Sveučilište u Zagrebu
Fakultet kemijskog
inženjerstva i tehnologije

FKITMCMXIX

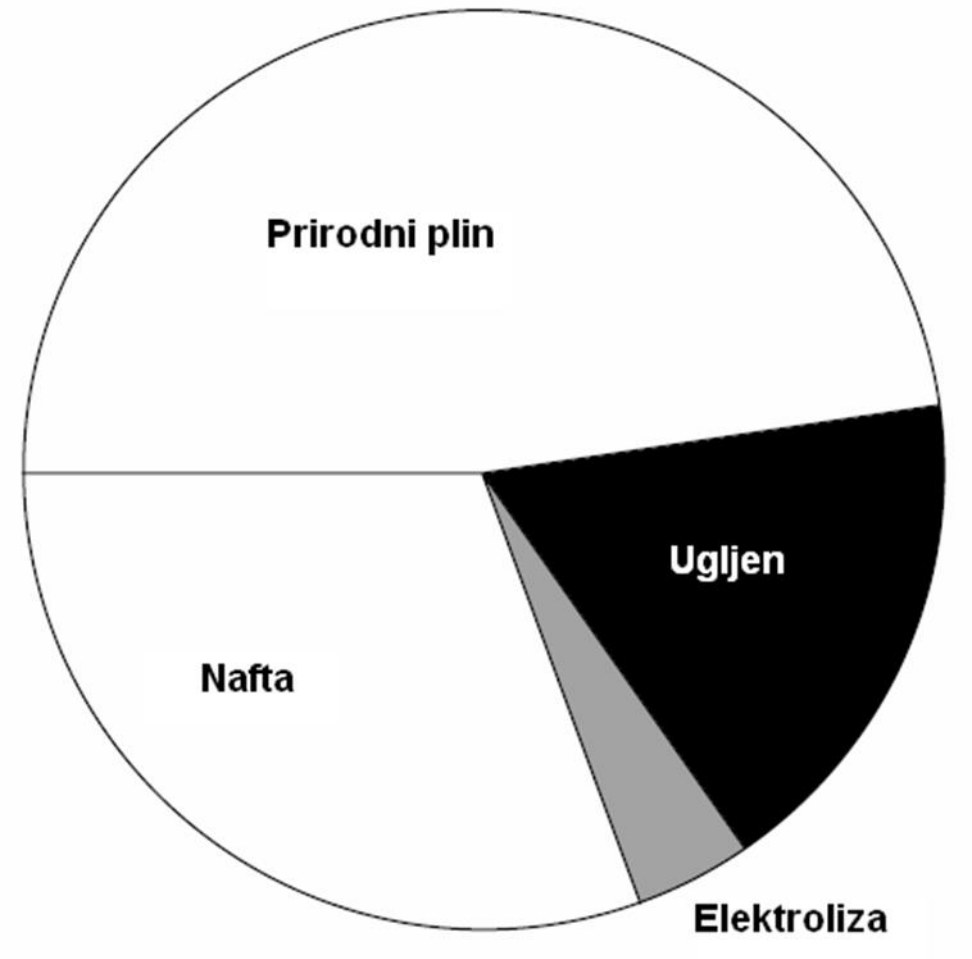
VODIK – PROIZVODNJA

Doc. dr. sc. Fabio Faraguna

Zavod za tehnologiju nafte i petrokemiju / Savska cesta 16
tel. 01- 4597 161 / fabio.faraguna@fkit.hr

