SPROŠČANJE IN PRENOS TOPLOTE V BIOPROCESIH

Sproščanje toplote pri reakcijah

Pri reakciji sproščena ali absorbirana toplota je enaka razliki entalpij reaktantov in produktov:

$$\Delta H_r = \sum_{produkti} Mh - \sum_{reaktanti} Mh$$

$M \ldots masa\ (kg)$

$h \ldots specifična\ entalpija\ (J/kg)$

Toplota zgorevanja: $\Delta h_c\ (J/kg)$ ali (J/mol)

Standardna toplota zgorevanja (pri 25°C, 1 atm): $\Delta h^{\circ}_c\ (J/kg)$ ali (J/mol)

Dogovor: $\Delta h^{\circ}_c = 0$ za produkte oksidacij, kot so CO_2 (*g*), N_2, H_2O (*l*), za ostale produkte je vselej $\Delta h^{\circ}_c < 0$

Standardna toplota reakcije:

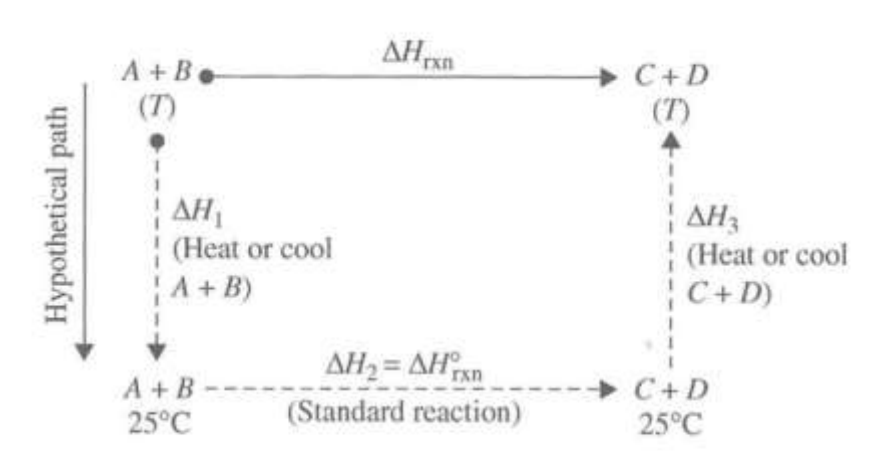
$$\Delta H^{\circ}_r = \sum_{reaktanti} n\Delta h^{\circ}_c - \sum_{produkti} n\Delta h^{\circ}_c$$

TABLE C.8 Heats of Combustion (Continued)

