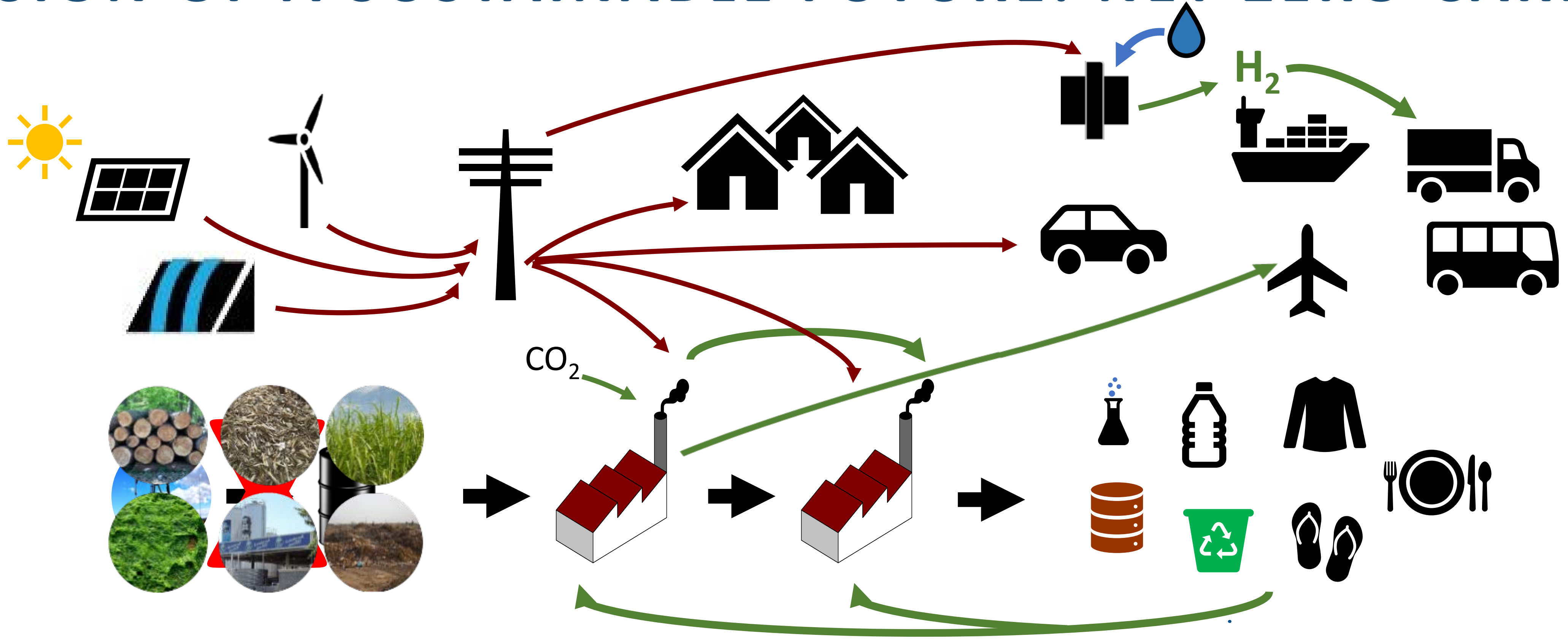
RENEWABLE ENERGY STORAGE AND CONVERSION TOWARDS NET ZERO CARBON ECONOMIES

Ana Inés Torres -Instituto de Ingeniería Química, Facultad de Ingeniería, UdelaR

Seminar Energy Systems Initiative- CAPD- December 4, 2021

VISION OF A SUSTAINABLE FUTURE: NET ZERO CARBON



- Energy - electricity : wind, solar, hydropower => houses, industries
  - transportation: electrification → passenger cars
  low carbon fuels → heavy duty, maritime and aviation
- Chemicals, materials, consumer products: renewable carbon sources

Figures: Wikimedia Commons,

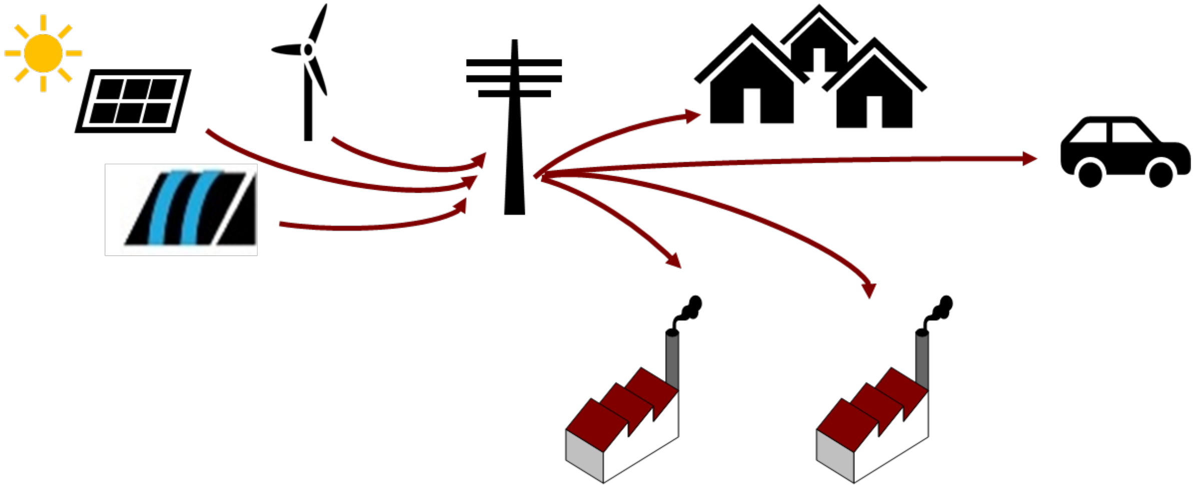
UNITED NATIONS SUSTAINABLE DEVELOPMENT GOALS

- Collection of global goals and targets set for the 2030 Agenda

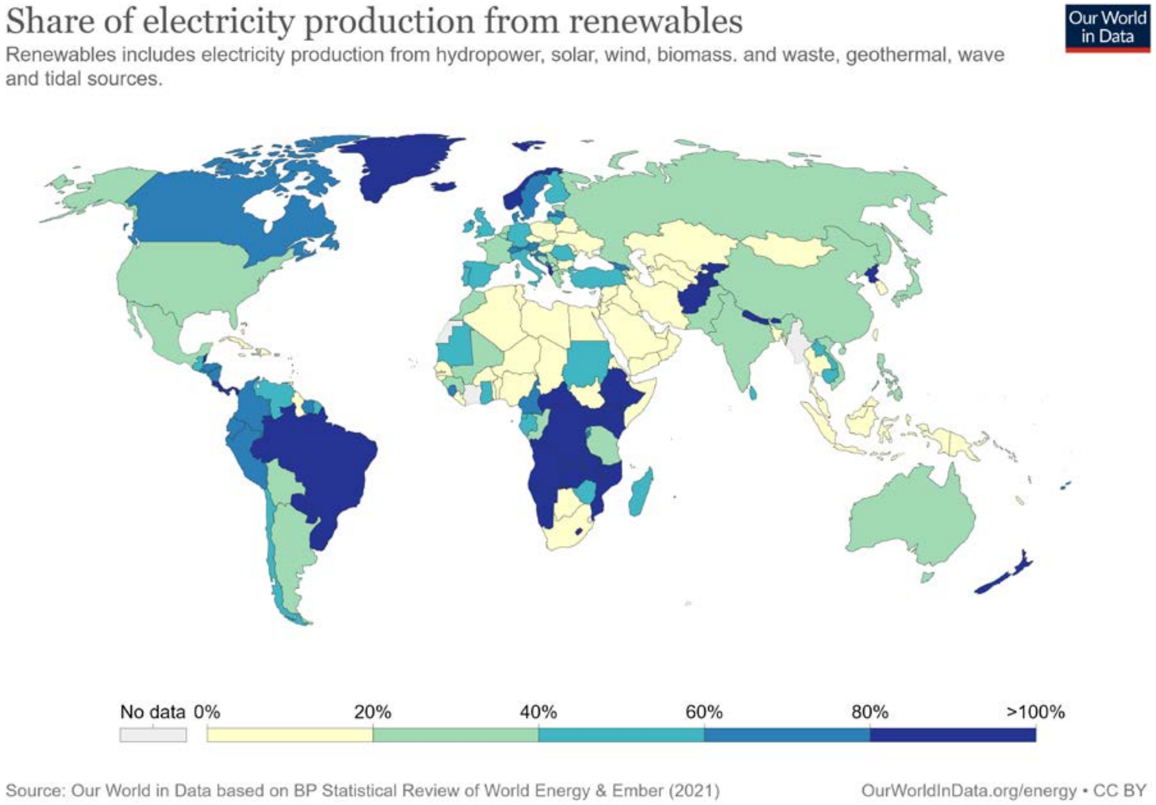
- Balance the three dimensions of sustainability: economic social and environmental

STATUS: RENEWABLE ENERGY- ELECTRICITY

- RE Sources: already integrated in the grid



- **Programmable sources**: hydropower, hydrothermal, nuclear, biomass & waste
- **Non-programmable sources**: wind, sun


Share of electricity production from renewables

Renewables includes electricity production from hydropower, solar, wind, biomass. and waste, geothermal, wave and tidal sources.