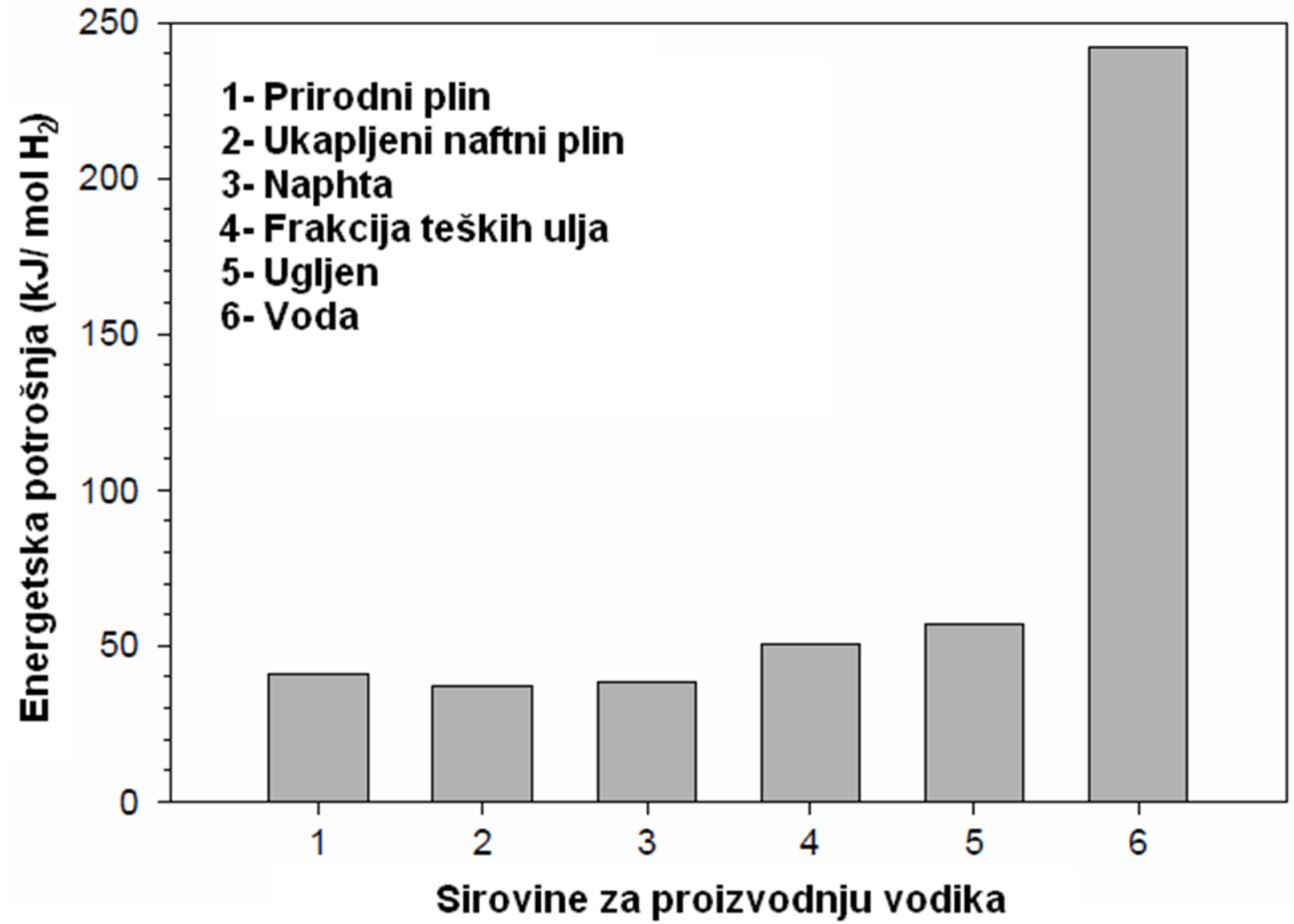
Mogućnosti proizvodnje vodika

Struktura svjetske proizvodnje vodika



Hydrogen Association; Evers, 2008.