Compound	Formula	Molecular weight	State	Heat of combustion Δh_c° (kJ gmol^{-1})
Alanine (L-)	$C_3H_7O_2N$	89.094	c	−1576.9
			g	−1715.0
Ammonia	NH_3	17.03	g	−382.6
Ammonium ion	NH_4^+			−383
Arginine (D-)	$C_6H_{14}O_2N_4$	174.203	c	−3738.4
Asparagine (L-)	$C_4H_8O_3N_2$	132.119	c	−1928.0
Aspartic acid (L-)	$C_4H_7O_4N$	133.104	c	−1601.1
Benzaldehyde	C_7H_6O	106.124	l	−3525.1
			g	−3575.4
Butanoic acid	$C_4H_8O_2$	88.106	l	−2183.6
			g	−2241.6
1-Butanol	$C_4H_{10}O$	74.123	l	−2675.9
			g	−2728.2
2-Butanol	$C_4H_{10}O$	74.123	l	−2660.6
			g	−2710.3
Butyric acid	$C_4H_8O_2$	88.106	l	−2183.6
			g	−2241.6
Caffeine	$C_8H_{10}O_2N_4$		s	−4246.5*
Carbon	C	12.011	c	−393.5
Carbon monoxide	CO	28.010	g	−283.0
Citric acid	$C_6H_8O_7$		s	−1962.0
Codeine	$C_{18}H_{21}O_3N \cdot H_2O$		s	−9745.7*
Cytosine	$C_4H_5ON_3$	111.103	c	−2067.3
Ethane	C_2H_6	30.070	g	−1560.7
Ethanol	C_2H_6O	46.069	l	−1366.8
			g	−1409.4
Ethylene	C_2H_4	28.054	g	−1411.2
Ethylene glycol	$C_2H_6O_2$	62.068	l	−1189.2
			g	−1257.0
Formaldehyde	CH_2O	30.026	g	−570.7
Formic acid	CH_2O_2	46.026	l	−254.6
			g	−300.7
Fructose (D-)	$C_6H_{12}O_6$		s	−2813.7
Fumaric acid	$C_4H_4O_4$	116.073	c	−1334.0
Galactose (D-)	$C_6H_{12}O_6$		s	−2805.7
Glucose (D-)	$C_6H_{12}O_6$		s	−2805.0
Glutamic acid (L-)	$C_5H_9O_4N$	147.131	c	−2244.1
Glutamine (L-)	$C_5H_{10}O_3N_2$	146.146	c	−2570.3
Glutaric acid	$C_5H_8O_4$	132.116	c	−2150.9
Glycerol	$C_3H_8O_3$	92.095	l	−1655.4
			g	−1741.2
Glycine	$C_2H_5O_2N$	75.067	c	−973.1
Glycogen	$(C_6H_{10}O_5)_x$ per kg		s	−17,530.1*
Guanine	$C_5H_5ON_5$	151.128	c	−2498.2
Hexadecane	$C_{16}H_{34}$	226.446	l	−10,699.2
			g	−10,780.5
Hexadecanoic acid	$C_{16}H_{32}O_2$	256.429	c	−9977.9
			l	−10,031.3
			g	−10,132.3
Histidine (L-)	$C_6H_9O_2N_3$	155.157	c	−3180.6
Hydrogen	H_2	2.016	g	−285.8
Hydrogen sulphide	H_2S	34.08		−562.6
Inositol	$C_6H_{12}O_6$		s	−2772.2*
Isoleucine (L-)	$C_6H_{13}O_2N$	131.175	c	−3581.1
Isoquinoline	C_9H_7N	129.161	l	−4686.5
Lactic acid (D,L-)	$C_3H_6O_3$		l	−1368.3
Lactose	$C_{12}H_{22}O_{11}$		s	−5652.5
Leucine (D-)	$C_6H_{13}O_2N$	131.175	c	−3581.7
Leucine (L-)	$C_6H_{13}O_2N$	131.175	c	−3581.6
Lysine	$C_6H_{14}O_2N_2$	146.189	c	−3683.2
Malic acid (L-)	$C_4H_6O_5$		s	−1328.8
Malonic acid	$C_3H_4O_4$		s	−861.8
Maltose	$C_{12}H_{22}O_{11}$		s	−5649.5
Mannitol (D-)	$C_6H_{14}O_6$		s	−3046.5*
Methane	CH_4	16.043	g	−890.8
Methanol	CH_4O	32.042	l	−726.1
			g	−763.7

