



# **SPROŠČANJE IN PRENOS TOPLOTE V BIOPROCESIH**

# Sproščanje toplote pri reakcijah

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

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

$M$  ... masa (kg)  
 $h$  ... specifična entalpija (J/kg)

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

**Standardna toplota zgorevanja** (pri 25°C, 1 atm):  $\Delta h_c^\circ$  (J/kg) ali (J/mol)

Dogovor:  $\Delta h_c^\circ$  za produkte oksidacij, kot so CO<sub>2</sub> (g), N<sub>2</sub>, H<sub>2</sub>O (l),  
za ostale produkte je vselej  $\Delta h_c^\circ < 0$

**Standardna toplota reakcije:**

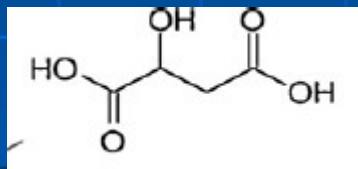
$$\Delta H_r^\circ = \sum_{\text{reaktanti}} n\Delta h_c^\circ - \sum_{\text{produkti}} n\Delta h_c^\circ$$

**TABLE C.8** Heats of Combustion (Continued)

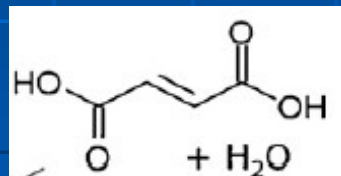
Compound	Formula	Molecular weight	State	Heat of combustion $\Delta h_c^\circ$ (kJ gmol <sup>-1</sup> )					
Alanine (L-)	C <sub>3</sub> H <sub>7</sub> O <sub>2</sub> N	89.094	c	-1576.9	Fumaric acid	C <sub>4</sub> H <sub>4</sub> O <sub>4</sub>	116.073	c	-1334.0
Ammonia	NH <sub>3</sub>	17.03	g	-382.6	Galactose (D-)	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>		s	-2805.7
Ammonium ion	NH <sub>4</sub> <sup>+</sup>			-383	Glucose (D-)	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>		s	-2805.0
Arginine (D-)	C <sub>6</sub> H <sub>14</sub> O <sub>2</sub> N <sub>4</sub>	174.203	c	-3738.4	Glutamic acid (L-)	C <sub>5</sub> H <sub>9</sub> O <sub>4</sub> N	147.131	c	-2244.1
Asparagine (L-)	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub> N <sub>2</sub>	132.119	c	-1928.0	Glutamine (L-)	C <sub>5</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub>	146.146	c	-2570.3
Aspartic acid (L-)	C <sub>4</sub> H <sub>7</sub> O <sub>4</sub> N	133.104	c	-1601.1	Glutaric acid	C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>	132.116	c	-2150.9
Benzaldehyde	C <sub>7</sub> H <sub>6</sub> O	106.124	l	-3525.1	Glycerol	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	92.095	l	-1655.4
Butanoic acid	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88.106	l	-2183.6				g	-1741.2
1-Butanol	C <sub>4</sub> H <sub>10</sub> O	74.123	l	-2675.9	Glycine	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> N	75.067	c	-973.1
2-Butanol	C <sub>4</sub> H <sub>10</sub> O	74.123	l	-2660.6	Glycogen	(C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ) <sub>x</sub> per kg		s	-17,530.1*
Butyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88.106	l	-2183.6	Guanine	C <sub>5</sub> H <sub>5</sub> ON <sub>5</sub>	151.128	c	-2498.2
Caffeine	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> N <sub>4</sub>		s	-4246.5*	Hexadecane	C <sub>16</sub> H <sub>34</sub>	226.446	l	-10,699.2
Carbon	C	12.011	c	-393.5				g	-10,780.5
Carbon monoxide	CO	28.010	g	-283.0	Hexadecanoic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	256.429	c	-9977.9
Citric acid	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>		s	-1962.0				l	-10,031.3
Codeine	C <sub>18</sub> H <sub>21</sub> O <sub>3</sub> N•H <sub>2</sub> O		s	-9745.7*				g	-10,132.3
Cytosine	C <sub>4</sub> H <sub>5</sub> ON <sub>3</sub>	111.103	c	-2067.3	Histidine (L-)	C <sub>6</sub> H <sub>9</sub> O <sub>2</sub> N <sub>3</sub>	155.157	c	-3180.6
Ethane	C <sub>2</sub> H <sub>6</sub>	30.070	g	-1560.7	Hydrogen	H <sub>2</sub>	2.016	g	-285.8
Ethanol	C <sub>2</sub> H <sub>6</sub> O	46.069	l	-1366.8	Hydrogen sulphide	H <sub>2</sub> S	34.08		-562.6
Ethylene	C <sub>2</sub> H <sub>4</sub>	28.054	g	-1411.2	Inositol	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>		s	-2772.2*
Ethylene glycol	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	62.068	l	-1189.2	Isoleucine (L-)	C <sub>6</sub> H <sub>13</sub> O <sub>2</sub> N	131.175	c	-3581.1
Formaldehyde	CH <sub>2</sub> O	30.026	g	-570.7	Isoquinoline	C <sub>9</sub> H <sub>7</sub> N	129.161	l	-4686.5
Formic acid	CH <sub>2</sub> O <sub>2</sub>	46.026	l	-254.6	Lactic acid (D,L-)	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>		l	-1368.3
Fructose (D-)	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>		s	-2813.7	Lactose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>		s	-5652.5
			g	-300.7	Leucine (D-)	C <sub>6</sub> H <sub>13</sub> O <sub>2</sub> N	131.175	c	-3581.7
			s	-2813.7	Leucine (L-)	C <sub>6</sub> H <sub>13</sub> O <sub>2</sub> N	131.175	c	-3581.6
					Lysine	C <sub>6</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub>	146.189	c	-3683.2
					Malic acid (L-)	C <sub>4</sub> H <sub>6</sub> O <sub>5</sub>		s	-1328.8
					Malonic acid	C <sub>3</sub> H <sub>4</sub> O <sub>4</sub>		s	-861.8
					Maltose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>		s	-5649.5
					Mannitol (D-)	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>		s	-3046.5*
					Methane	CH <sub>4</sub>	16.043	g	-890.8
					Methanol	CH <sub>4</sub> O	32.042	l	-726.1
								g	-763.7