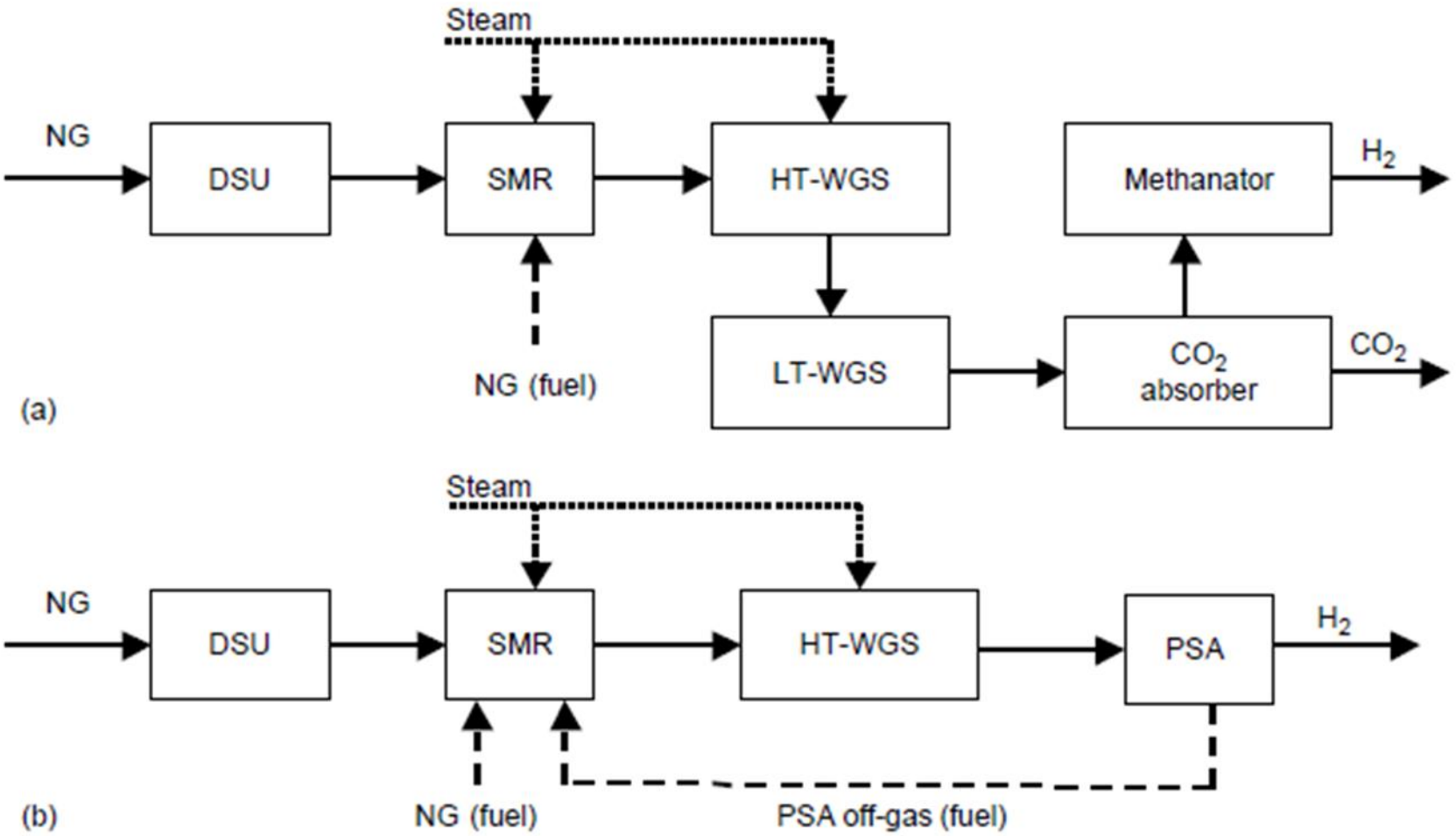
Teorijska potrošnja energije za proizvodnju vodika iz različitih sirovina



Proizvodnja vodika iz ugljikovodika

Maksimalno teoretsko iskorištenje za dobivanje vodika parnim reformiranjem iz različitih sirovina

Shema parnog reformiranja



a) Odvajanje CO_2 pomoću otapala i metanacijom
b) Odvajanje CO_2 tlačno izmjeničnom adsorpcijom

Parno reformiranje

- DSU – postojenje za hidrodesulfurizaciju
  - Tioli, tiofeni, sulfidi, disulfidi…
  - $C_2H_5SH + H_2 \rightarrow C_2H_6 + H_2S$ (primjer!)
  - Co/Mo 290–370 °C
  - $H_2S + ZnO \rightarrow ZnS + H_2O$
  - 340–390 °C

