



UNIVERSITY OF TARTU



Biovesiniku roll Eesti rohepöörde elluviimisel - energiatehnoloogiakompleksi moderniseerimisel

Enn Lust ja kaastöötajad

Füüsikalise keemia professor, Tartu Ülikool

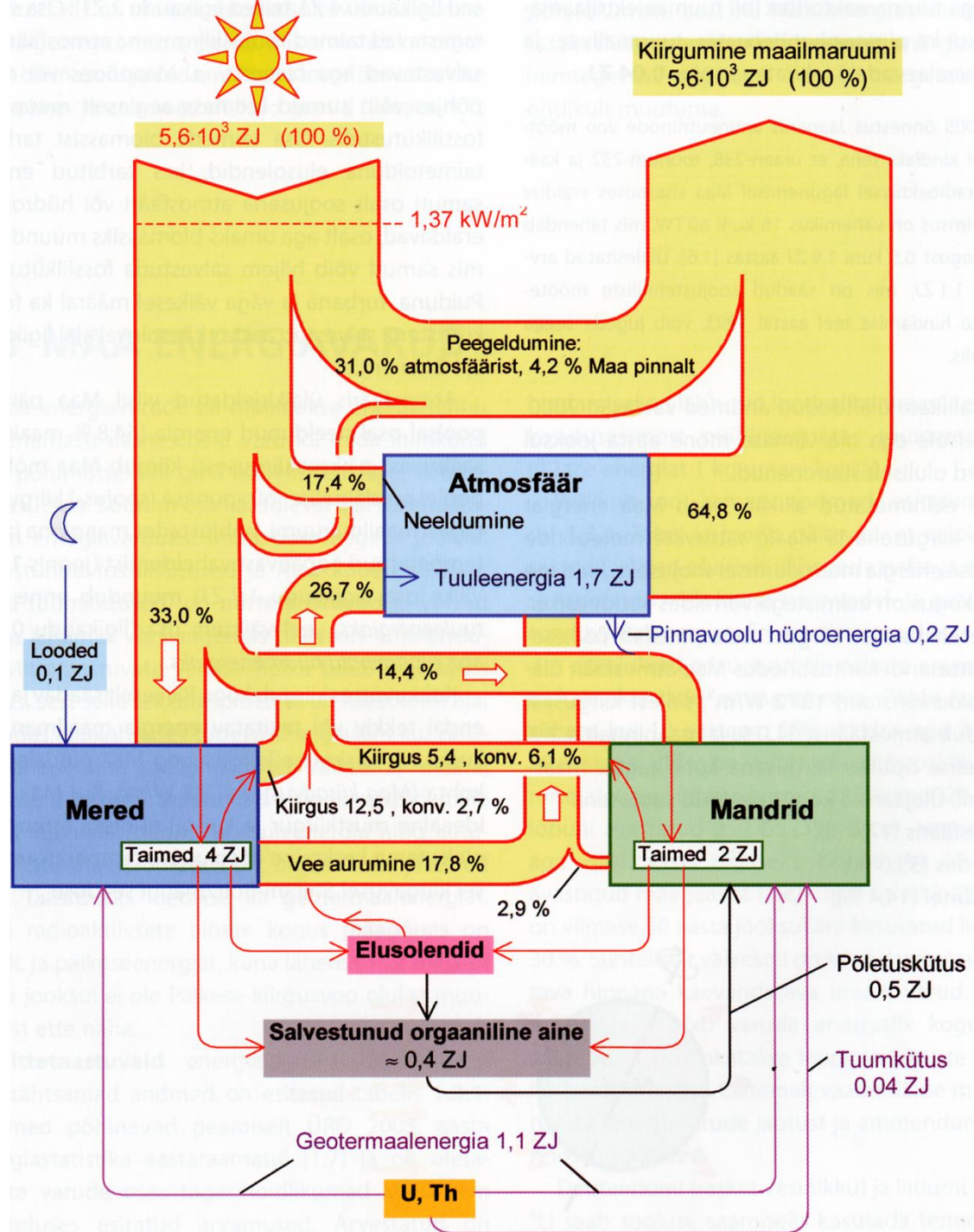
Eesti Teaduste Akadeemia liige

EASAC Energeetika arenduskomitee liige

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Keemia instituut, Tartu Ülikool

Tartu, 07.03. 2023



Maa energiabilanss

Inimkond kasutab/käitleb momendil ainult 0.44 ZJ energiat, kusjuures Maale langeb 5600 ZJ energiat, seega kasutame ainult 0.01% Maale langevast energiast.

T. Risthein, Sissejuhatus energiatehnikasse, Kirj. Elektriajam, Tallinn, 2007.

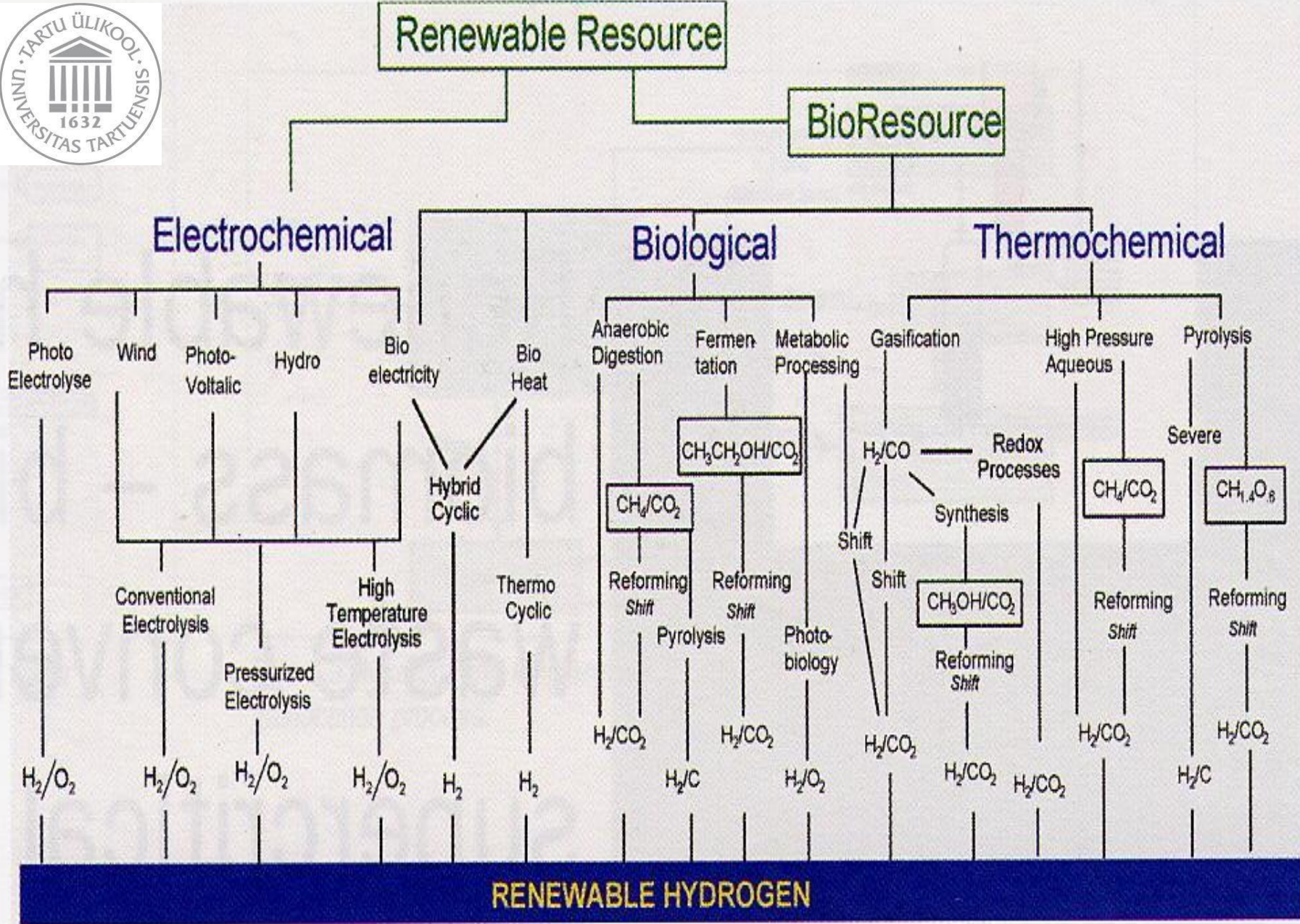


Figure 2: Overview of possible pathways to produce renewable hydrogen.

- Vesinikku saab toota vähemalt **15-20 erineval** meetodil;
- vesinik on kõige suurema kaalulise energiatihedusega energiakandja;
 - **H_2 LHV on 33.6 KWh /kg;**
 - 3 kWh /Nm³;**
 - 119.7 +/-0.5 MJ/kg** (LHV kasutatakse, kui pole otsene põlemine)
- **HHV:**
 - 39.39kWh/kg;**
 - 3.54kWh/Nm³**
- **Energiasaldused:**
 - **1 dm³ H₂ = 0,27 dm³ bensiini;**
 - **1kg H₂ = 3.3 kg bensiini**

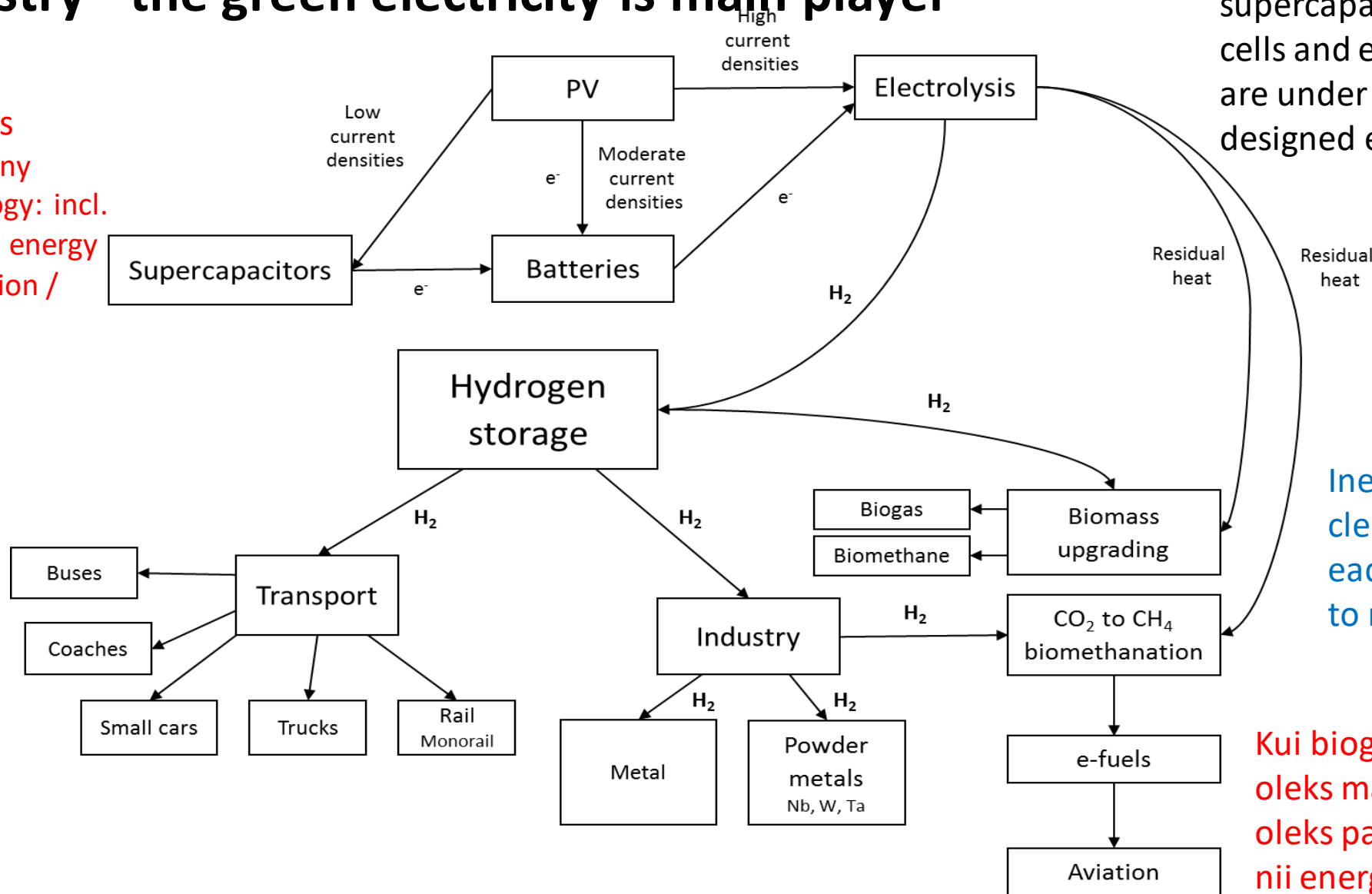


Possibilities for modernisation of Estonian Industry - the green electricity is main player

Hydrogen technology is generating changes in many fields of classical technology: incl.

- pulsating PV and wind energy generation / stabilisation / storage;
- transport;
- classical chemical and biochemical industry;
- metallurgy;
- central heating etc.

Combination of different heat pumps by PV and wind electricity for local and central heating



Novel Na-ion batteries, supercapacitors, fuel cells and electrolyzers are under tests in designed energy complex

Inevitable for cleaning/upgrading of biogas to methane

Kui biogaasi hind oleks madalam, siis oleks palju võimlusi nii energeetikas kui ka keemiatööstuses

CO₂, NO_x, VOC, SO_x, NP clean transport Silmet (Molycorp)



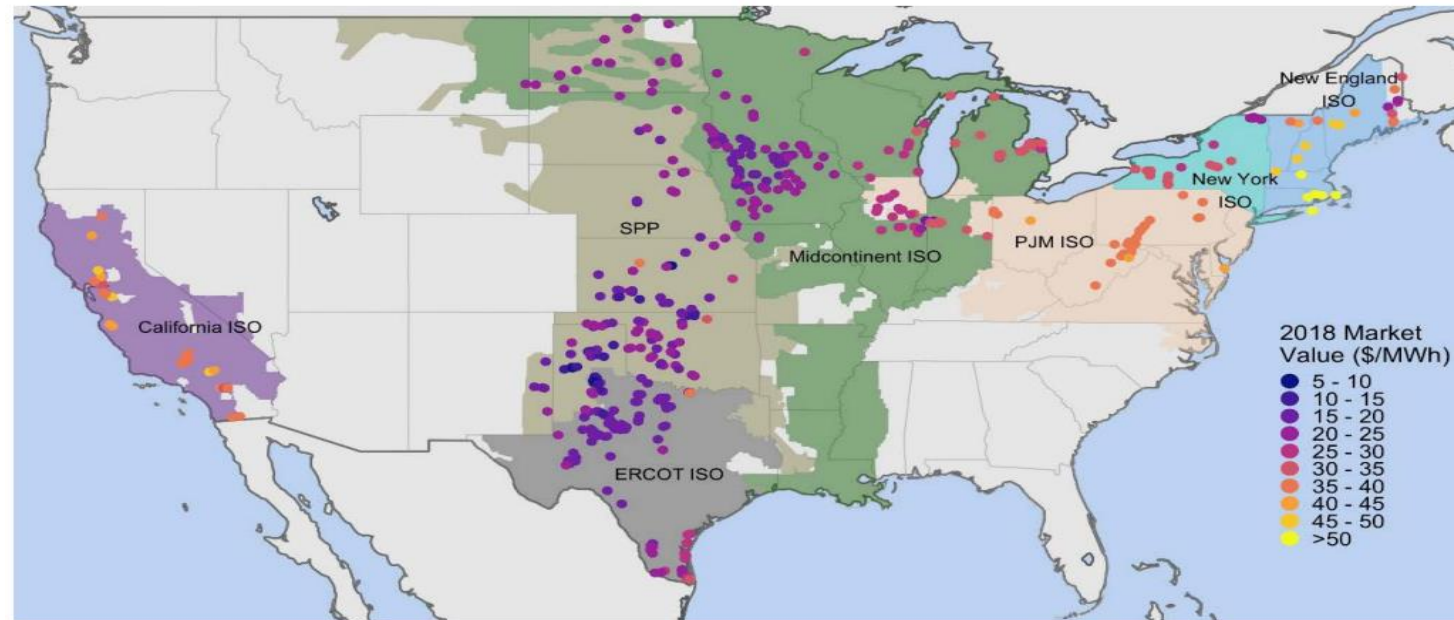
Biogaasi ökonoomseks käitlemiseks on vaja odavat elektrit!

Odavat elektrit saame meretuulest, PV päikesest jne, vajalik omavaheline koostootmine ja salvestamine

- **1kg H₂ = 0.35 \$ (1kg electrolysis needs 50 kWh electricity - 1kg H₂ small car 120-180 km ; 6-9 times more efficient than gasoline car;**
- **12 m bus hydrogen consumption: 6.3 -7.5 kg H₂ per 100 km travel - the same bus needs 40 dm³ diesel and 80-120 kg CO₂ is forming !!!**

Wind park position and technical characteristics (height of turbine central position, power, etc.) must be well optimised taking into account the geographical and meteorological conditions (laminar flow of wind)

The Wholesale Market Value of Wind Energy in 2018 Varied by Region: Lowest in ERCOT, Highest in ISO-NE



- Market value estimates in 2018 at project level span a wide range, from a low of \$7/MWh to a high of \$72/MWh, with a median value of \$22/MWh

U.S. DEPARTMENT OF ENERGY OFFICE OF ENERGY EFFICIENCY & RENEWABLE ENERGY

- **1kg H₂ = 3.685 dm³ gasoline (for equivalent run gasolin price = 0.1 \$).**
- **Small car ... 3.685 dm₃ only 45-70 km / 40 dm³ diesel = 55 €, but 6.4 kg H₂ = max 40 € (6.3 kg = 2 USD in USA wind park (fully optimised))**



Vesinikutanklad maailmas

Vesiniku tootmise, salvestamise, transportimise, jaotamise ja kasutamise tehnoloogiad on olemas. Võiksime toota ka biogaasist, kuid hind liiga kõrge, senini!

6 põhilist piirkonda:

- Euroopa,
- Jaapan,
- Korea,
- Hiina,
- USA idarannik
- USA läänerannik

kokku juba 59 riigis!

USA Biden-Harrise plaan:

- 350 tuhat km H₂highway-sid;
- iga 120-150 km tagant H₂ tankla!
- Patareide laadimisjaam iga 60-120 km järel!





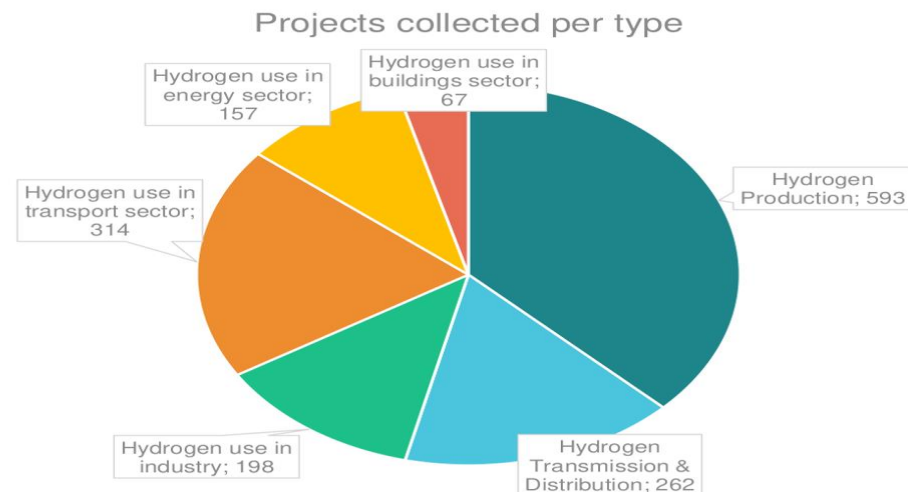
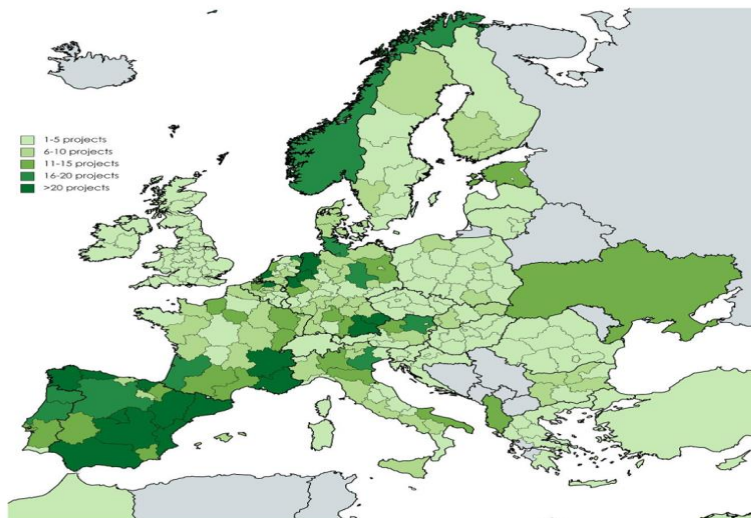
Eestise 8
vesinikutanklat 2030.
aasta lõpuks. See on
lõplik kohustus EL ees.