# Naloga

- Izračunajte standardno energijo reakcije za tvorbo fumarne kisline iz jabolčne kisline.
- Reakcija:



jabočna kislina



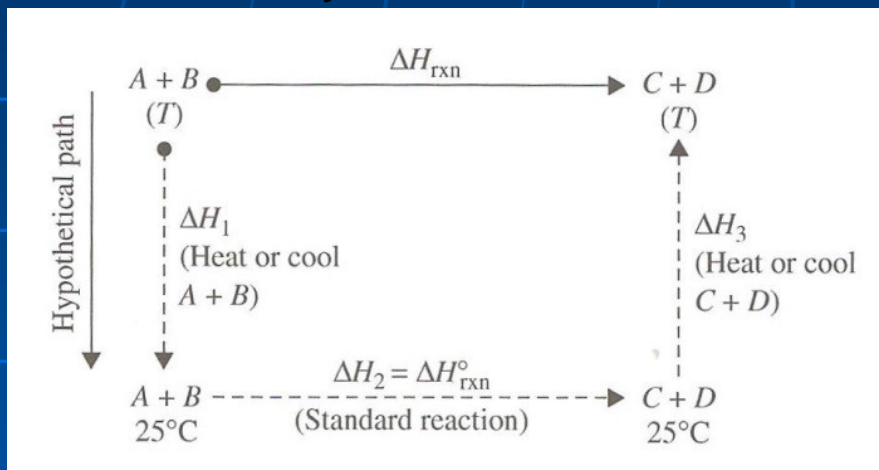
fumarna kislina

Odgovor:  $\Delta H_r^\circ = 5,2 \text{ kJ}$

Toplota se absorbira – reakcija je endotermna.

# Toplota reakcije pri nestandardnih pogojih

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



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

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

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

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

Razlika lahko zanemarimo

# Toplota reakcije za procese s proizvodnjo biomase

Termodinamika rasti celic:



Vsebnost energije organskih spojin je sorazmerna njihovi stopnji redukcije

$$\Delta h_c^\circ = -q \cdot \gamma \cdot x_C$$

$\Delta h_c^\circ$  ..... molarna toplota zgorevanja pri standardnih pogojih

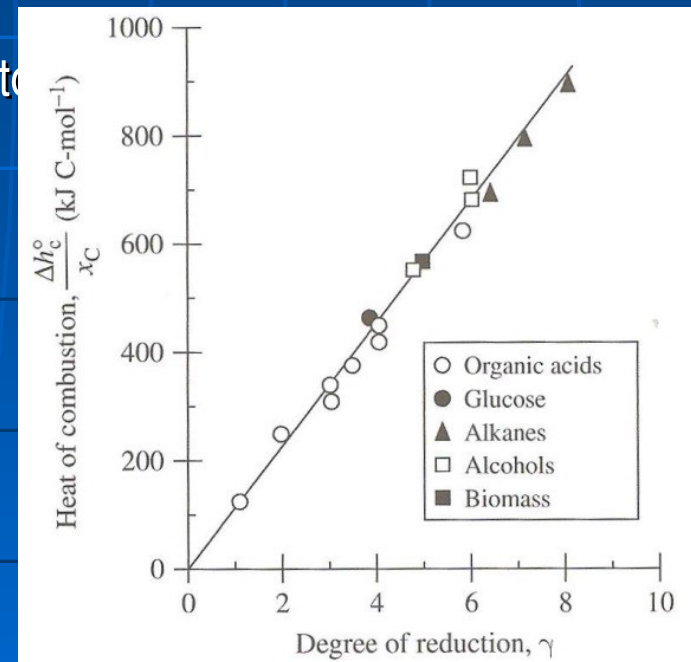
$q$ ..... Energija sproščena na mol prostih elektronov