Toplota reakcije pri nestandardnih pogojih

- reakcija $A+B \longrightarrow C+D$



$\Delta H_r(\text{pri T}) = \Delta H_1 + \Delta H^\circ_r + \Delta H_3$

- Primer: $C_6H_{12}O_6 + 6\ O_2 \longrightarrow 6\ CO_2 + 6\ H_2O$

$\Delta H_r(\text{pri } 37\ ^\circ C) = -2801{,}7\ kJ$

$\Delta H^\circ_r = -2805{,}0\ kJ$

Razliko lahko zanemarimo

Toplota reakcije za procese s proizvodnjo biomase

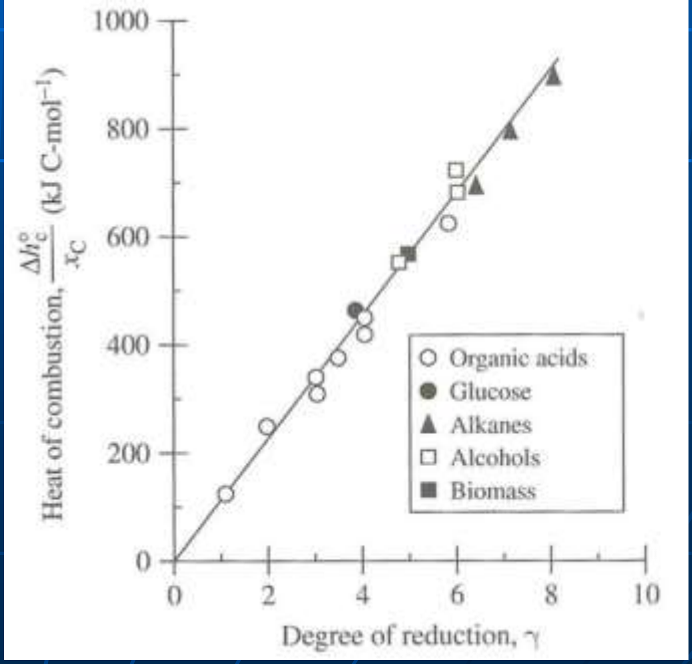
Termodinamika rasti celic:

$$C_wH_xO_yN_z + a\ O_2 + b\ H_gO_hN_i \longrightarrow c\ CH_\alpha O_\beta N_\delta + d\ CO_2 + e\ H_2O$$

substrat vir dušika suha biomasa

Vsebnost energije organskih spojin je sorazmerna njihovi stopnji redukcije:

$$\Delta h^\circ_c = -q \cdot \gamma \cdot x_C$$



Δh°_c ……. molarna toplota zgorevanja pri standardnih pogojih

q….. Energija sproščena na mol prostih elektronov

γ……stopnja redukcije spojine glede na N_2

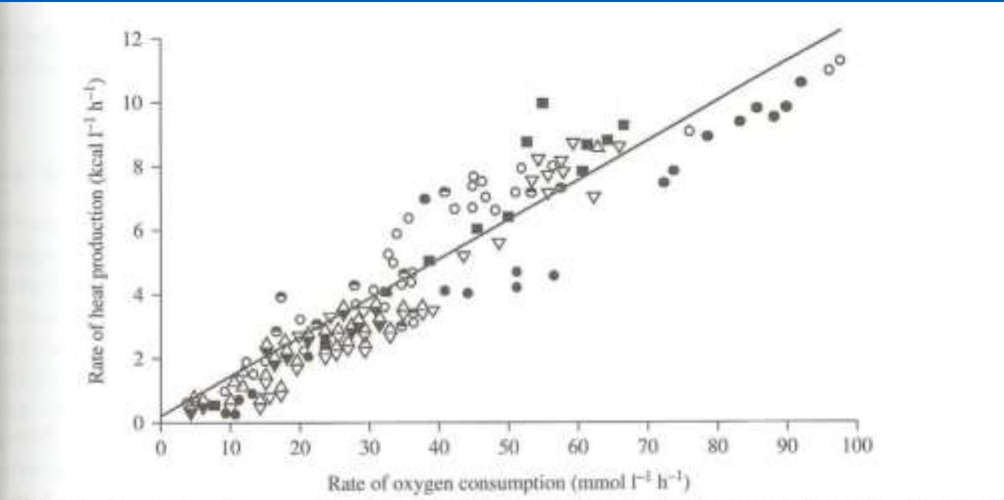
x_C…..število atomov C v molekuli

Številne kemijske in biokemijske spojine, tudi biomasa:

q = 115 kJ/mol

Toplota reakcije s kisikom kot akceptorjem e^-

Ker je stopnja redukcije neposredno povezana s količino kisika, potrebnega za popolno zgorenje, sta tudi Δh°_c in ΔH_r sorazmerna porabi O_2.