Projekt tHrive

- Eesti valiti “Project tHrive” piirkondade esimesse rühma
- Eelmisel aastal esitati Euroopa Puhta Vesiniku Liidu (ECH2A) projektikorjel üle 1000 projekti.
- Nagu kaardilt näha, olid Eesti ettevõtted väga aktiivsed, esitades projekte tootmisest tarbimiseni.
- Seda toetas lisaks Eesti **vesiniku IPCEI** (Important Projects of Common European Interest) initsiatiiv. **21 projekti**.
- Rahastatakse 3 projekti: **Elcogen OÜ/OY; Stargate Hydrogen OÜ ja Skeleton OÜ**.
- **Utilitas OÜ H₂ taksode projekt**, 49,1 miljonit eurot vesiniku tervikahela projektide arendamiseks jne.
- Lisaks: Eesti Vesiniku Org, Botnia H2 backbone, Hansa Hydrogen Hub, Läänemere Sadamate H2 projekt, Tallinna + Tartu Lennujaama osalus üle-Euroopalises H2 projektis; **Asi nagu liigub!**

Overview of all eligible projects collected*

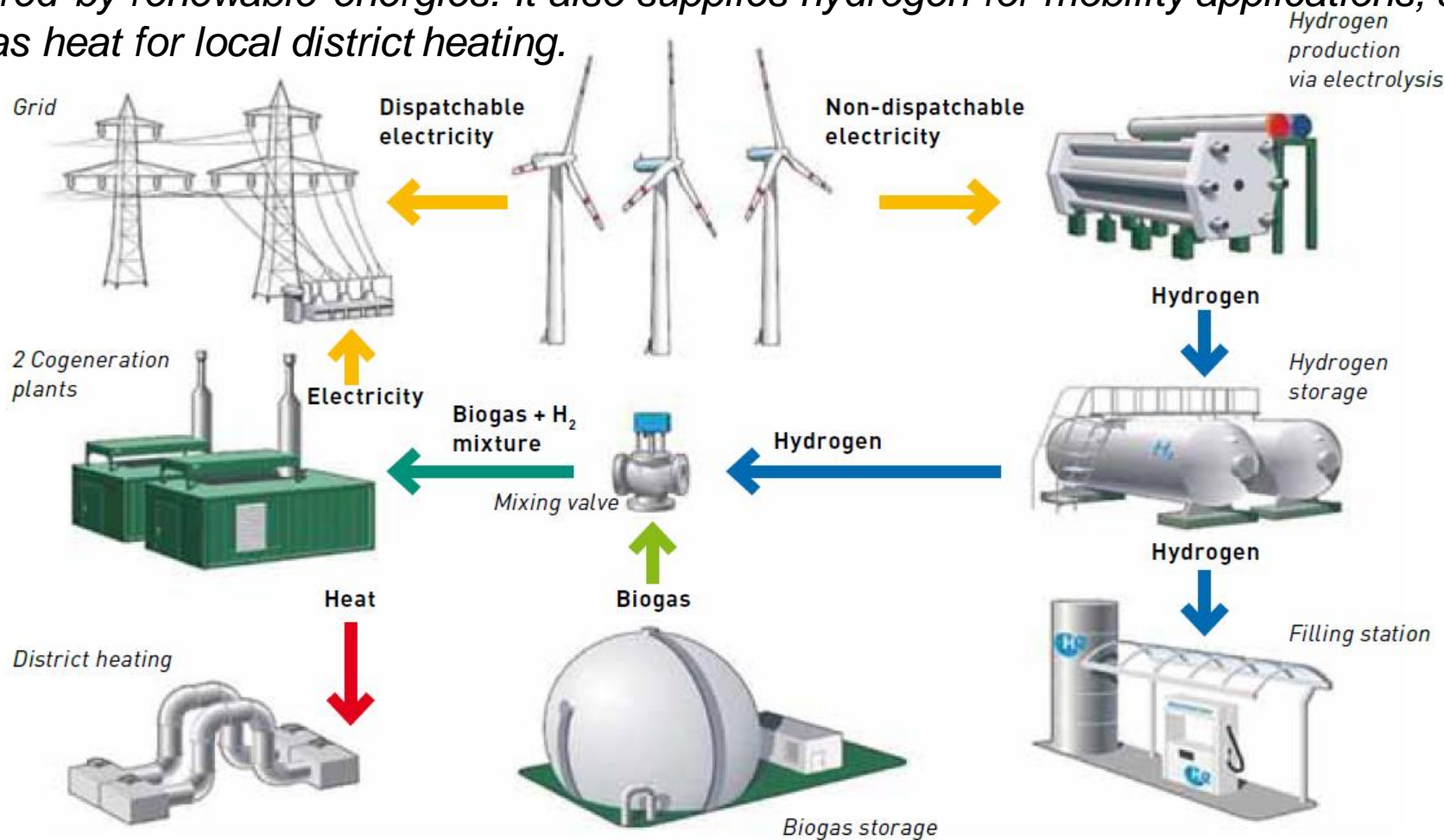


* Actual project location by NUTS2 region; a project covering more than one region appears more than once



ENERTRAG: Hybrid power plant

This innovative system allows the operation of a stabilized electricity grid entirely powered by renewable energies. It also supplies hydrogen for mobility applications, as well as heat for local district heating.



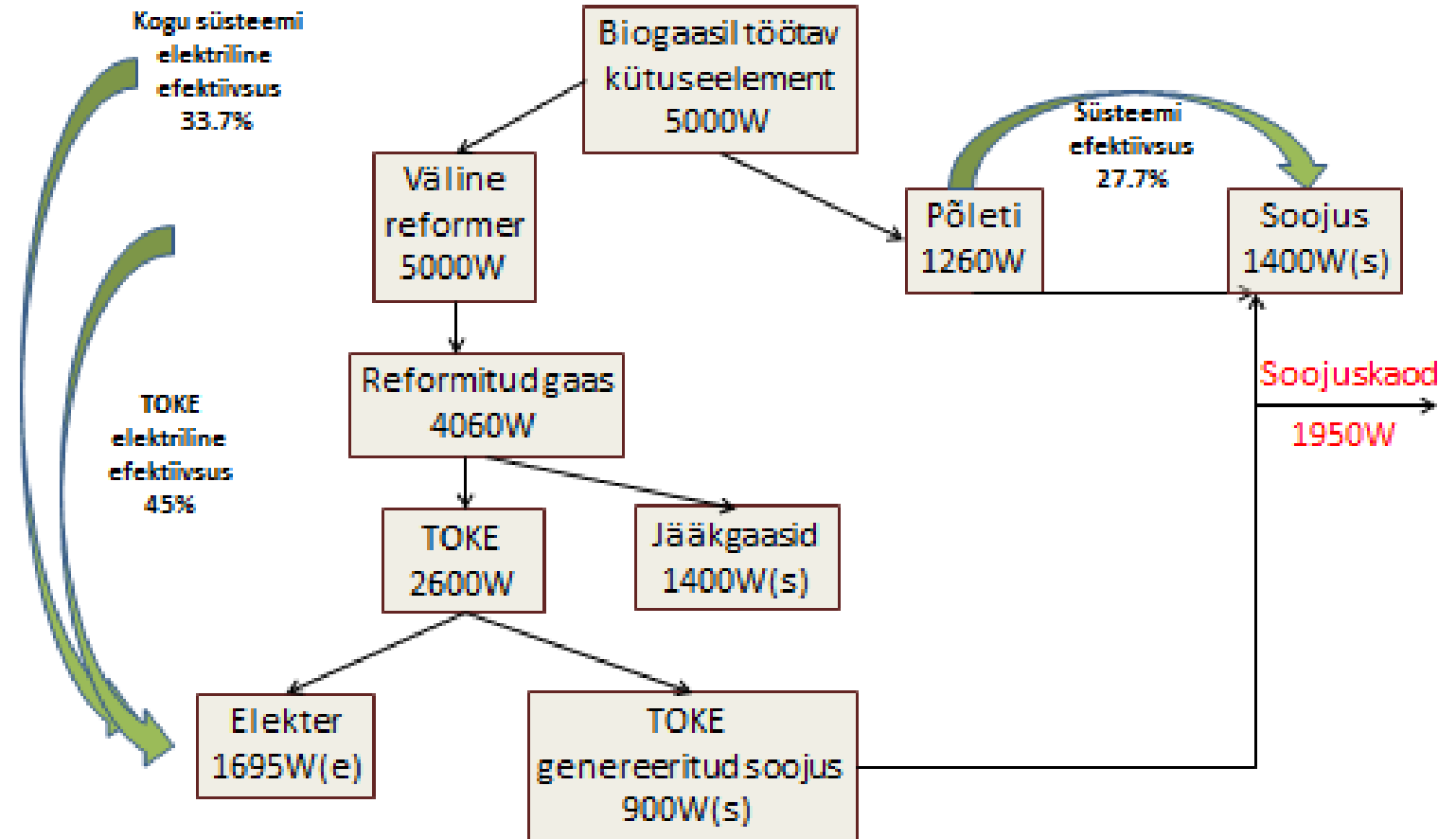
Biogaas on kombineeritav CO₂-vaba elektri ja sellest toodetud vesinikuga, kasutatav nii elektri kui soojuste koostootmiseks, CO₂ tuleb koguda ja võtta kasutusele.

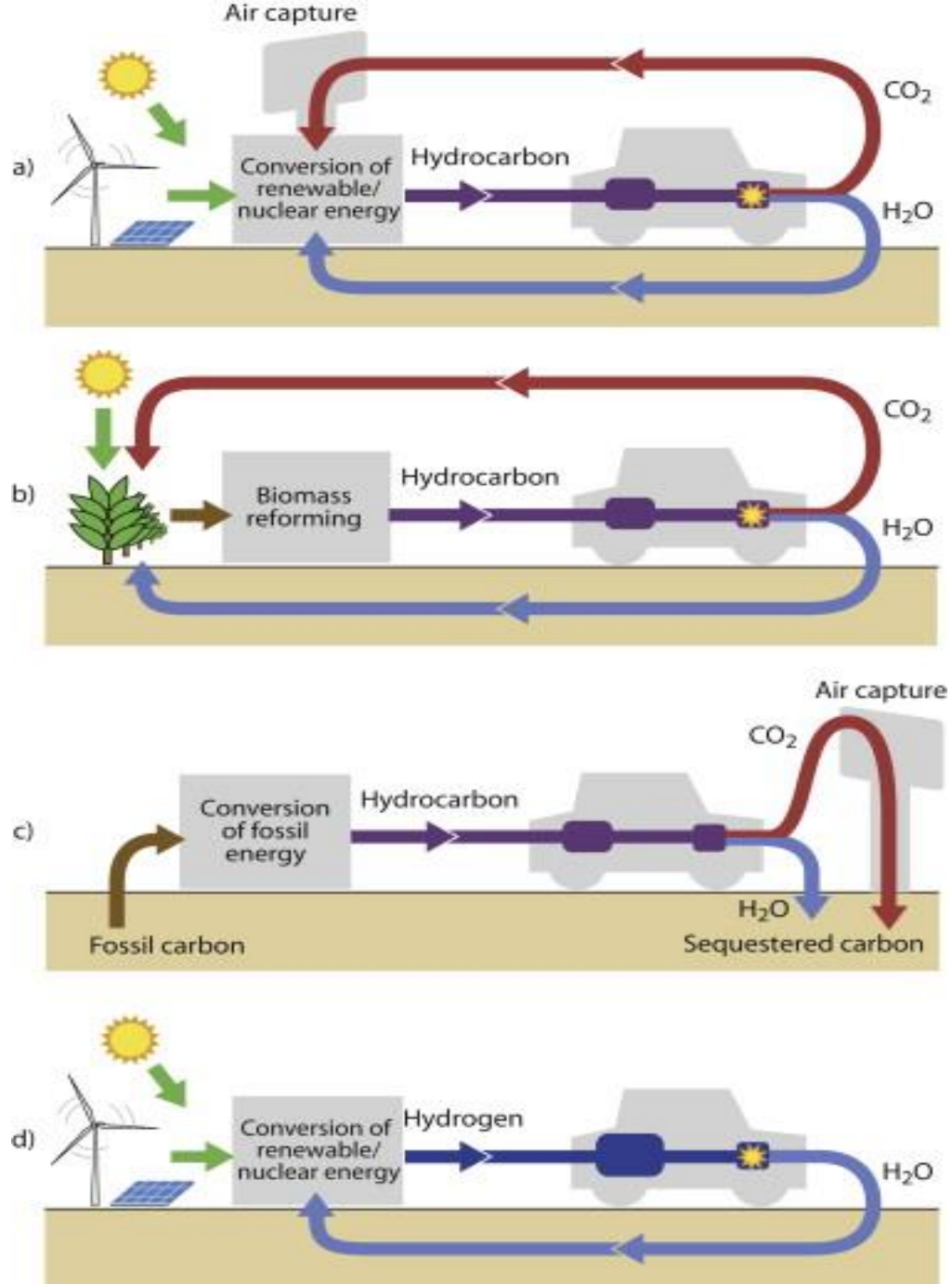
The prototype installation comprises 3 wind turbines (2 MW / unit) connected to the grid, but also to an electrolyser (gas production: 120 Nm³/h of hydrogen, 60 Nm³/h of oxygen; op. pressure: 15–20 mbar (atm.)), a compressor (nominal flow: 2 x 60 Nm³/h of hydrogen, output pressure: 43 bar (abs.)), a stationary hydrogen storage (3 pressure vessels, storage capacity: 1.350 kg H₂ at 43 bar (abs.)), a biogas production unit with a nominal production rate of about 300 m³/h, and a storage capacity of ca. 2.600 m³; and two CHP (combined-heat-and-power) units (max. yearly production capacity: 2.776 MWh of electricity each, and ca. 2.250 MWh heat). This thermal output is enough to heat about 80 single-family houses.



Biogaasil töötava TOKE (SOFC) põhimõtteline skeem koos tänapäeva tehnoloogilisi võimalusi arvestavate efektiivsustega. (s) tähistab soojust.

- Üks võimalus on kasutada kõrgtemperatuurseid kütuseelemente:
- Biogaasi otsest põletamist tuleb vältida:
- Muundada läbi kütuseelementide ja võimalusel CO₂ koguda ja toota kemikaale.





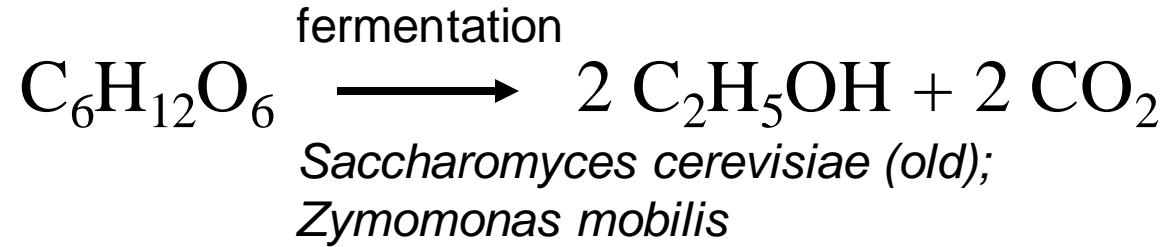
Comparison of carbon-neutral fuel cycles for hydrocarbons produced using

- (a) renewable energy (shown as solar and wind energy),
- (b) biomass,
- (c) fossil fuel.
- (d) Hydrogen produced by solar/wind energy is also shown for comparison with (a). Whereas the renewable energy based cycles (a, b, and d) are considered materially closed, the fossil fuel based cycle (b) is carbon-neutral but the carbon is stored in an oxidized form.

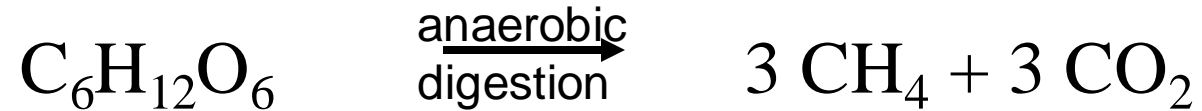


Glükoos kui kütus, lihtsamad näited

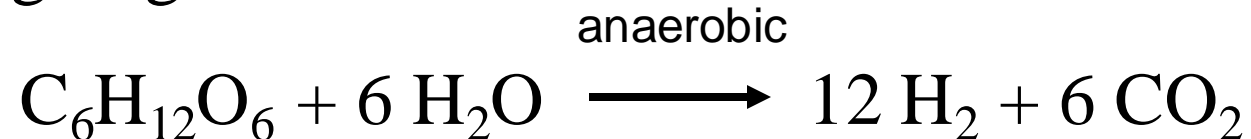
Bio-ethanol:



Biogas:



Hydrogen gas:



Microbial fuel cell:



Rabaey, K., G. Lissens, and W. Verstraete (2005) Microbial fuel cells: performances and perspectives. *In* P. N. Lens, P. Westermann, M. Haberbauer, and A. Moreno (ed.), *Biofuels for fuel cells: biomass fermentation towards usage in fuel cells*.



Table 20.1. Energetic yields of conventional biofuels
(after Lay *et al.* 1999, Logan 2004)

| • <i>Methane</i> | • <i>Bio-ethanol</i> | • <i>Hydrogen</i> |
|--|---|---|
| <i>Theoretical yield</i> (g/g glucose) 0.27 | <i>Theoretical yield</i> (g/g glucose) 0.51 | <i>Theoretical yield</i> (g/g glucose) 0.13 |
| <i>Yield in practice</i> (g/g glucose) 0.14-0.22 | <i>Yield in practice</i> (g/g glucose) 0.3-0.46 | <i>Yield in practice</i> (g/g glucose) 0.02-0.04 Only! |
| <i>Energetic yield</i> (kJ/g glucose) 7.8-12.2 | <i>Energetic yield</i> (kJ/g glucose) 8-12.3 | <i>Energetic yield</i> (kJ/g glucose) 2.4-4.9 Only! |

Rabaey, K., G. Lissens, and W. Verstraete (2005) Microbial fuel cells: performances and perspectives. *In* P. N. Lens, P. Westermann, M. Haberbauer, and A. Moreno (ed.), *Biofuels for fuel cells: biomass fermentation towards usage in fuel cells.*

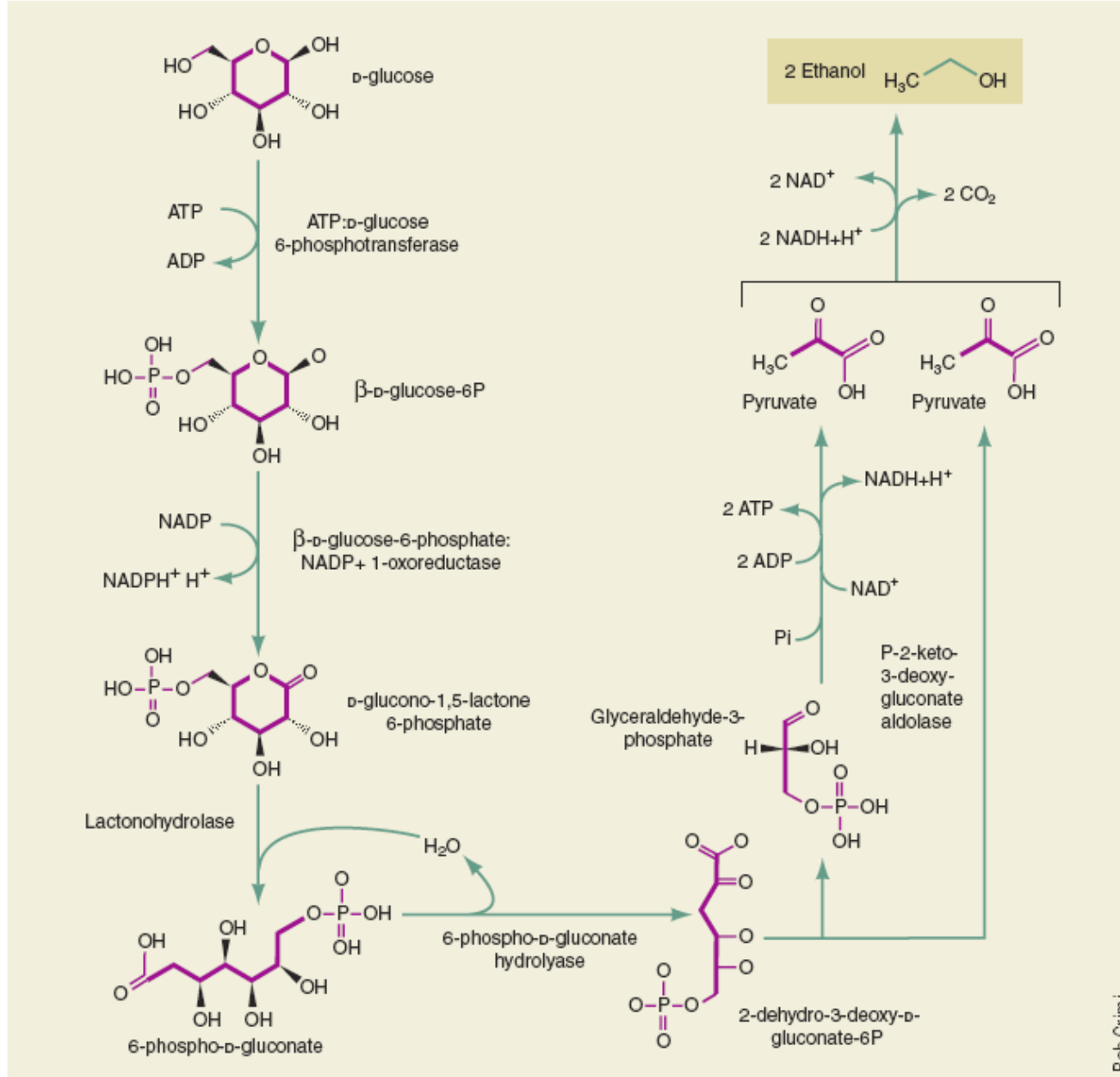


Figure 1 Ethanol fermentation in *Zymomonas mobilis*. The conversion of glucose into two moles of ethanol nets 1 mole of ATP. This pathway is commonly used by aerobic pseudomonads for the metabolism of glucose, but *Z. mobilis* makes use of it uniquely for anaerobic metabolism. The low ATP yield results in a low cell mass and the potential for higher ethanol yields.

Väga efektiivne on toota etanooli, mis võiks olla nii

- keemiatööstuse tooraine,
- toiduaine tööstuse lähteaine
- kui ka energiakandja.