$\gamma$ .....stopnja redukcije spojine glede na  $N_2$

$x_C$ .....število atomov C v molekuli

Številne kemijske in biokemijske spojine, tudi biomasa:

$$q = 115 \text{ kJ/mol}$$



# Toplota reakcije s kisikom kot akceptorjem e<sup>-</sup>

Ker je stopnja redukcije neposredno povezana s količino kisika, potrebnega za popolno zgorenje, sta tudi in sorazmerna porabi O<sub>2</sub>.

$$\Delta h_c \quad \Delta H_r$$

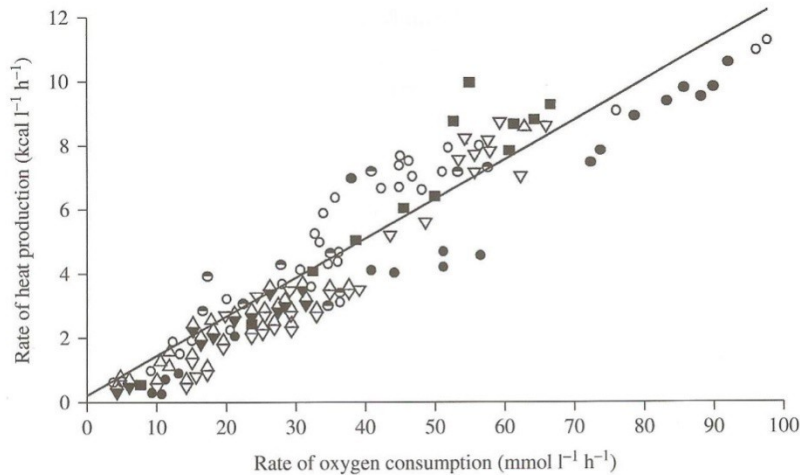


FIGURE 5.8 Correlation between rate of heat evolution and rate of oxygen consumption for a variety of microbial fermentations. (○) *Escherichia coli*, glucose medium; (◐) *Candida intermedia*, glucose medium; (△) *C. intermedia*, molasses medium; (▽) *Bacillus subtilis*, glucose medium; (■) *B. subtilis*, molasses medium; (●) *B. subtilis*, 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 in microbial growth, Biotechnol. Bioeng. 11, 269–281; Copyright © 1968. Reprinted by permission of John Wiley.

$$\Delta H_r \approx -460 \text{ kJ/mol O}_2$$

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

$$\dot{Q} = (460 \text{ kJ/mol}) \cdot r_{\text{O}_2} \cdot V$$

$$U \cdot A \cdot \Delta T = (460 \text{ kJ/mol}) q_{\text{O}_2} \cdot X \cdot V$$

Če je  $\Delta T$  max, potem:

$$X_{\text{max}} = \frac{U A (T_F - T_{h,v})}{460 \frac{\text{kJ}}{\text{mol}} q_{\text{O}_2} V}$$

# Toplota reakcije z drugimi akceptorji e<sup>-</sup>



Če je vir N NH<sub>3</sub>:

$$\Delta H^{\circ}_r = (n \Delta h^{\circ}_c)_{\text{substrat}} + (n \Delta h^{\circ}_c)_{\text{NH}_3} - (n \Delta h^{\circ}_c)_{\text{biomasa}} - (n \Delta h^{\circ}_c)_{\text{produkt}}$$