RE 5.8 Correlation between rate of heat evolution and rate of oxygen consumption for a variety of bial fermentations. (○) *Escherichia coli*, glucose medium; (◈) *Candida intermedia*, glucose medium; (△) *ermedia*, molasses medium; (▽) *Bacillus subtilis*, glucose medium; (■) *B. subtilis*, molasses medium; (◓) *tilis*, soybean meal medium; (⊕) *Aspergillus niger*, glucose medium; (●) *Asp. niger*, molasses medium. C.L. Cooney, D.I.C. Wang, and R.I. Mateles, *Measurement of heat evolution and correlation with oxygen consumption microbial growth*, Biotechnol. Bioeng. 11, 269–281; Copyright © 1968. Reprinted by permission of John Wiley.

$\Delta H_r \approx -460$ kJ/mol O_2

Če je vsa toplota na račun rasti, potem je: $\dot{Q} = -\Delta H_r$

$\dot{Q} = (460\ \text{kJ/mol}) \cdot r_{O2} \cdot V$

$U \cdot A \cdot \Delta T = (460\ \text{kJ/mol})\ q_{O2} \cdot X \cdot V$

Če je ΔT max, potem:

$$X_{max} = \frac{U\,A\,(T_F - T_{h\,v})}{460\frac{kJ}{mol}\,q_{O2}\,V}$$

Toplota reakcije z drugimi akceptorji e$^-$

$$C_wH_xO_yN_z + b\, H_gO_hN_i \longrightarrow c\, CH_\alpha O_\beta N_\delta + d\, CO_2 + e\, H_2O + f\, C_jH_kO_lN_m$$

Če je vir N NH_3:

$$\Delta H^\circ_r = (n\, \Delta h^\circ_c)_{substrat} + (n\, \Delta h^\circ_c)_{NH3} - (n\, \Delta h^\circ_c)_{biomasa} - (n\, \Delta h^\circ_c)_{produkt}$$