Thomas W Jeffries, Ethanol fermentation on the move, Nature Biotechnology 23, 40-41 (01 Jan 2005) News and Views

Biogaasi tootmine läbi anaeroobse kääritamise

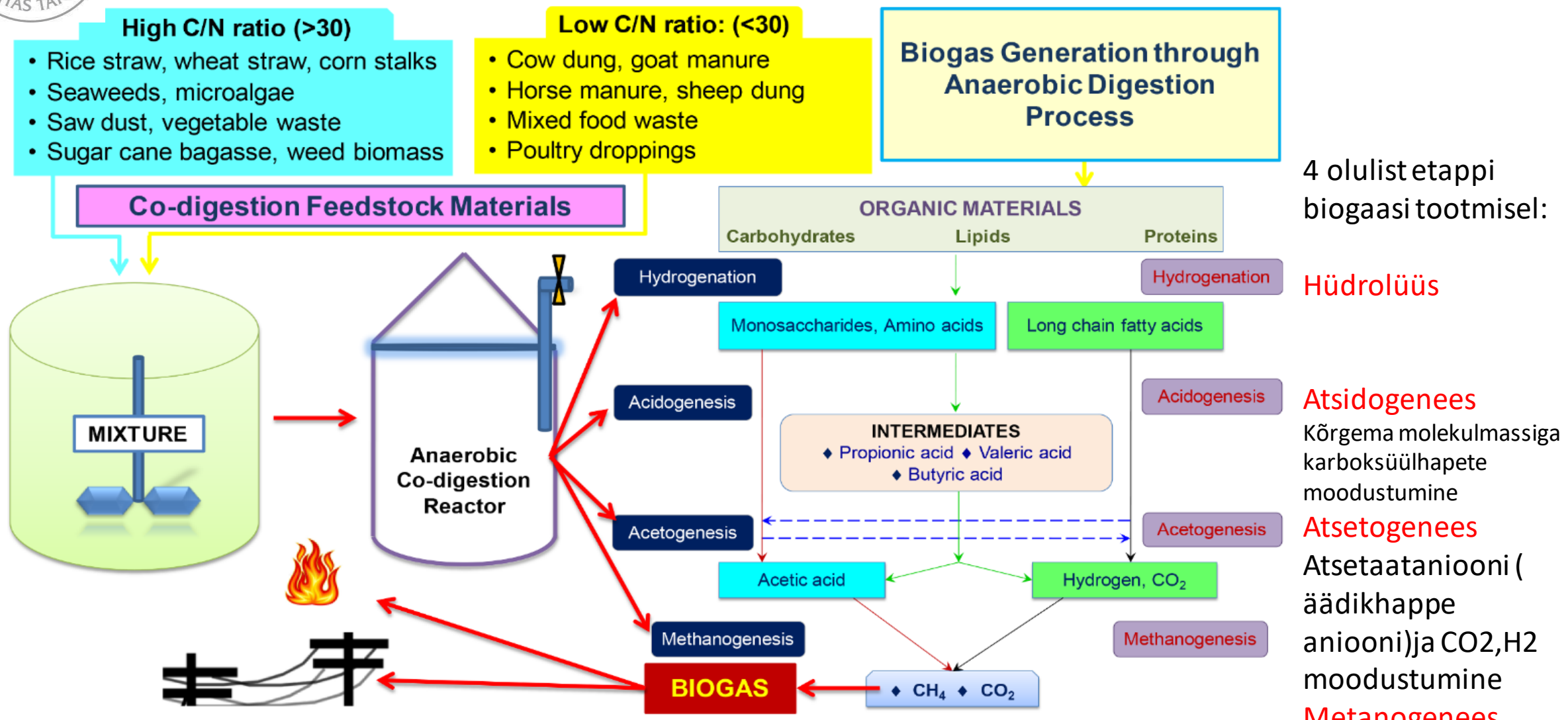


Fig. 1. Different substrates for anaerobic co-digestion process and biogas generation.

Erinevatest lähteainetest saab väga erinevaid vaheühendeid kuid sarnaseid lõppprodukte

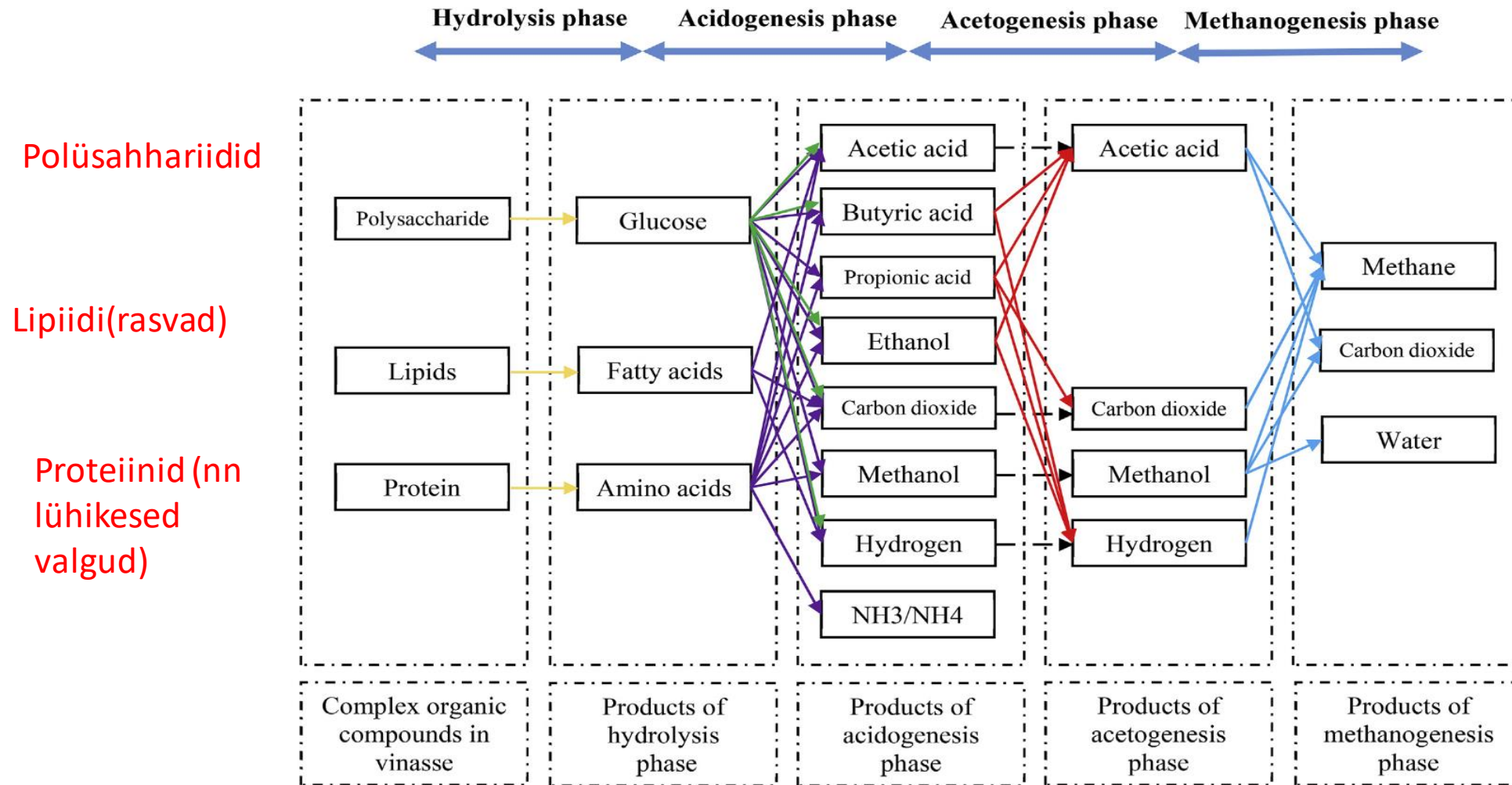


Fig. 4. Simultaneous production of biogas from the activity of anaerobic bacteria [102].



Kuidas toimub biogaasi biokeemiline tootmine/süntees?

Anaeroobsed bakterid lagundavad biomassi 4 astmes (tuntud ka kui anaeroobne kääritamine):

- I etapis ehk hüdrogenisatsiooni (tuntud ka kui hydrolysis (hüdrolüüsi)) etapis lagundatakse (hüdrolüüsitakse) lipiidid, proteiinid, süsivesikud ja suhkrud väiksemateks biomolekulideks anaeroobsetes tingimustes mikrobioloogilise seguga nagu **Bacillus, Clostridium, Erwinia, Streptomyces** jt.
- II acidification (alkoholide, hapete) etapis toimub bakterite osalusel (Lactobacillus, Streptococcus, Salmonella jt) happeid tekitavate (acidogenic) bakterite vahendusel **alkoholide ja pikema ahelaga kaboksüülhapete moodustamine**.
- III acetogenesis (äädikhape) etapis toimub bakterite **Acetobacterium, Eubacterium, Thermosyntrophia** jt happeid moodustavate bakterite osalusel **äädikhape, CO₂ ja H₂ moodustumine**.
- IV methanogenesis etapis toimub anaeroobne lagundamine (digastation), mille tulemusena moodustub **biogaas**. IV etapis osalevad **Methanococcus ja Methanobus archaea**, mis sünteesivad **äädikhapest CO₂ ja vesinikust lõpuks metaani**. Osa CO₂ ja H₂ ning H₂O jääb metaaniks muundamata ja sageli on biogaasi koostis **55-70% CH₄, 35-40% CO₂, kuni 5% H₂O, 1-2% H₂, NH₃, lisanditena H₂S jt väävlit sisaldavad ühendid, silaanid jne**.

Biogaasi koostis sõltub väga palju sellest, milline on lähtesegu biokeemiline koostis. Kasutatavad on kõik bioloogilise päritoluga segud, nagu puude ja toidu jäänused, marjade ja puuviljade jäägid (koored, kivid), uriin ja sõnnik, õled (põhk), rohi, pilliroog, munitsipaalreovesi, loomade jäänused jne.

Ka lignotselluloos (LC) on hea biogaasi tootmise tooraine.

Biogaas vajab tavaliselt enne kasutamist kaheastmelist puhastamist: esmane nn biokeemiline ja teine tavaliselt füüsikaline (kas adsorptsioon söega) või keemiline CO₂ jääkide, H₂S ja teiste väävli- ja lämmastikühendite või silaanide keemiline sidumine, ka vee eraldamine enne, kui gaasi saab loodusliku gaasi trassi suunata.

Kasutatavad ka vesipuhastus või selexol (dimetüüleeter + polüetüleenglükooli segu) meetod, erinevad separaatormembraanid ja **Pressure Swing Adsorption (PSA/VSA) st. surve all adsorbeerimise** meetodid, külmutamismeetodid, tseoliitide ja modifitseeritud tseoliitide kasutamine, nitroosamiinid H₂S sidumiseks (kui palju H₂S biogaasis).

Nanoosakeste roll biogaasi tootmisel lignotselluloosist: katalüsaatorid

- Nanokatalüsaatorite kasutamine võimaldab tõsta reaktsioonide kulgemise aktiivset pindala (kuna tegemist on pindadel toimuvate reaktsioonidega)
- Samas suureneb massiüleande kiirus ja väheneb massiülekanne teepikkus ja seega reaktsioonitsoonis kontsentratsioon kasvab.
- Katalüsaatori pinna kättesaadavus.

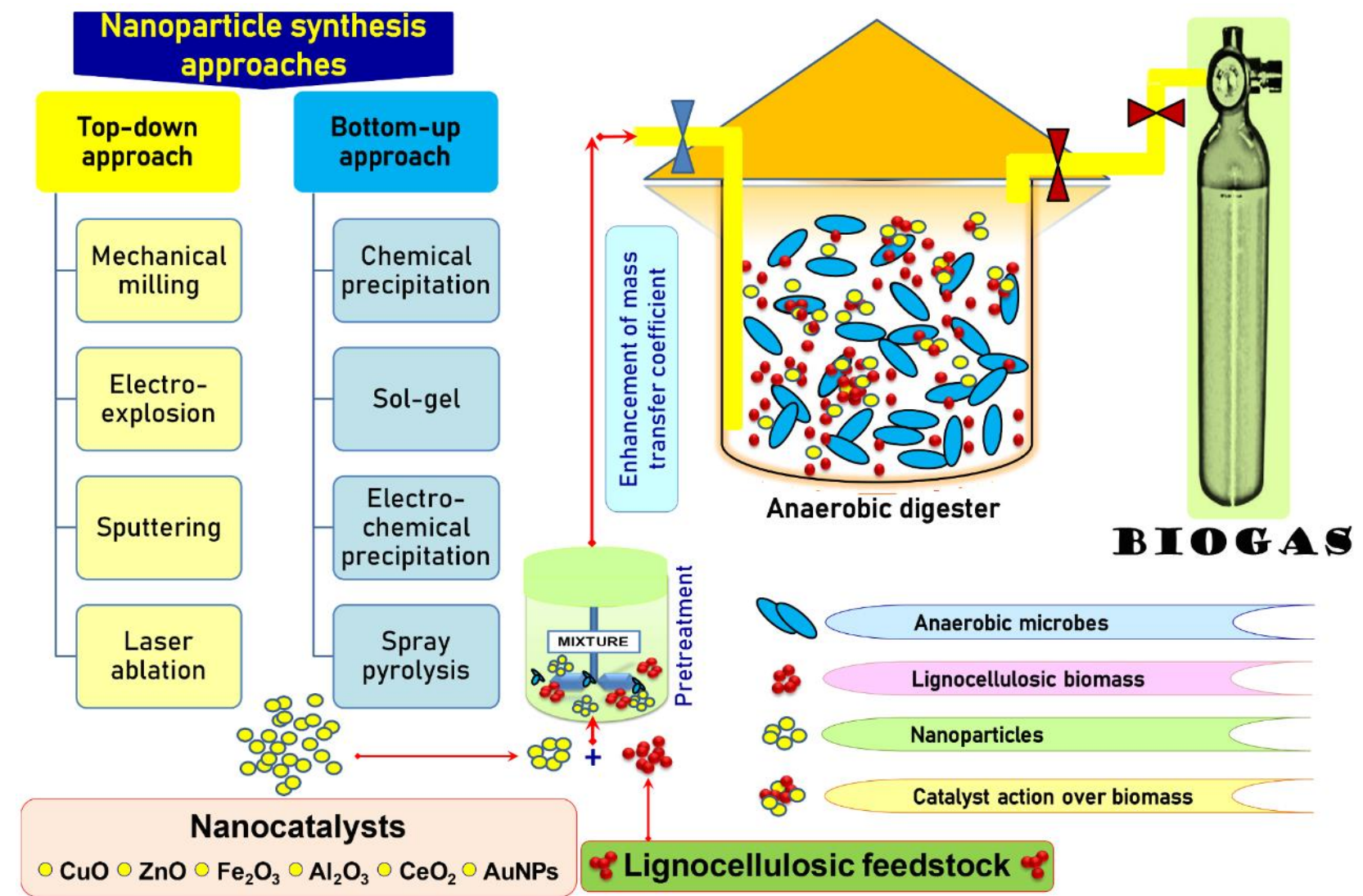


Fig. 2. The pathway of nanocatalyst mediated lignocellulosic biomass conversion into biogas.



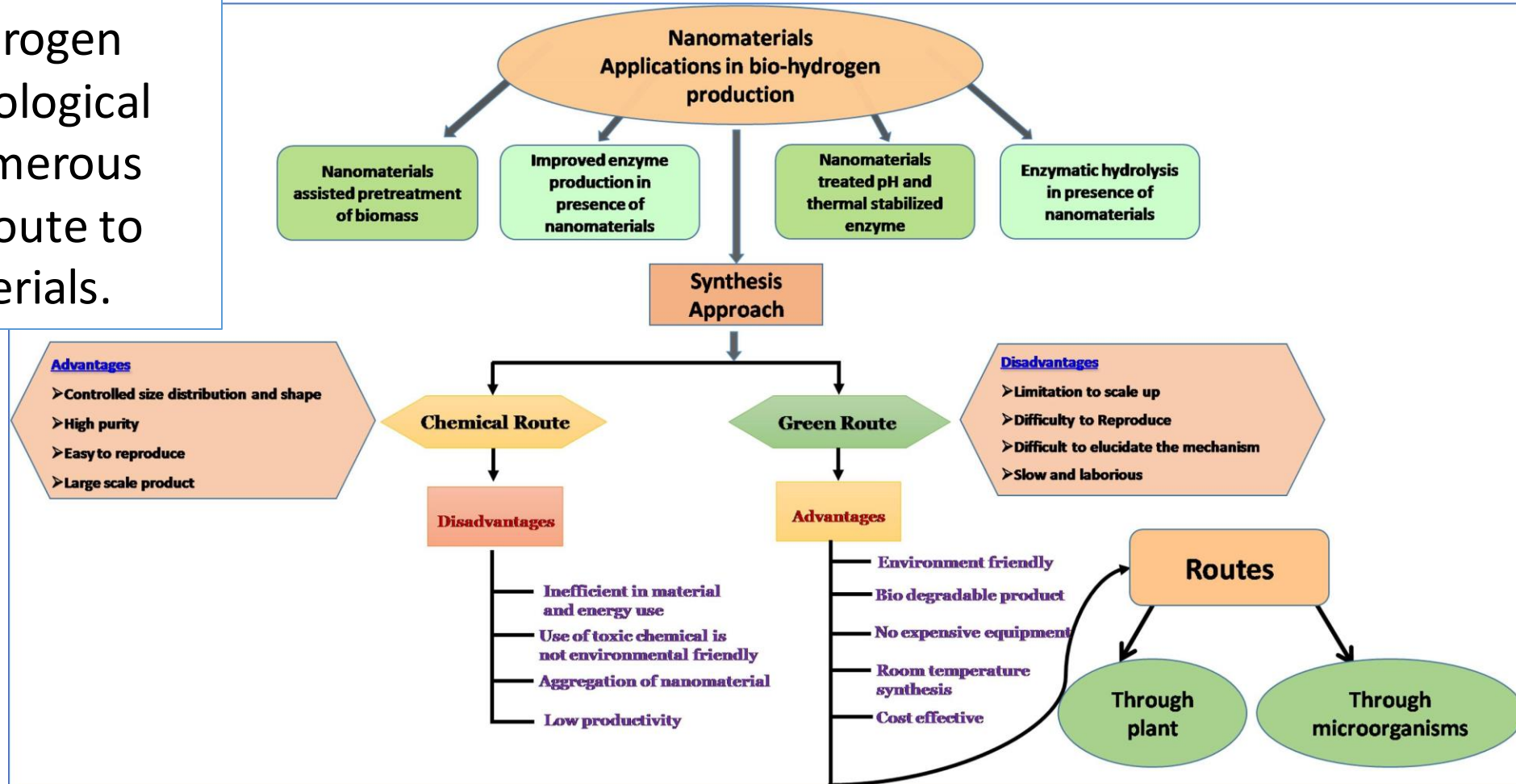
Biogaasi (biometaani) lagundamine

- Biogaasi (biometaani) võib lagundada nn elektrolüüsi (plasmolüüsi) meetodil: tegija **Graforce (üliuudne meetod, detailid esitatakse 7. või 8. märtsil 2023 rahvusvahelisel konverentsil)**
- CH₄ elektrolüüs (plasmolüüs) toodab kõrgel temperatuuril vesinikku: $\text{CH}_4 = \text{C} + 2\text{H}_2$.
 - 20 MW tehas lagundab 70,000 metric ton* LNG või biogaasi H₂ (15,55m ton) ja C(pulber) (54,44 metric ton), jättes tootmata 200,000 metric ton CO₂.
 - CH₄ plasmolüüsil energia kulu 4 korda väiksem kui vee elektrolüüsil (st sama koguse vesiniku tootmisel!!!) (1kg H₂ tootmiseks kulub 12-15 kWh elektrit!)
 - Kui tõsi, siis ühe kg H₂ tootmine (operation cost) maksab: 12x 5 senti = 60 USA senti!!!!!! Või 15 x 10 senti = 1,5USD! No odav ikkagi! Määrav on elektri hind!
 - Kui see on tõsi, siis on üks lahendusvõimalus jälle juures.

*tons = metric tons × 1.102311

Nanomaterjalide mõju keemilisele ja biokeemilisele vesiniku tootmise tsüklile: nn roheline tootmismeetodi eelised

Applications of nanomaterials at different steps of hydrogen production through biological routes, along with numerous advantages of green route to synthesize nanomaterials.





Vesiniku tootmine biomassi gasifitseerimisega H_2 -ks koos CO_2 kogumisega

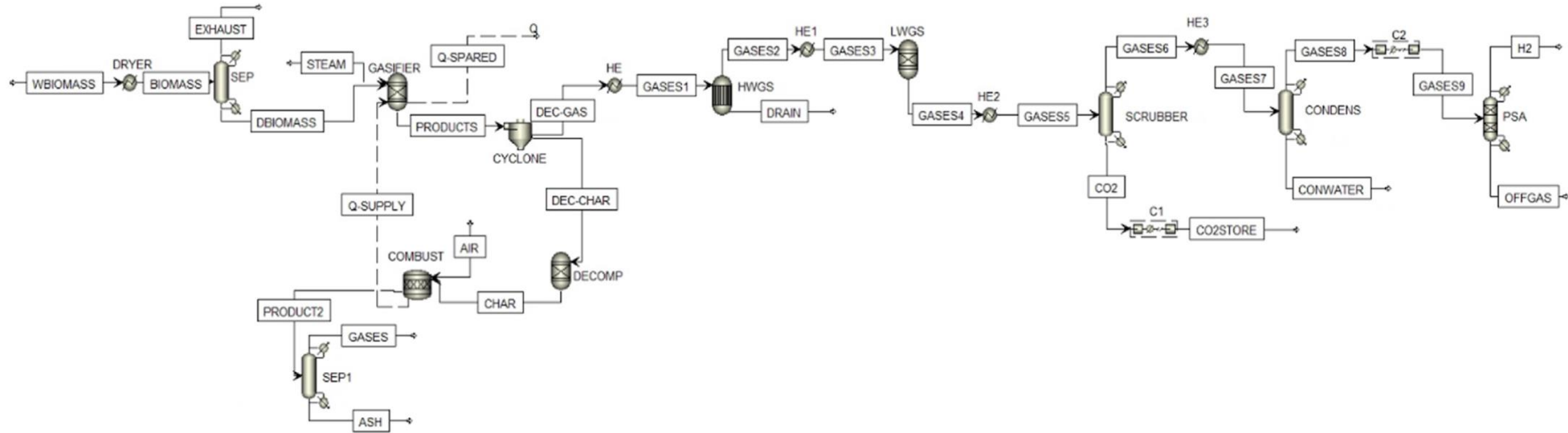
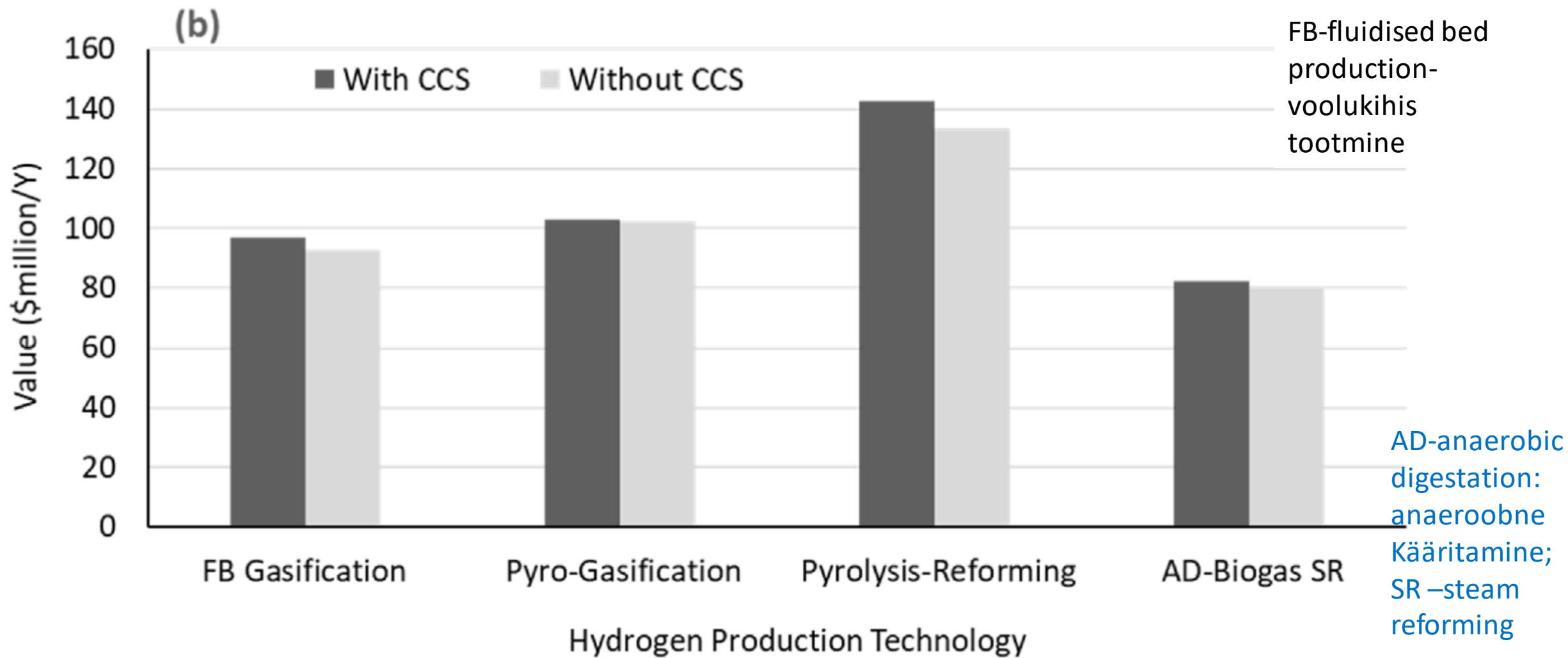


Fig. 1. An ASPEN Plus simulation depicting the Process Flow Diagram of Hydrogen Production from Biomass Gasification with Carbon Capture and Sequestration.