TABLE 5.1 Heats of Combustion of Bacteria and Yeast

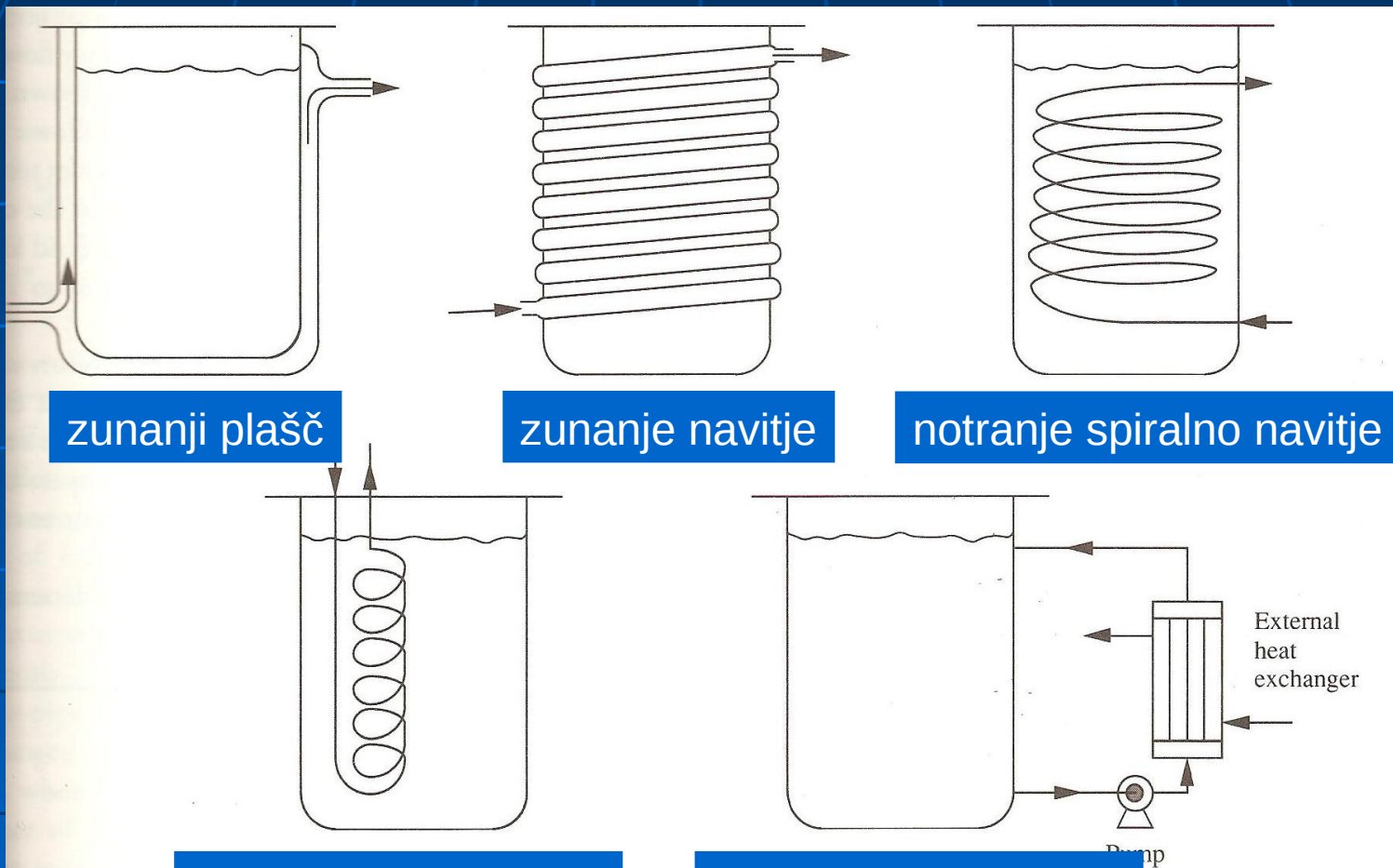
Organism	Substrate	$\Delta h_c$ (kJ g <sup>-1</sup> )
<b>BACTERIA</b>		
<i>Escherichia coli</i>	glucose	-23.04 ± 0.06
	glycerol	-22.83 ± 0.07
<i>Enterobacter cloacae</i>	glucose	-23.22 ± 0.14
	glycerol	-23.39 ± 0.12
<i>Methylophilus methylotrophus</i>	methanol	-23.82 ± 0.06
<i>Bacillus thuringiensis</i>	glucose	-22.08 ± 0.03
<b>YEAST</b>		
<i>Candida lipolytica</i>	glucose	-21.34 ± 0.16
<i>Candida boidinii</i>	glucose	-20.14 ± 0.18
	ethanol	-20.40 ± 0.14
	methanol	-21.52 ± 0.09
<i>Kluyveromyces fragilis</i>	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<sup>-1</sup>, 0.061 h<sup>-1</sup>, 0.158 h<sup>-1</sup>, and 0.227 h<sup>-1</sup>, 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

