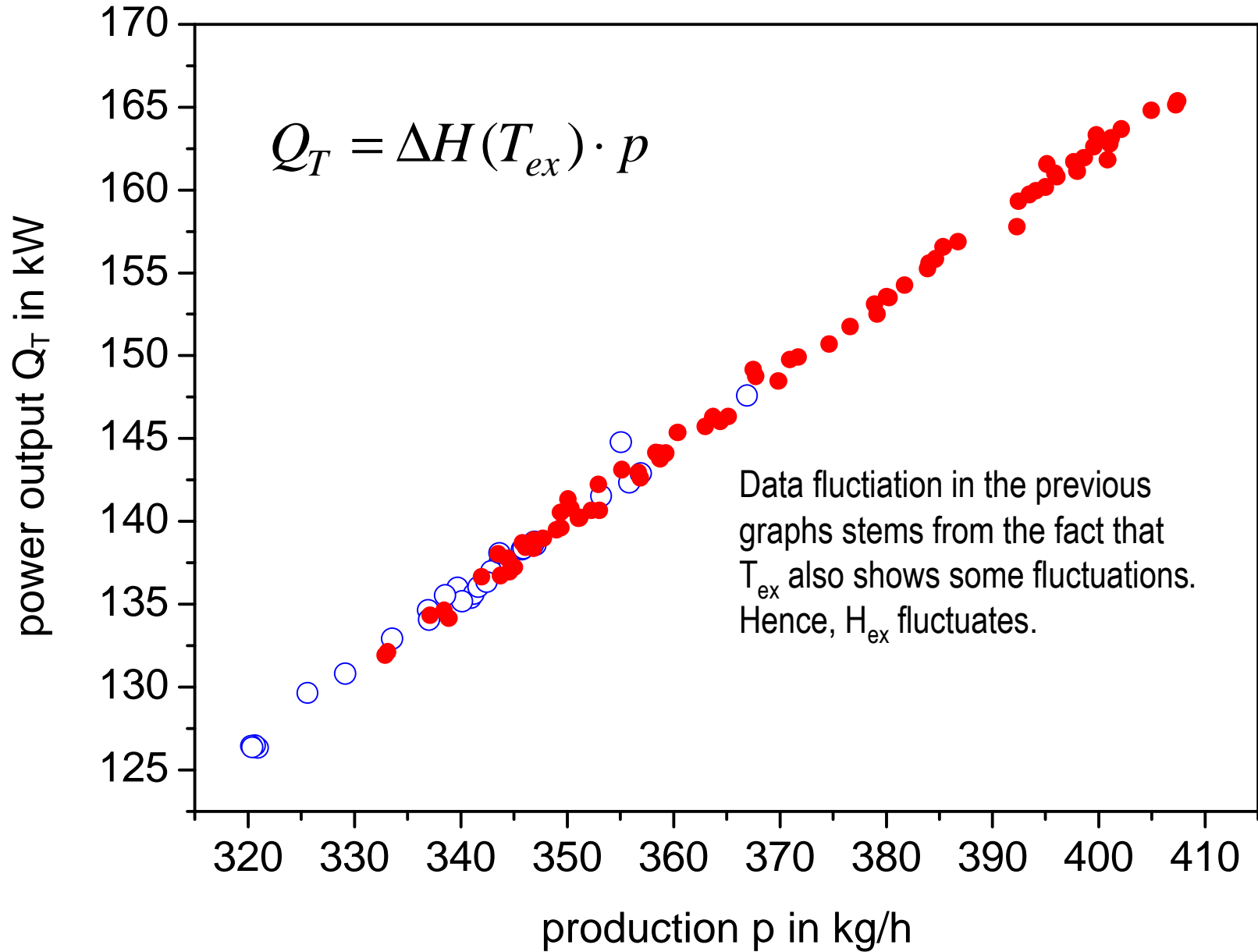








The best way of evaluation is the assessment of the true output power.



practice

#furnace data.XLS

#heat balance.xls

examples

melting behavior

=

heat demand

⊕

quartz dissolution rate

⊕

gas release rate

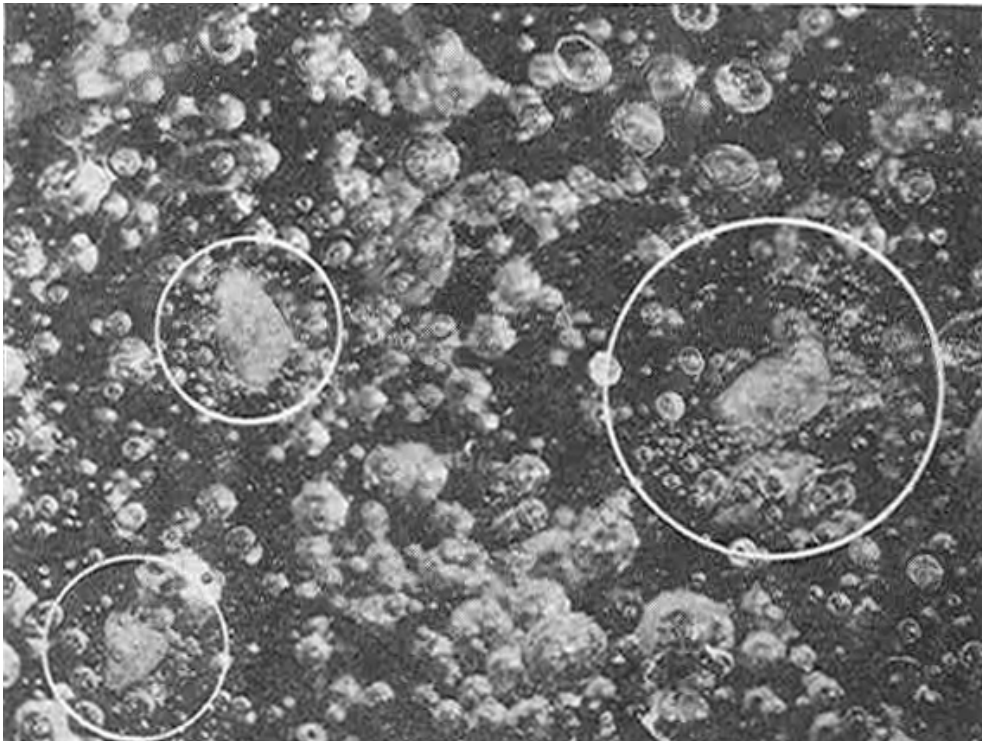
DH_{chem} does not tell the whole story!

quartz: $H^\circ = 910.9 \text{ kJ/mol}$

silica glass: $H^\circ = 901.4 \text{ kJ/mol}$

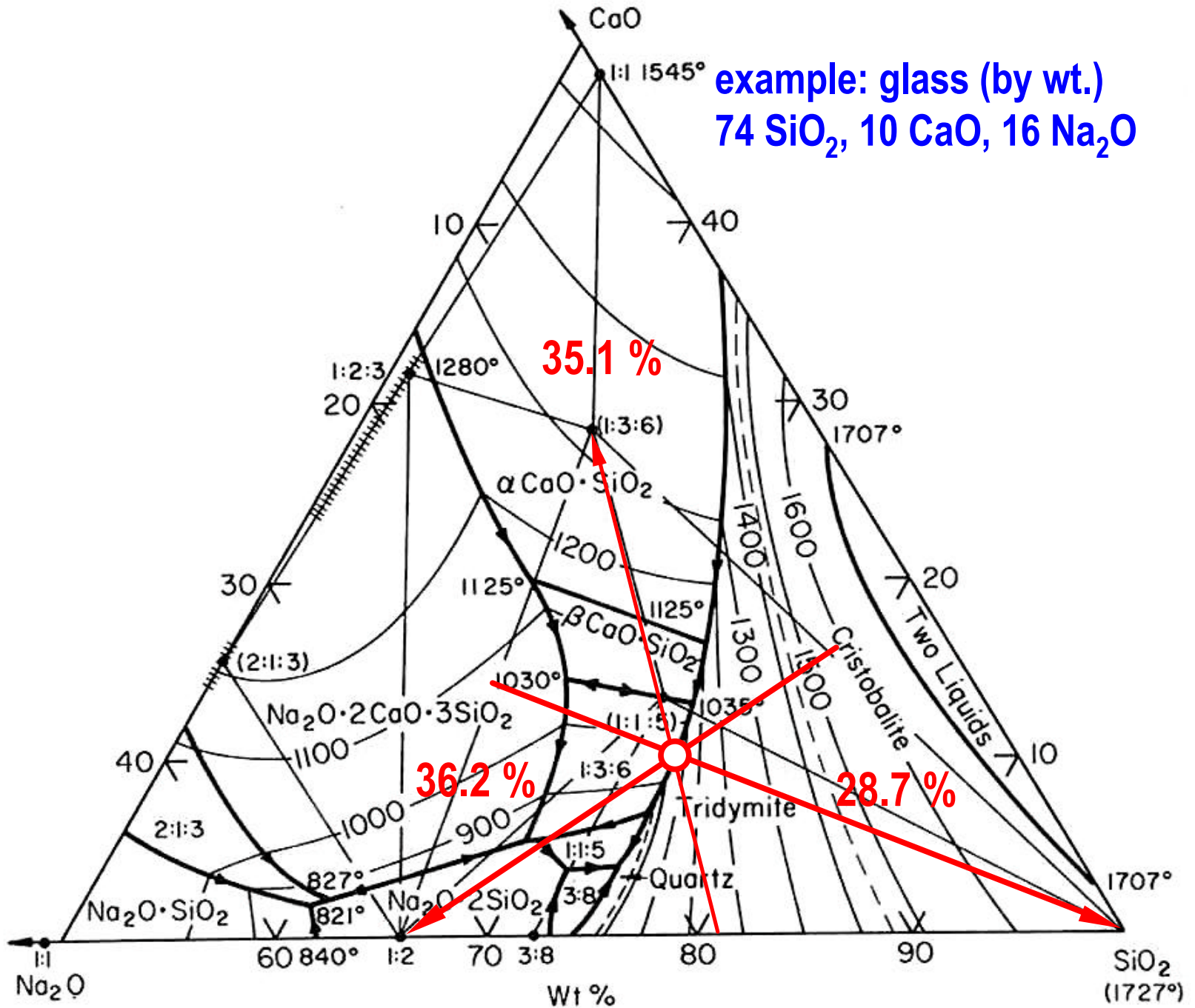
$DH_{chem} = 9.5 \text{ kJ/mol}$
 $= 43.9 \text{ kWh/t}$

As DH_{chem} for a conventional batch is approx. 140 kWh/t, is adding quartz sand a good way to save energy? **OF COURSE NOT!** Slow quartz dissolution is a main reason for late fining, long dwell times, high energy consumption.