Parno reformiranje

- SMR – parno reformiranje metana
  - $CH_4 + H_2O \rightarrow 3H_2 + CO$
  - Vodena para 2,6 MPa, 500 °C
  - 850–900 °C
  - $2CO \rightarrow C + CO_2$ (nepoželjno)

Parno reformiranje

- HT-WGS
  - $CO + H_2O \rightarrow H_2 + CO_2$
  - 340–360 °C
  - 90–95% Fe_3O_4, 5–10% Cr_2O_3
- LT-WGS
  - $CO + H_2O \rightarrow H_2 + CO_2$
  - 200 -300 °C
  - 90–95% Fe_3O_4, 5–10% Cr_2O_3
  - 15–30% CuO, 30–60% ZnO, Al_2O_3

Zadaci – proizvodnja vodika

Specifične entalpije i entropije komponenata i slobodna Gibbsova energija reakcije

$$H_i = H_i^\circ + \int_{298}^{T} C_{Pi} \cdot dT$$

$$\Delta H = \left(\sum_i n_i \cdot H_i \right)_{izlaz} - \left(\sum_i n_i \cdot H_i \right)_{ulaz}$$

$$S_i = S_i^\circ + \int_{298}^{T} \frac{C_{Pi}}{T} \cdot dT$$

$$\Delta S = \left(\sum_i n_i \cdot S_i \right)_{izlaz} - \left(\sum_i n_i \cdot S_i \right)_{ulaz}$$

$$\Delta G = \Delta H - T \cdot \Delta S$$

$$C_p = f(T) = a + b \cdot T + c \cdot T^2$$

	M/(g mol^{-1})	$\Delta_f H^\ominus$/(kJ mol^{-1})	$\Delta_f G^\ominus$/(kJ mol^{-1})	$S_m^\ominus$/(J K^{-1} mol^{-1})†	$C_{p,m}^\ominus$/(J K^{-1} mol^{-1})
CO_2(g)	44.040	−393.51	−394.36	213.74	37.11
CH_4(g), methane	16.04	−74.81	−50.72	186.26	35.31
C(s) (graphite)	12.011	0	0	5.740	8.527
C(s) (diamond)	12.011	+1.895	+2.900	2.377	6.113
C(g)	12.011	+716.68	+671.26	158.10	20.838
H_2(g)	2.016	0	0	130.684	28.824
H(g)	1.008	+217.97	+203.25	114.71	20.784
H_2O(s)	18.015			37.99	
H_2O(l)	18.015	−285.83	−237.13	69.91	75.291
H_2O(g)	18.015	−241.82	−228.57	188.83	33.58
O_2(g)	31.999	0	0	205.138	29.355
O(g)	15.999	+249.17	+231.73	161.06	21.912
CO(g)	28.011	−110.53	−137.17	197.67	29.14

1 kWh = 3600 kJ


FKITMCMXIX


UNIVERSITAS STUDIORUM ZAGRABIENSIS
MDCLXIX

1. ZADATAK

- Izračunaj potrebne mase reaktanata i potrebnu energiju-uloženi rad za dobivanje 1 kg vodika reakcijom parnog reformiranja pri standardnim uvjetima (298 K).

- $CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$

1. ZADATAK

- $CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$
- $n(H_2) = \frac{m(H_2)}{M(H_2)} = 496\ \text{mol}$
- $3n(H_2) = n(CH_4) = n(H_2O)$
- $m(H_2O) = n(H_2O) \times M(H_2O) = 2{,}978\ \text{kg}$
- $m(CH_4) = n(CH_4) \times M(CH_4) = 2{,}652\ \text{kg}$

1. ZADATAK

- $CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$
- $\Delta H = \left(3 \times H_{H_2} + H_{CO}\right) - \left(H_{CH_4} + H_{H_2O}\right) = 206{,}1\ \text{kJ/mol}$
- $\Delta S = \left(3 \times S_{H_2} + S_{CO}\right) - \left(S_{CH_4} + S_{H_2O}\right) = 214{,}6\ \text{J/K mol}$
- $\Delta G = \Delta H - T\Delta S = 142{,}15\ \text{kJ/mol}$
- $W_{\text{po 1kg}} = \frac{1}{3}\Delta G \times n\,(H_2) = 23502\ \text{kJ} = 6{,}528\ \text{kWh}$