Source: Our World in Data based on BP Statistical Review of World Energy & Ember (2021)

OurWorldInData.org/energy • CC BY

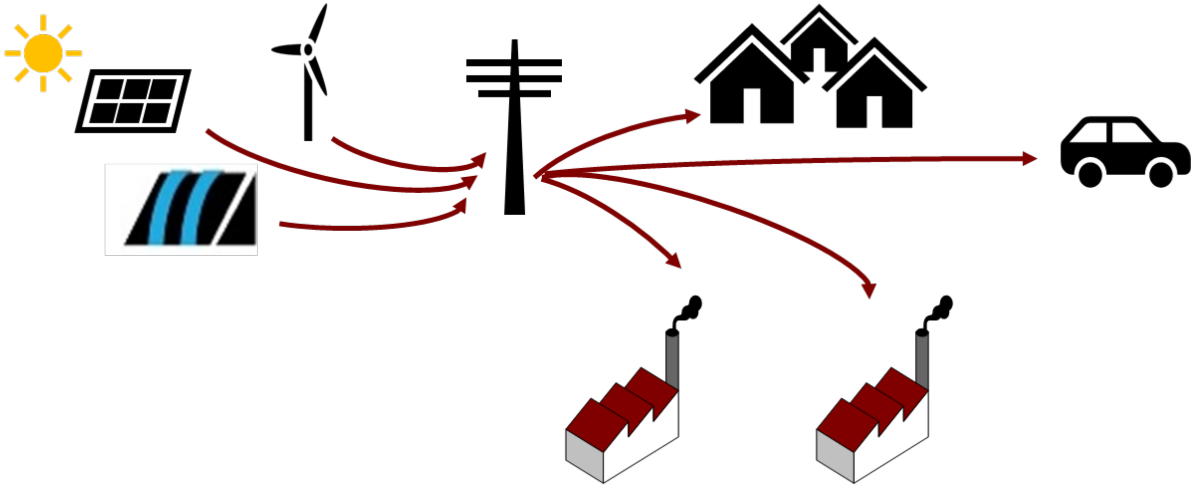
2019: 10 countries > 99% share

Figures: Wikimedia Commons,

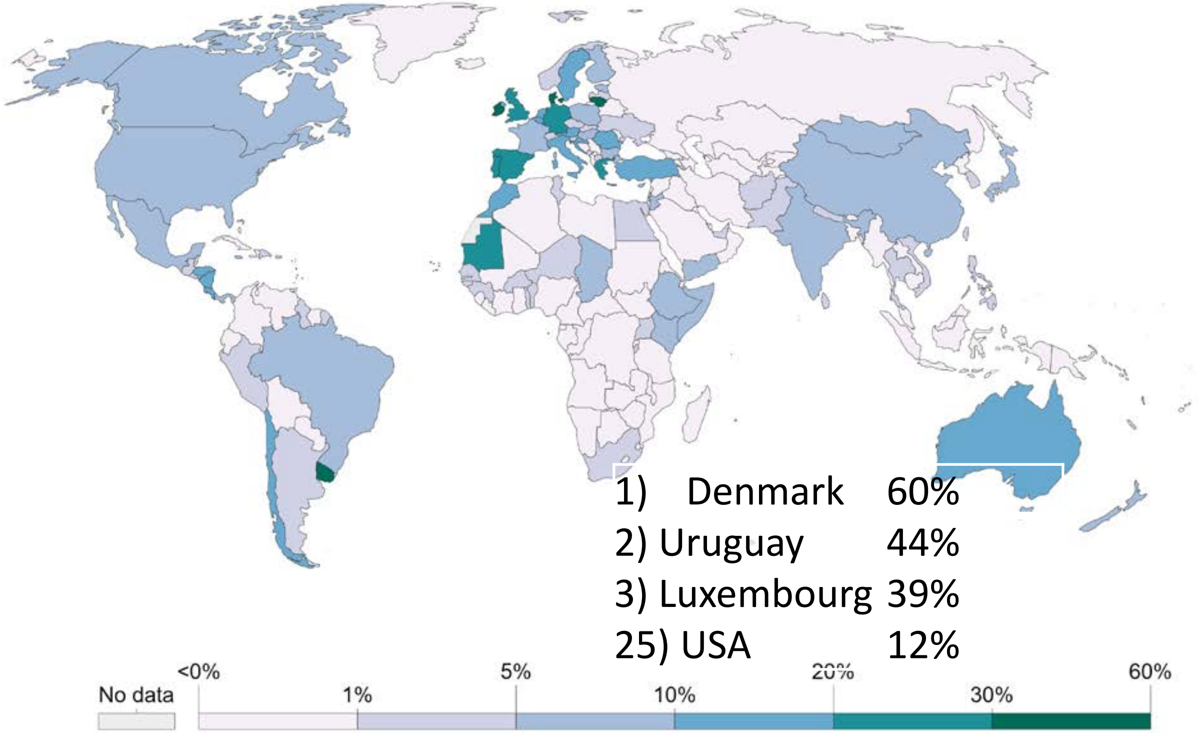
Figure: On the basis of Our world in data https://ourworldindata.org/grapher/share-electricity-renewables

STATUS: RENEWABLE ENERGY- ELECTRICITY

- RE Sources: already integrated in the grid



Share of wind + solar



1) Denmark	60%
2) Uruguay	44%
3) Luxembourg	39%
25) USA	12%

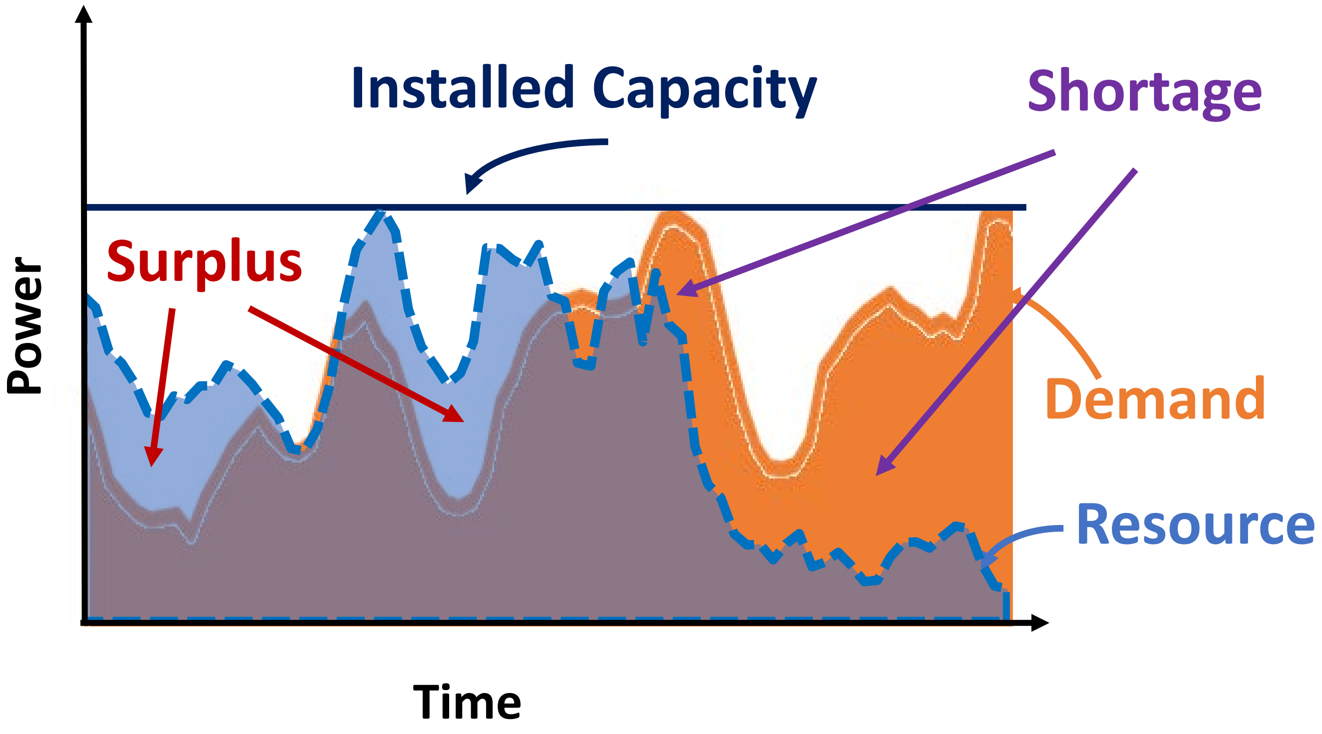
- **Programmable sources**: hydropower, hydrothermal, nuclear, biomass & waste
- **Non-programmable sources**: wind, sun

Figures: Wikimedia Commons,

Figure: Our world in data https://ourworldindata.org/grapher/share-electricity-renewables