DESIGN LOW RESIDAL SILICA BATCHES!

example: glass (by wt.)
74 SiO₂, 10 CaO, 16 Na₂O



raw material i	kg/t	oxide j	kg/t	phase k	kg/t
sand	666.96	SiO ₂	720.00	SiO ₂	227.05
feldspar	77.15	Al ₂ O ₃	15.00	Na ₂ O·Al ₂ O ₃ ·6SiO ₂	77.15
dolomite	182.98	MgO	40.00	MgO·SiO ₂	99.62
limestone	34.54	CaO	75.00	Na ₂ O·3CaO·6SiO ₂	263.34
soda ash	240.91	Na ₂ O	150.00	Na ₂ O·2SiO ₂	332.84
		CO ₂	202.54		
sum	1202.54		1202.54		1000.00

H°(batch) = 4589.5 kWh

H°(gl) = 3942.3 kWh

H°(gas) = 503.0 kWh;

DH°_{chem} = 144.2 kWh

DH_T(gl) = 404.1 kWh, T = 25 to 1200 °C

DH_T(gas) = 90.2 kWh, T = 25 to 1400 °C

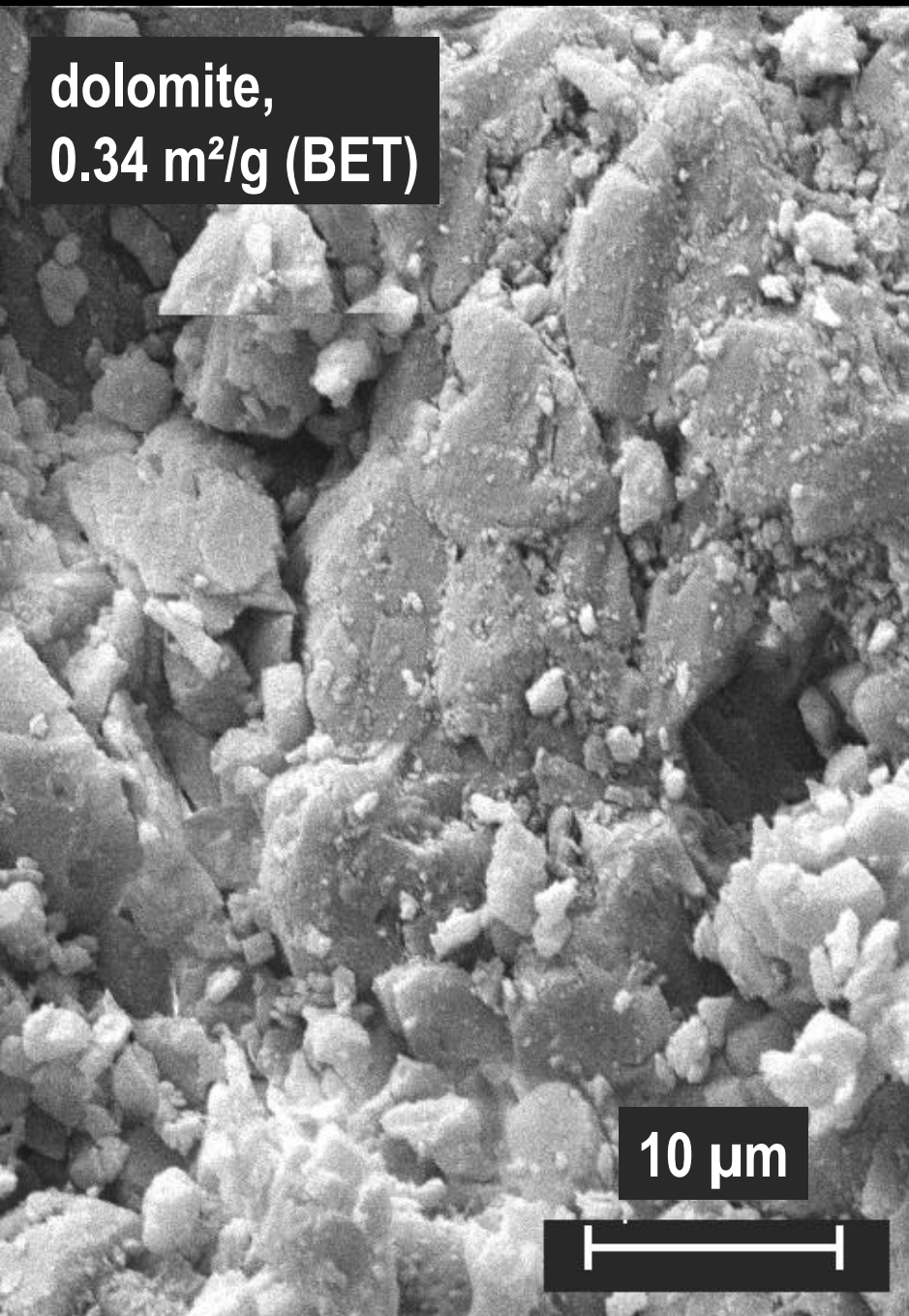
raw material i	kg/t	oxide j	kg/t	phase k	kg/t
sand	666.96	SiO ₂	720.00	SiO ₂	227.05
feldspar	77.15	Al ₂ O ₃	15.00	Na ₂ O·Al ₂ O ₃ ·6SiO ₂	77.15
dolomite	182.98	MgO	40.00	MgO·SiO ₂	99.62
limestone	34.54	CaO	75.00	Na ₂ O·3CaO·6SiO ₂	263.34
soda ash	240.91	Na ₂ O	150.00	Na ₂ O·2SiO ₂	332.84
		CO ₂	202.54		
sum	1202.54		1202.54		1000.00

H°(batch) = 4589.5 kWh
 H°(gl) = 3942.3 kWh
 H°(gas) = 503.0 kWh;
 DH°_{chem} = 144.2 kWh
 DH_T(gl) = 404.1 kWh, T = 25 to 1200 °C
 DH_T(gas) = 90.2 kWh, T = 25 to 1400 °C

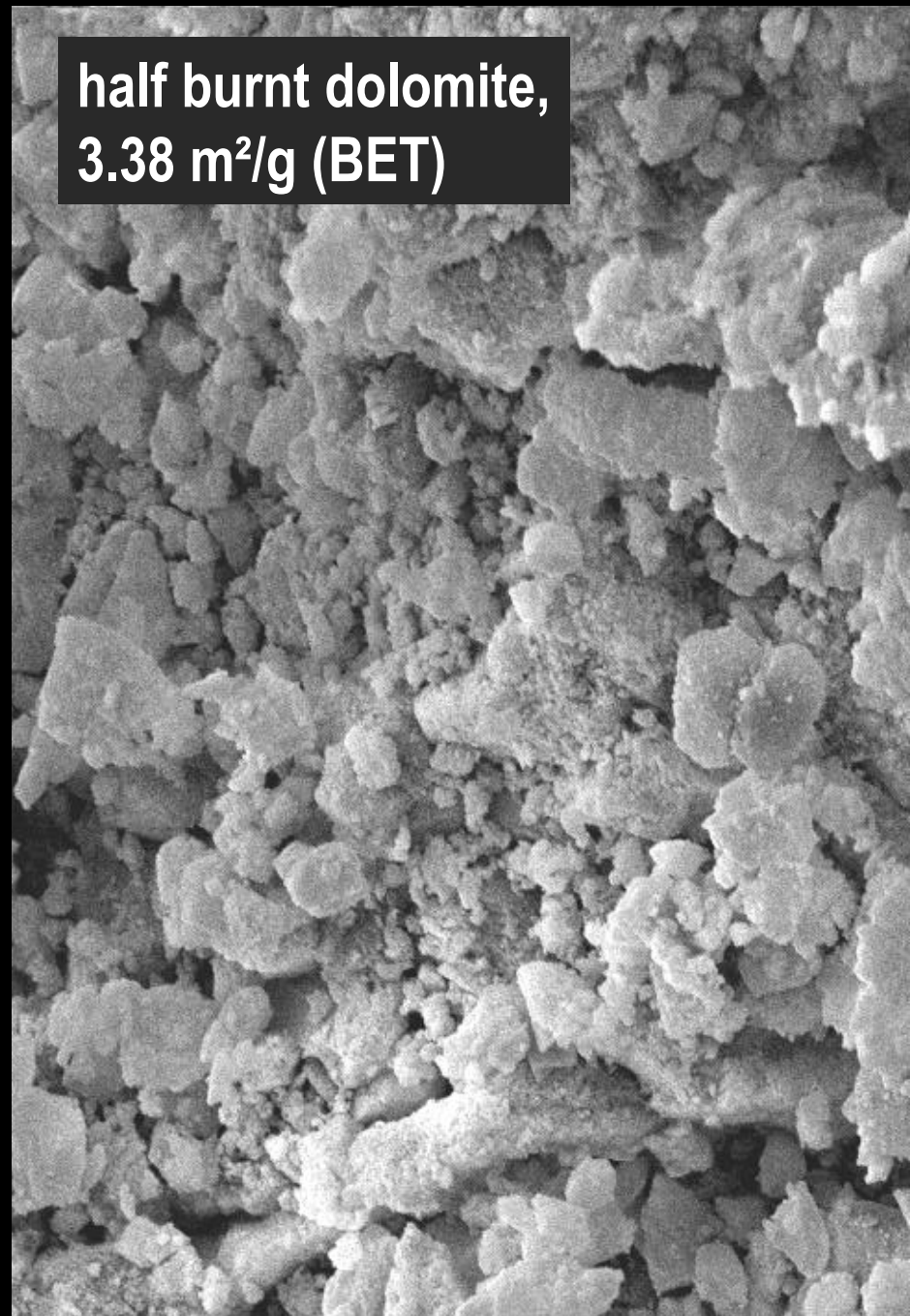
residual amount of
 crystalline SiO₂: >23 %,
 dissolved by diffusion,
 not by chem reaction

NOTE: Each raw material by itself is a multioxide mineral system.

dolomite,
0.34 m²/g (BET)