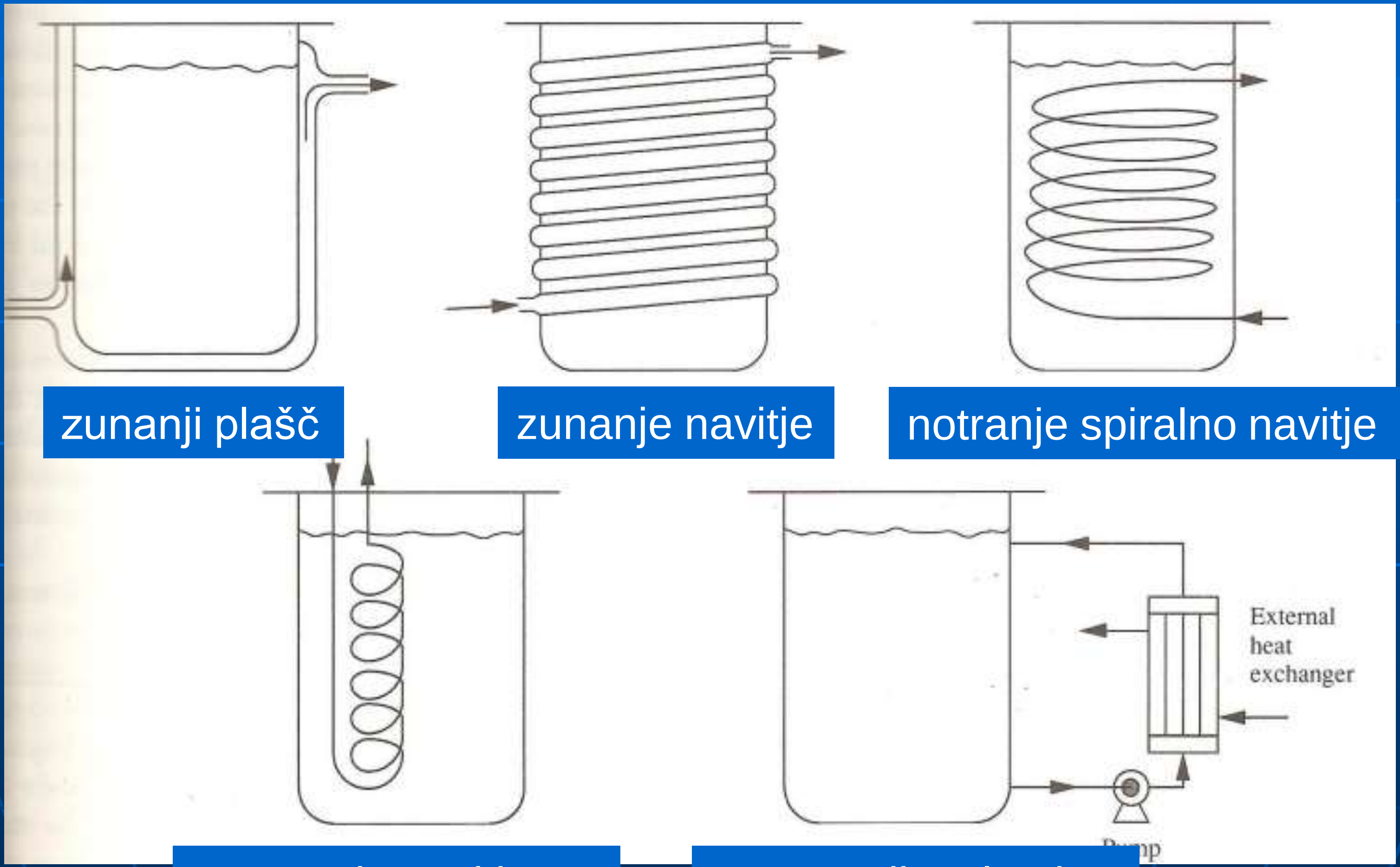
TABLE 5.1 Heats of Combustion of Bacteria and Yeast

Organism	Substrate	Δh_c (kJ g^{-1})
BACTERIA		
Escherichia coli	glucose	-23.04 ± 0.06
	glycerol	-22.83 ± 0.07
Enterobacter cloacae	glucose	-23.22 ± 0.14
	glycerol	-23.39 ± 0.12
Methylophilus methylotrophus	methanol	-23.82 ± 0.06
Bacillus thuringiensis	glucose	-22.08 ± 0.03
YEAST		
Candida lipolytica	glucose	-21.34 ± 0.16
Candida boidinii	glucose	-20.14 ± 0.18
	ethanol	-20.40 ± 0.14
	methanol	-21.52 ± 0.09
Kluyveromyces fragilis	lactose	-21.54 ± 0.07
	galactose	-21.78 ± 0.10
	glucose	-21.66 ± 0.19
	glucose*	-21.07 ± 0.07
		-21.30 ± 0.10
		-20.66 ± 0.26
		-21.22 ± 0.14

Chemostat rather than batch culture: dilution rates were 0.036 h^{-1}, 0.061 h^{-1}, 0.158 h^{-1}, and 0.227 h^{-1}, respectively.

From J.-L. Cordier, B.M. Butsch, B. Birou, and U. von Stockar, 1987, The relationship between elemental composition and heat of combustion of microbial biomass, Appl. Microbiol. Biotechnol. 25. 305–312.