STATUS: RENEWABLE ENERGY-ELECTRICITY

- Modern non-programmable renewable energy sources complicate operations

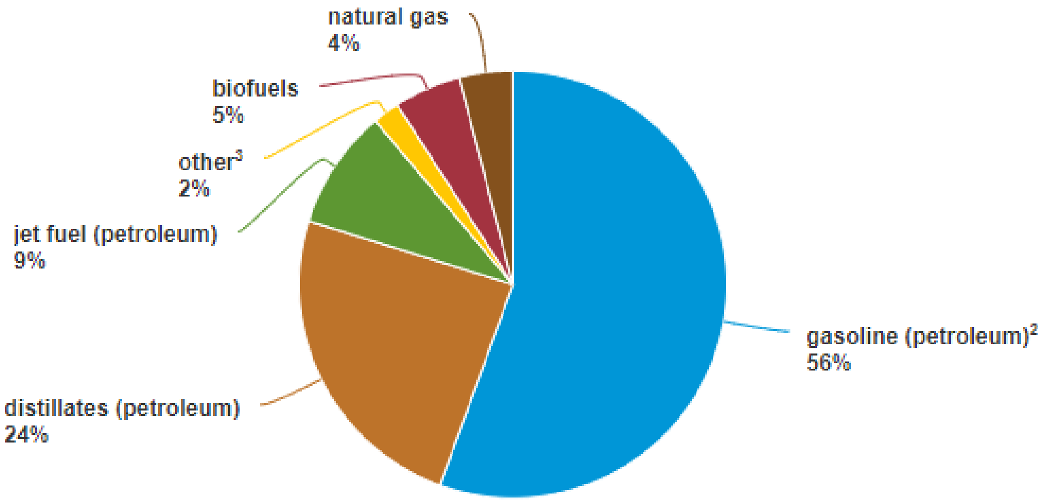


- Large shares of wind/solar energy => imbalances between availability and demand

Challenge: keep growing and use surpluses

STATUS: TRANSPORTATION SECTOR

- USA 2020

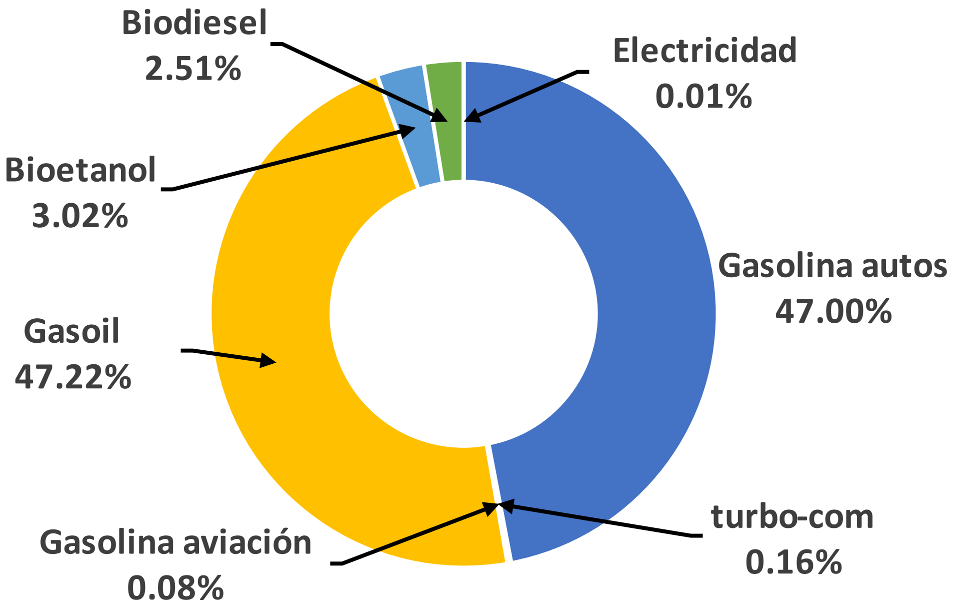


1. Based on energy content
2. Motor gasoline and aviation gas; excludes ethanol
3. Includes residual fuel oil, lubricants, hydrocarbon gas liquids (mostly propane), and electricity (includes electrical system energy losses).

Source: U.S. Energy Information Administration, *Monthly Energy Review*, Tables 2.5, 3.8c, and 10.2b, April 2021, preliminar data

Note: Sum of individual components may not equal 100% because of independent rounding.

- Uruguay, 2020 (1)



- Europe(2): 8% renewables 2018

2020 Target: 10%

Challenge: Advance on decarbonization of transportation sector

Figure: https://www.eia.gov/energyexplained/use-of-energy/transportation.php

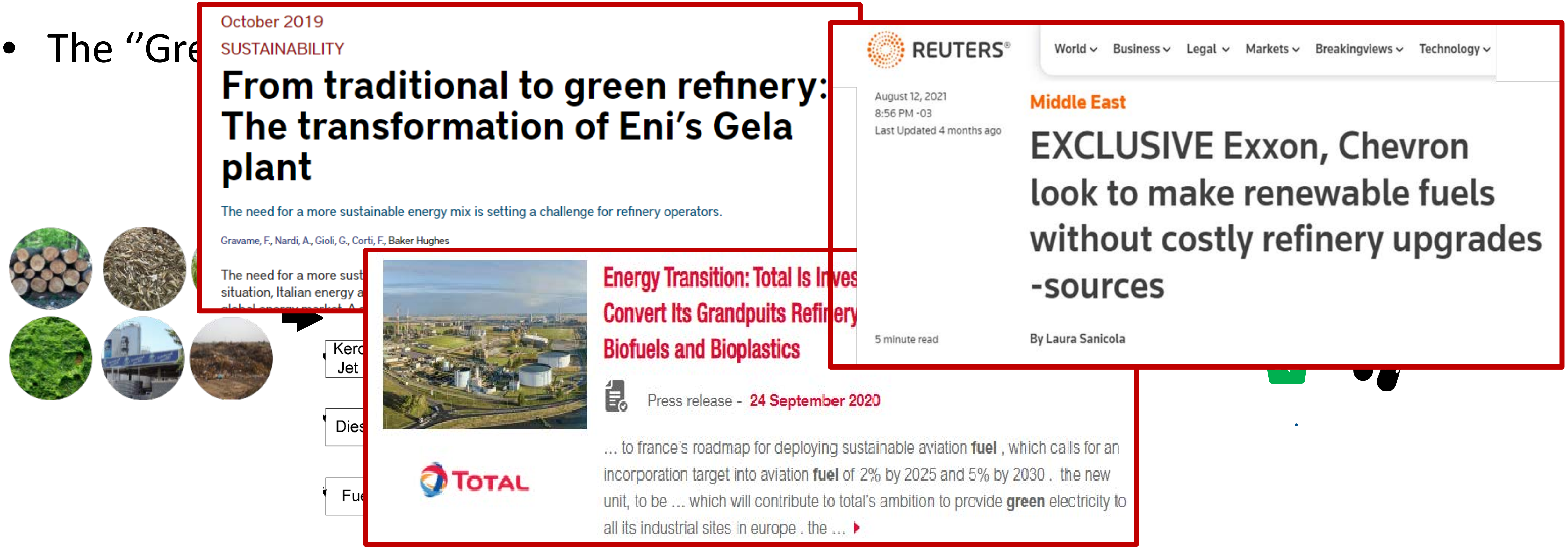
=> more than 90% fossil based

(1) Balance Energético Nacional (MIEM)

(2) Eurostat https://ec.europa.eu/eurostat/web/products-eurostat-news/-/ddn-20200123-2

STATUS: CHEMICALS MATERIALS END PRODUCTS

- **Bio-refineries: Process biomass into fuels materials and chemicals**
- The ‘’Gre



October 2019

SUSTAINABILITY

From traditional to green refinery: The transformation of Eni's Gela plant

The need for a more sustainable energy mix is setting a challenge for refinery operators.

Gravame, F., Nardi, A., Gioli, G., Corti, F., Baker Hughes

The need for a more sust
situation, Italian energy a

August 12, 2021
8:56 PM -03
Last Updated 4 months ago

Middle East

EXCLUSIVE Exxon, Chevron look to make renewable fuels without costly refinery upgrades -sources

5 minute read

By Laura Sanicola

Energy Transition: Total Is Inves
Convert Its Grandpuits Refinery
Biofuels and Bioplastics