2. ZADATAK

- Izračunaj potrebne mase reaktanata i potrebnu energiju-uloženi rad za dobivanje 1 kg vodika reakcijom parnog reformiranja i WGS jedinice pri standardnim uvjetima (298 K).
- $CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$
- $CO(g) + H_2O(g) \rightarrow H_2(g) + CO_2(g)$
- $CH_4(g) + 2H_2O(g) \rightarrow 4H_2(g) + CO_2(g)$

2. ZADATAK

- $CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$
- $CO(g) + H_2O(g) \rightarrow H_2(g) + CO_2(g)$
- $CH_4(g) + 2H_2O(g) \rightarrow 4H_2(g) + CO_2(g)$
- $n(H_2) = \frac{m(H_2)}{M(H_2)} = 496\ \text{mol}$
- $4n(H_2) = n(CH_4) = 2n(H_2O)$
- $m(H_2O) = n(H_2O) \times M(H_2O) = 4{,}468\ \text{kg}$
- $m(CH_4) = n(CH_4) \times M(CH_4) = 1{,}989\ \text{kg}$

2. ZADATAK

- $CH_4(g) + 2H_2O(g) \rightarrow 4H_2(g) + CO_2(g)$
- $\Delta H = \left(4 \times H_{H_2} + H_{CO_2}\right) - \left(H_{CH_4} + 2 \times H_{H_2O}\right) =$

  $= 164{,}94\ \text{kJ/mol}$
- $\Delta S = \left(4 \times S_{H_2} + S_{CO_2}\right) - \left(S_{CH_4} + 2 \times S_{H_2O}\right) =$

  $= 172{,}6\ \text{J/K mol}$
- $\Delta G = \Delta H - T\Delta S = 113{,}51\ \text{kJ/mol}$
- $W_{\text{po 1kg}} = \frac{1}{4}\Delta G \times n\,(H_2) = 14074\ \text{kJ} = 3{,}910\ \text{kWh}$

3. ZADATAK

- Izračunaj potrebne mase reaktanata i potrebnu energiju-uloženi rad za dobivanje 1 kg vodika procesom katalitičke parcijalne oksidacije pri standardnim uvjetima (298 K).

- $CH_4(g) + 1/2O_2(g) \rightarrow CO(g) + 2H_2(g)$

3. ZADATAK

- $CH_4(g) + 1/2O_2(g) \rightarrow CO(g) + 2H_2(g)$
- $n(H_2) = \frac{m(H_2)}{M(H_2)} = 496\ \text{mol}$
- $2n(H_2) = n(CH_4) = 1/2n(O_2)$
- $m(O_2) = n(O_2) \times M(O_2) = 3{,}966\ \text{kg}$
- $m(CH_4) = n(CH_4) \times M(CH_4) = 3{,}976\ \text{kg}$

3. ZADATAK

- $CH_4(g) + 1/2O_2(g) \rightarrow CO(g) + 2H_2(g)$
- $\Delta H = \left(2 \times H_{H_2} + H_{CO} \right) - \left(H_{CH_4} + \frac{1}{2} \times H_{O_2} \right) =$
- $= -35{,}7 \text{ kJ/mol}$
- $\Delta S = \left(2 \times S_{H_2} + S_{CO} \right) - \left(S_{CH_4} + \frac{1}{2} \times S_{O_2} \right) =$
- $= 170{,}2 \text{ J/K mol}$
- $\Delta G = \Delta H - T\Delta S = -86{,}42 \text{ kJ/mol}$
- $W_{\text{po 1kg}} = \frac{1}{2} \Delta G \times n(H_2) = -21423 \text{ kJ} = -5{,}953 \text{ kWh}$