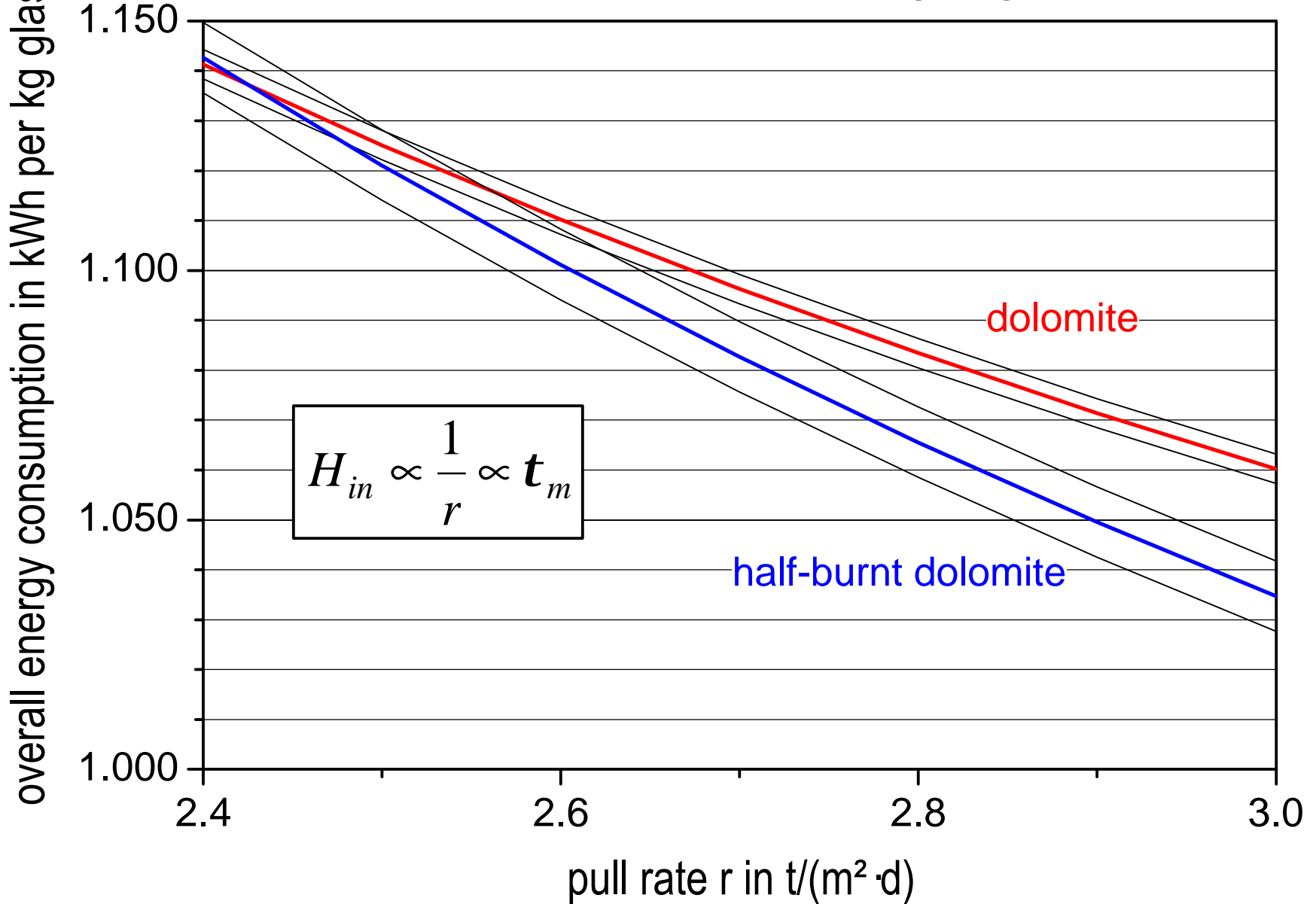
half burnt dolomite,
3.38 m²/g (BET)



	H°	DrH°	DrH° per [MgO]		4 % MgO
	kJ/mol	kJ/mol	MJ/kg	kWh/kg	kWh/t glass
dolomite	2314.2	290.7	7.21	2.00	80
half-burnt	1808.5	178.5	4.43	1.23	49
difference		112.2	2.78	0.77	31

depending on hex (30 – 55 %) P 60 – 105 kWh (0 % cullet)
43 – 80 kWh (25 %)

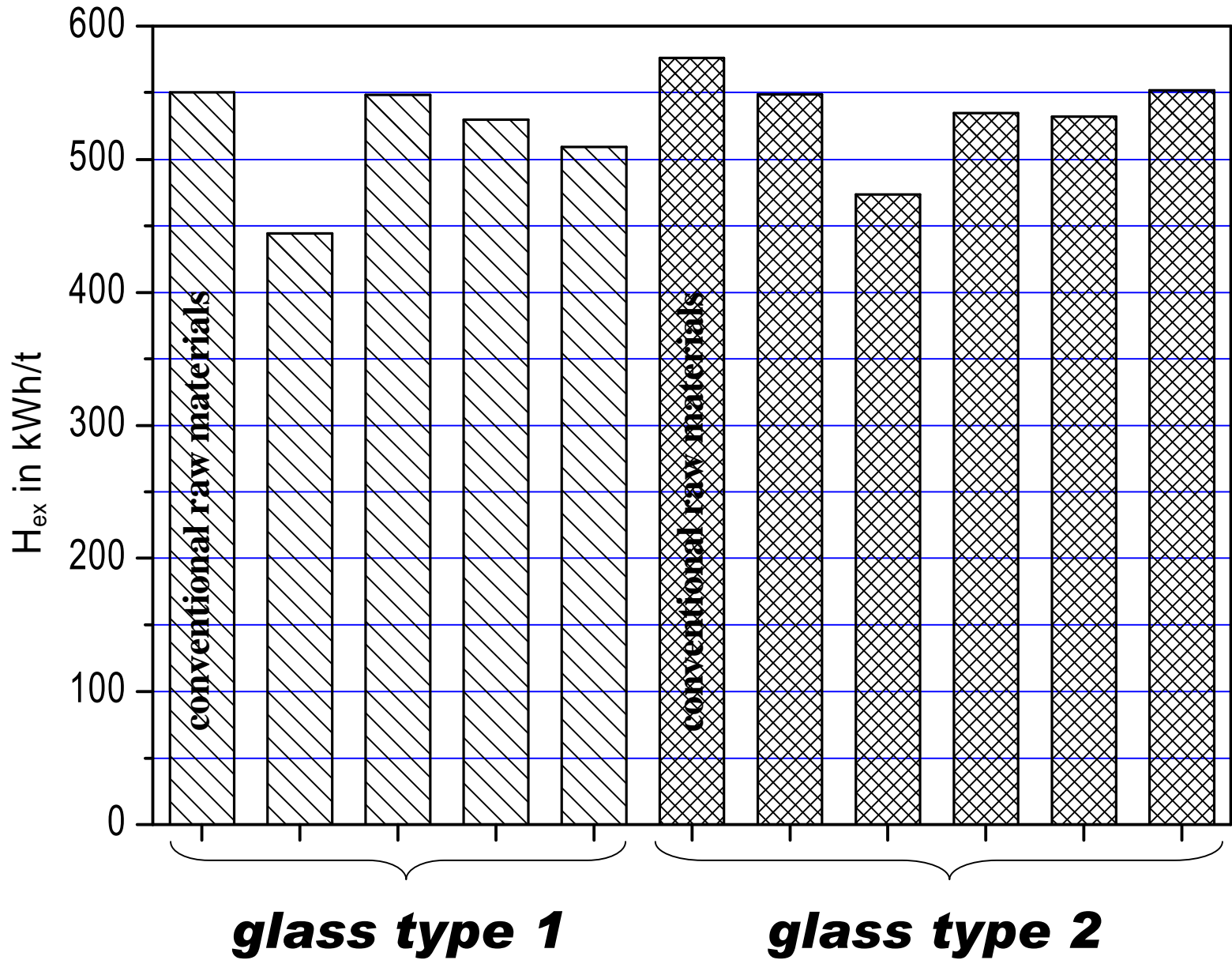
horseshoe flame furnace: 40 m², large regenerator



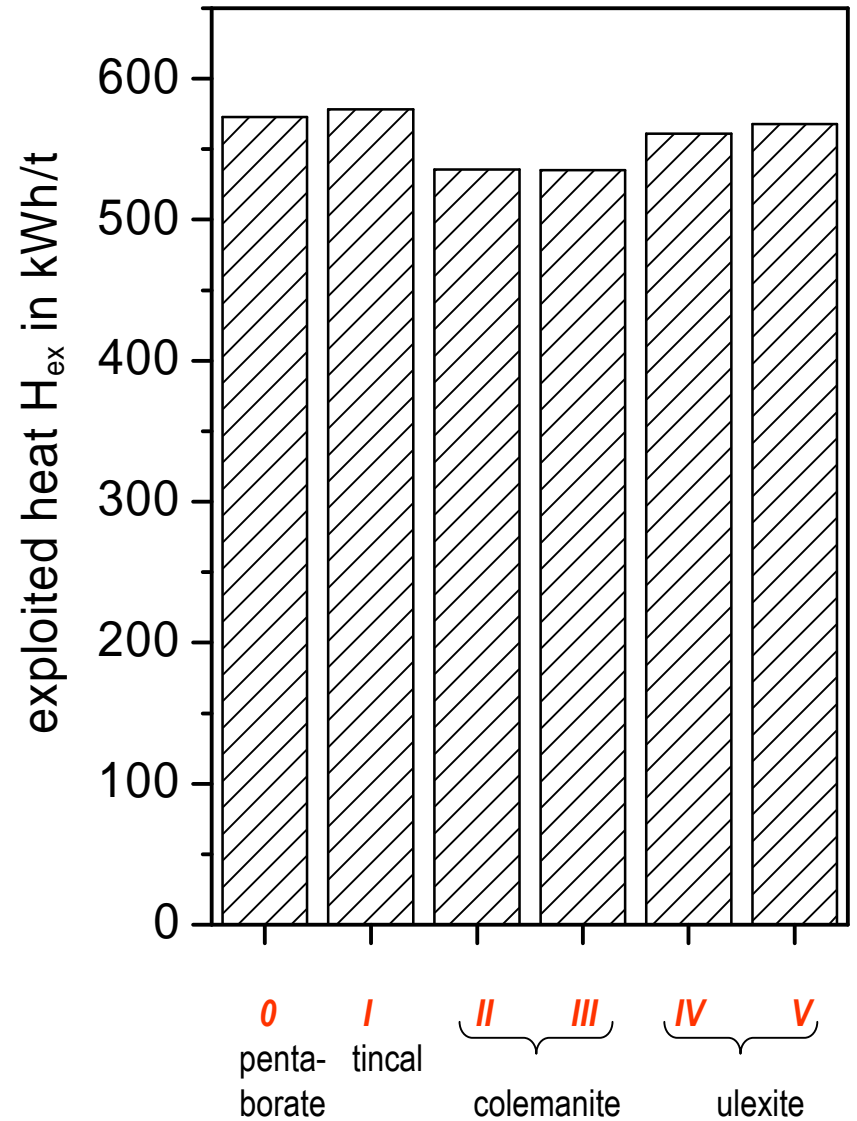
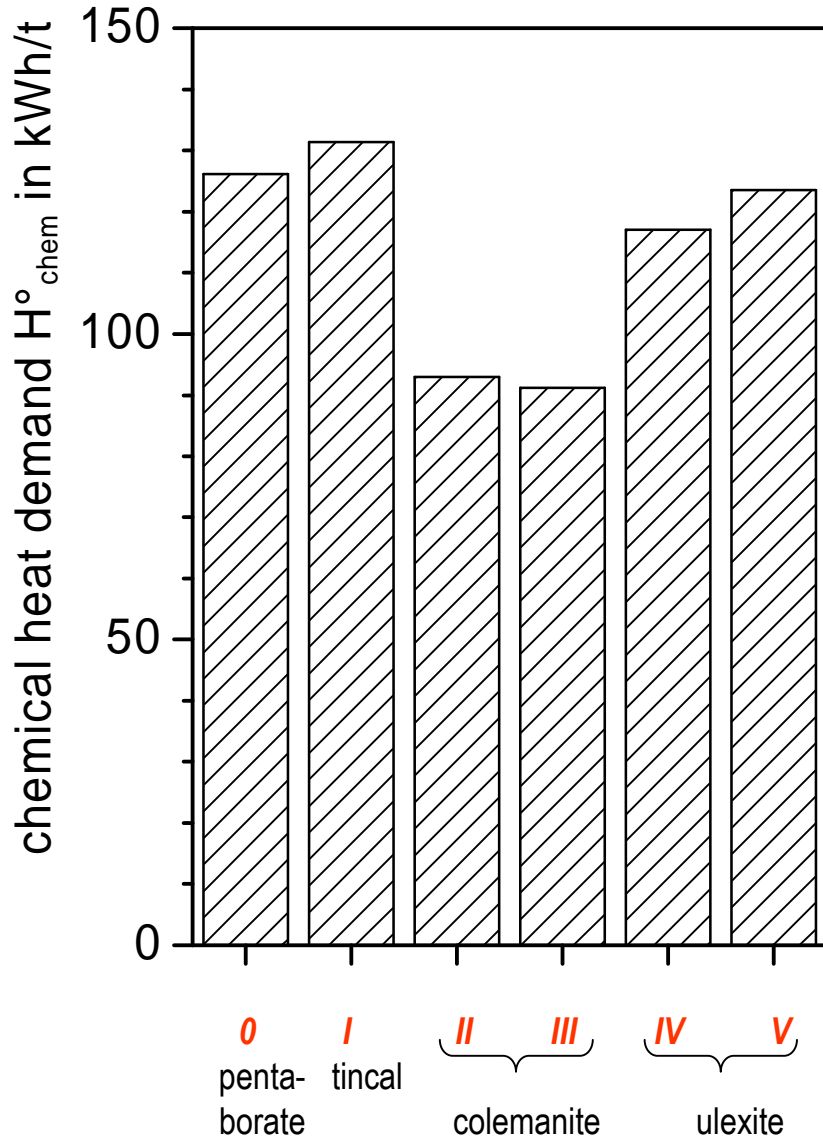
Normalized composition of theoretical and real raw materials