Press release - 24 September 2020

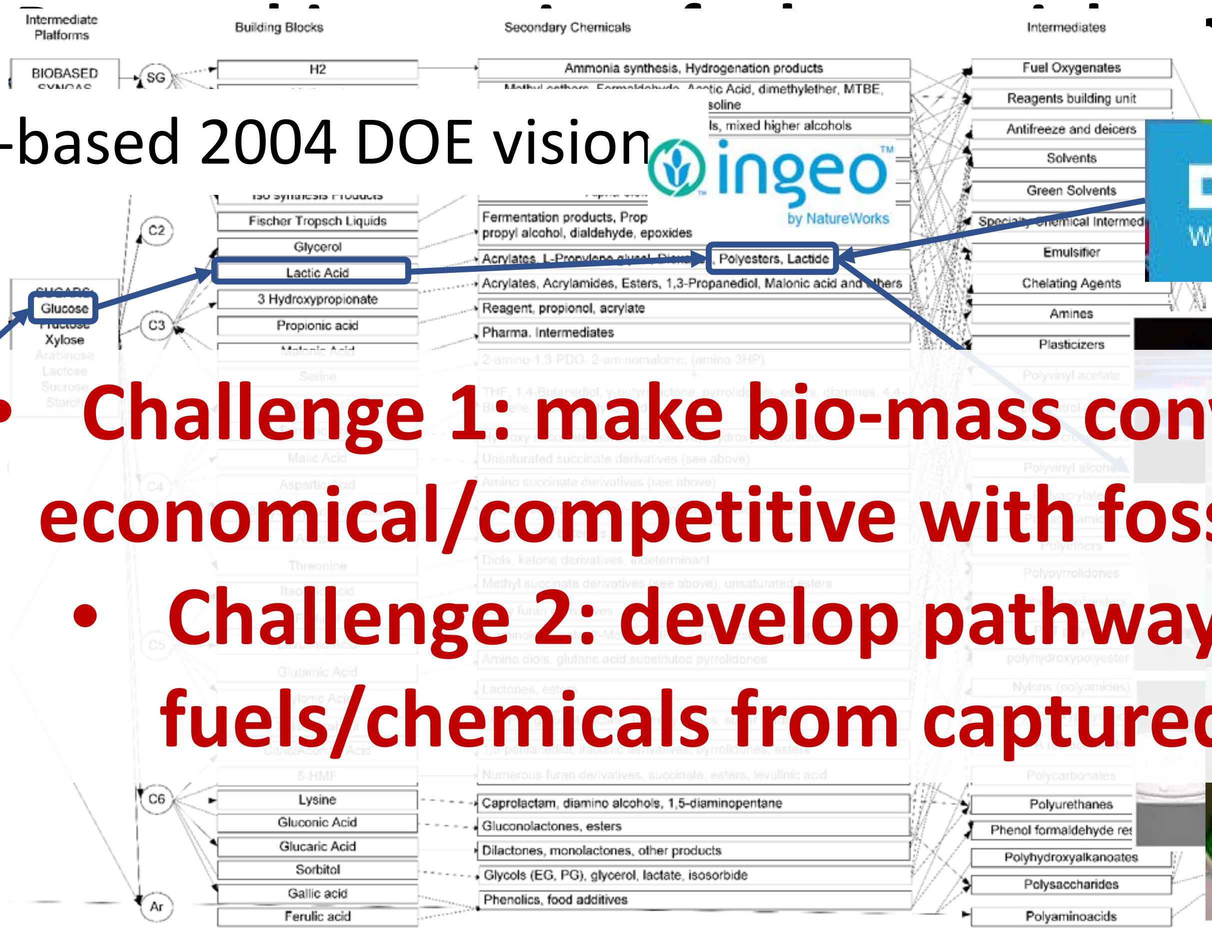
... to france's roadmap for deploying sustainable aviation **fuel** , which calls for an incorporation target into aviation **fuel** of 2% by 2025 and 5% by 2030 . the new unit, to be ... which will contribute to total's ambition to provide **green** electricity to all its industrial sites in europe . the ...

- Popular among oil companies as it uses existing infrastructure
- Keeps petrochemical industry “as is”

Figures: Wikimedia Commons
Honewywell Uop ’s website
Eni’s website
Total’s website

CURRENT STATUS: MATERIALS & CHEMICALS

- **Bio-refineries:** nd chemicals
- The older sugar-based 2004 DOE vision



- **Challenge 1: make bio-mass conversion economical/competitive with fossil based**
  - **Challenge 2: develop pathways for fuels/chemicals from captured CO_2**

- Analogues of current petrochemicals
- Popular in industries that already process biomass

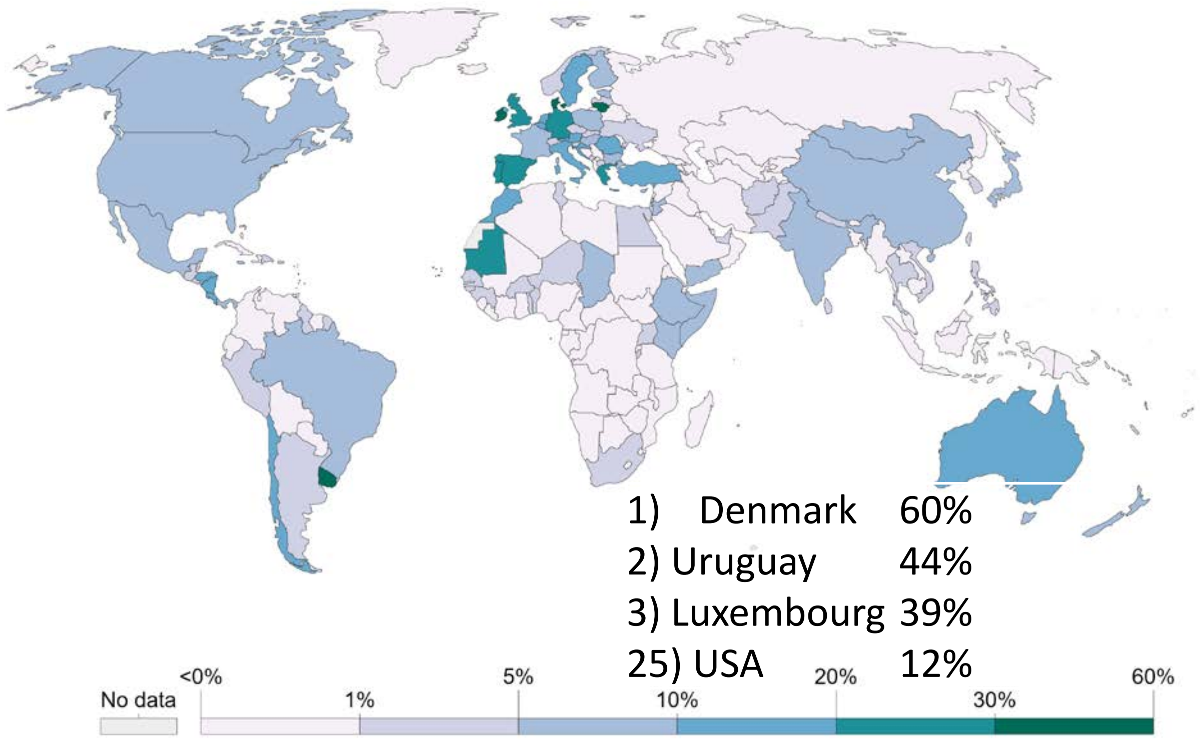
Figures: Wikimedia Commons, Natureworks LLC website
Cargill's website BASF website

OUTLINE OF THE TALK

- **Research group: Analysis & Development of tools for transitioning to a zero/low carbon future**
- **Today: Processes that may be coupled to intermittent renewable energy (P2X)**
  1. Self-storage as a solution to imbalances between generation and demand: tools for assessing self-storage convenience/TOU policies (P2P)
  2. Production of green-hydrogen using surpluses (P2G): selection of technology and production capacities
  3. Electro-reduction of CO_2: Recent advances in reaction network definition
- **Focus mostly on Uruguay, ideas & discussion useful for other regions**

HOW DID URUGUAY BECAME A LEADER IN RENEWABLE ENERGY?

Share of wind + solar



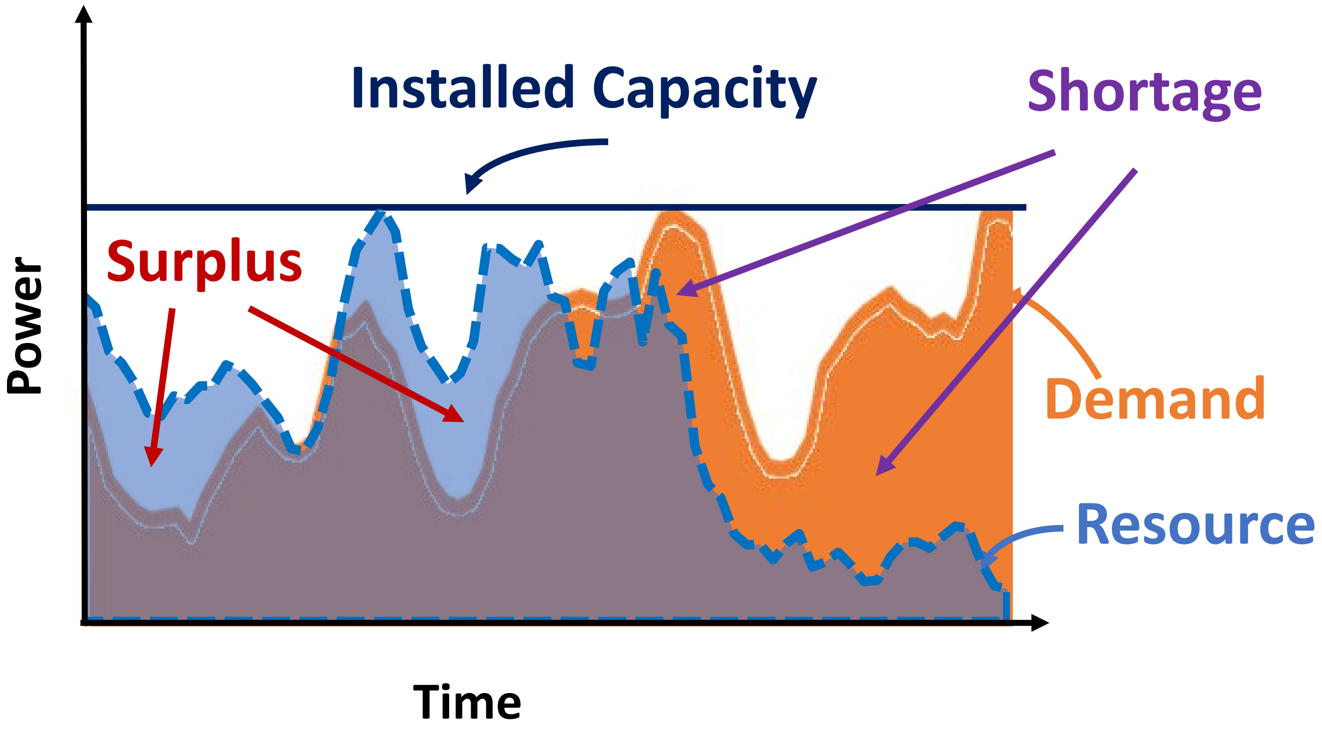
1)	Denmark	60%
2)	Uruguay	44%
3)	Luxembourg	39%
25)	USA	12%