Oprema za gretje/hlajenje



zunanji plašč

zunanje navitje

notranje spiralno navitje

notranje navitje v obliki tuljave

zunanji toplotni menjalnik

TOPLOTNA BILANCA
ZA HLADNEJŠI MEDIJ

$$\Phi_m \cdot c_p \cdot \left(T_{h,2} - T_{h,1}\right) = U \cdot A \cdot \Delta T_{\ln}$$

LOGARITEMSKA SREDNJA TEMPERATURNA RAZLIKA

$$\Delta T_{\ln} = \frac{\left(T_{p,1} - T_{h,1}\right) - \left(T_{p,2} - T_{h,2}\right)}{\ln \dfrac{T_{p,1} - T_{h,1}}{T_{p,2} - T_{h,2}}}$$

Površina za hlajenje

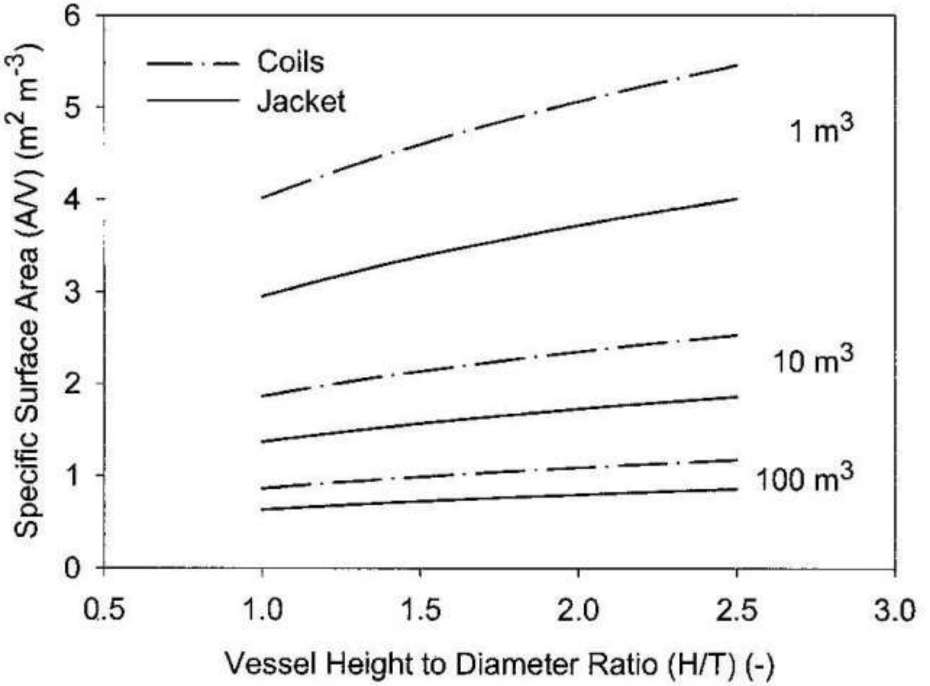
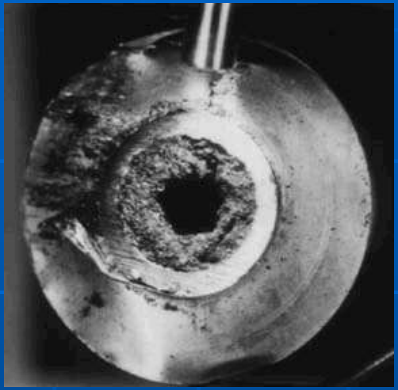


Figure 7. Variation of specific surface area with aspect ratio and scale for external jackets and internal coils. Data: Jacket and coils extend over 80% of height. Coils: $D_c = T/30$; Pitch = $2D_c$; Wall clearance = $2D_c$.