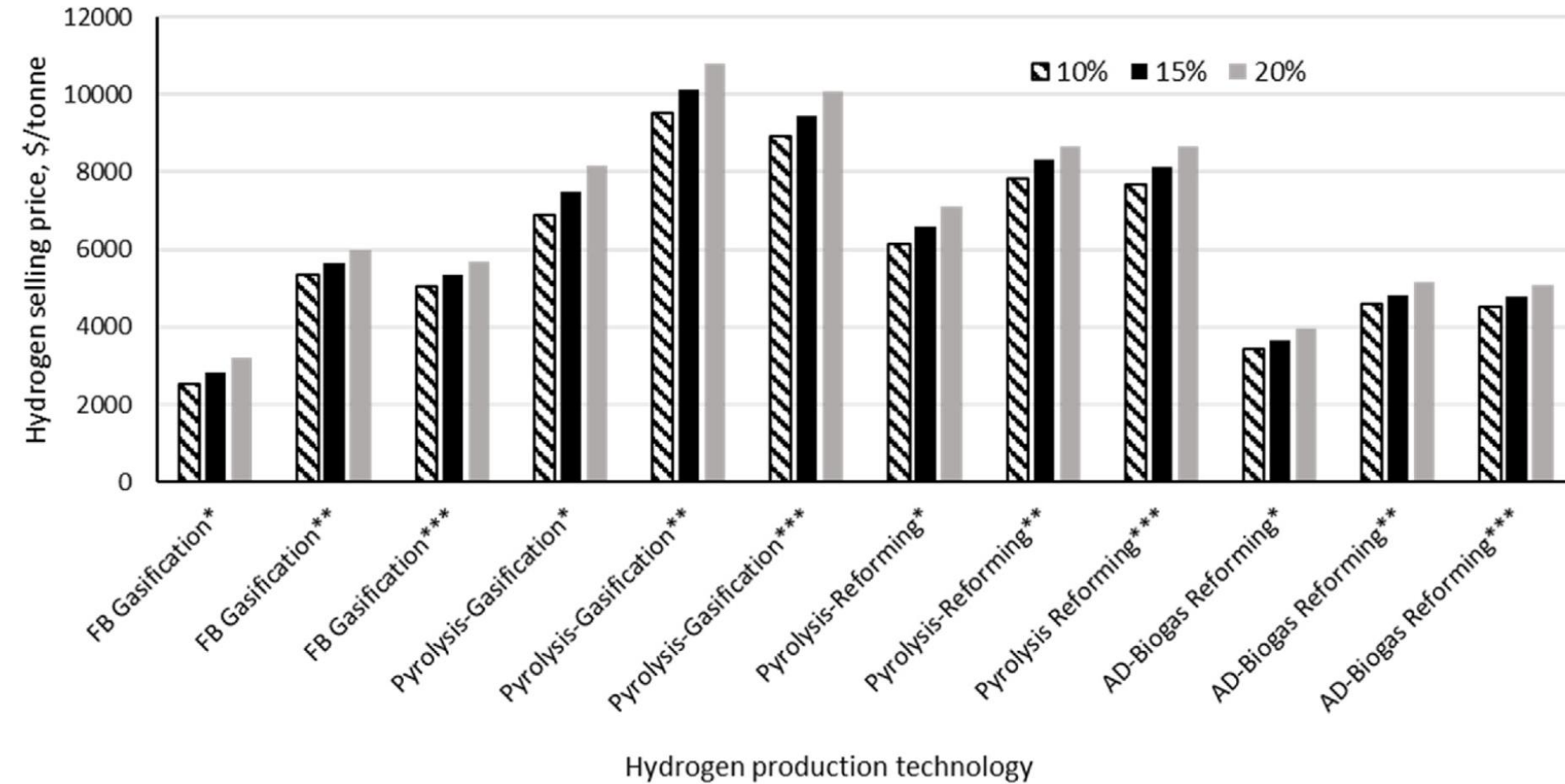


H₂ production systems operating costs: Kõige odavam on ehitada biometaani arurfaasis lagundamise süsteem





Vesiniku müügihind sõltuvalt tootmisviisist ja realiseerimise (ka CO₂ müük) tingimustest



Kõige odavam vesinik, kui toimub nn FB gasifitseerimine ja CO₂ kogutakse ja müüakse keemiatööstuse-sse (toiduainetetöös-tusesse) kasutamiseks!

Veelgi odavam vesinik saadakse märja biomassi superkriitilisel gasifitseerimisel!

Fig. 8. Influence of changes in internal rate of return on the minimum selling price of hydrogen from the different technologies

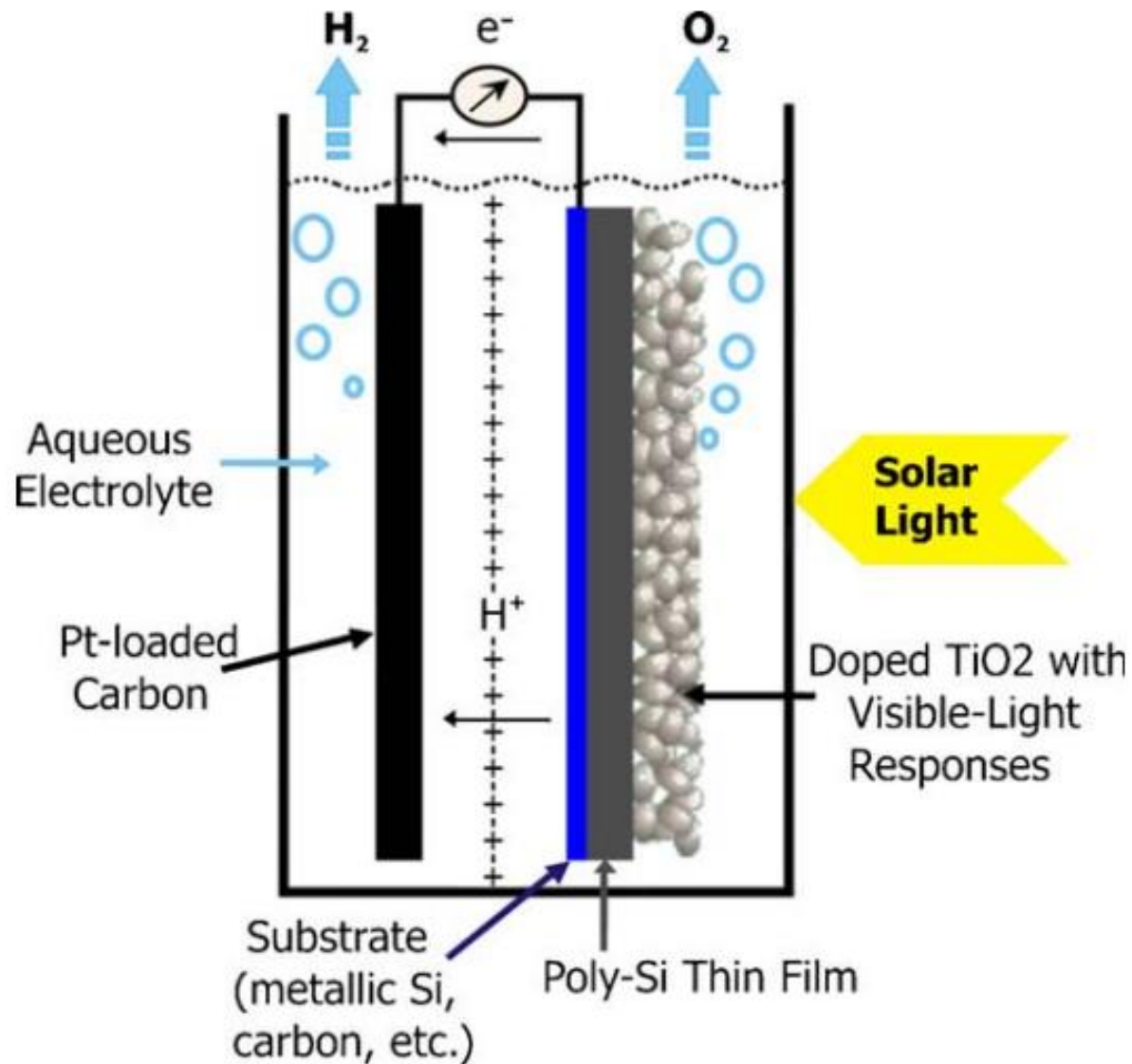
(* with CCS, CO₂ sold; ** with CCS, CO₂ not sold; *** without CCS).



Vesiniku tootmine biomassist 2000 bussile UKs; tasuvusaeg koos CO₂ müümisega 5,19 aastat, ilma CO₂ müümiseta 7,3 aastat

Case study data used for hydrogen production for 2000 buses

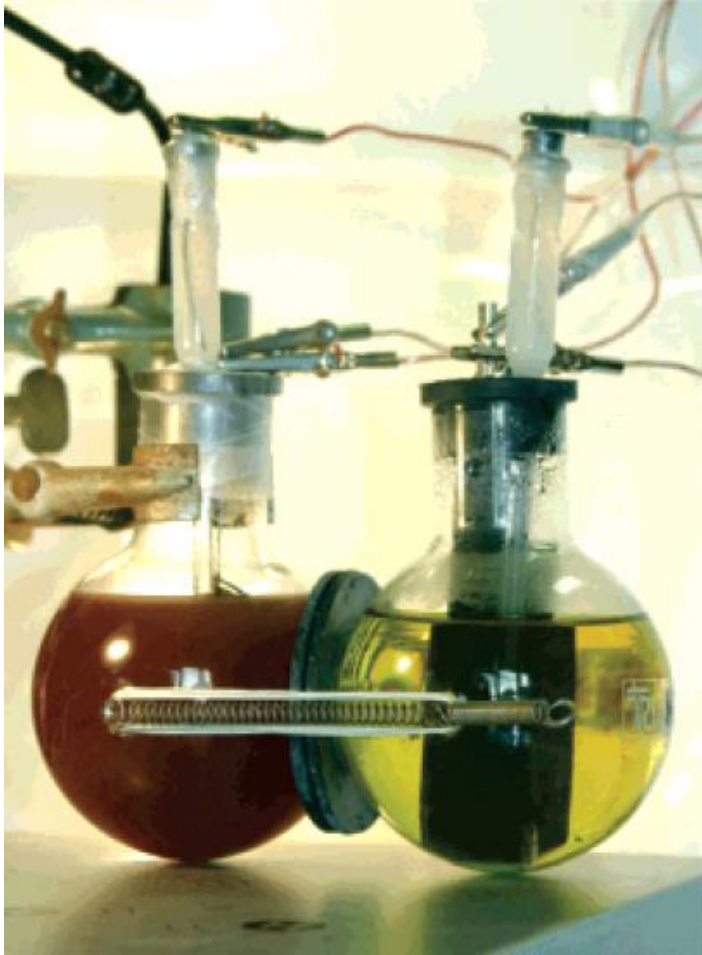
| Production Details | Value | Units |
|--|----------|-------------------|
| Average hydrogen consumption by buses | 0.09 | kg/km |
| Distance travelled by one bus | 257.5 | km/day |
| No. of days the bus is driven | 330 | days/year |
| No. of buses in West Midlands, England | 2300 | — |
| Yearly hydrogen requirement | 17589.83 | tonnes/year |
| Adjusted yearly hydrogen requirement | 22031.78 | tonnes/day |
| Yearly hydrogen plant operating hours | 7920 | hours/year |
| Adjusted hydrogen production capacity | 2781.79 | kg/h |
| Density of hydrogen at RTP | 0.0813 | kg/m ³ |
| Volumetric production capacity | 34216.36 | m ³ /h |



- Fotoelektrolüüs pakub väga palju uusi arendusvõimalusi
- Väga palju katalüütiliselt aktiivseid elektrodimaterjale

Fig. 4. Schema of solar water splitting system a composite polycrystalline-Si/doped TiO_2 semiconductor thin-film electrode. Adapted from Ref. [76].

Mikroobne kütuseelement



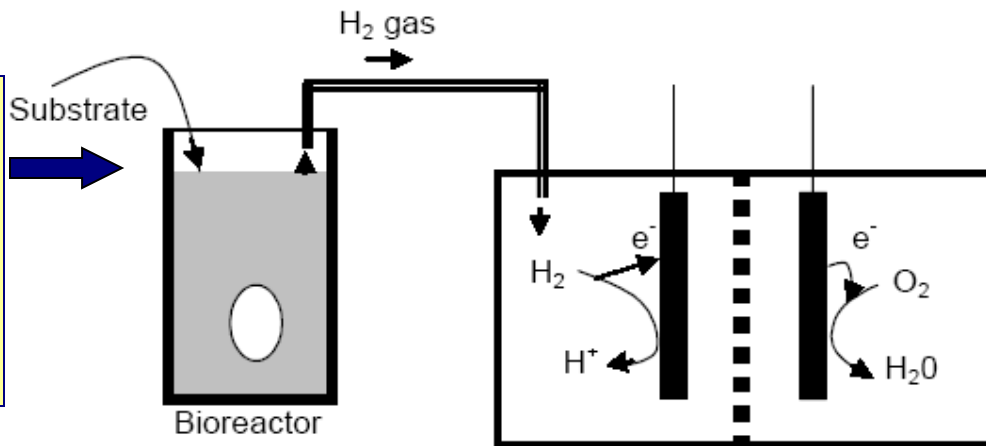
Vesiniku hinna sõltuvus tootmismeetodist:

Cost of hydrogen based on various production processes.

| Process | Cost of hydrogen (\$US per kg) |
|---|--------------------------------|
| Natural gas reforming | 1.03 |
| Natural gas and CO ₂ capture | 1.22 |
| Coal gasification | 0.96 |
| Coal with CO ₂ capture | 1.03 |
| Wind electrolysis | 3.64 |
| Biomass gasification | 4.63 |
| Biomass pyrolysis | 3.8 |
| Nuclear thermal splitting of water | 1.63 |
| Gasoline (for reference) | 0.93 |

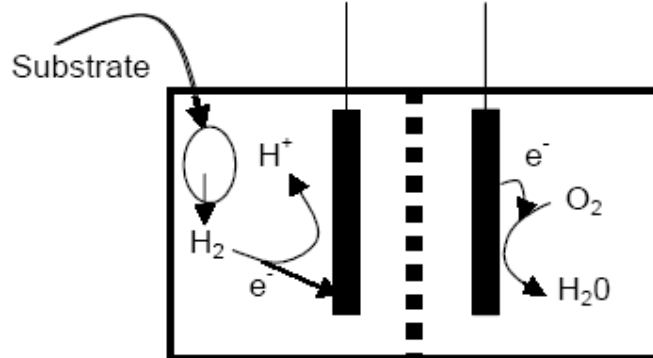
Mikroobse reaktori (MFC) tüübid

The *uncoupled bioreactor MFC*:
microbiological hydrogen or methane production (with subsequent reforming) in a separate bioreactor followed by a chemical fuel cell (generally high temperature SOFC) to convert hydrogen gas into electricity



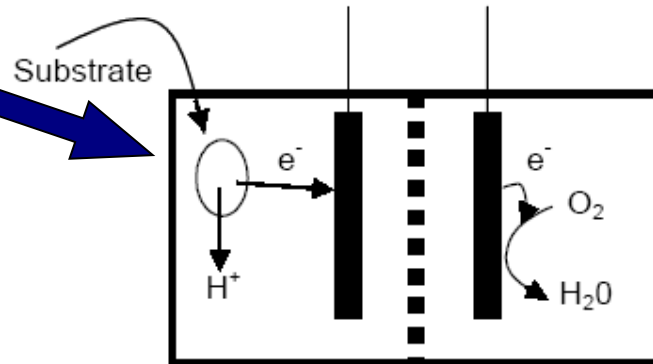
Kaheastmeline, töötab korralikult, kuid H₂S jt tuleb gaasist ärastada

The *integrated bioreactor MFC*:
microbiological hydrogen production and hydrogen to electricity conversion in a single cell



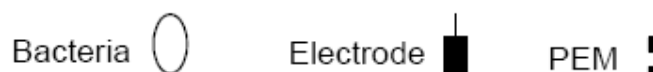
Töötab, kuid saastub kiiresti.

The *MFC with direct electron transfer*:
microbiological electricity generation and direct electron transfer to the anode



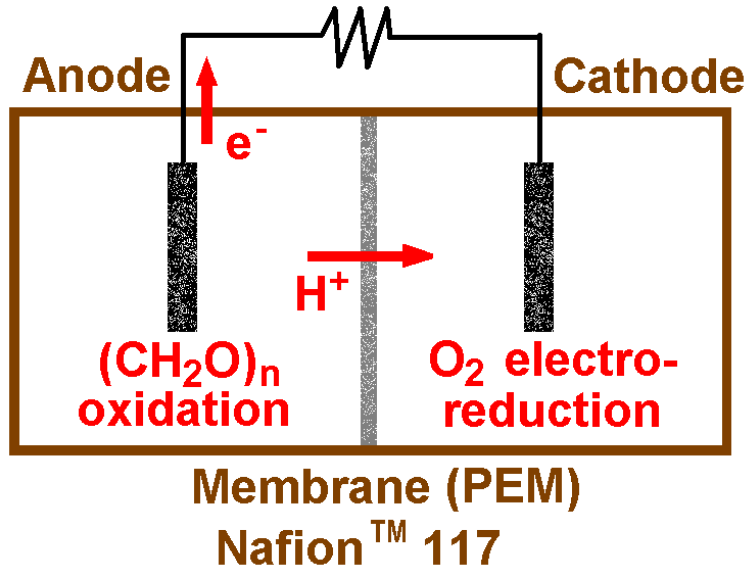
Töötab, kuid redoksmediaator nõuab uuendamist

The *MFC with mediated electron transfer*:
microbiological electricity generation and electron transport towards anode by means of electron shuttling mediators





Mikroobne kütuseelement



Anood: Pt | poorne Pt; süsinik|poorne Pt;
Elektrit juhtiv polümeer | poorne Pt|Pt

Cathode: poorne Pt; poorne süsinik;
Pt(poorne süsinik); Mn⁴⁺|Mn²⁺ — ;

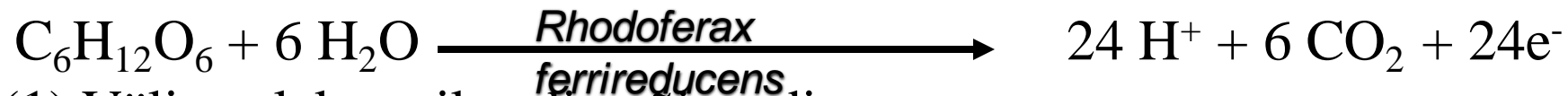
Co³⁺|Co²⁺ — porfüriin- ja

ptalotsüaniinkompleks-modifitseeritud
elektroodid

Katoodiruum: (aeroobne) O₂ elektoreduktsioon $4H^+ + O_2 + 4e^- \rightarrow 2H_2O$

Anoodiruum: (anaeroobne)

substraat oksüdeerub bakteri toimel ja tekib H⁺



(1) Väline elektronikandja või mediaator

(Na₃[Fe(CN)₆]; thioniin; neutraalpunane)

(2) e⁻ transport otse anoodile respiratoorsete ensüümide abil

NB! Mediaatorid – kallid, bakterimürgid, limiteeritud kasutus aeg, tuleb uuendada