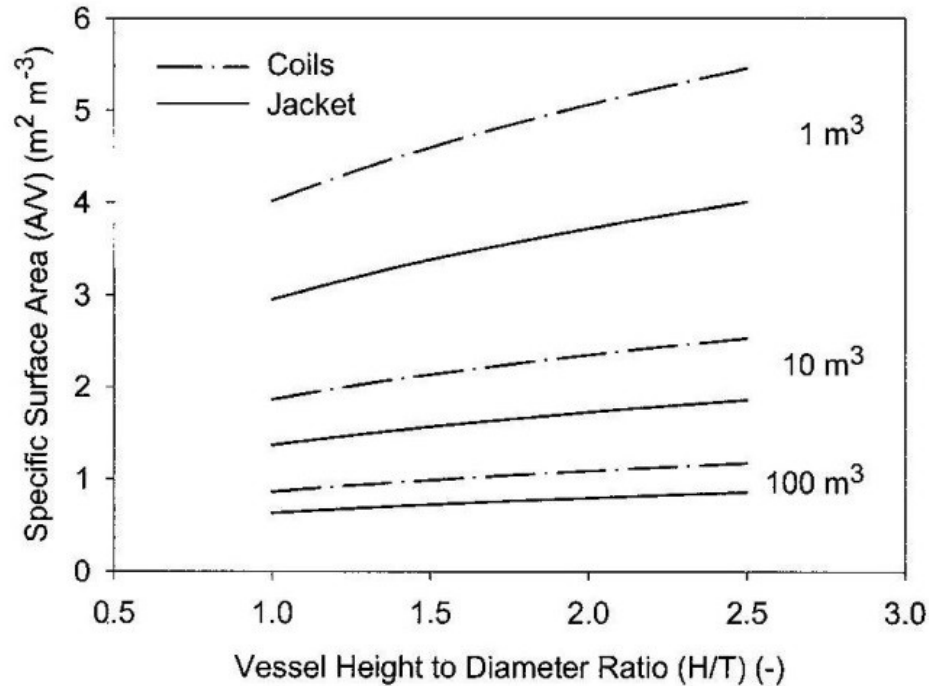
zunanje navitje

notranje spiralno navitje

notranje navitje v  
obliki tuljave

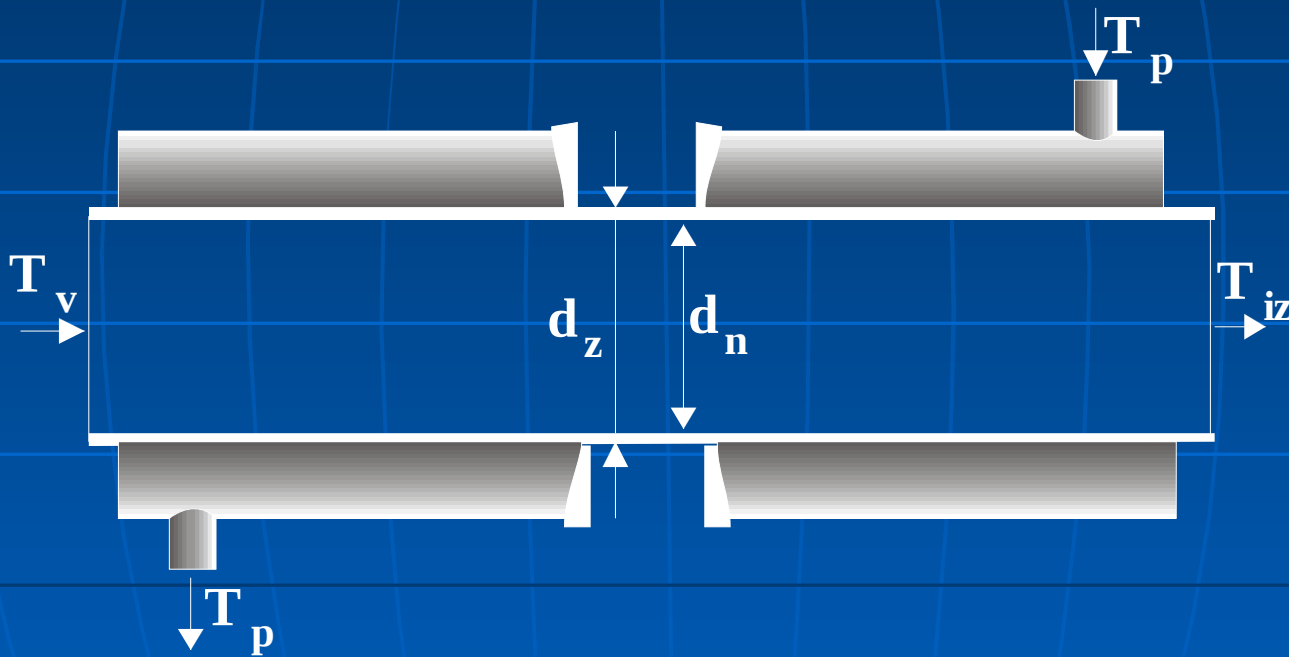
zunanji toplotni  
menjalnik

# Površina za hlajenje

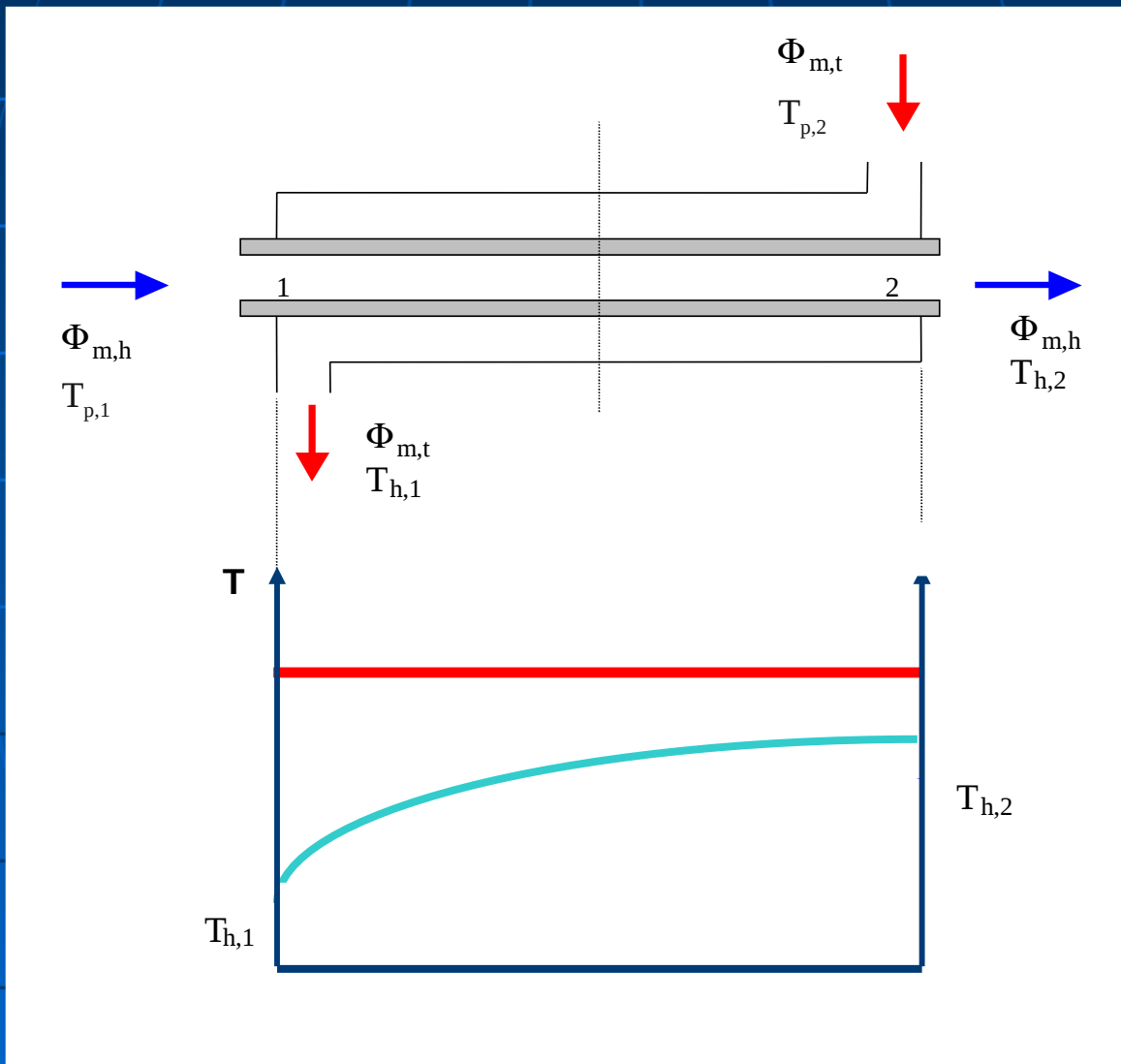


**Figure 7.** Variation of specific surface area with aspect ratio and scale for external jackets and internal coils. Data: Jacket and coils extend over 80% of height. Coils:  $D_c = T/30$ ; Pitch =  $2D_c$ ; Wall clearance =  $2D_c$ .