	NB ₂ H ₅	NB ₂ H ₁₀	tincal	C ₂ B ₃ H ₅	colemanite	NC ₂ B ₅ H ₁₆	ulexite
	penta	deca	real		real		real
oxide content in kg per kg of raw material							
SiO ₂			0.0220		0.0370		0.0290
TiO ₂			0.0001		0.0001		
Al ₂ O ₃			0.0016		0.0014		0.0008
B ₂ O ₃	0.4780	0.3651	0.4830	0.5081	0.4310	0.4295	0.3770
Fe ₂ O ₃			0.0006		0.0006		0.0030
MgO			0.0242		0.0161		0.0142
CaO			0.0289	0.2728	0.2670	0.1384	0.1670
SrO			0.0027		0.0095		0.0061
Na ₂ O	0.2128	0.1625	0.2220		0.0008	0.0765	0.0636
K ₂ O			0.0011		0.0005		0.0003
released gases in kg per kg of raw material							
CO ₂ (g)					0.0455		0.0340
H ₂ O(g)	0.3092	0.4724	0.2126	0.2191	0.1859	0.3556	0.3043
SO ₂ (g)			0.0010		0.0026		0.0006
O ₂ (g)			0.0002		0.0021		0.0001
balance in kg per kg raw material							
sum	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
glass	0.6908	0.5276	0.7862	0.7809	0.7640	0.6444	0.6610
gases	0.3092	0.4724	0.2138	0.2191	0.2360	0.3556	0.3390
heat of formation in kWh per kg of raw material							
H ^o _{raw mat}	4.5676	4.5625	4.4834	4.6891	4.5453	4.6353	4.5145

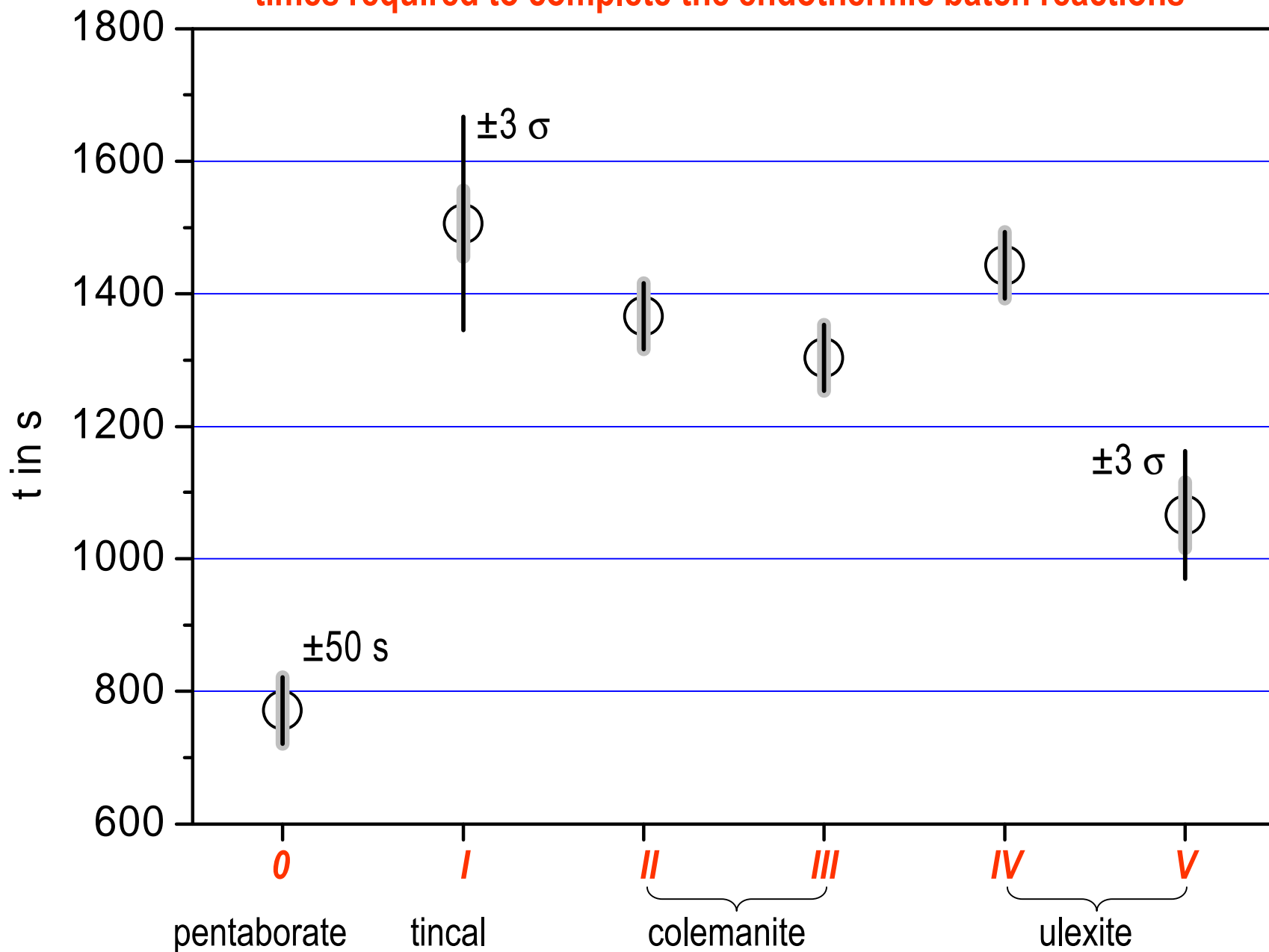
H_{ex} for $T_{ex} = 1300\text{ }^{\circ}\text{C}$ (no cullet)



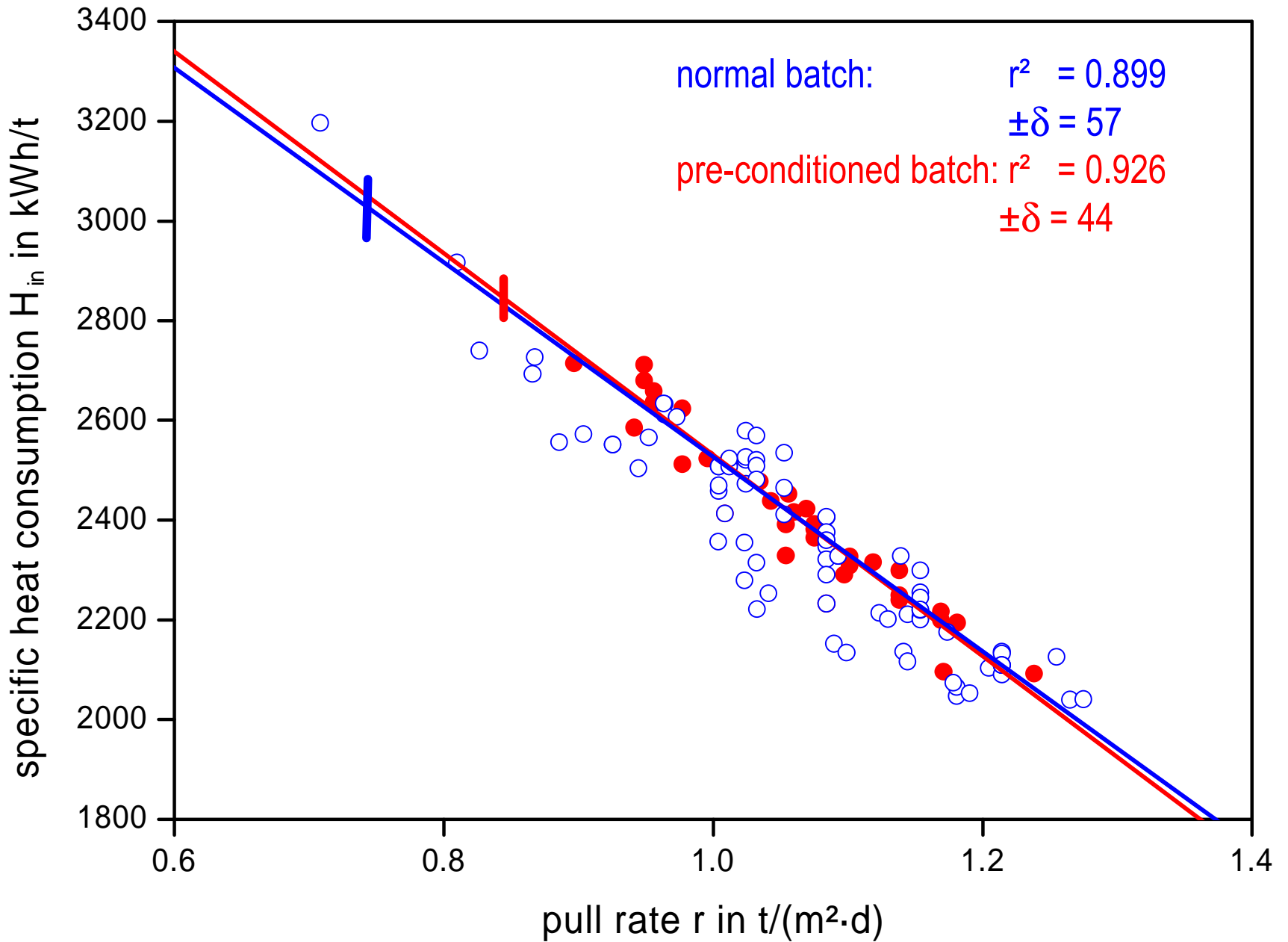
energy demand, calculated from real raw material composition