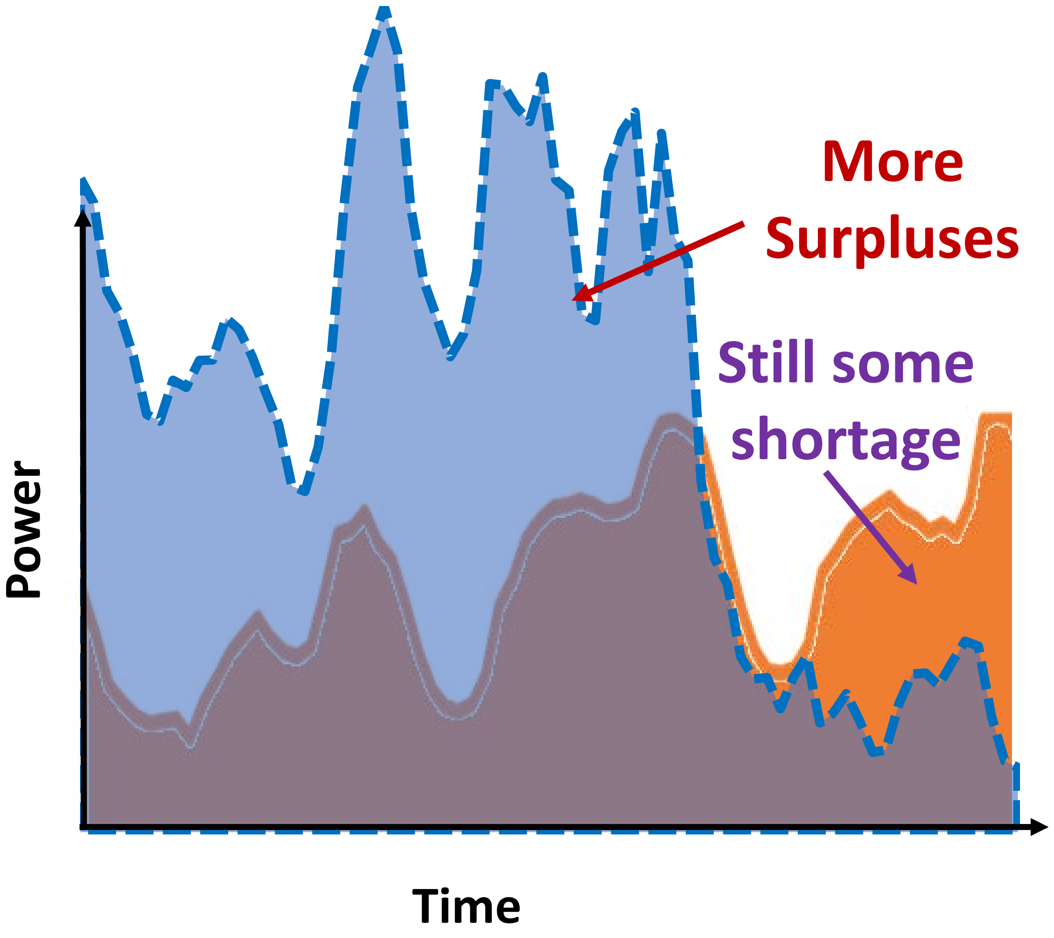
Figure: Our world in data https://ourworldindata.org/grapher/share-electricity-renewables

- **0** fossil fuels: import 100% petroleum & gas needs
  - 2005: Big energy problem: scheduled blackouts
  - 2006: Industries self-generate using biomass -> grid
  - 2009: First 10 MW wind park
  - 2017: Doubled 2005 generation capacity, 70% non-programmables

TRANSITION TO RENEWABLE ENERGY

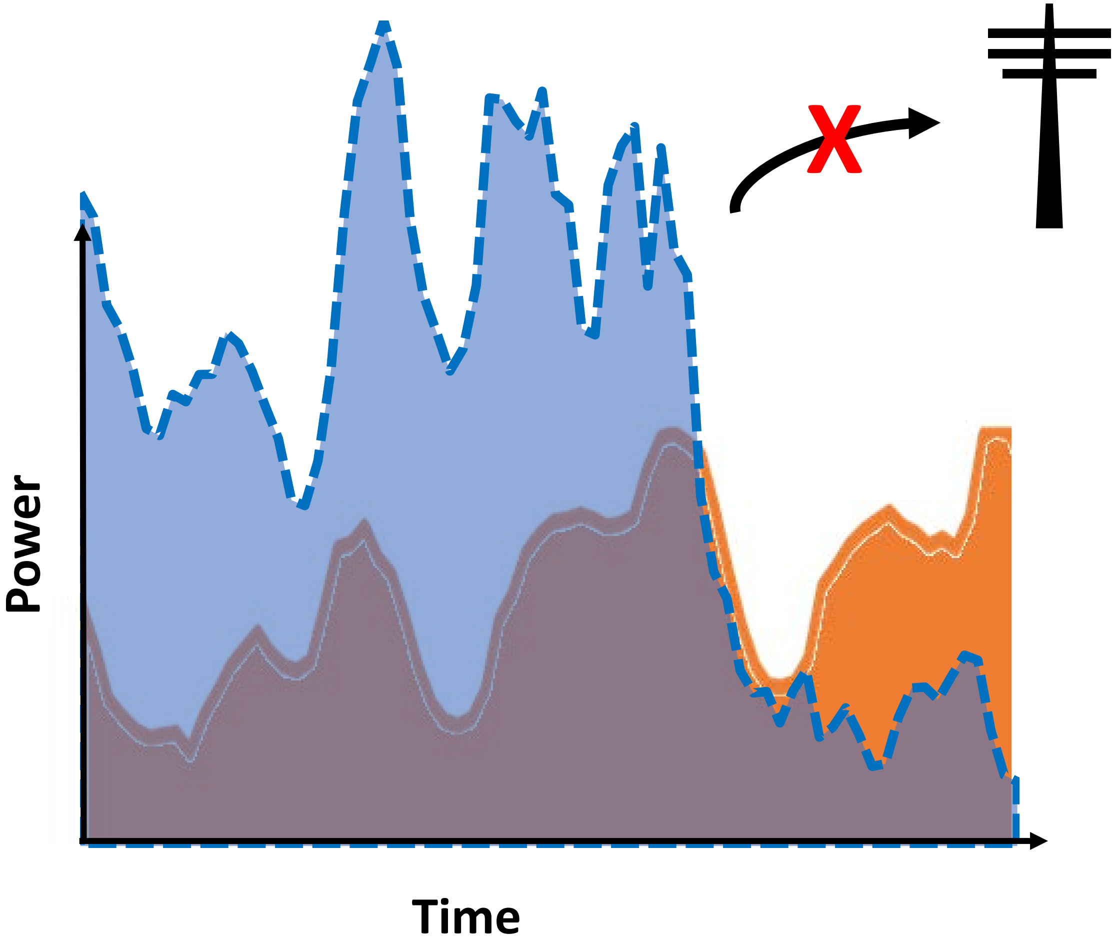
- Not that planned process = > satisfy demand installing very large capacities