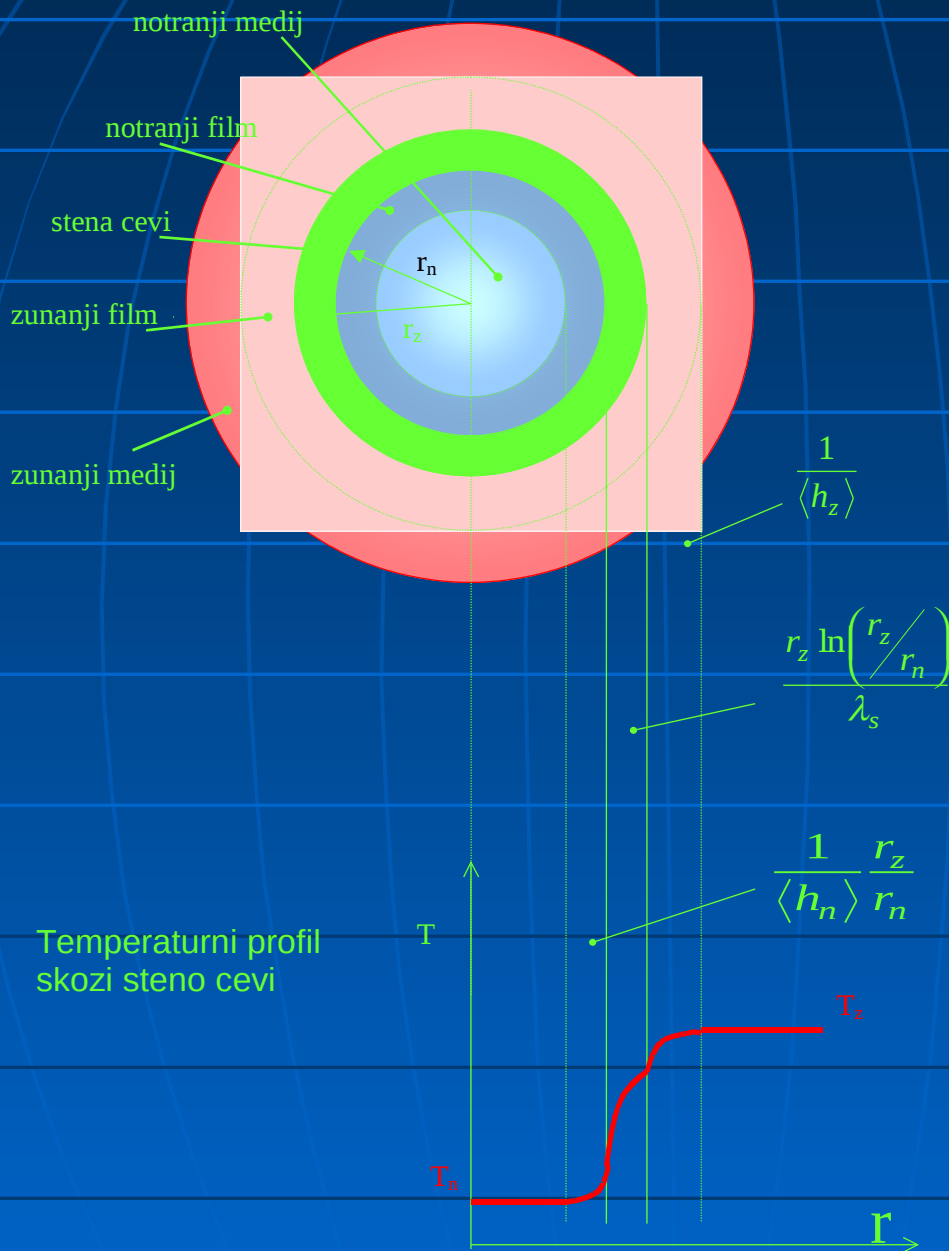
# TOPLOTNI MENJALNIK



# TEMPERATURNI PROFIL V CEVI



# TEMPERATURNI PROFIL SKOZI STENO CEVI TOPLITNEGA MENJALNIKA



Temperaturni profil skozi steno cevi

# TOPLOTNA BILANCA ZA HLADNEJŠI MEDIJ

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

## LOGARITEMSKA SREDNJA TEMPERATURNI RAZLIKA

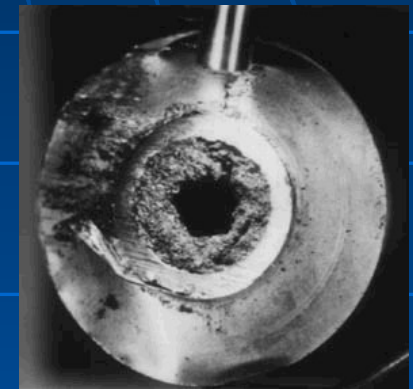
$$\Delta T_{\ln} = \frac{(T_{p,1} - T_{h,1}) - (T_{p,2} - T_{h,2})}{\ln \frac{T_{p,1} - T_{h,1}}{T_{p,2} - T_{h,2}}}$$

# POVPREČNI KOEFICIENT TOPLOTNEGA PREHODA

$$\frac{1}{\bar{U}_z} = \frac{1}{h_z} + \frac{r_z \cdot \ln(r_z / r_n)}{\lambda_s} + \frac{1}{h_n} \cdot \left( \frac{r_z}{r_n} \right)$$

# POVPREČNI KOEFICIENT TOPLLOTNEGA 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/m<sup>2</sup> K]

$h_{fz}$ ...koeficient toplotnega prestopa na strani brozge, v plasti na zunanji strani cevi [W/m<sup>2</sup> K]

$\lambda_s$ ...prevodnost stene [W/m K]

$l_s$ ... debelina stene [m]

$h_{fn}$ ...koeficient toplotnega prestopa v plasti v notranjosti cevi [W/m<sup>2</sup> K]

$h_n$ ...koeficient toplotnega prestopa na strani brozge [W/m<sup>2</sup> K]