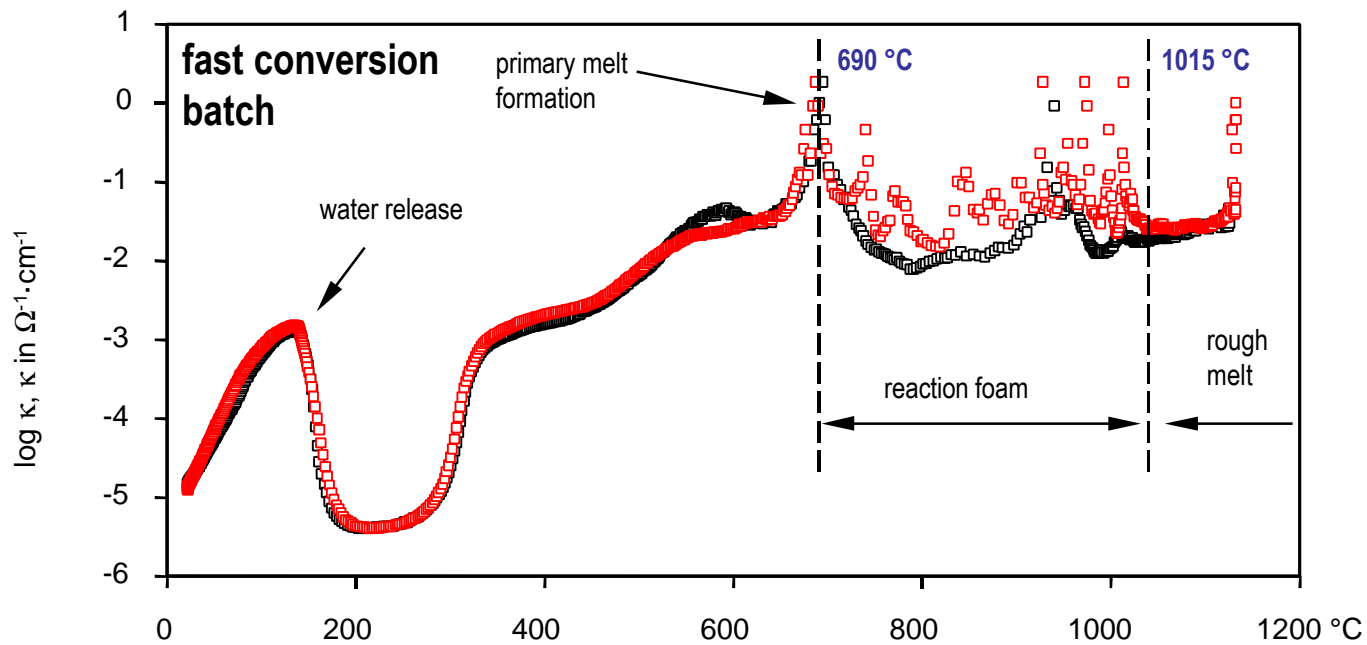
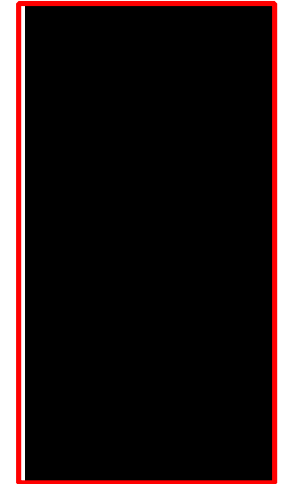
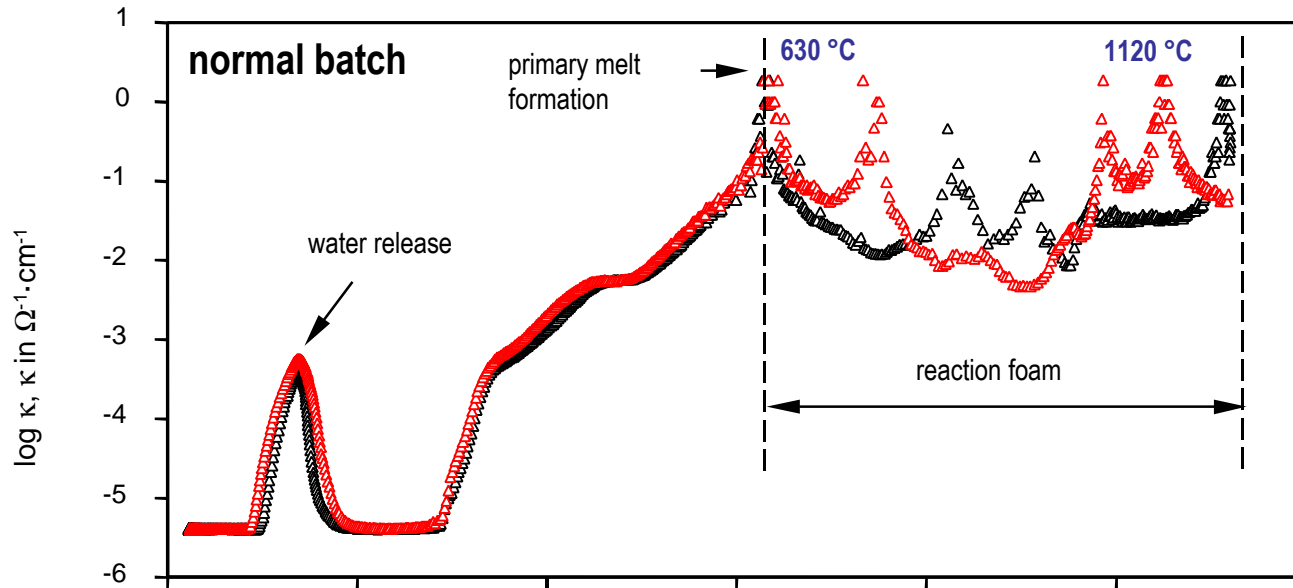


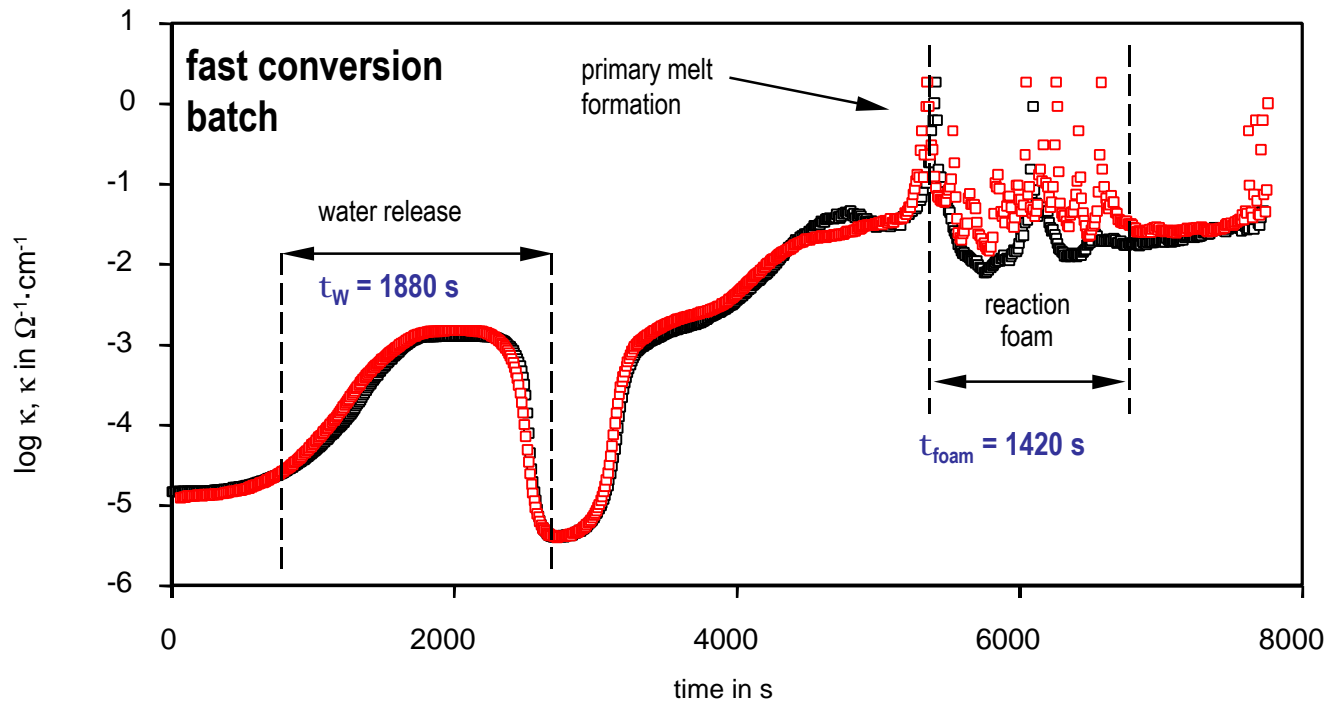
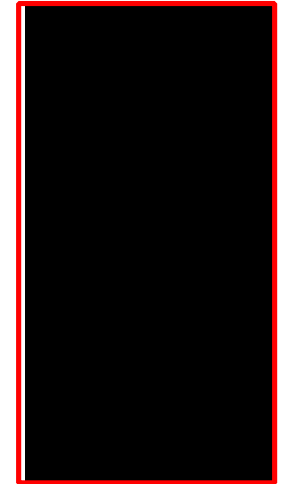
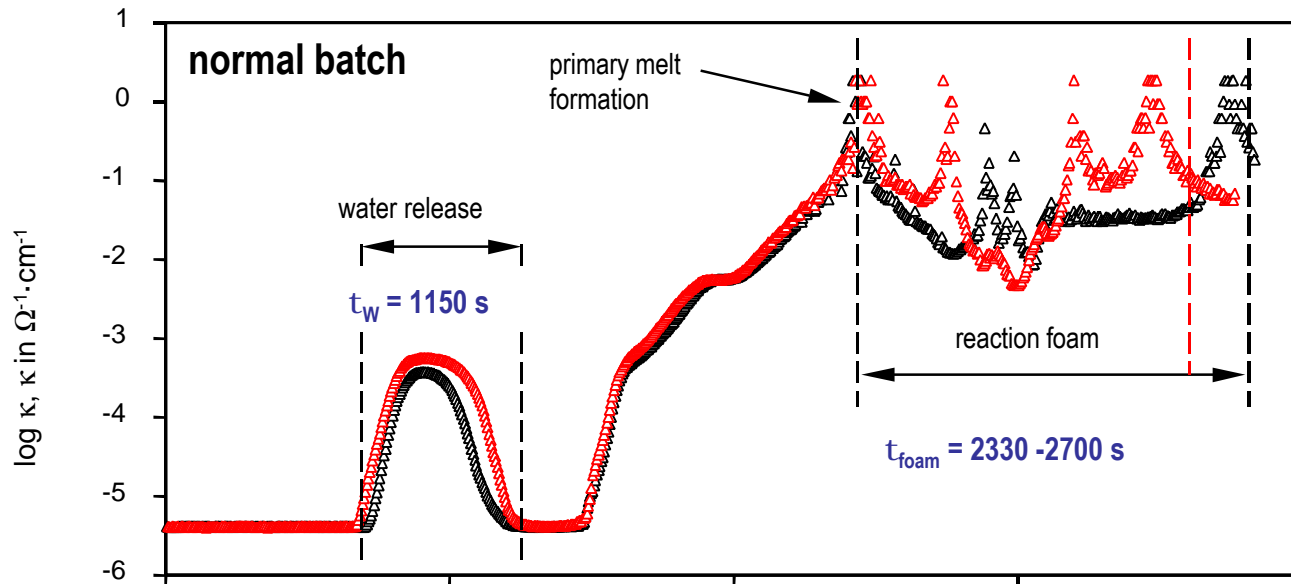
times required to complete the endothermic batch reactions