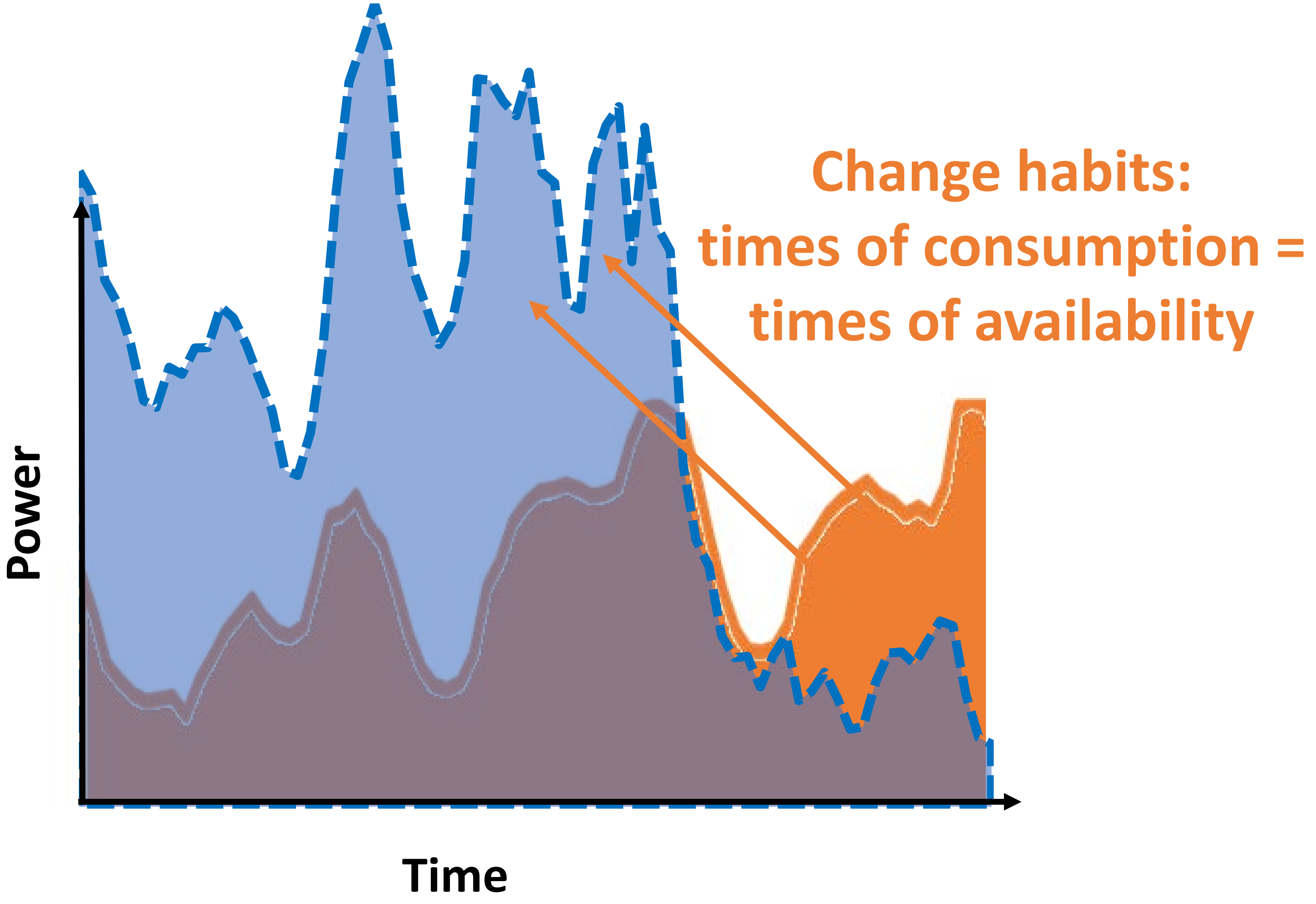
- Planned: Lara et. al, *EJOR*, 2018

OPTIONS TO BALANCE DEMAND AND AVAILABILITY



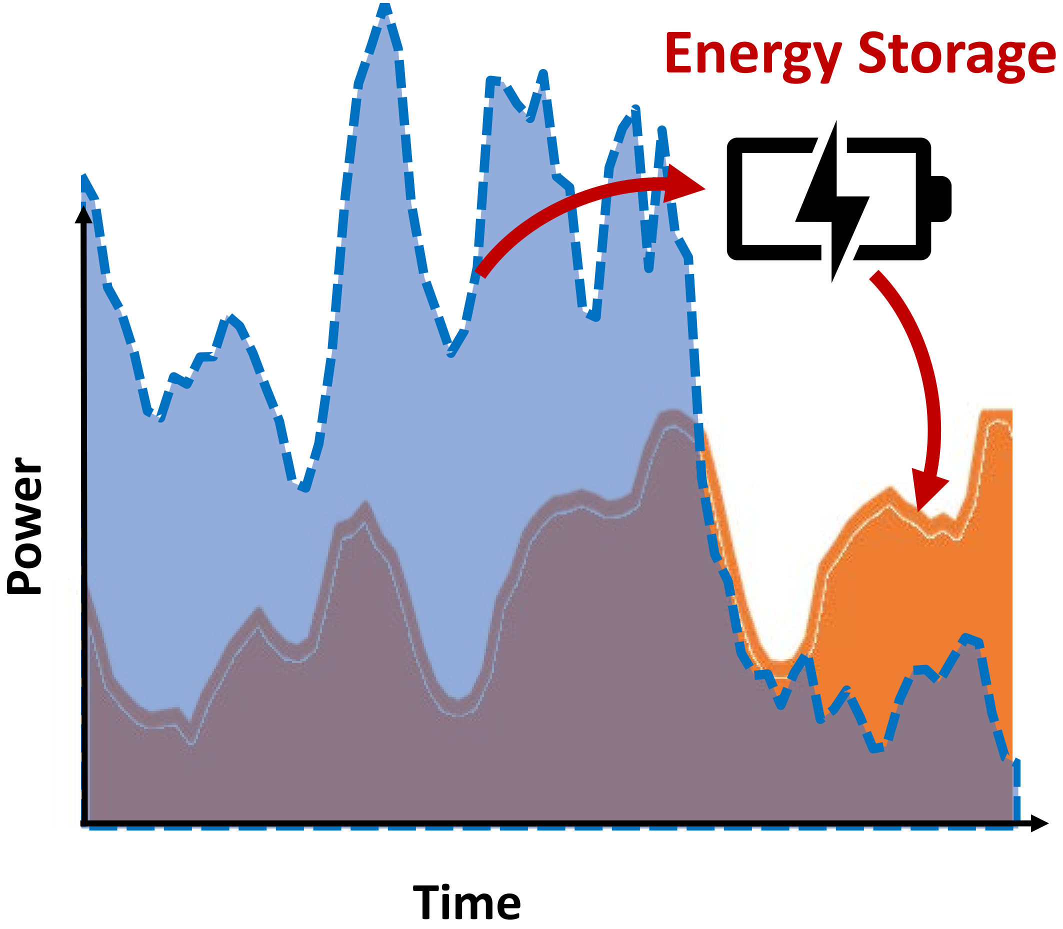
1. Curtailment: Discard any excess energy: do not turn on generators

OPTIONS TO BALANCE DEMAND AND AVAILABILITY



1. Curtailment: Discard any excess energy/ do not turn on generators
2. Demand response programs: time of use (TOU) pricing

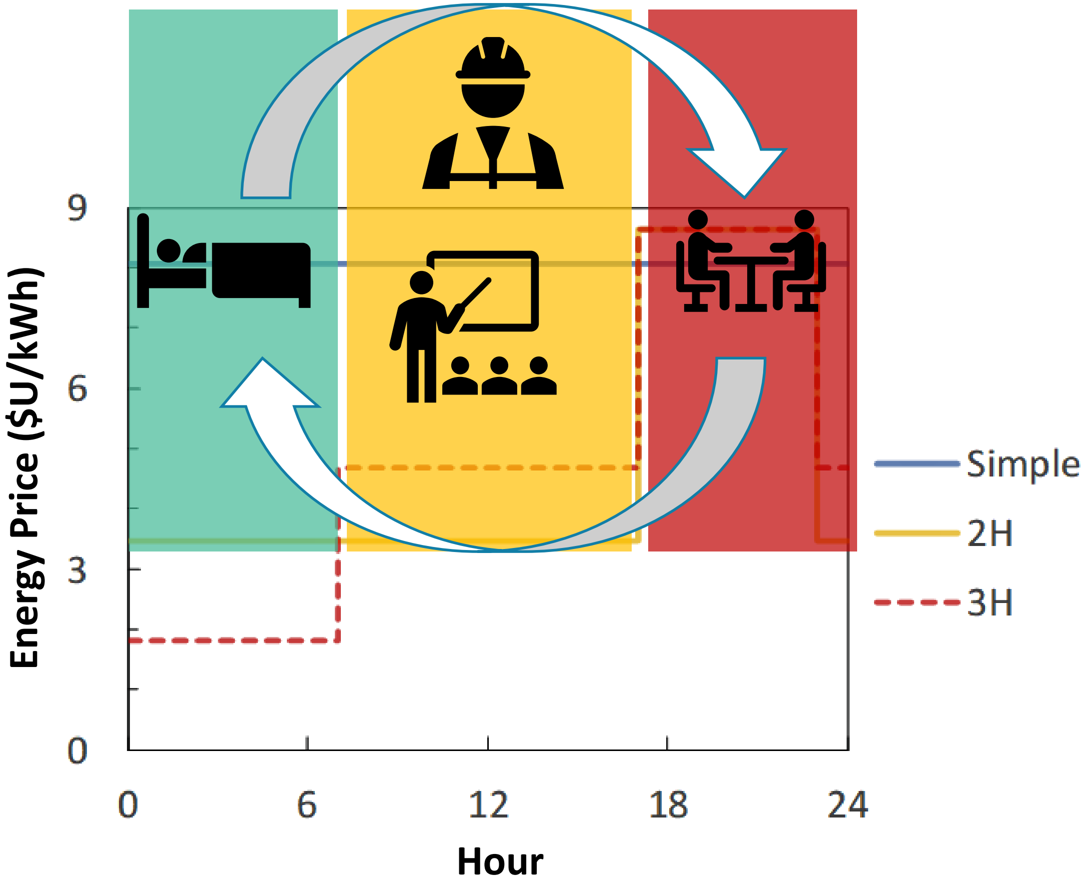
OPTIONS TO BALANCE DEMAND AND AVAILABILITY