4. ZADATAK

- Izračunaj potrebne mase reaktanata i potrebnu energiju-uloženi rad za dobivanje 1 kg vodika reakcijom reformiranja metana ugljičnim dioksidom pri standardnim uvjetima (298 K).
- $CH_4(g) + CO_2(g) \rightarrow 2CO(g) + 2H_2(g)$

4. ZADATAK

- $CH_4(g) + CO_2(g) \rightarrow 2CO(g) + 2H_2(g)$
- $n(H_2) = \frac{m(H_2)}{M(H_2)} = 496\ \text{mol}$
- $2n(H_2) = n(CH_4) = n(CO_2)$
- $m(CO_2) = n(CO_2) \times M(CO_2) = 10{,}912\ \text{kg}$
- $m(CH_4) = n(CH_4) \times M(CH_4) = 3{,}976\ \text{kg}$

4. ZADATAK

- $CH_4(g) + CO_2(g) \rightarrow 2CO(g) + 2H_2(g)$
- $\Delta H = \left(2 \times H_{H_2} + 2 \times H_{CO}\right) - \left(H_{CH_4} + H_{CO_2}\right) =$
- $= 248{,}26\ \text{kJ/mol}$
- $\Delta S = \left(2 \times S_{H_2} + 2 \times S_{CO}\right) - \left(S_{CH_4} + S_{CO_2}\right) =$
- $= 256{,}6\ \text{J/K mol}$
- $\Delta G = \Delta H - T\Delta S = 171{,}79\ \text{kJ/mol}$
- $W_{\text{po 1kg}} = \frac{1}{2}\Delta G \times n\,(H_2) = 40285\ \text{kJ} = 11{,}190\ \text{kWh}$

5. ZADATAK

- Izračunaj potrebne mase reaktanata i potrebnu energiju-uloženi rad za dobivanje 1 kg vodika reakcijom termalne dekompozicije prirodnog plina pri standardnim uvjetima (298 K).
- $CH_4(g) \rightarrow C(s) + 2H_2(g)$

5. ZADATAK

- $\mathrm{CH_4(g) \rightarrow C(s) + 2H_2(g)}$
- $n(\mathrm{H_2}) = \frac{m(\mathrm{H_2})}{M(\mathrm{H_2})} = 496\ \mathrm{mol}$
- $2n(H_2) = n(\mathrm{CH_4})$
- $m(CH_4) = n(\mathrm{CH_4}) \times M(\mathrm{CH_4}) = 3{,}976\ \mathrm{kg}$