NB!
Pt elektroodide
kasutamine teeb
tehnoloogia
väga kalliks



$$E = 1.2288 + 0.0148 \log p - 0.05915 \text{ pH}$$

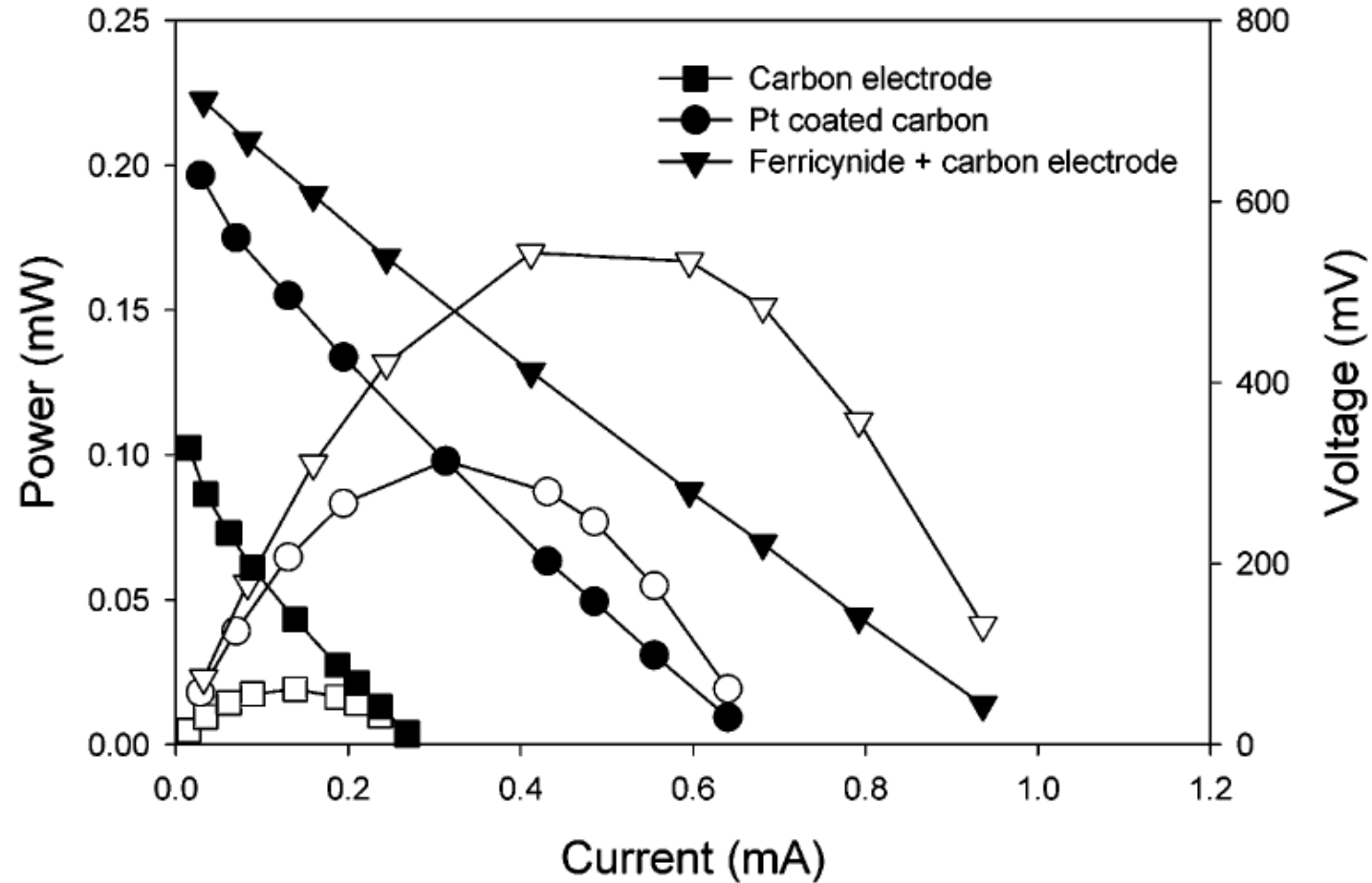
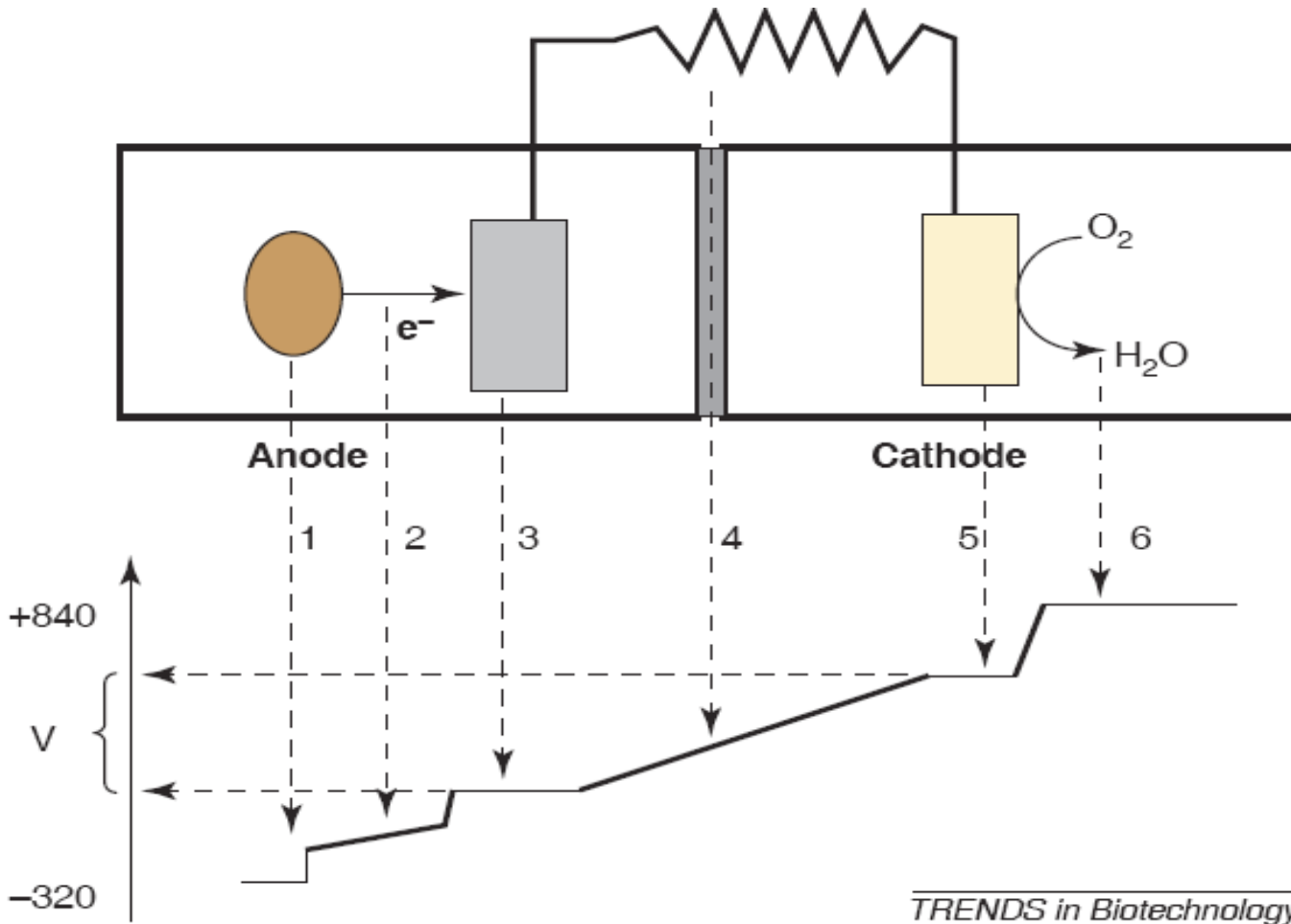


FIGURE 4. Comparison of voltage and power generated as a function of current when using plain carbon, Pt-coated carbon, or ferricyanide and plain carbon electrodes. (Open symbols indicate power; filled symbols indicate voltage.)

Elektroodidel potentsiaali kaotus laenguülekanandel metanooli kütuseelemendis ja biokütuseelemendis



$$DG = -nFE$$

$$P = IU$$

$$E = Pt$$

I – current density (A)

U – cell voltage (V)

P – power density (W)

E – energy density

(Wh)

t – time (s)

1. Loss owing to bacterial electron transfer. 2. Losses owing to electrolyte resistance. 3. Losses at the anode. 4. Losses at the MFC resistance (useful potential difference) and membrane resistance losses. 5. Losses at the cathode. 6. Losses owing to electron acceptor reduction.

TRENDS in Biotechnology

Rabaey, K., and W. Verstraete (2005) Microbial fuel cells: sustainable core technology. Trends in Biotechnology 23: 291-298

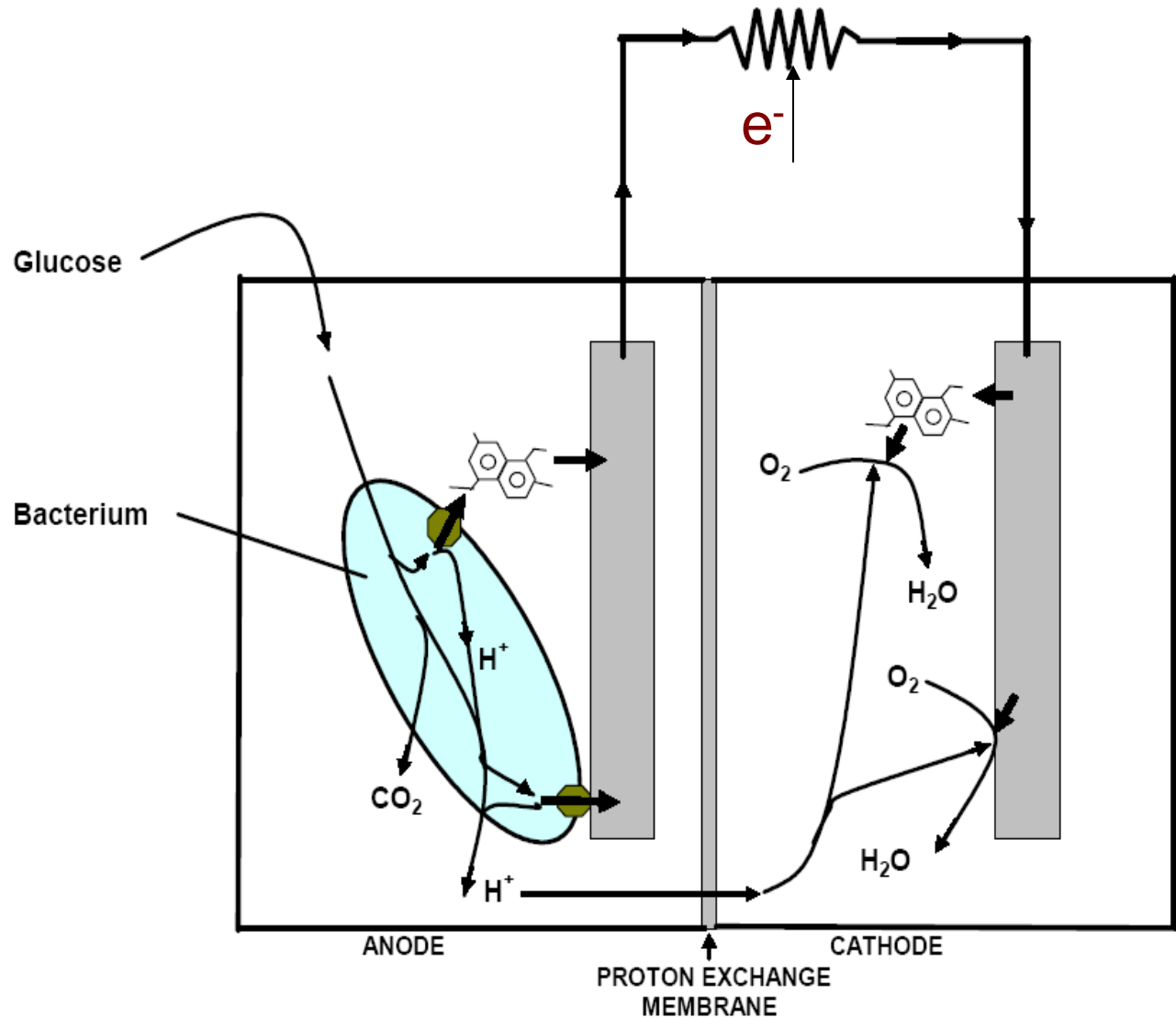


Mikroob-kütuseelement

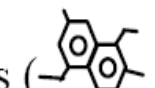

- Cost of 400 € per m³ (1kW power output per 1m³ anode, only!!!!) gives electricity 10-150 times more expensive than chemical fuel cells or wind turbines

However

- The sludge treatment cost of wastewater treatment facilities can amount up to 500 € per ton of dry matter! — Some compensation effect!
- Kuna H₂S saastemaksud on USAs väga kõrged, siis kasutatakse SOFCd puhastamata biogaasidest (60-65 % CH₄, 30-35% CO₂, 3-5% H₂O + x%CO, y%H₂S jt lisandid) elektri ja soojuste koostootmiseks, heitgaasid kogutakse!
- Ja ikkagi tasuvat selline tegevus ära??????

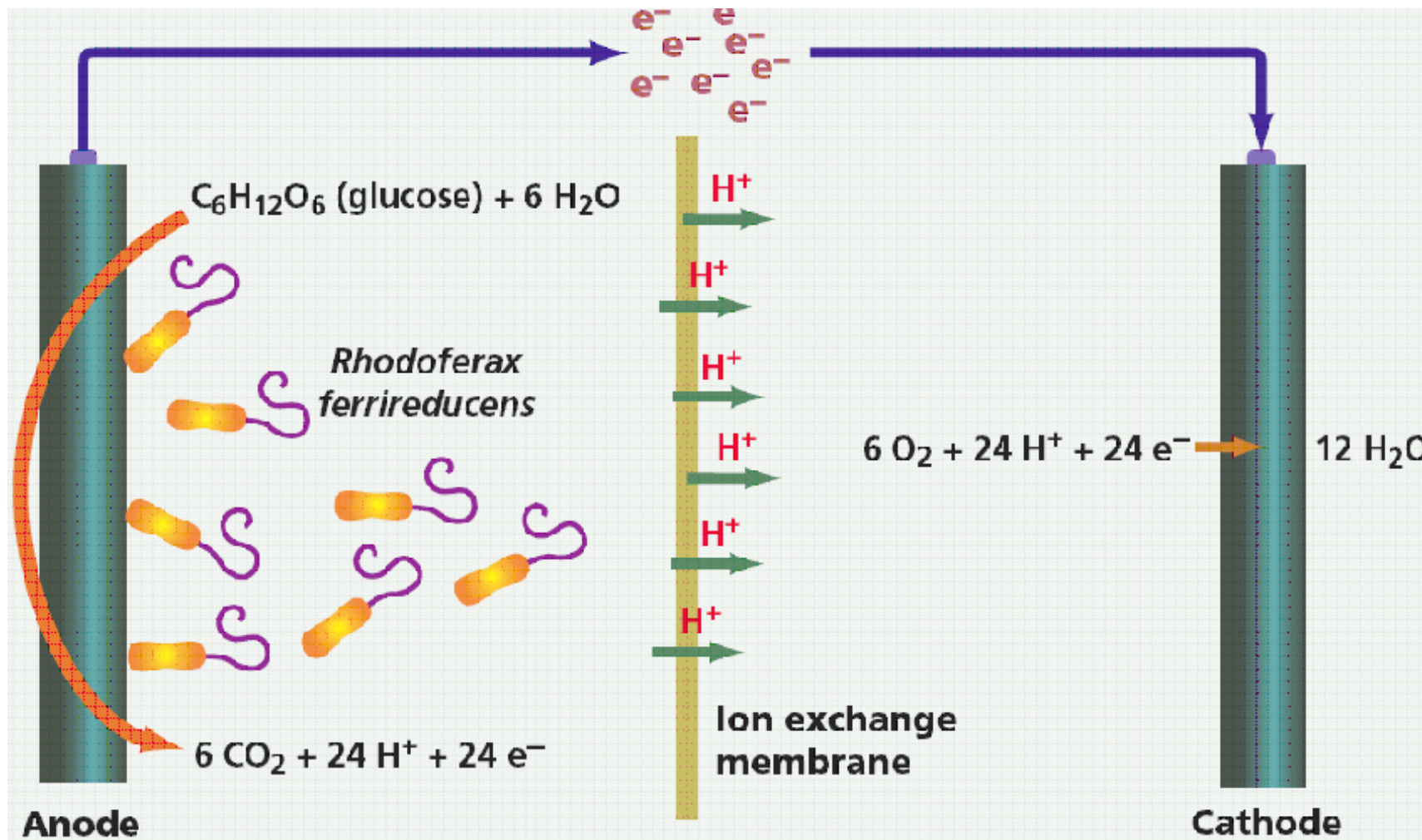


- Võimalikud väga erinevad biokütuseelemendi mudelid:
Elektroni ülekande toimub kas:
- läbi lahustunud redoksmediaatori;
 - läbi membraanile adsorbeerunud redoksmediaatori.

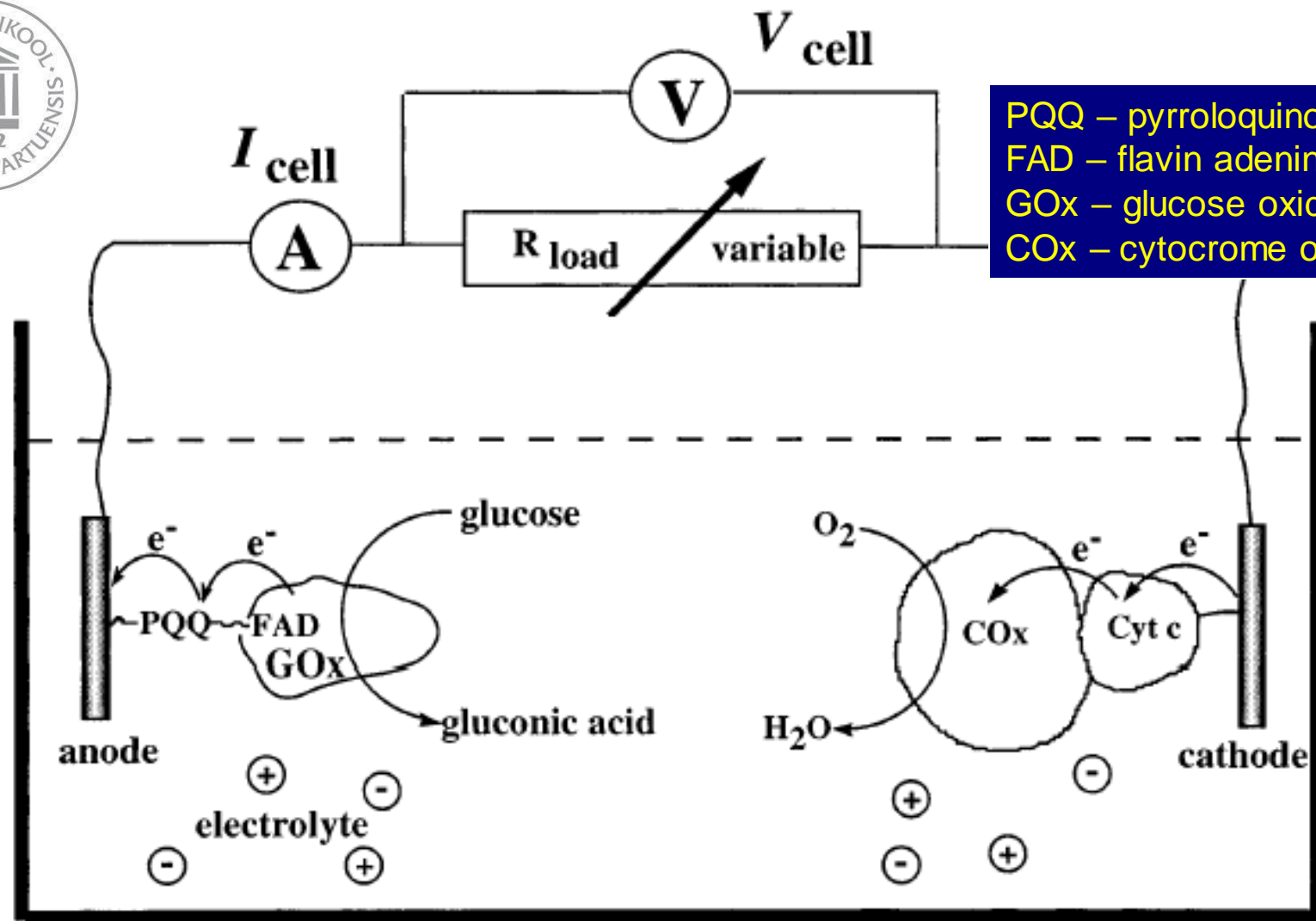
Figure 20.1. Schematic drawing of a microbial fuel cell. Electron transfer can occur through either soluble redox mediators () or membrane bound complexes ()

Rabaey, K., G. Lissens, and W. Verstraete (2005) Microbial fuel cells: performances and perspectives. In P. N. Lens, P. Westermann, M. Haberbauer, and A. Moreno (ed.), Biofuels for fuel cells: biomass fermentation towards usage in fuel cells.

Rhodospirillum rubrum microbial fuel cell



R. ferrireducens burns carbohydrates to CO_2 in the anodic compartment, a process that produces free electrons which are directly captured by the anode. From there, the electrons are channeled to the cathode, where they reduce oxygen to water. The transfer of electrons from the anode to the cathode results in the generation of an electrical current



PQQ – pyrroloquinoline quinone
 FAD – flavin adenin dinucleotide
 GOx – glucose oxidase
 COx – cytochrome oxidase

Biokütuseelement, mis töötab glükoosil kui kütusel, mis oksüdeerub ja O₂ mis redutseerub
 Anoodil pürroloquinoliin + flaviin (adeniin dinukleotiid) glükoosi oksüdeerimiseks ja katoodil tsütokroom C + tsütokroomoksidaas, mis on funktsionaliseeritud (adsorb.) hapniku redutseerimiseks.
 Vaja pidevalt uuendada elektroode või biokeemiliselt aktiivseid aineid lahuses.

Scheme 1. Schematic configuration of a biofuel cell employing glucose and O₂ as a fuel and an oxidizer, respectively, and PQQ-FAD | GOx and Cyt. *c* | COx-functionalized electrodes as biocatalytic anode and cathode, respectively.