1. Curtailment: Discard any excess energy/ do not turn on generators
2. Demand response programs: time of use (TOU) pricing
3. Energy Storage: P2P, P2X industrial or consumer level

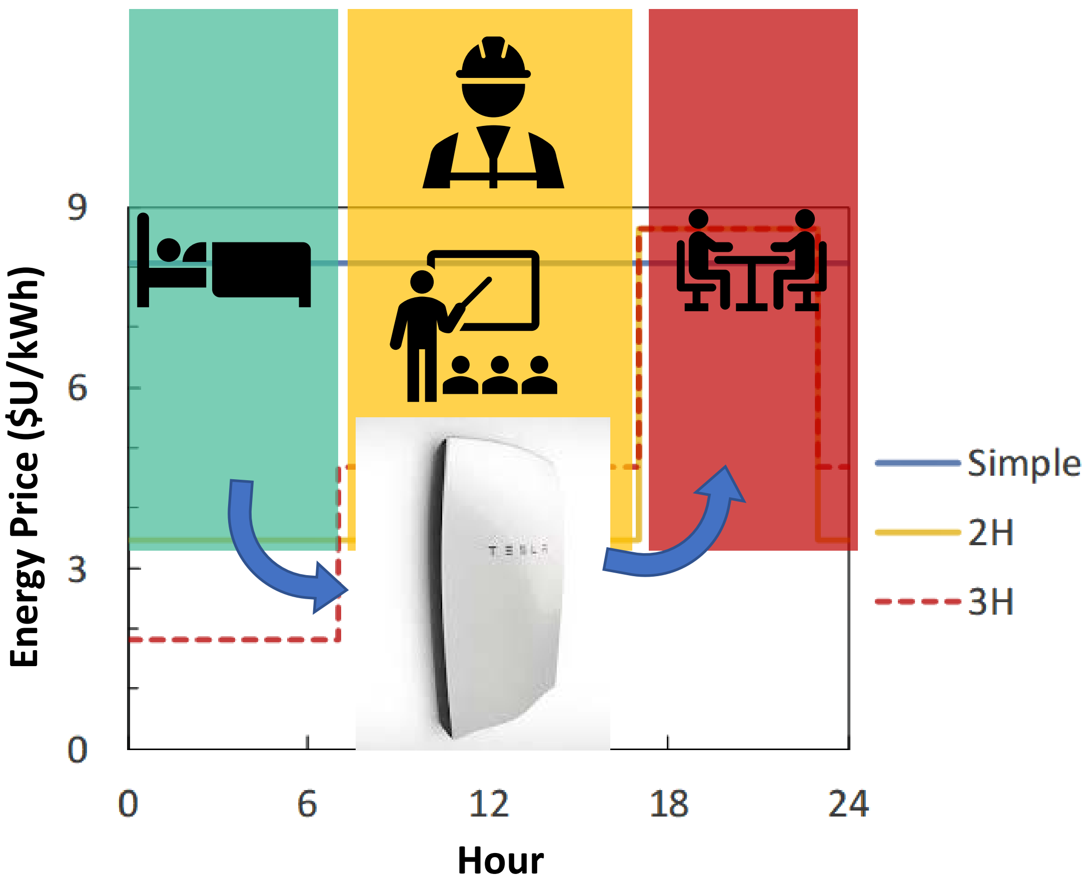
SMART TARIFFS?