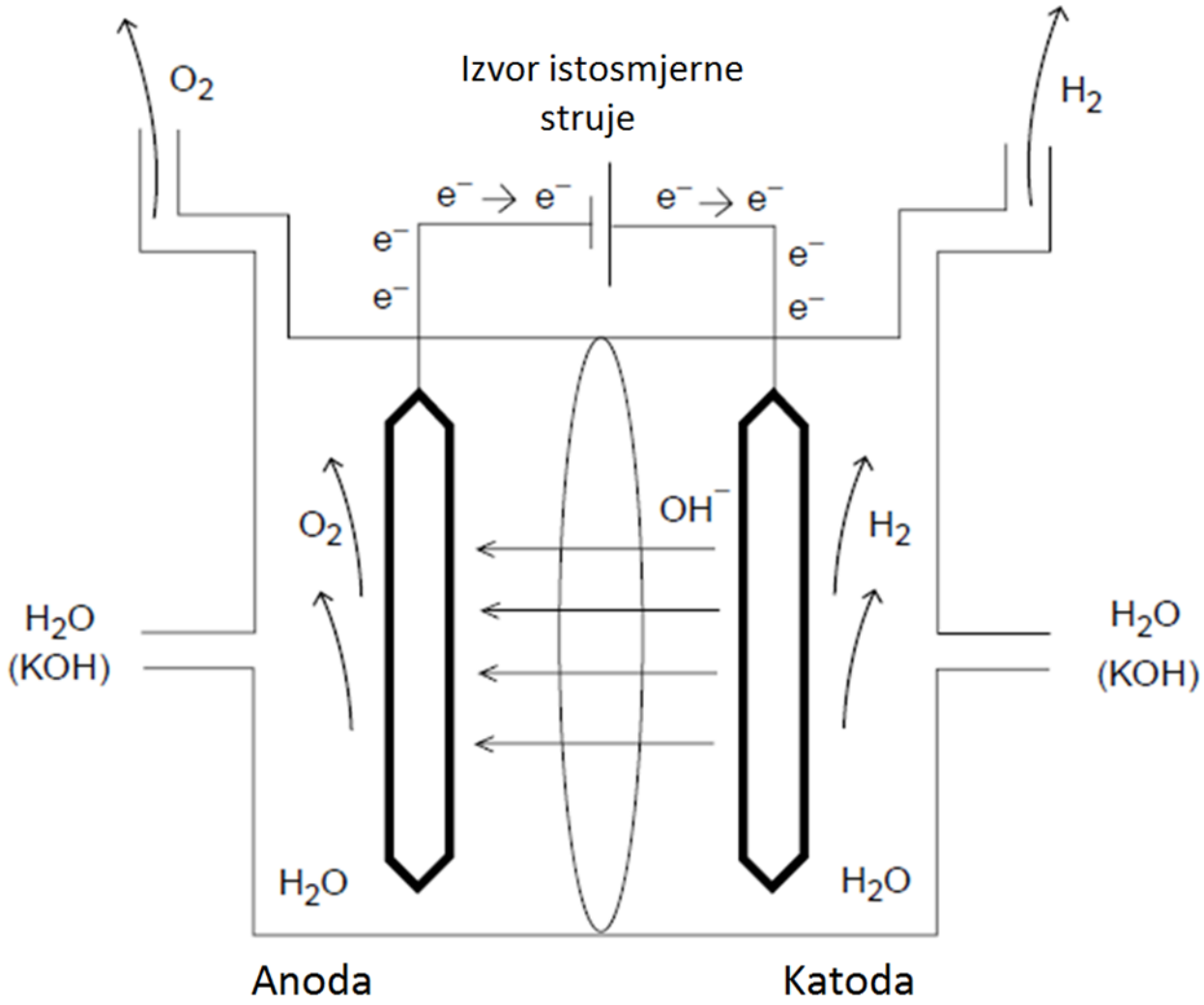
5. ZADATAK

- $CH_4(g) \rightarrow C(s) + 2H_2(g)$
- $\Delta H = \left(2 \times H_{H_2} + H_C\right) - \left(H_{CH_4}\right) = 74{,}8\ \text{kJ/mol}$
- $\Delta S = \left(2 \times S_{H_2} + S_C\right) - \left(S_{CH_4}\right) = 80{,}9\ \text{J/K mol}$
- $\Delta G = \Delta H - T\Delta S = 50{,}7\ \text{kJ/mol}$
- $W_{\text{po } 1kg} = \frac{1}{2}\Delta G \times n\,(H_2) = 12574\ \text{kJ} = 3{,}931\ \text{kWh}$