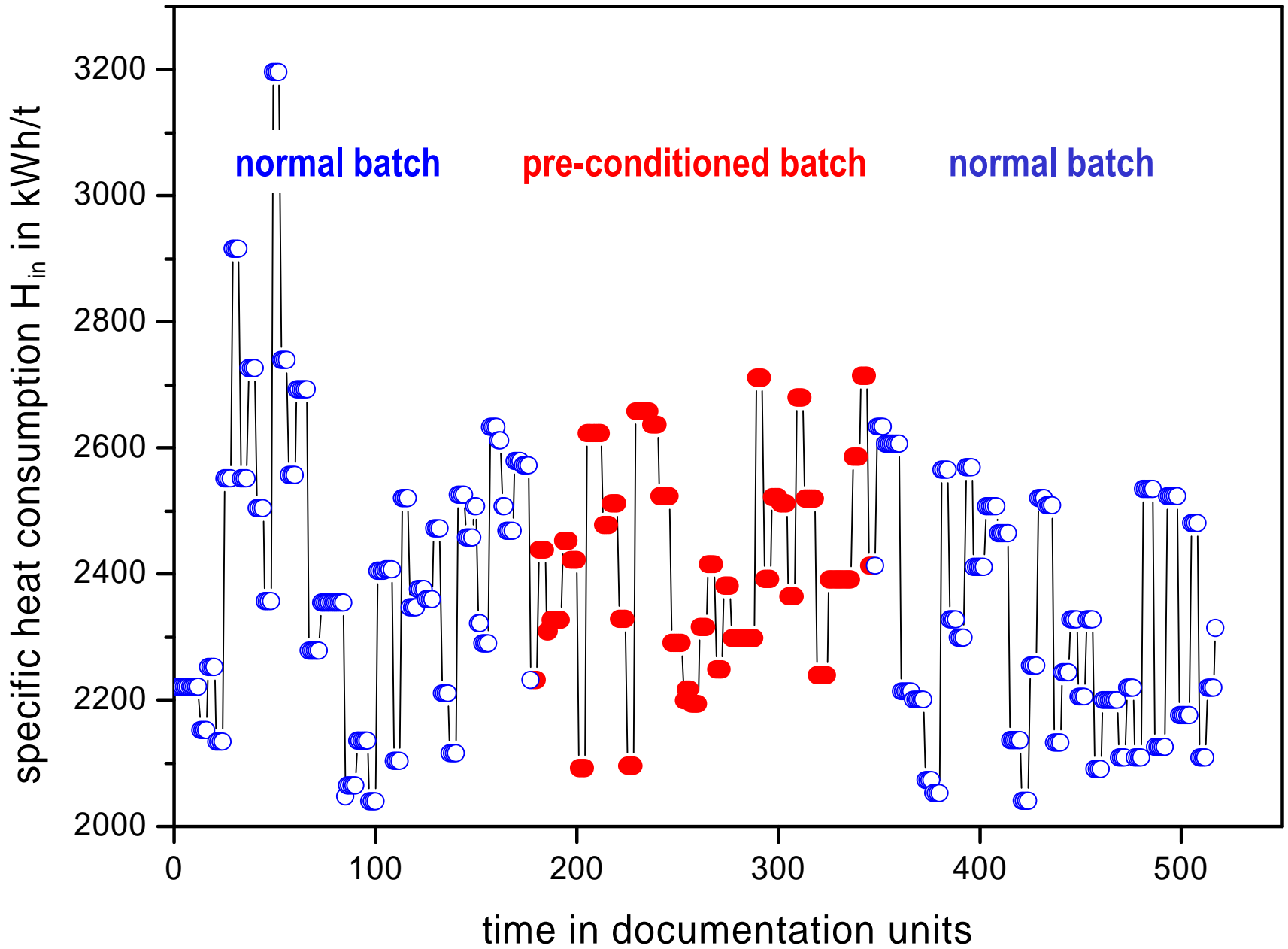
... although the new batch quickly makes the furnace more stable.



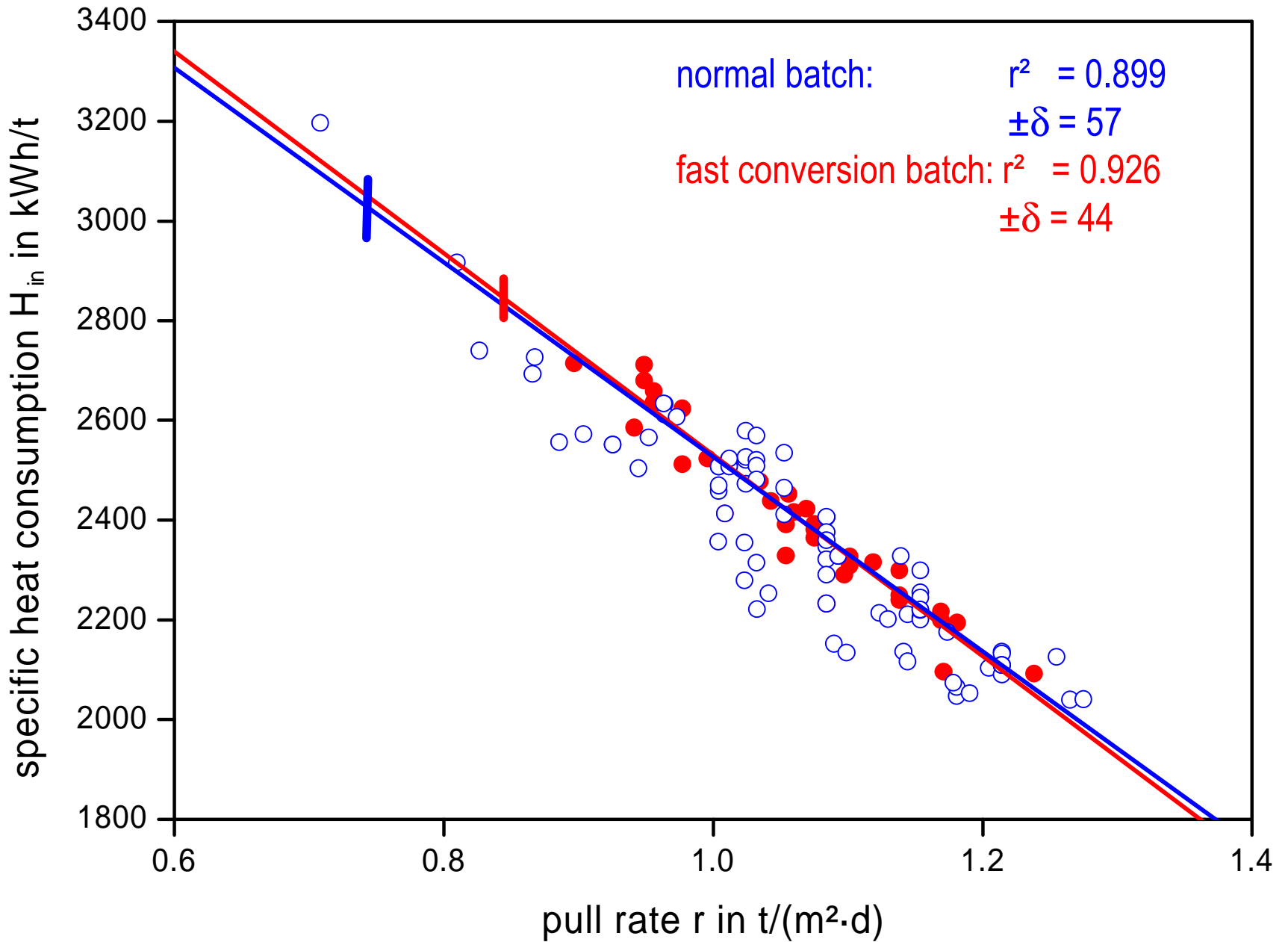




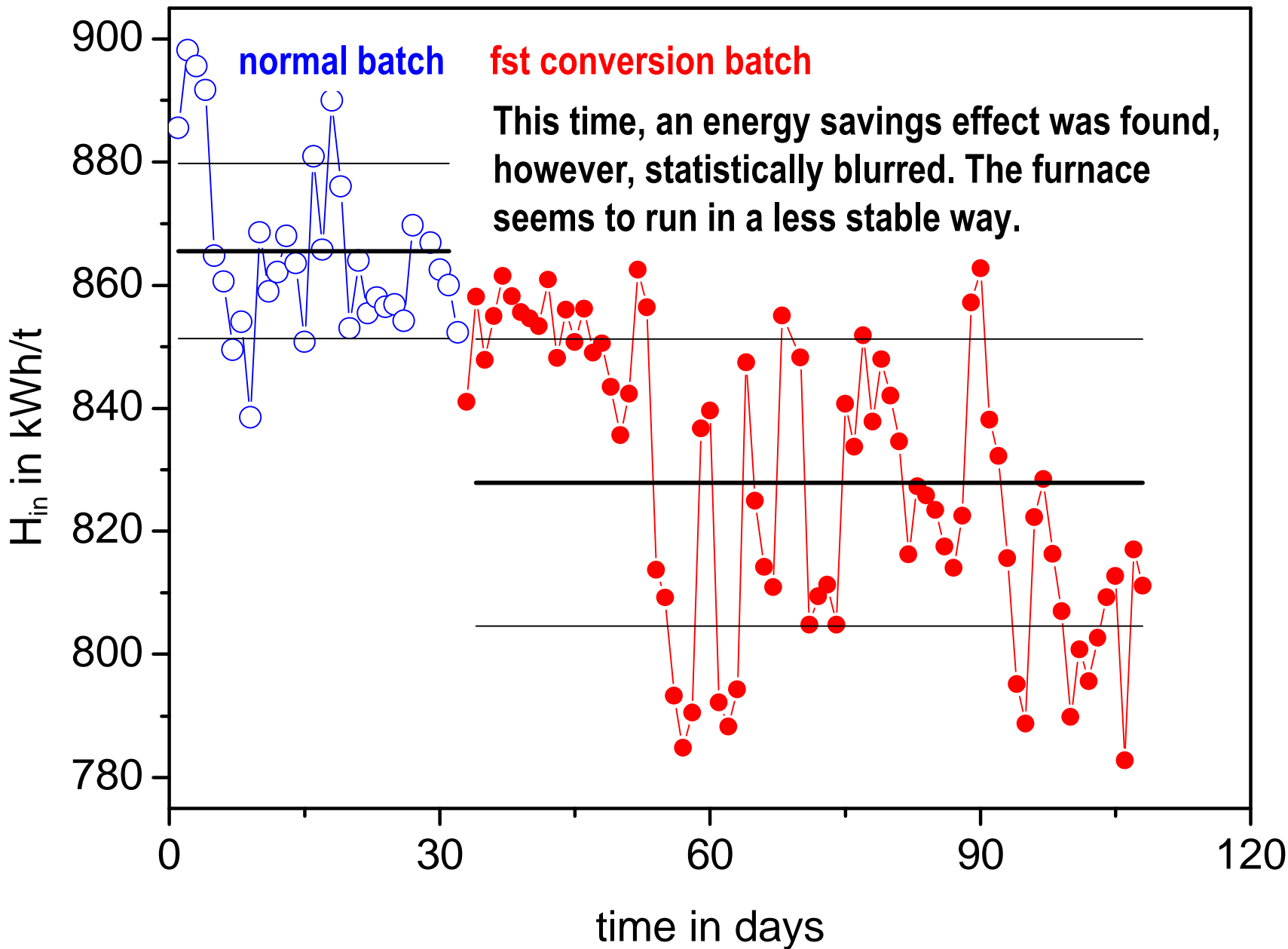
Due to the manager's impatience, no significant difference was found ...