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

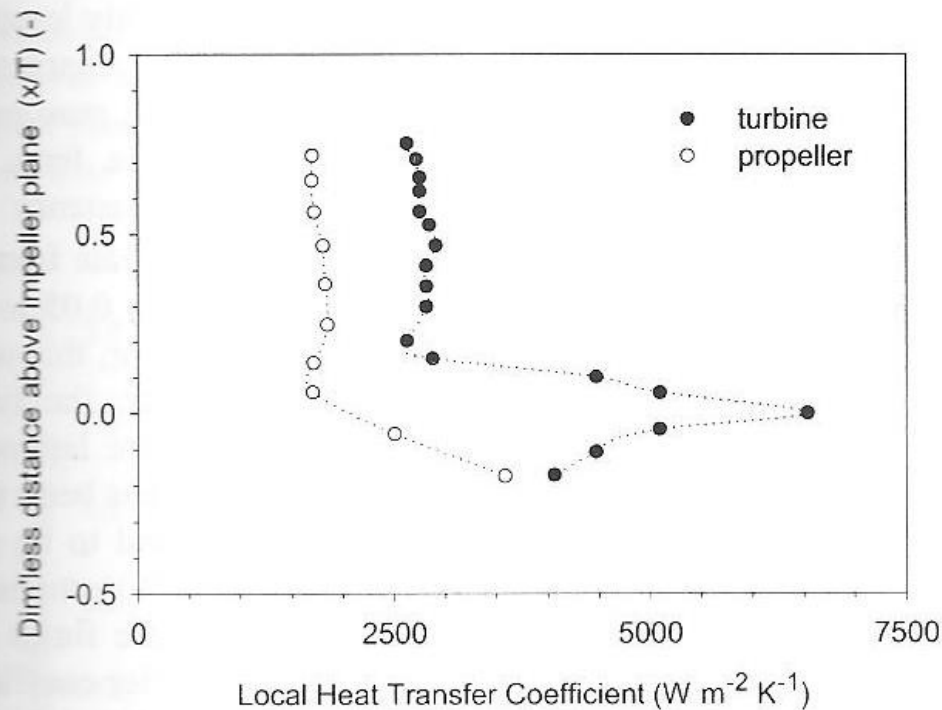
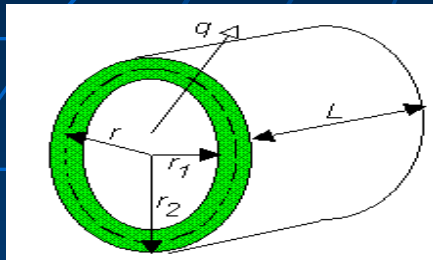


Figure 2. Variation of local heat transfer coefficients with axial position for turbine and propeller impellers,  $D/T = 1/3$ ,  $N = 0.5 s^{-1}$  (Man *et al.*, 1984).



hidrodinamski pogoji  
na obeh straneh cevi

snovne lastnosti obeh  
strujajočih medijev

$\langle U_z \rangle$

debelina stene  
 $r_2/r_1$  in njena toplotna  
prevodnost  $\lambda_s$

# OKVIRNE VREDNOSTI KOEFICIENTOV TOPLOTNEGA PRESTOPA

Pojav	$h$ (W/m <sup>2</sup> K)
Naravna konvekcija, zrak	5-50
Prisilna konvekcija, zrak	25-250
Prisilna konvekcija, voda	250-15.000
Ogrevanje vode, naravna konvekcija	50-1.000
Vretje vode	3.500-45.000
Kondenzacija pare v filmu	5.000-15.000

# NAPOVEDI KOEFICIENTOV TOPLOTNEGA PRESTOPA

$$h_z = 0,72 \cdot \left[ \frac{g \cdot \Delta H_{\text{kond}} \cdot \rho^2 \cdot \lambda^3}{\eta \cdot (T_p - T_s) \cdot d_z} \right]^{0,25}$$

$$\text{Nu} = 0,023 \text{ Re}^{0,8} \text{ Pr}^n$$

segrevanje:  $n = 0,4$

ohlajanje:  $n = 0,3$

$$h_n = \frac{0,023 \cdot \lambda \cdot \text{Re}^{0,8} \cdot \text{Pr}^{0,4}}{d_n} = \frac{0,023 \cdot \lambda \cdot \left( \frac{4 \cdot \Phi_v \cdot \rho}{\pi \cdot d_n \cdot \eta} \right)^{0,8} \cdot \left( \frac{c_p \cdot \eta}{\lambda} \right)^{0,4}}{d_n}$$

# Brezdimenzijska števila

## ■ Reynoldsovo število

$$Re = \frac{\rho v D}{\eta} \quad \text{za cev,}$$

premer cevi

sile vztrajnosti  
sile viskoznosti

$$Re = \frac{\rho N D^2}{\eta} \quad \text{za mešalnik}$$

premer mešala

## ■ Nusseltovo število

$$Nu = \frac{hD}{\lambda}$$

prenos toplote s konvekcijo  
prenos toplote s prevajanjem  
sile viskoznosti

## ■ Prandtlovo število

$$Pr = \frac{c_p \eta}{\lambda}$$

kinematična viskoznost  
toplotna difuzivnost

# Naloga

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

$$c_p \text{ vode} = 4190 \text{ J/kg K} \quad \text{oz.} \quad 75,4 \text{ J/mol K}$$

$$\rho \text{ vode} = 1000 \text{ kg/m}^3$$

Odgovor:  $T = 25 \text{ }^\circ\text{C}$