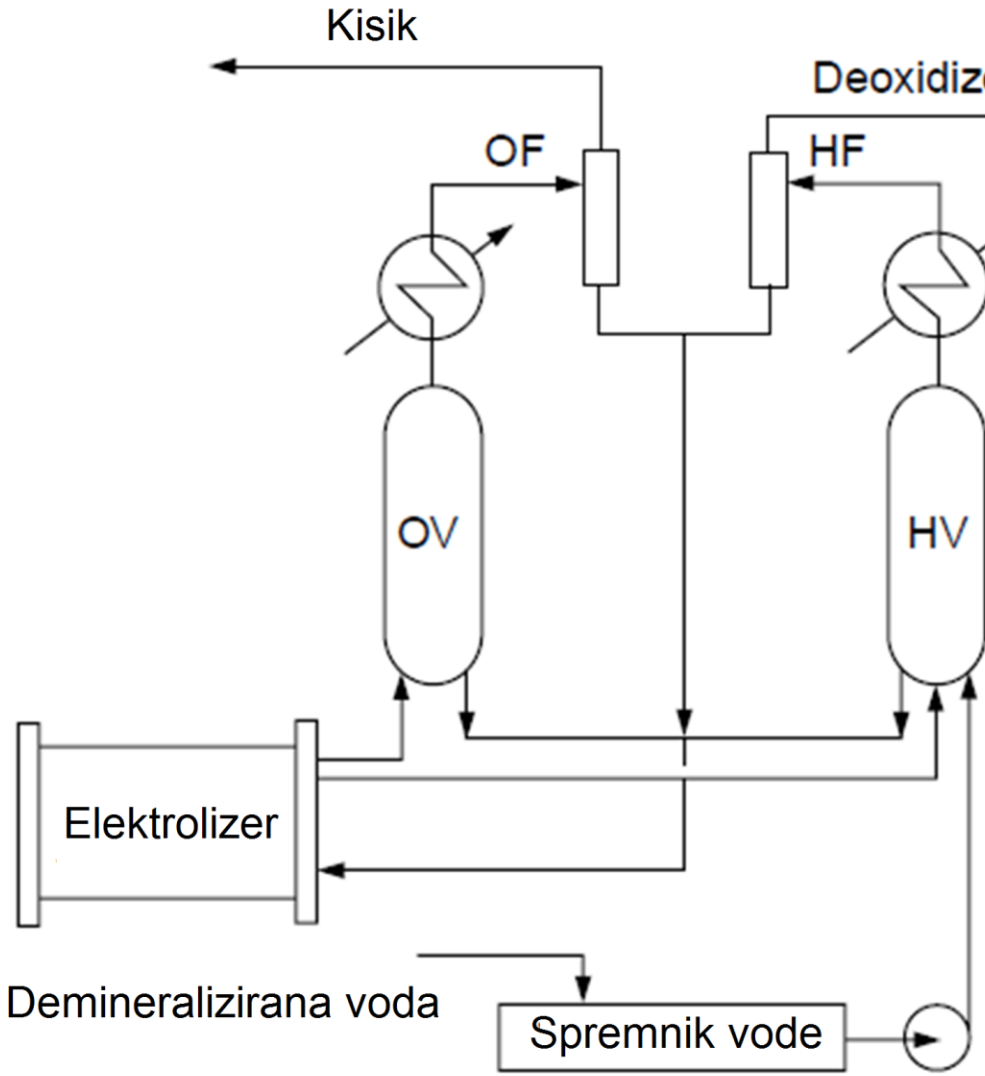
6. ZADATAK

- Izračunaj potrebne mase reaktanata i potrebnu energiju-uloženi rad za dobivanje 1 kg vodika elektrolizom iz vode pri standardnim uvjetima (298 K).

Shema elektrolizera za elektrolizu vode



Shema sustava za elektrolizu vode



HF/OF - razdvajanje vodik/elektrolit ili kisika/elektrolit smjese filtriranjem

HV/OV - hladenje smjese vodik/elektrolit kisik/elektrolit

6. ZADATAK

- A(+): $H_2O \rightarrow 2H^+ + 1/2O_2 + 2e^-$
- K(-): $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
- $H_2O(l) \rightarrow H_2(g) + 1/2O_2(g)$
- $n(H_2) = \frac{m(H_2)}{M(H_2)} = 496\ \text{mol}$
- $n(H_2) = n(H_2O)$
- $m(H_2O) = n(H_2O) \times M(H_2O) = 8{,}933\ \text{kg}$

6. ZADATAK

- $H_2O(l) \rightarrow H_2(g) + 1/2O_2(g)$
- $\Delta H = \left(H_{H_2} + \frac{1}{2} H_{O_2} \right) - \left(H_{H_2O} \right) = 285{,}83 \text{ kJ/mol}$
- $\Delta S = \left(S_{H_2} + \frac{1}{2} S_{O_2} \right) - \left(S_{H_2O} \right) = 163{,}6 \text{ J/K mol}$
- $\Delta G = \Delta H - T\Delta S = 237{,}06 \text{ kJ/mol}$
- $W_{\text{po 1kg}} = \Delta G \times n\,(H_2) = 117584 \text{ kJ} = 32{,}662 \text{ kWh}$