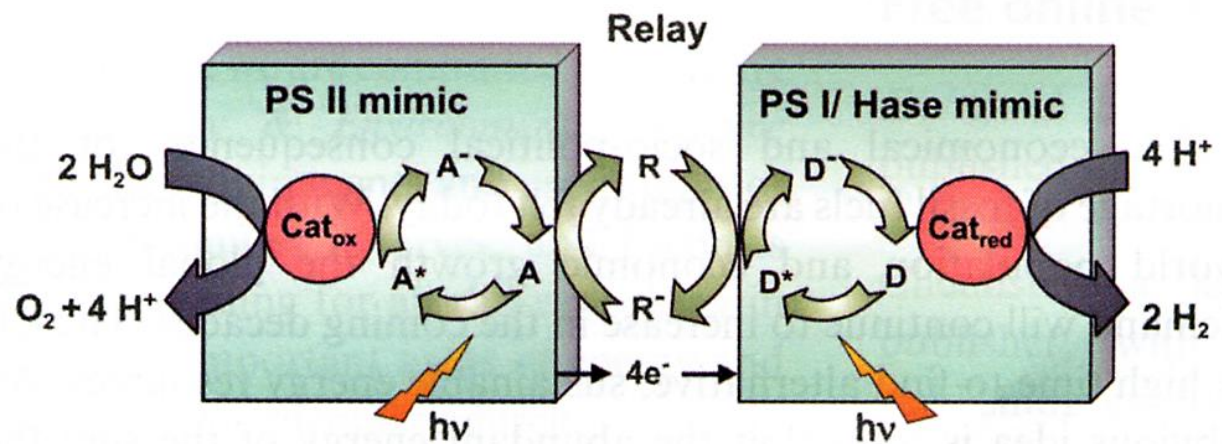
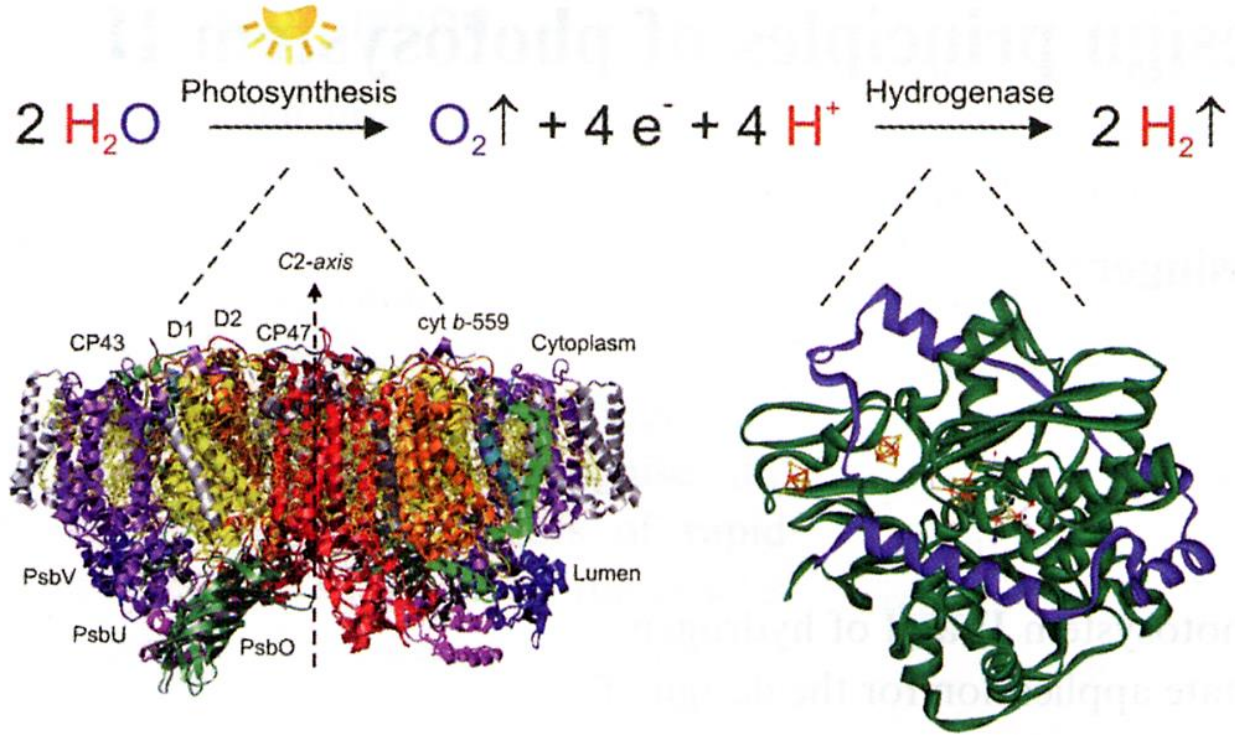


Fig. 1 Light induced water splitting by photosystem II in photosynthesis and hydrogen production by an [FeFe] hydrogenase shown together with the structure of respective protein complexes^{17,18} and a possible scheme¹⁹ for mimicking the natural process.



Rakupotentsiaalid sõltuvad elektrodipotentsiaalidest

| Redox reaction | E'_0 (mV) |
|--|-------------|
| $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ | -420 |
| Ferredoxin(Fe^{3+}) + $\text{e}^- \rightarrow$ Ferredoxin(Fe^{2+}) | -420 |
| $\text{NAD}^+ + \text{H}^+ + 2\text{e}^- \rightarrow \text{NADH}$ | -320 |
| $\text{S} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{S}$ | -274 |
| $\text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e}^- \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$ | -220 |
| Pyruvate $^{2-} + 2\text{H}^+ + 2\text{e}^- \rightarrow$ Lactate $^{2-}$ | -185 |
| $\text{FAD} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{FADH}_2$ | -180 |
| Fumarate $^{2-} + 2\text{H}^+ + 2\text{e}^- \rightarrow$ Succinate $^{2-}$ | +31 |
| Cytochrome <i>b</i> (Fe^{3+}) + $\text{e}^- \rightarrow$ Cytochrome <i>b</i> (Fe^{2+}) | +75 |
| Ubiquinone + $2\text{H}^+ + 2\text{e}^- \rightarrow$ UbiquinoneH $_2$ | +100 |
| Cytochrome <i>c</i> (Fe^{3+}) + $\text{e}^- \rightarrow$ Cytochrome <i>c</i> (Fe^{2+}) | +254 |
| $\text{NO}_3^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O}$ | +421 |
| $\text{NO}_2^- + 8\text{H}^+ + 6\text{e}^- \rightarrow \text{NH}_4^+ + 2\text{H}_2\text{O}$ | +440 |
| $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ | +771 |
| $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ | +840 |

Tegelikult väga vähe võimalusi, kus dE oleks kas võrdne või üle 1.23 V!!!!

$$\Delta E \approx \sim 1.16 \text{ V}$$

The energy gained is calculated as $\Delta G = -nF \Delta E$

n is the number of electrons exchanged;

F is Faraday's constant,

ΔE is potential difference between electron donor and acceptor

Täna tähelepanu eest!

Tänuavaldused:

- ETAG (IUT20-13, PRG676)
- Euroopa Strukturiifond
 - Eesti tippkeskused TK 117 ja TK 141,
 - Energiatehnoloogiaprojekt SLOKT10209T,
 - Materjalitehnoloogia projektid SLOKT12180T ja SLOKT12181T
 - Eesti osalemine ESS arenduses
- Iseauto projekt AuveTECH OÜ

European cities face big challenges if they want to comply with the Paris Agreement to reduce greenhouse gas emissions. Fuel cells and hydrogen (FCH) technology can contribute significantly towards reducing emissions and facilitating the necessary green energy transition in European regions and cities.



Safe, clean and competitive: Europeans cities and regions want to improve local air quality with hydrogen-fueled fleets.



Selleks, et vältida kliima katastroofi, on EL ja kogu maailm seadnud oma kliima eesmärgid:

Euroopa eesmärgid 2050. aastaks vältimaks kliimakatastroofi (70 % ulatuses CO₂ genereerimise vähendamine 2030; 100% vähendamine nn null % uut süsinikdioksiidi tootmist 2050).

Koostatud: Green Deal, Covid Recovery Plan, Strategy for Energy System Integration and a Climate –Neutral Europe, AIT industry, Botnia Hydrogen Backbone, jt TEN-T transpordi koridorid, H-ICPEI programmid jt andmetel.

- Alalisvooluvõrkude arendamine ja H₂ energeetika intensiivne juurutamine, elektri salvestusvõimsuste arendamine
- Elektrolüüserite võimsuse tõstmine: 60 MW (2018) - 6GW (2024) (24-42 miljardit € ning 80-120 miljardit € PV ja tuuleelektri genereerimiseks); kuni 40 GW (2030) 220-340 miljardit €;
- Elektrolüüserite hinnad on momendil 800-1000 €/kW, aga langevad: 450-480 €/kW 2030. a. Momendil Hiinas toodetud elektrolüüser: 220-240 €/kW:
- 65 miljardit H₂ transpordi (H₂ torustikud, H₂ tsisternveokid, tankurlaevad, tankurrongid) ja jaotussüsteemi (H₂ tankurid tanklates, survepaagid, kompressorid, jne) prototüübib juba ammu olemas ja reaalses igapäevases kasutamises arendamiseks
- Euroopas 2050. a 500 GW ja kulutused ehitamiseks 2.2 triljonit (Goldman Sachs); kogu maailmas 2050.a 4.0- 5.0 TW, kulutused 11 triljonit (Bank of America prognoos 2020 a);
- 2020. a 1kg H₂ maksab tanklas 2.5-5.5 €, 2030. peaks langema 1.1-2.4 €-le; (kui toota tuulest siis on omahind 1kg H₂ = 0.28 € (momendil tuuleelekter 14 €/MWh ja (2030) 8-9 €/MWh (siis 1kg H₂ = 0.16-0.18 € tuulejaamas kohapeal)
- 11 miljardit € H₂ fossiilsest allikatest H₂ tootmise muutmiseks CCUS (carbon capturing, utilisation and storage) vastavaks tehnoloogiaks.

Kõik kokku: 320-458 miljardit €.

Momendil toodetakse 75-85 miljonit tonni (115-130 miljardit USD) vesinikku: 46-48 % metaanist, 28-30% naftast, 16-18% söest, 5-8% elektrolüüsil. Põhiliselt kasutatakse tööstuses: toornafta ja toor maagaasi puhastamiseks, ammoniaagi (Haberiprotsess: 3H₂+N₂=NH₃) sünteesiks ja muudeks keemiatööstuse protsessideks.

CO₂ puhastamine ja tagasimüümimine vähendab vesiniku müügihinda

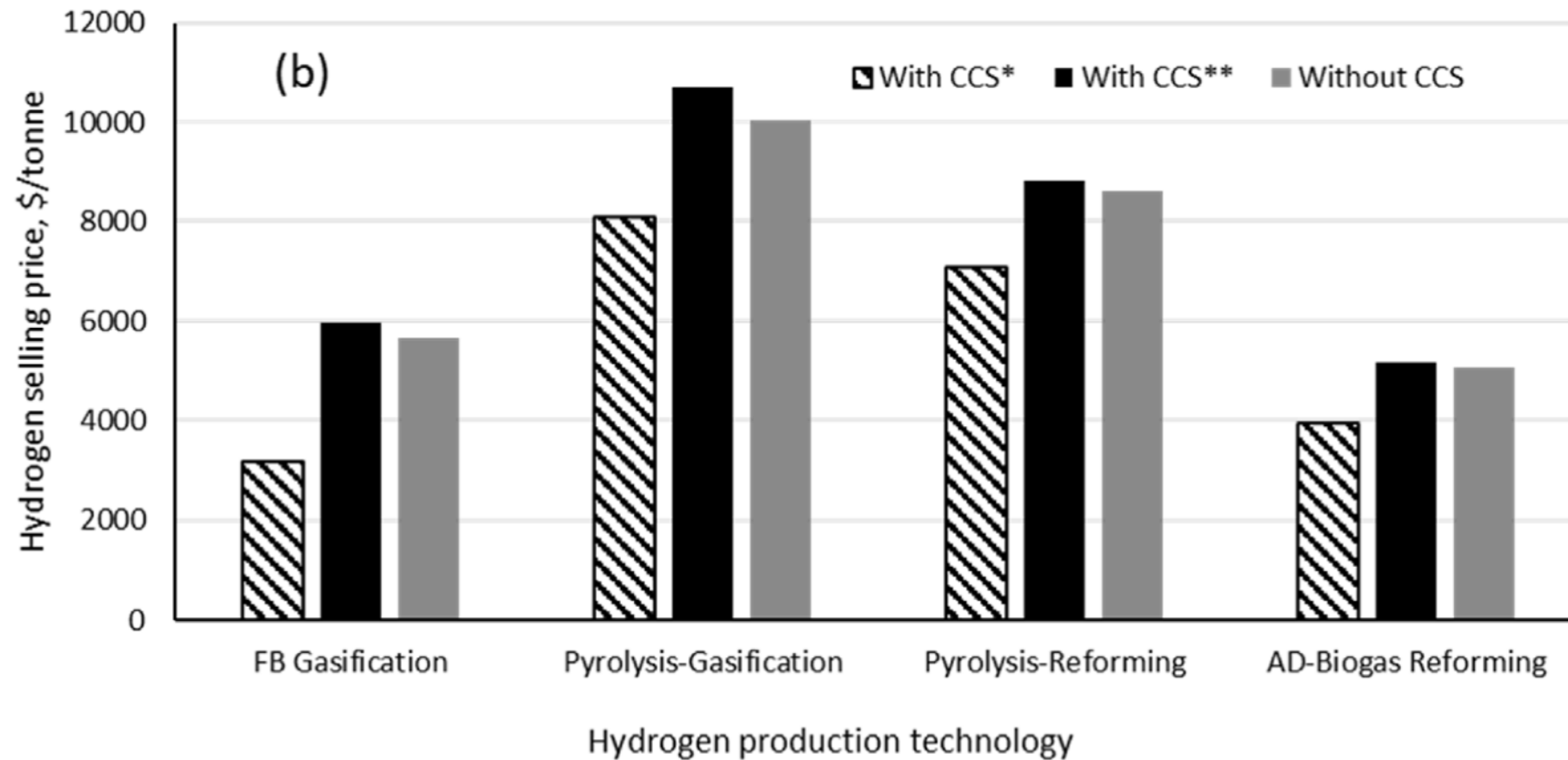


Fig. 7. Influence of changes in raw materials cost on the minimum selling price of hydrogen from the different technologies at +20% of nominal values.

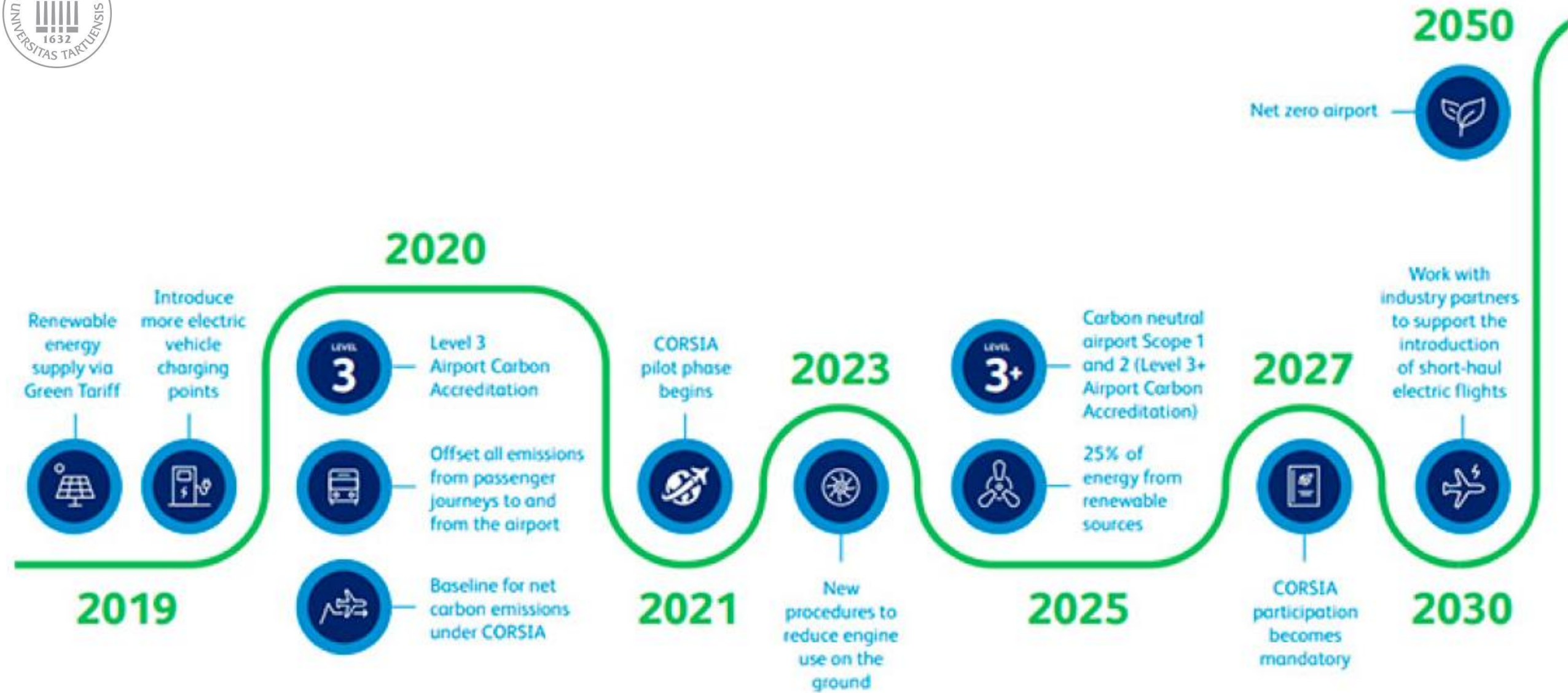
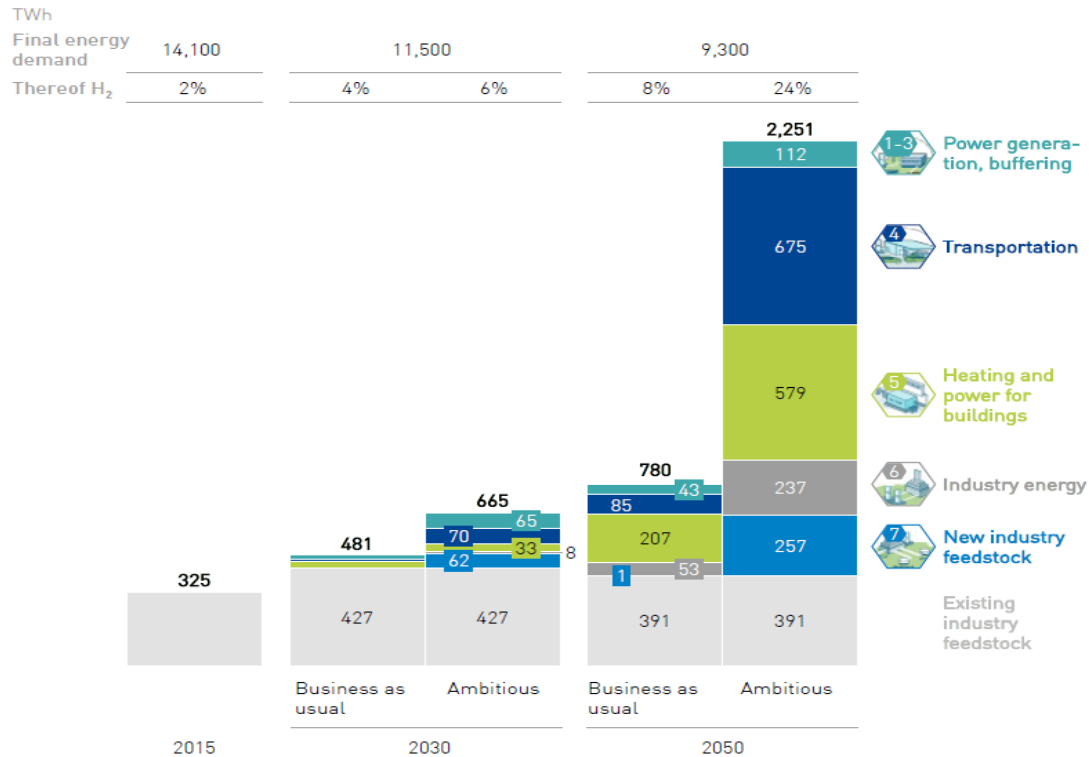


Fig. 4. Prediction of future of vehicles development [54].



Main development directions of green energy : generation of energy storage methods and completing of recycling economy cycle methods

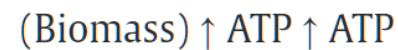
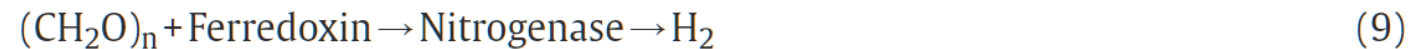
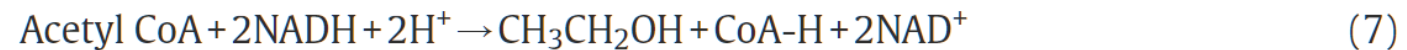
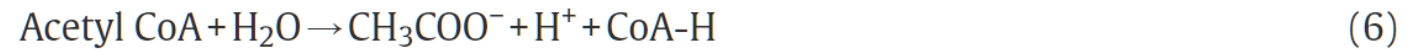
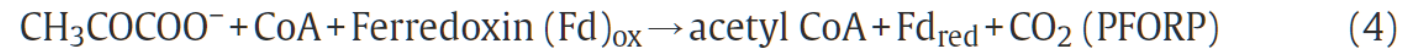
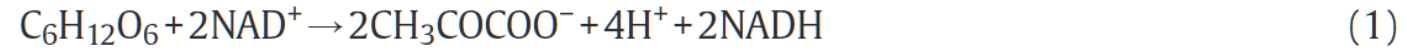
EXHIBIT 2: HYDROGEN COULD PROVIDE UP TO 24% OF TOTAL ENERGY DEMAND, OR UP TO ~2,250 TWH OF ENERGY IN THE EU BY 2050



3 As part of the Paris agreement, EU member states have committed to achieving the 2-degree scenario and making efforts towards achieving a 1.5-degree scenario. This study anchors on achieving the 2-degree scenario – the necessity for hydrogen and the amount of deployment would be even greater in a 1.5-degree scenario.