Vir: P. Kieran, Heat management in Bioreactors, Bioprocess engineering course notes (P. Kieran, M. Berovič, ur.), 2001, FKKT, Ljubljana

POVPREČNI KOEFICIENT TOPLOTNEGA PREHODA

$$\frac{1}{U} = \frac{1}{h_z} + \frac{1}{h_{fz}} + \frac{l_s}{\lambda_s} + \frac{1}{h_{fn}} + \frac{1}{h_n}$$



plast (biološka, korozija, karbonat...) na notranji površini menjalnika – angl. fouling

h_z...koeficient toplotnega prestopa na strani brozge [W/m² K]

h_{fz}...koeficient toplotnega prestopa na strani brozge, v plasti na zunanji strani cevi [W/m² K]

λ_s...prevodnost stene [W/m K]

l_s... debelina stene [m]

h_{fn}...koeficient toplotnega prestopa v plasti v notranjosti cevi [W/m² K]

h_n...koeficient toplotnega prestopa na strani brozge[W/m² K]

Odvisnost lokalne vrednosti koeficienta snovnega prestopa na strani brozge od razdalje od mešala

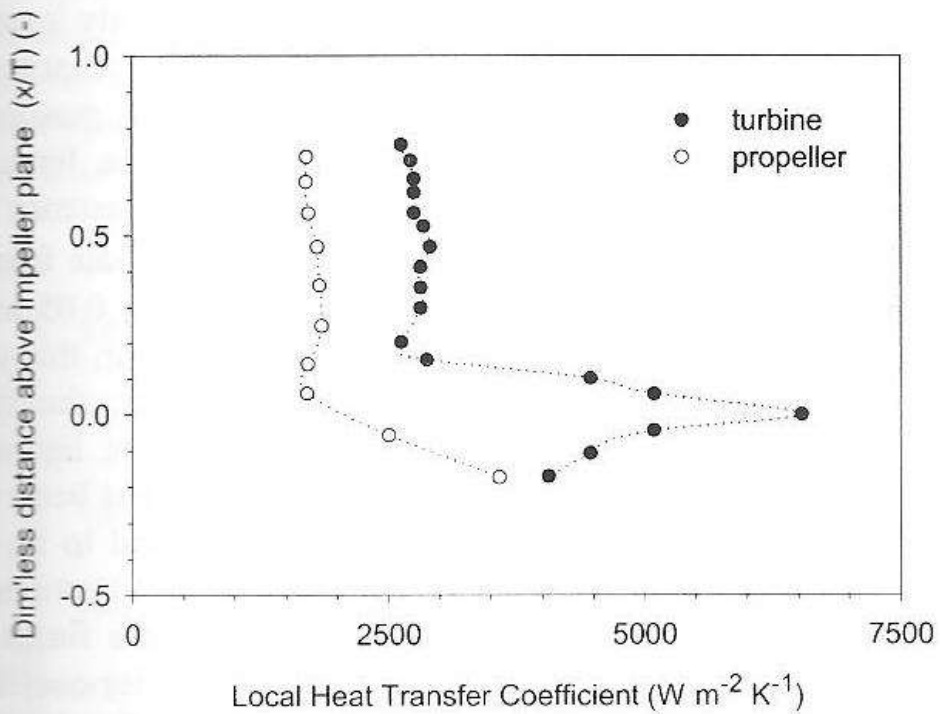


Figure 2. Variation of local heat transfer coefficients with axial position for turbine and propeller impellers, $D/T = 1/3$, $N = 0.5\ s^{-1}$ (Man *et al.*, 1984).

Vir: P. Kieran, Heat management in Bioreactors, Bioprocess engineering course notes (P. Kieran, M. Berovič, ur.), 2001, FKKT, Ljubljana

Naloga

Bioreaktor prostornine 150 m^3, kjer proizvajamo biomaso iz glukoze, deluje pri 35 °C. Kultura porablja kisik s hitrostjo 1,5 kg/m^3h; mešalo oddaja 1 kW/m^3 energije. Hladilna voda iz bližnje reke, ki ima 10 °C, prehaja skozi notranjo cev v fermentorju s hitrostjo 60 m^3/h. Če sistem deluje v stacionarnem stanju in če ni izparevanja, kakšna je temperatura vode na izstopu?

c_p vode = 4190 J/kg K   oz.   75,4 J/mol K

ρ vode = 1000 kg/m^3

Odgovor: T= 25 °C