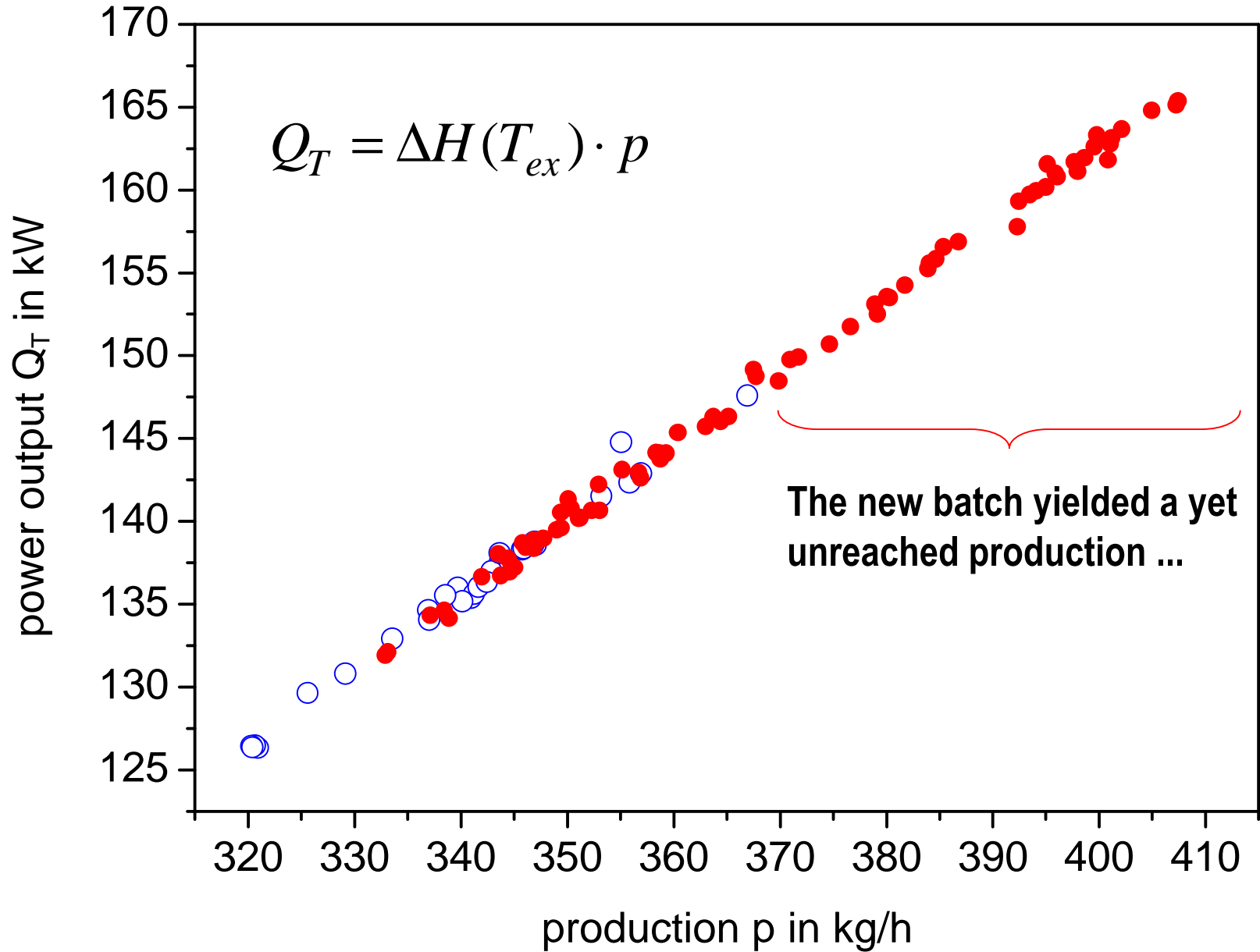
... although the new batch quickly makes the furnace more stable.

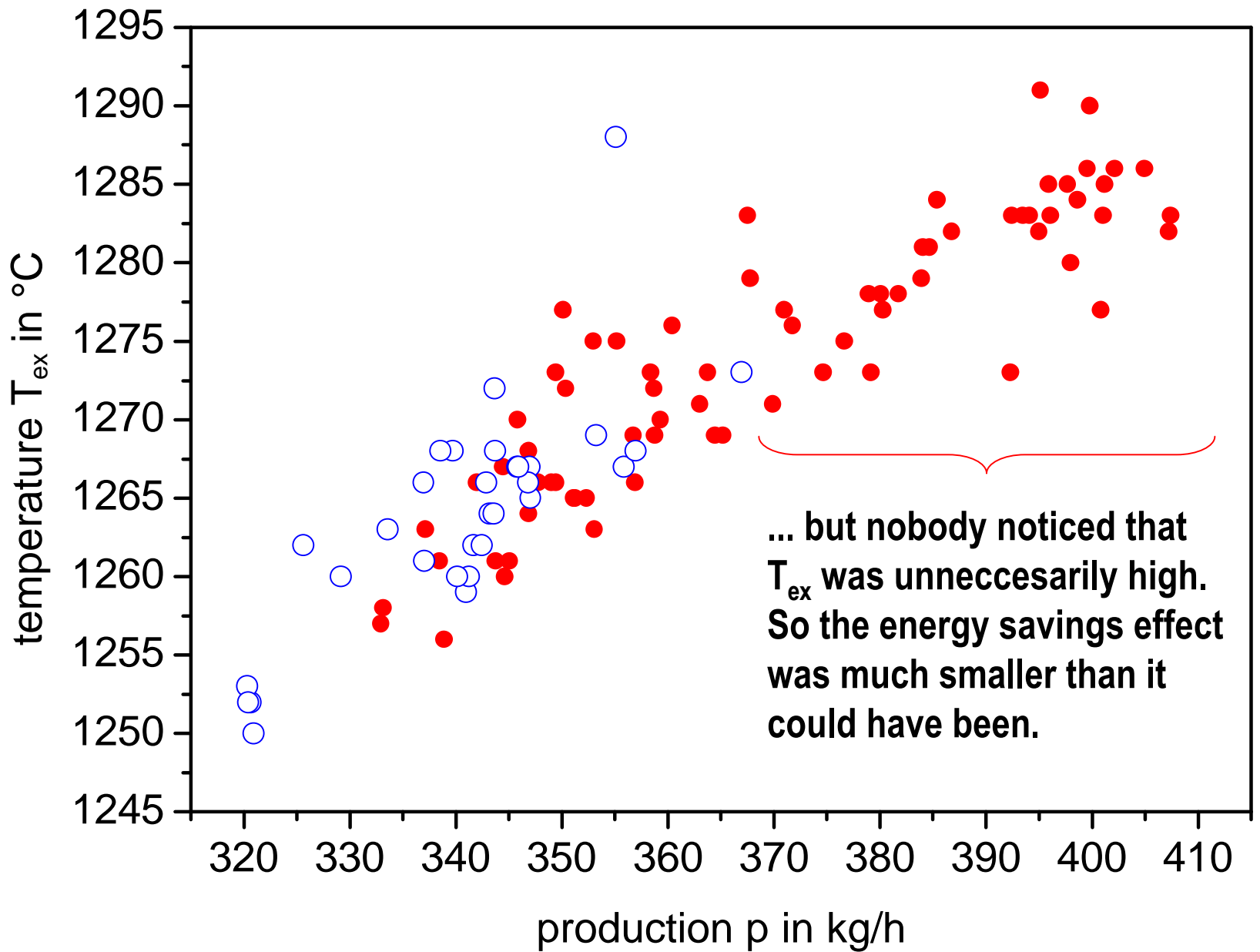


Same type of batches in a different factory.



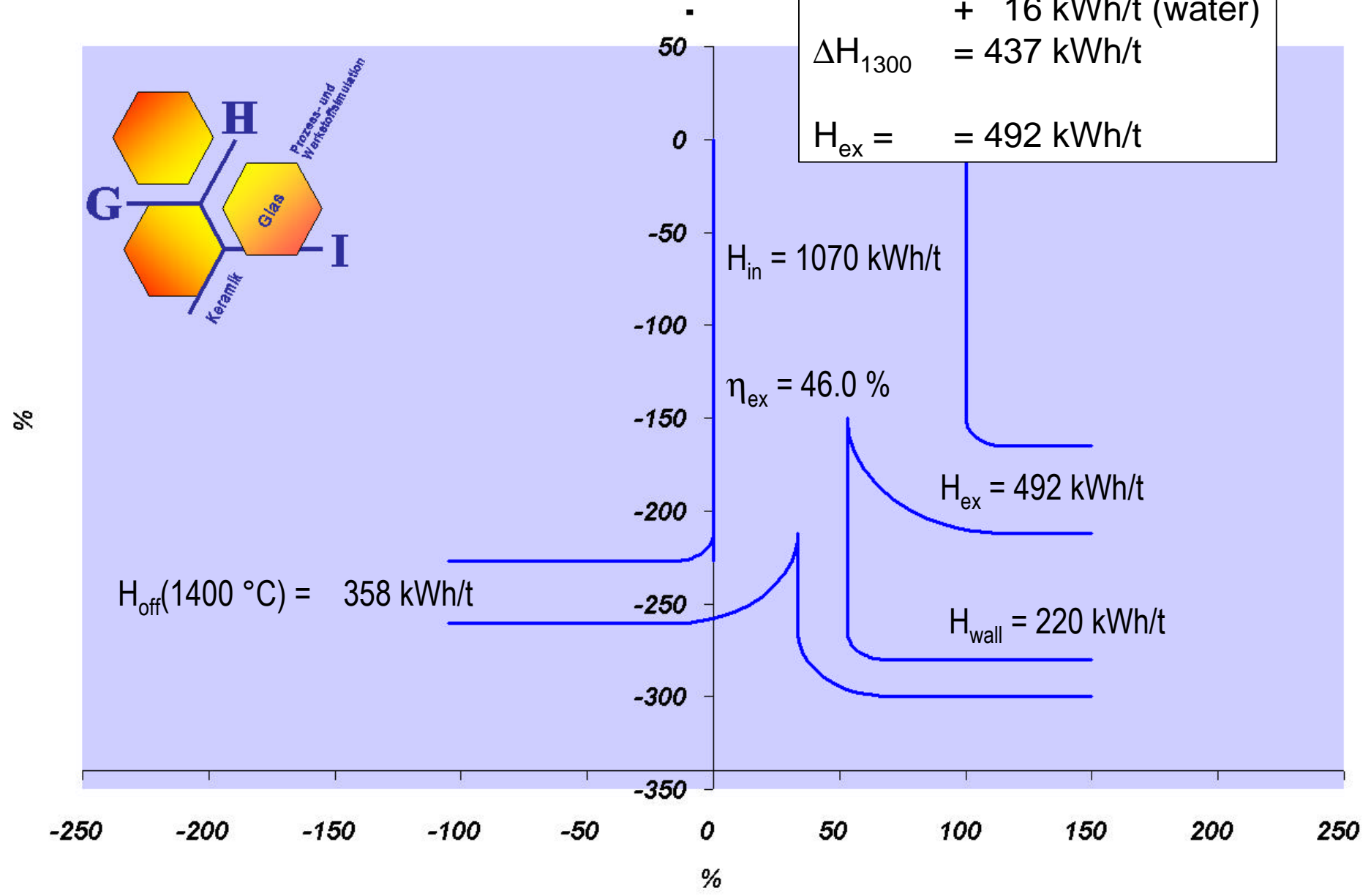
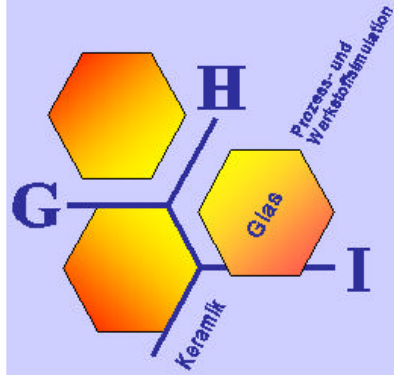
Evaluating the mass and power pulled from the furnace speaks a different language!