- Energy storage of PV and wind current peaks, stabilisation of wind and solar DC regime
Busses, coaches trucks, tractors, trains, maritime, planes, lifting machines, **Electrical heating solutions, heating pumps combined with PV, CSP and fuel cells**
- (hydrogen can be used only as a fuel for fuel cells!)
- Endothermal industrial processes combined with exothermal processes: glas melting, CaO production , cement production
- H2 reductant for steel and Al industry, rare earth and high temperature melting point metals powder production, biogas methanogenic upreading, ammonia generation

Biokeemilised reaktsioonid, mis toimuvad, et saada vesinikku



Süsinikdioksiidi müügi hind mõjutab vesiniku müügi hinda

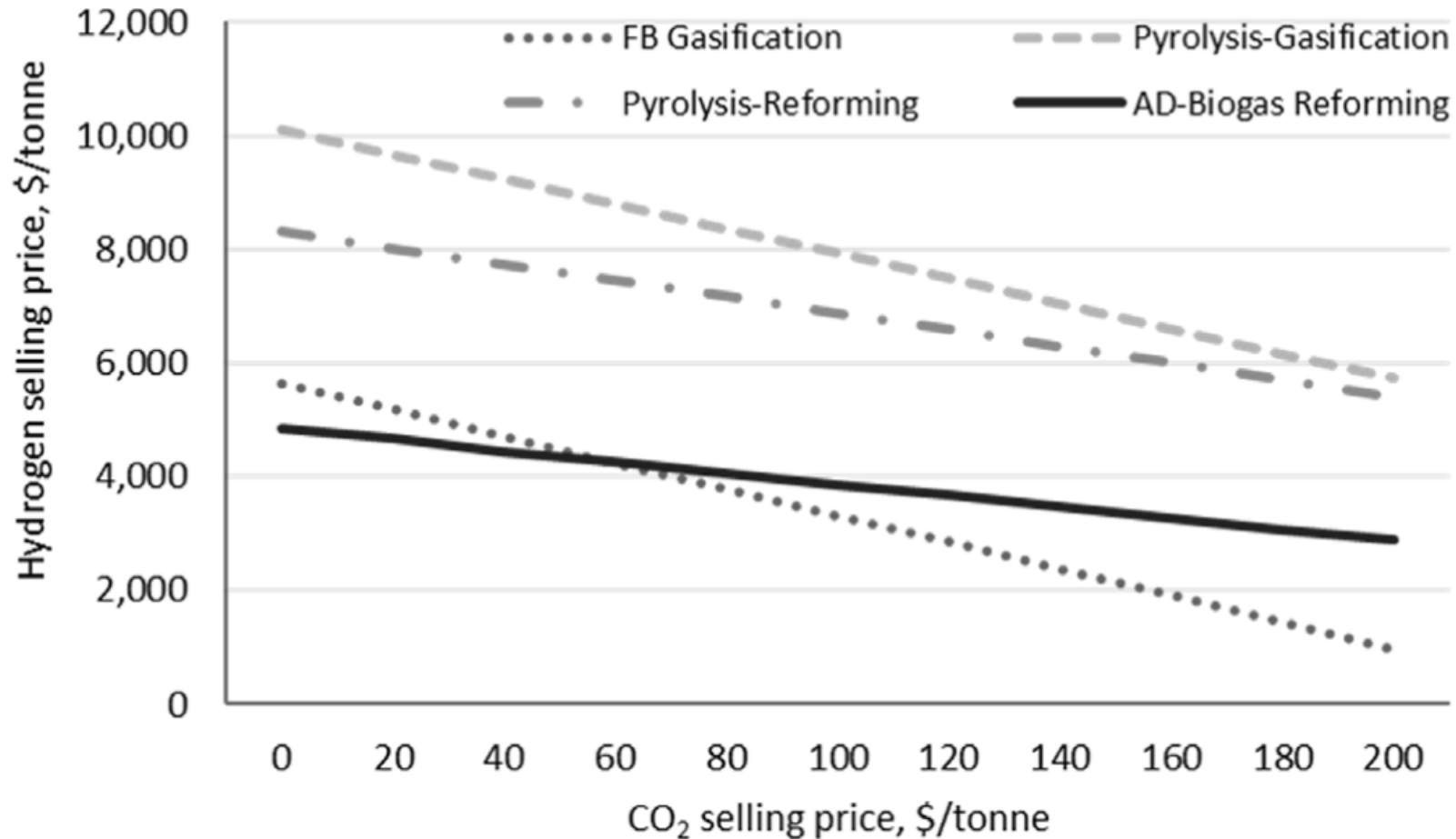
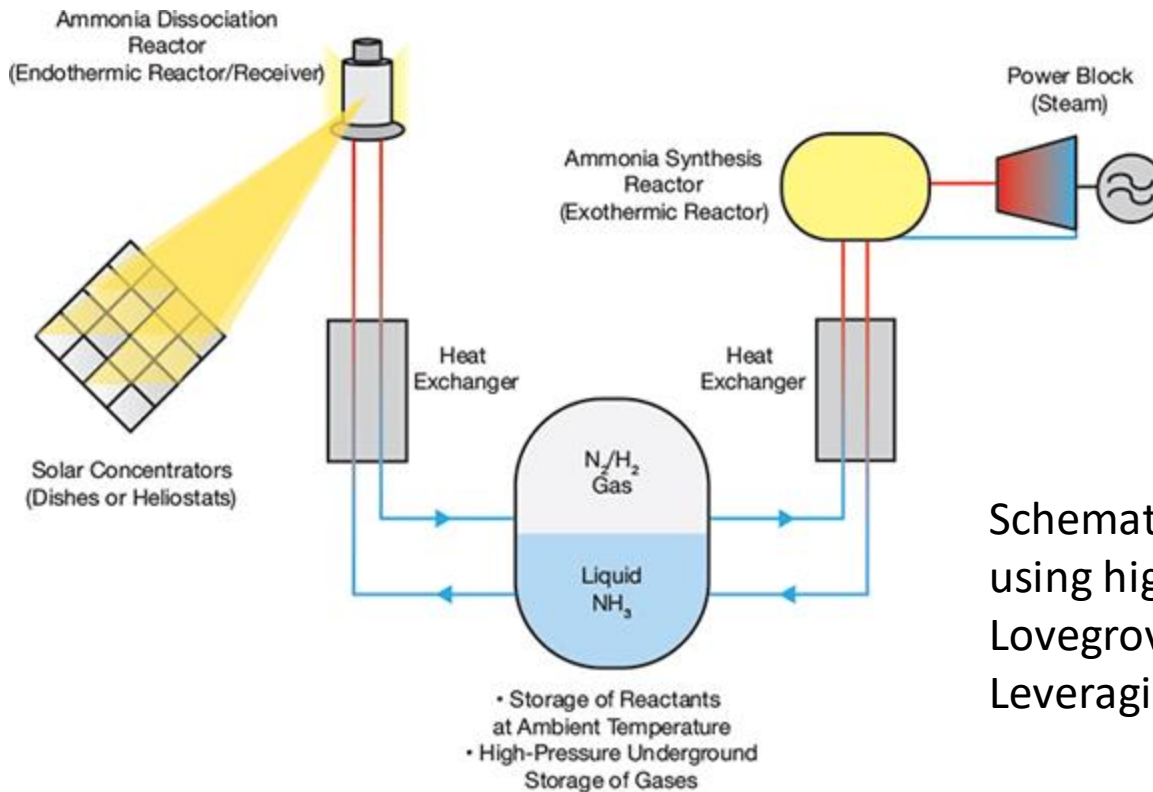


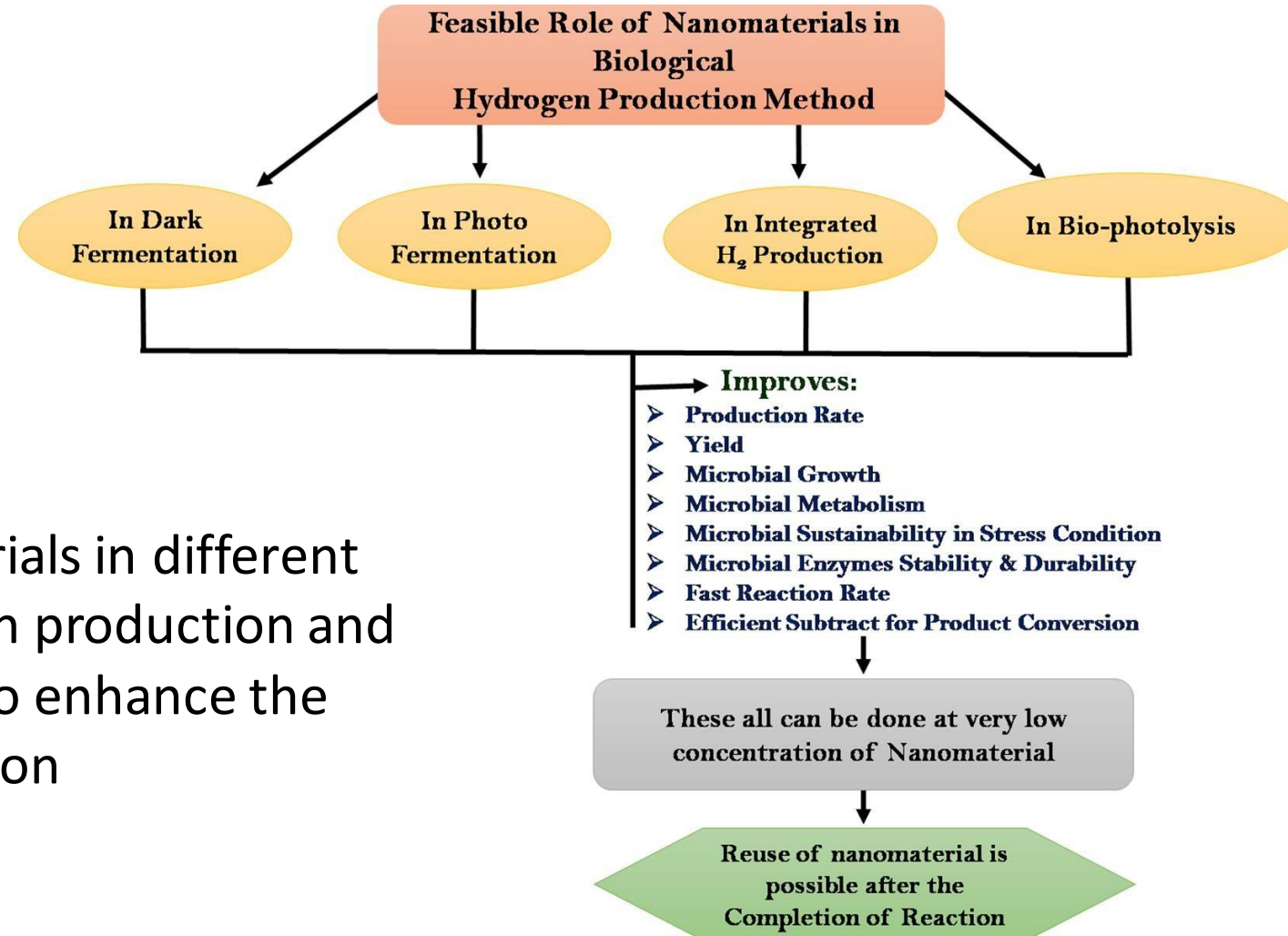
Fig. 9. Influence of CO₂ selling price on the minimum hydrogen selling price for the different technologies.

Concentrated solar power (CSP) can be used for synthesis of green ammonia, (Haber-Bosch: 300-550 °C and 15-30 MPa) catalysed by Fe-Ni or Ru based catalysts, but only 15 % NH_3 ; CSP for production of clean metals , sulphur, hydrogen, etc



Schematic diagram of an ammonia thermochemical storage system using high-temperature solar concentrators. Source: Keith Lovegrove, Adrienne Lavine, Hamarz, Aryafar and Chen Chen: Leveraging the Ammonia Industry for Solar Energy Storage.

Nanomaterjalide mõju erinevate biovesiniku tootmisprotsessides



Role of nanomaterials in different modes of hydrogen production and their advantages to enhance the hydrogen production

Vesiniku tootmise skeem pürolüüsi+reformimise meetodil koos CO2 kogumise ja kasutamisega (ka müümisega keemiatööstusele)

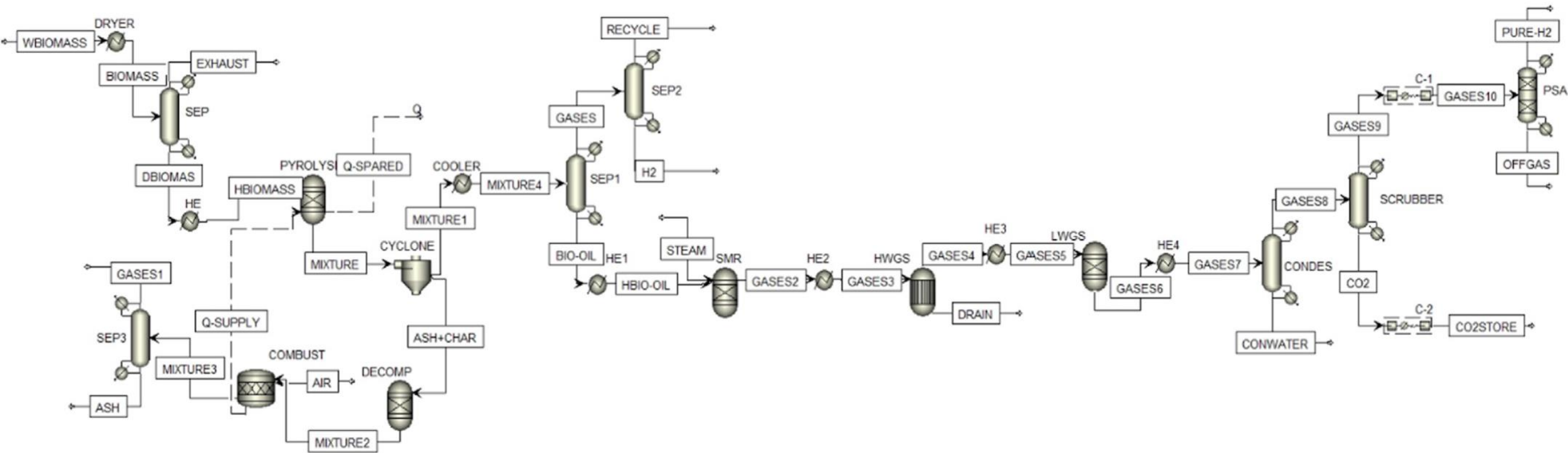
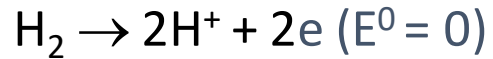


Fig. 3. An ASPEN Plus simulation picturing the Process Flow Diagram of Hydrogen Production from Pyrolysis-Reforming with Carbon Capture and Sequestration.

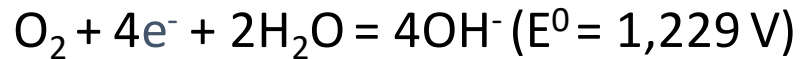
H₂-O₂ kütuseelement ; teoreetilised alused W.Ostwald

- H₂-O₂ kütuseelement - 1839 Sir W.Grove, 1893-1898 W. Ostwald (teooria, TÜ professor) (Pt/Pt +happeline lahus)
- PEMFC - 1955 T. Grubb, 1958 L. Niedrach (General Electric, NASA), pH < 7, prootonjuhtivusega kütuseelement

Anoodil vesinik (kütus) oksüdeerub



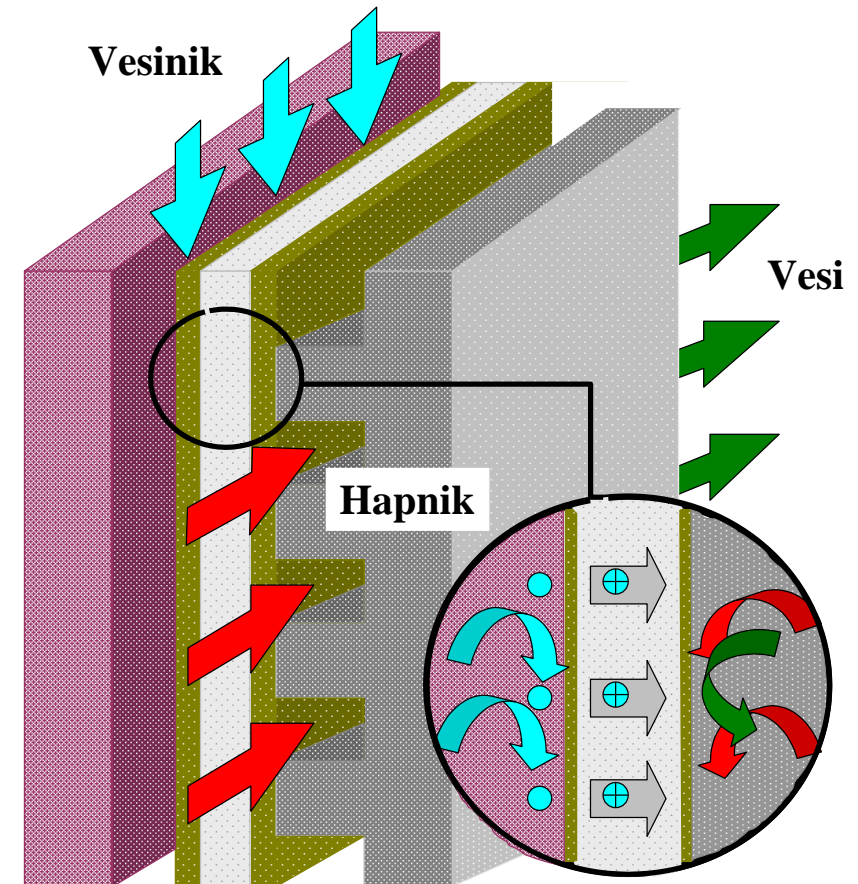
Katoodil hapnik redutseerub



Summaarne ioonreaktsioon: $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$

- Pole kõrvalprodukte!
- T = 60-80 °C
- Tekib elektrivool ja soojus ning ainult ülipuhas vesi!
- Vett saab koguda ja kasutada vesiniku taastootmiseks, kui PEMFC võimsus 50 kW ja rohkem!

$$\Delta E^0 = -\Delta G / nF = RT \ln K / nF$$



Biofermentation

Simple sugars – max. theoretical 4 mole H_2 per 1 mole glucose

$CH_3COO^-H^+$ only end prod.)

67% organic matter will remain in solution

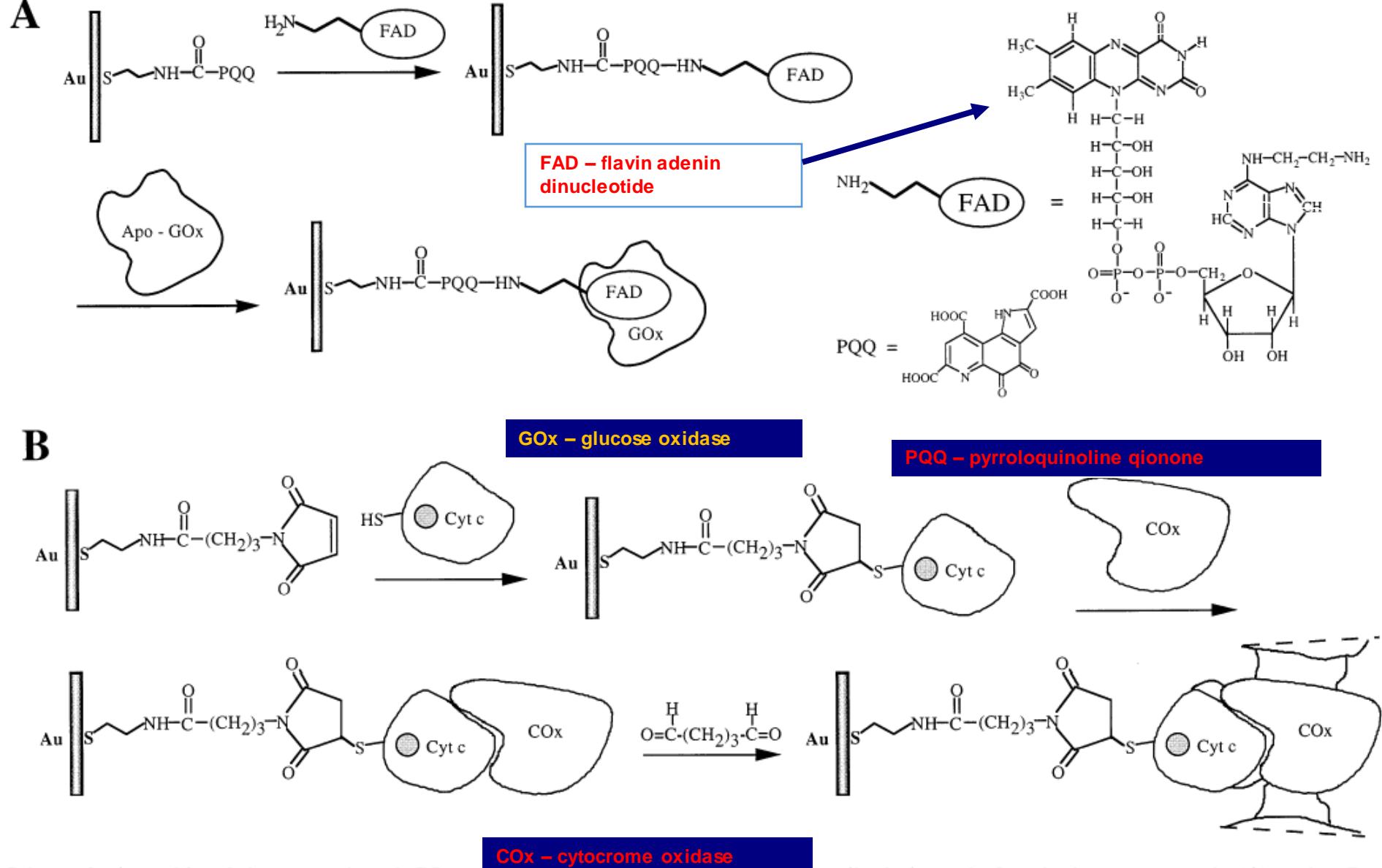
Typically, yield of H_2 is 1...2 mole/mole and 80...90 % organic matter will remain in solution (CH_3COOH , C_2H_5COOH , C_3H_7COOH , C_2H_5OH etc.)

More efficient

Two steps methane production (yield depends on the anaerobic fermentation conditions)

Bacteria in mediator-less MFC-s

- electrochemically active redox enzymes (cytochromes on anode outer surface)
- microorganisms able to reduce Fe^{3+} ions to Fe^{2+} ions (*Shewanella putrefaciens*, members of *Geobacteraceae*)
- fermentative bacteria (*Clostridium butyricum*, *Rhodospirillum rubrum*)

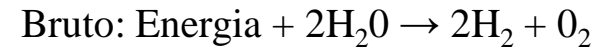
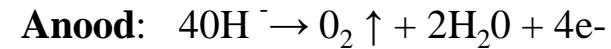
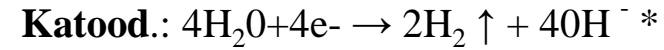
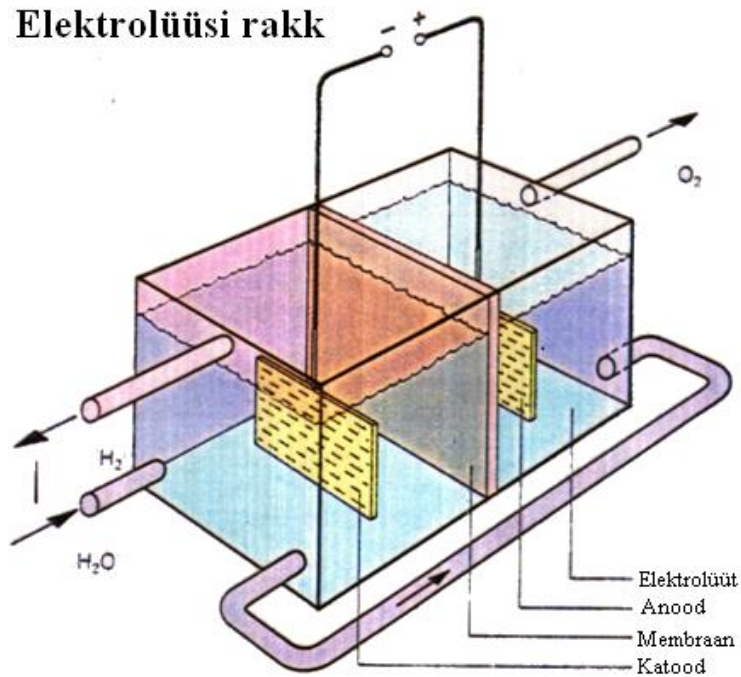


Scheme 2. Assembly of the reconstituted GOx on the PQQ-FAD monolayer-functionalized electrode functioning as an anode (A) and a Cyt *c* | COx-integrated electrode functioning as a cathode (B) in the biofuel cell.

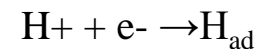
Vesiniku tootmine vee elektrolüüsil traditsioonilise aluselise elektrolüüdiga elektrolüüseris. **1kg vesiniku** tootmiseks minimaalselt **33kWh** (teoreetiline)-
39 kWh (reaalne kõrgT)- **55 kWh** elektrit (madalT) (normaalrõhul, sõltub volutihedusest)

Elektrolüüs

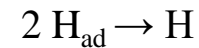
TÜKI-I lepingud
H2Electro OÜ
(kõrgtemperat
uurne
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* Sammud:

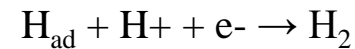


Volmer



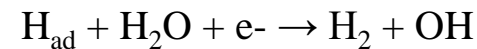
Tafel

or



Heyrowski

or



1m³ vajab 0.8 l vett

1 kWh ~ 250 cm³ vett



Electrolyser

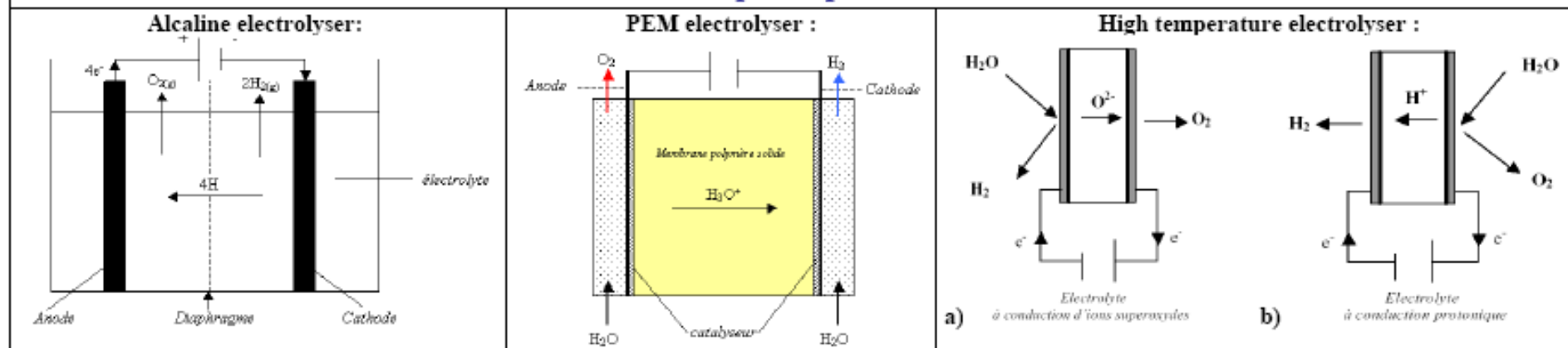
Different types

| type | Electrolyte / Membrane | Electrodes / Catalysers | global reaction |
|------------------|---|--|--|
| Alcaline | KOH/NiO, IMET™ (Inorganic Membrane Electrolysis Tech.) | Anode : Ni, Fer / Ni alloys, metal oxides Cathode : steel + Ni / Ni-Co | Anode : $4\text{HO}^-_{(l)} \Rightarrow \text{O}_{2(g)} + 2\text{H}_2\text{O}_{(l)} + 4e^-$ Cathode: $4\text{H}_2\text{O}_{(l)} + 4e^- \Rightarrow 2\text{H}_{2(g)} + 4\text{HO}^-_{(l)}$ |
| Acid PEM | Solid, proton exchange polymer membrane (Nafion®) | Anode : Graphite-PTFE + Ti / RuO ₂ , IrO ₂ Cathode : Graphite + Pt / Pt | Anode : $6\text{H}_2\text{O}_{(l)} \Rightarrow \text{O}_{2(g)} + 4\text{H}_3\text{O}^+_{(l)} + 4e^-$ Cathode: $4\text{H}_3\text{O}^+_{(l)} + 4e^- \Rightarrow 4\text{H}_{2(g)} + 4\text{H}_2\text{O}_{(l)}$ |
| High temp. steam | a) Zirconia ceramics (0,91ZrO ₂ -0,09Y ₂ O ₃) b) Zirconia oxide ceramics | Anode : ceramics (Mn, La, Cr) / Ni Cathode : Zr & Ni cermets / CeOx | a) Cathode: $2\text{H}_2\text{O}_{(g)} + 4e^- \Rightarrow 2\text{O}_2^- + 2\text{H}_{2(g)}$ Anode : $2\text{O}_2 \Rightarrow \text{O}_{2(g)} + 4e^-$ b) Anode : $2\text{H}_2\text{O} \Rightarrow 4\text{H}^+ + \text{O}_{2(g)} + 4e^-$ Cathode: $4\text{H}^+ + 4e^- \Rightarrow 2\text{H}_{2(g)}$ |

Aluseline FC, pole Pt vaja

PEMFC, Pt ja RuO₂ või IrO₂; SOFC pole vaja Pt-metalle

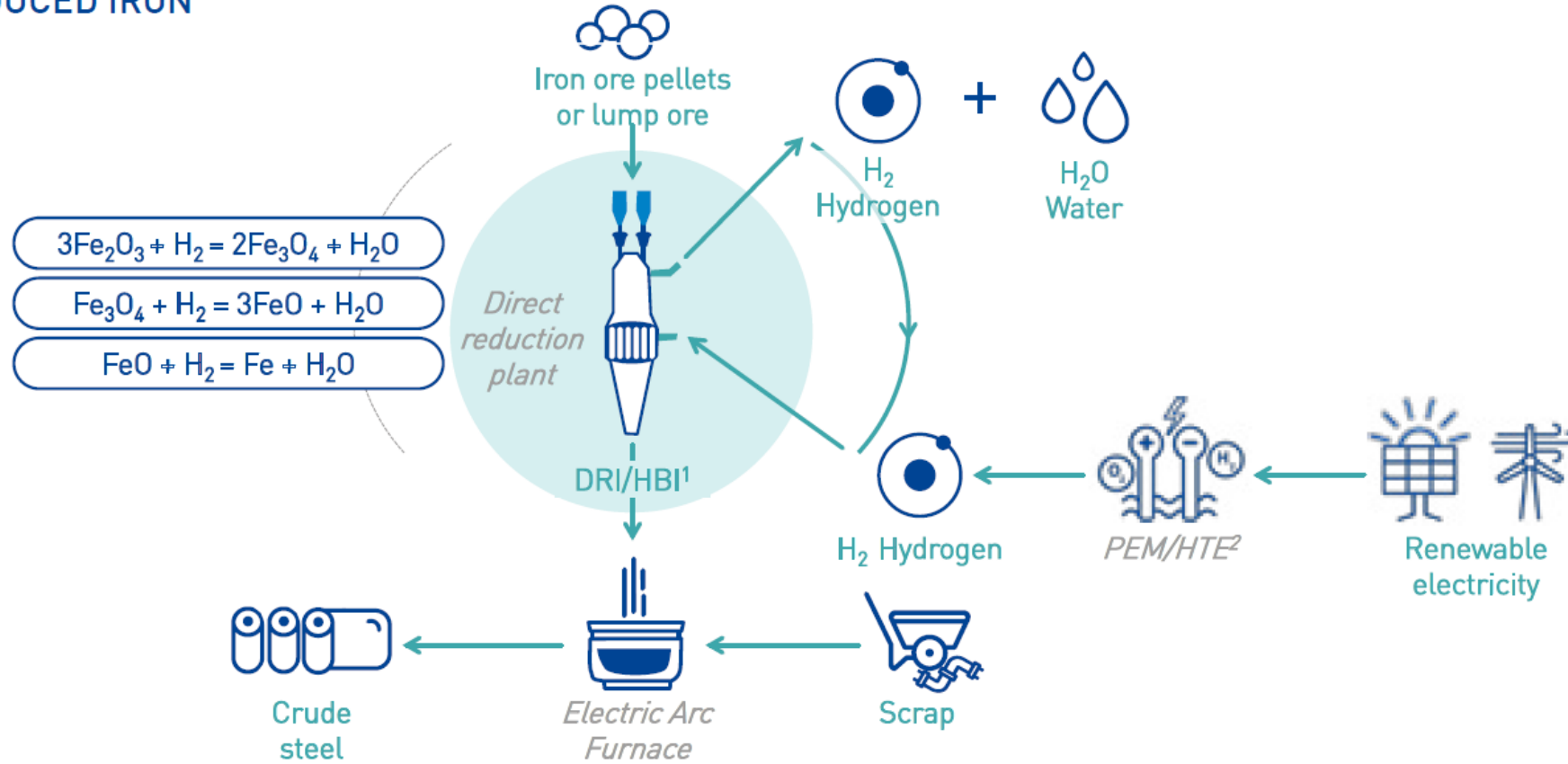
Principle of operation



Technical data

| type | Temperature of operation | Pressure of operation | Electric consumption | Energy Efficiency | Life duration | State of development |
|------------------|--------------------------|-----------------------|---|-------------------|---------------------------|----------------------|
| Alcaline | 50 - 100 °C | 3 - 30 bars | 4-5 kWh / Nm ³ of H ₂ | 75 - 90 % | 15 - 20 years | marketed |
| PEM | 80 - 100 °C | 1- 70 bars | 6 kWh / Nm ³ of H ₂ | 80 - 90 % | 150 000 hours (≈17 years) | development |
| High temp. steam | 800 - 1000 °C | ?? | 3-3.5 kWh / Nm ³ of H ₂ | 80 - 90 % | ?? | research |

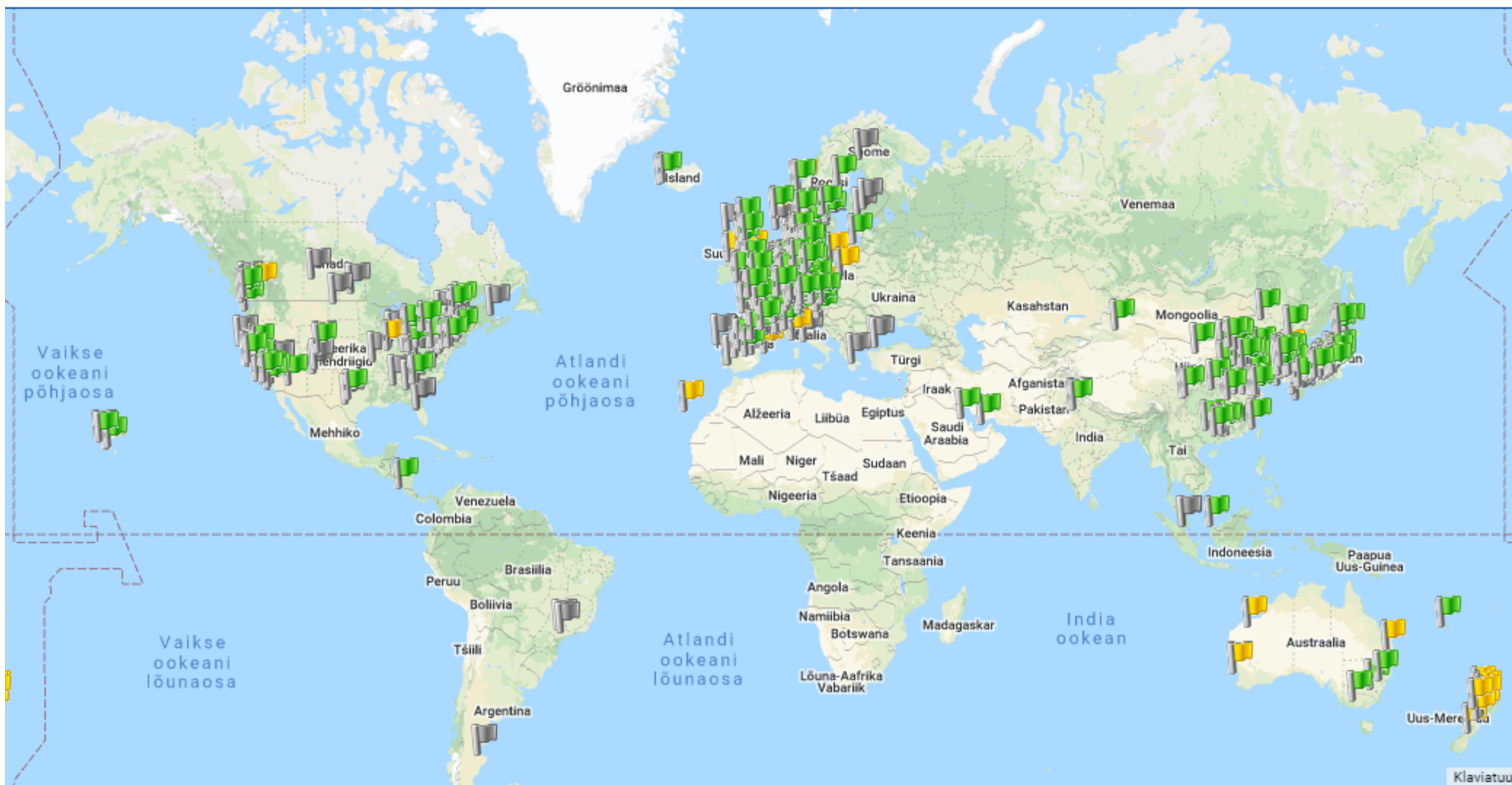
EXHIBIT 18: DEEPLY DECARBONIZED STEELMAKING THROUGH HYDROGEN-BASED DIRECT REDUCED IRON



1 Direct reduced iron/hot briquetted iron

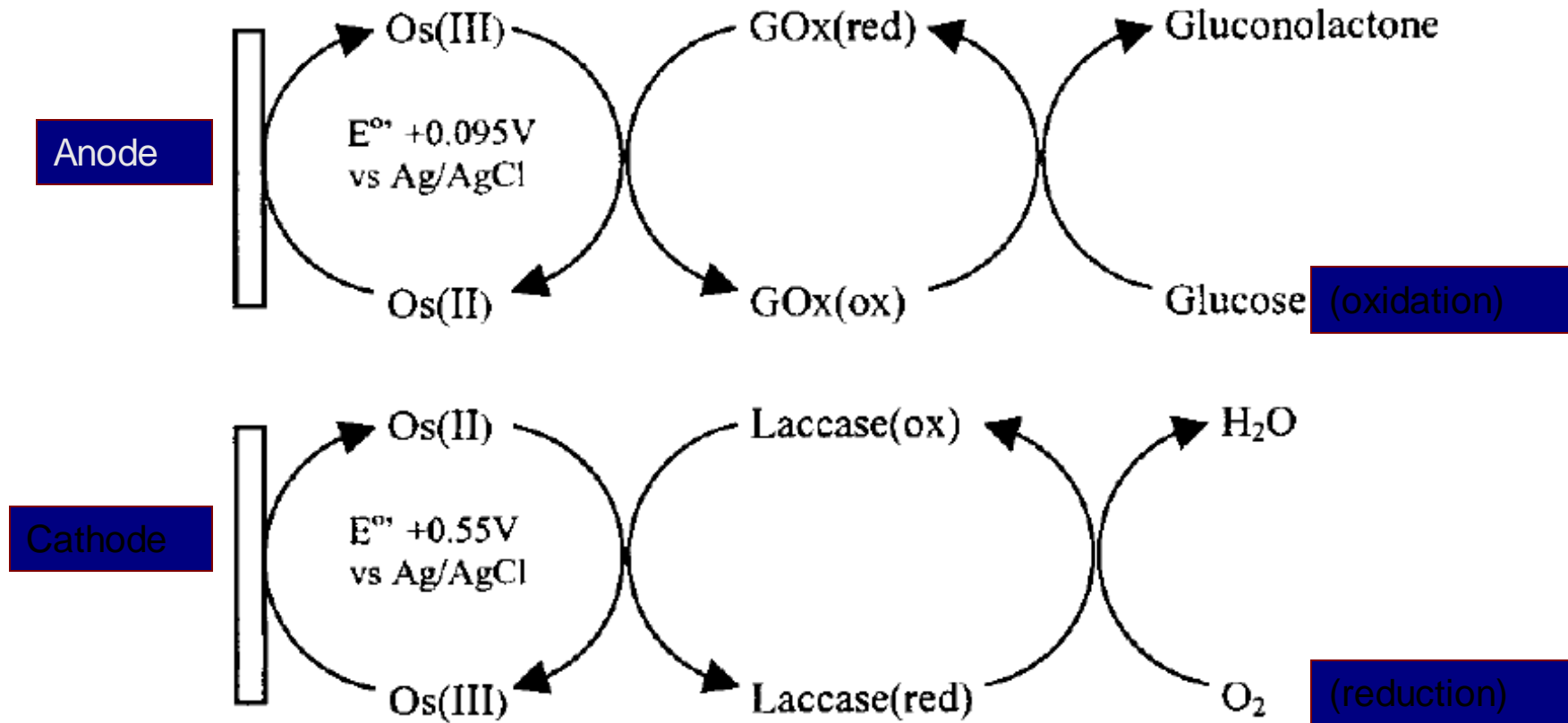
2 Polymer electrolyte membrane electrolysis/high temperature electrolysis

H2 Stations Map



Miniature Biofuel Cell

Scheme 1. Electron-Transferring Steps in the Electrocatalytic Oxidation of Glucose (top) and in the Electrocatalytic Reduction of O₂ (bottom)^a



^a The Os^{2+/3+} centers and the enzymes are immobilized in the electron-conducting redox-polymer films.

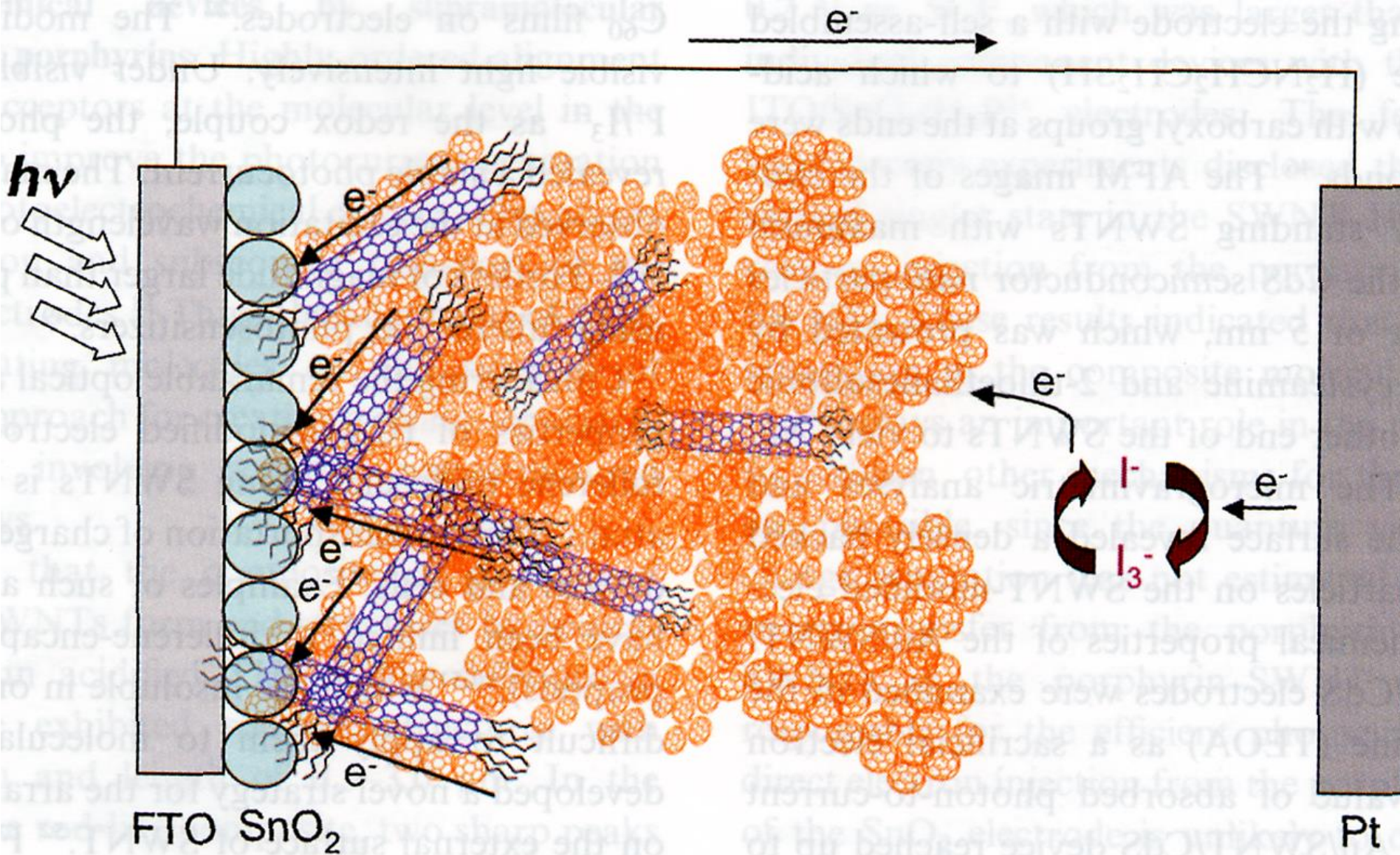


Fig. 11 Schematic illustration for photocurrent generation in the photoelectrochemical devices using FTO/SnO₂/(f-SWNT + C₆₀)_m electrode.