$$H_{\text{ex}} = (1 - y_C) \cdot \Delta H^{\circ}_{\text{chem}} + \Delta H_{1300}$$

y_C	= 62 %
$\Delta H^{\circ}_{\text{chem}}$	= 129 kWh/t
	+ 16 kWh/t (water)
ΔH_{1300}	= 437 kWh/t
H_{ex}	= 492 kWh/t



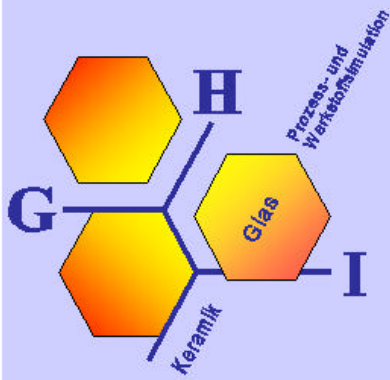
$H_{\text{off}}(1400\text{ °C}) = 358\text{ kWh/t}$

$H_{\text{in}} = 1070\text{ kWh/t}$

$\eta_{\text{ex}} = 46.0\%$

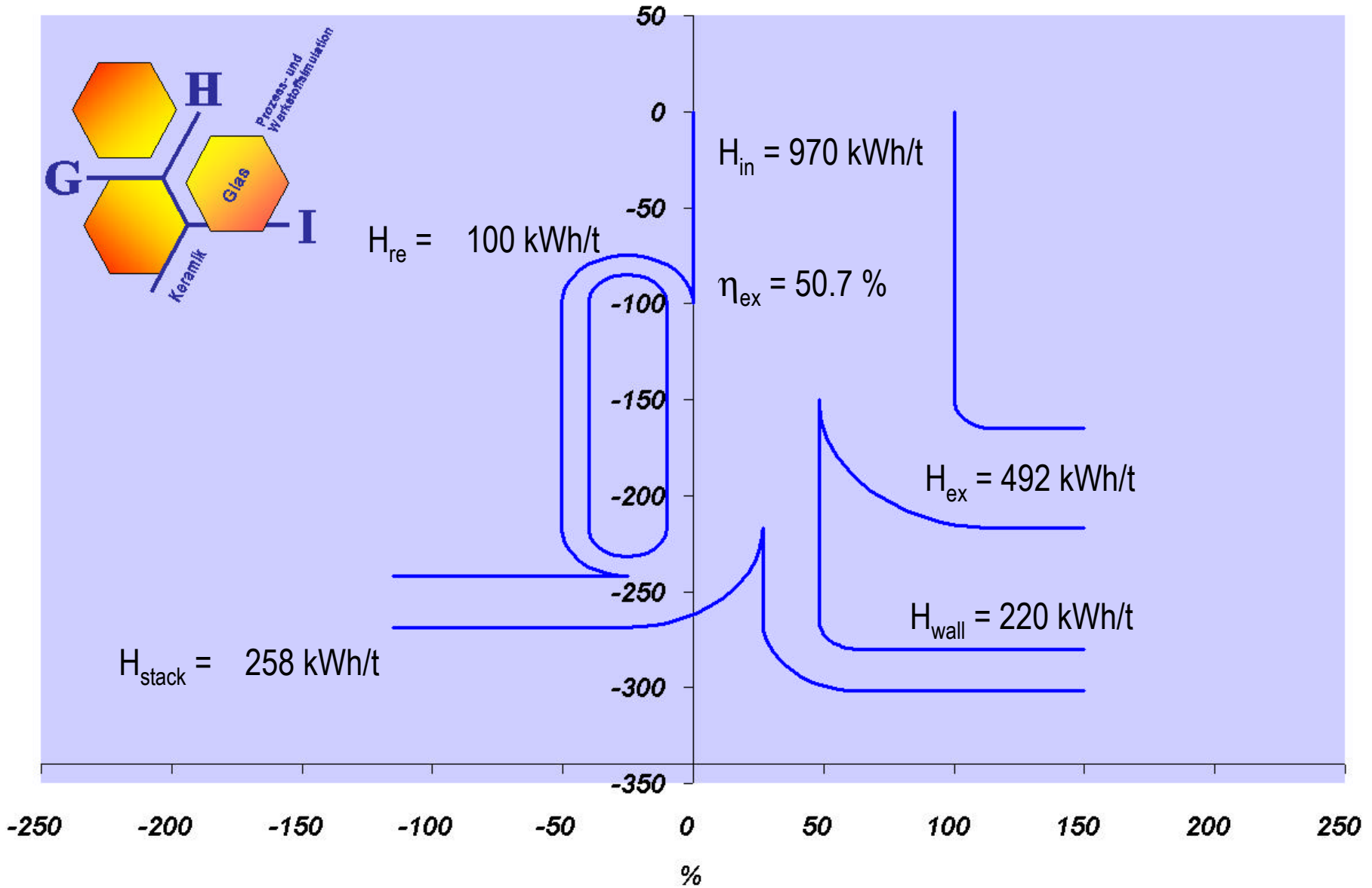
$H_{\text{ex}} = 492\text{ kWh/t}$

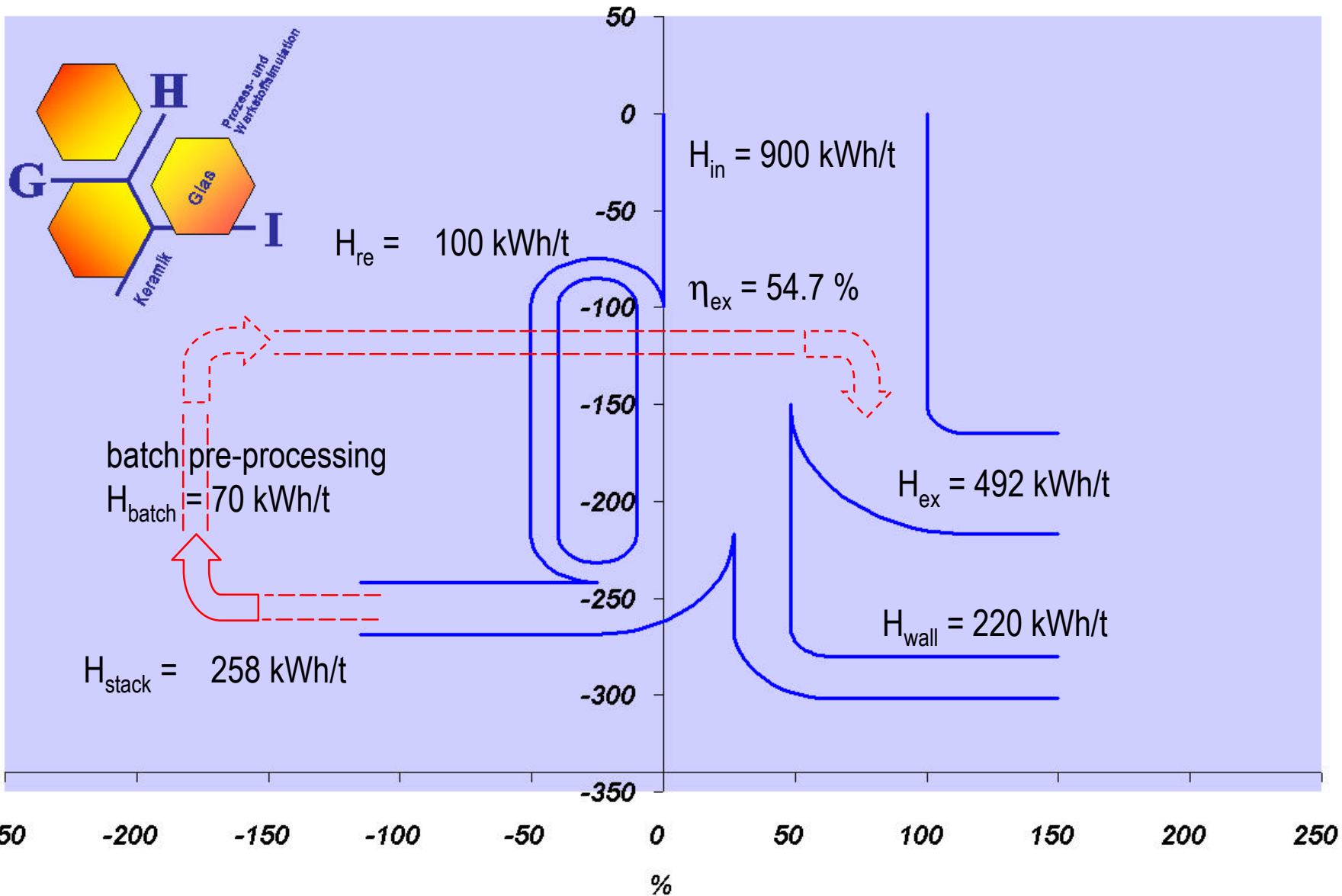
$H_{\text{wall}} = 220\text{ kWh/t}$



$H_{re} = 100 \text{ kWh/t}$

$H_{stack} = 258 \text{ kWh/t}$





**Thank you
for your kind attention!**