- Demand response programs



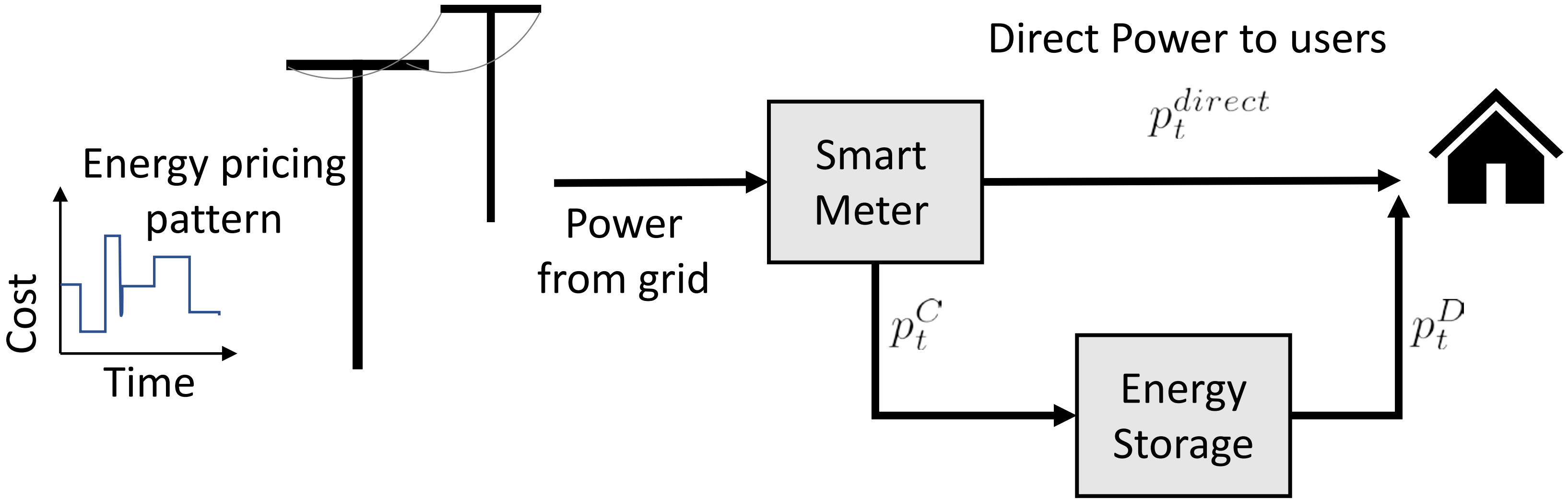
- Major habit changes

- Behind the meter storage



- Batteries degrade when used

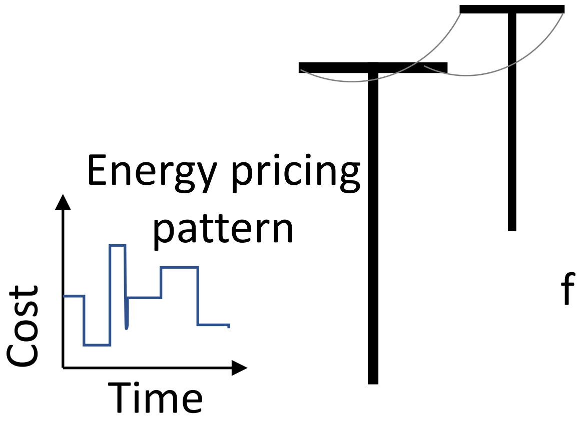
STATING THE PROBLEM

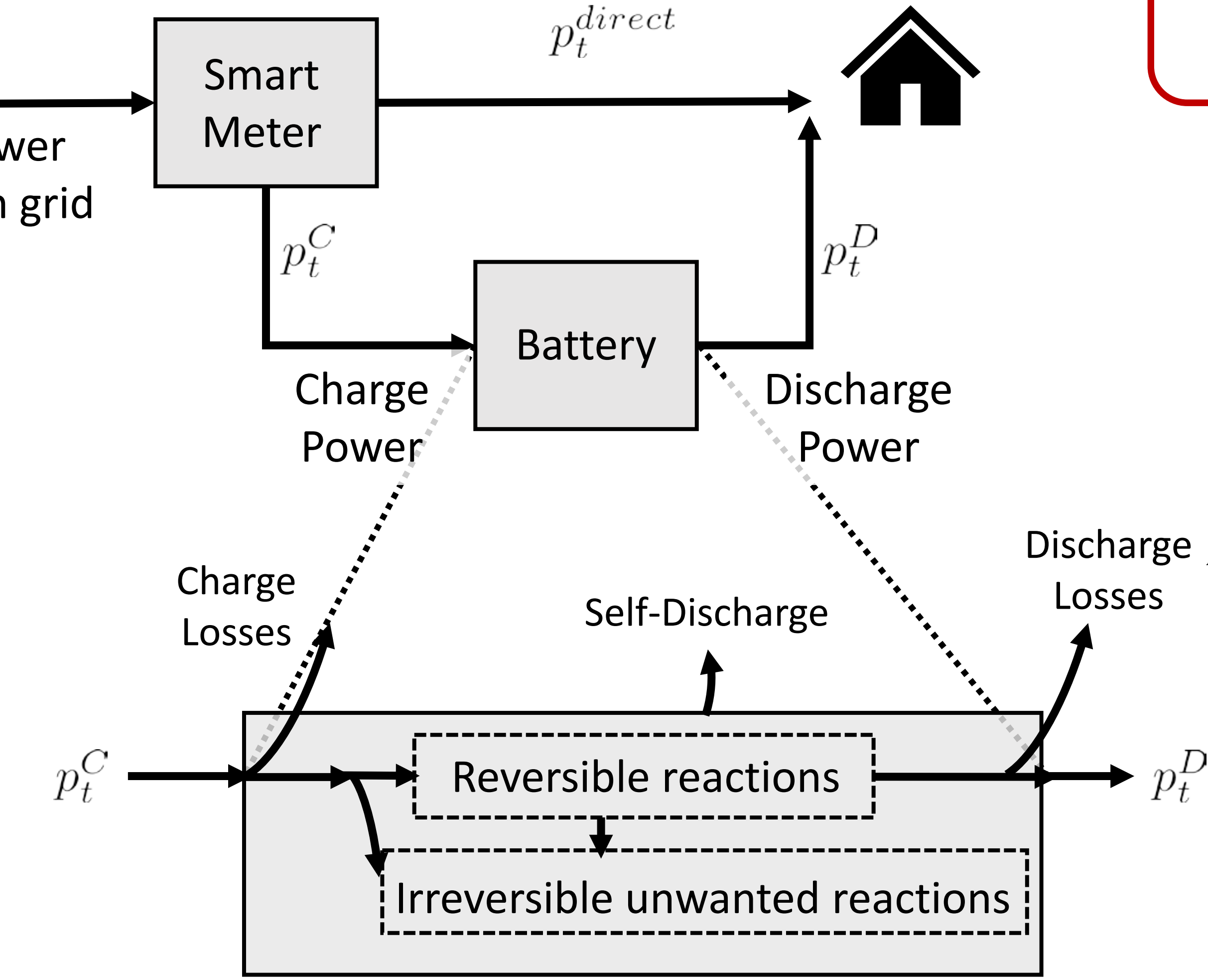


Goal: Maximize savings

- Strategy: Time-shift power signal
  - Consume & charge at power p_t^C when energy cost ($\$_t$) is low
  - Discharge (& consume a rest if needed) at power p_t^D when $\$_t$ high

STATING THE PROBLEM

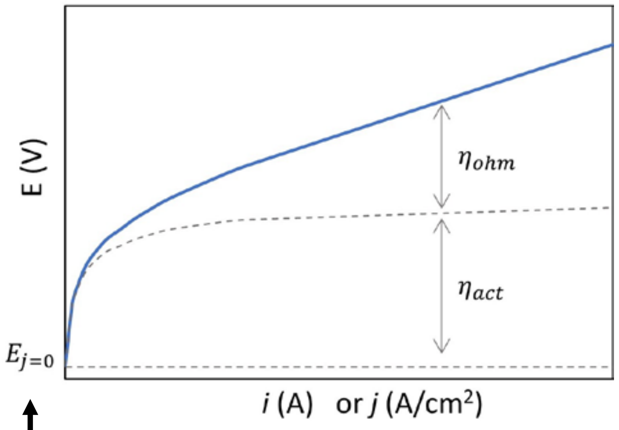




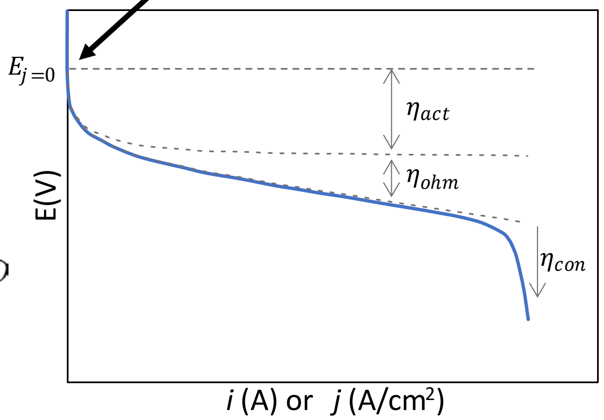
Charge/discharge patterns affect efficiency and life of the battery

⇑

ChemE phenomena



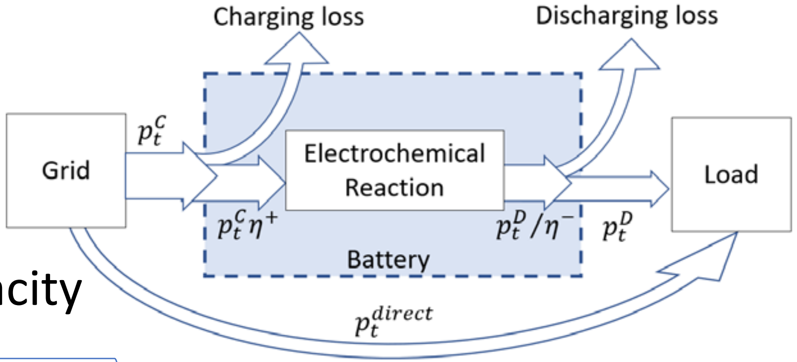
Nernst equation



Nernst equation

FORMULATION OF THE OPTIMIZATION PROBLEM

- Objective function



In the electricity bill

Penalty for losing capacity

$$\text{Savings} = \overbrace{\sum_t (\$_t \boxed{p_t^D} \Delta t - \$_t \boxed{p_t^C} \Delta t)}$$

Power not consumed from the grid when price is high

Power consumed from the grid when price is low

"Discretization" of the price signal

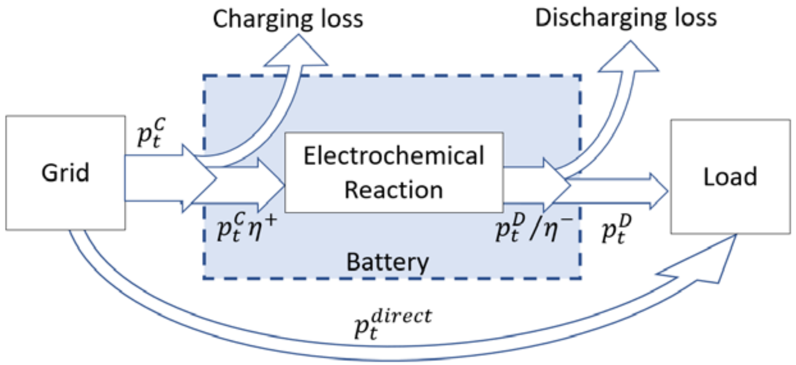
Fraction of capacity lost due to operation @ t

Installed capacity (@ t=0)

Cost of the device

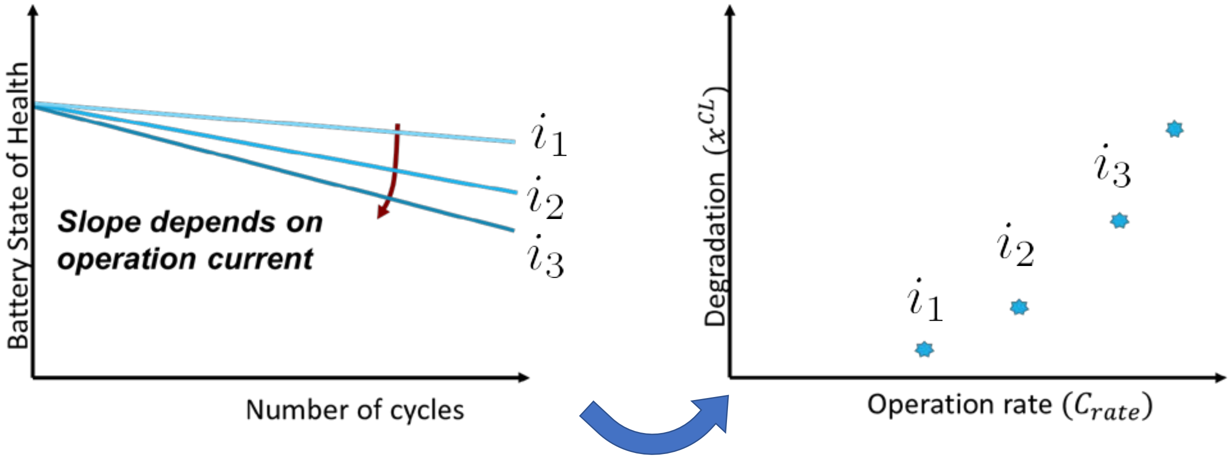
- p_t^D, p_t^C, x_t^{CL} **Degrees of freedom**

FORMULATION OF THE OPTIMIZATION PROBLEM



- Main constraints

1. Energy balance $SoC_t = SoC_{t-1} + \Delta t p_t^C \eta^+ - \Delta t \frac{p_t^D}{\eta^D}$
2. Non-simultaneous charge/discharge $p_t^C p_t^D = 0$
3. Models for capacity loss



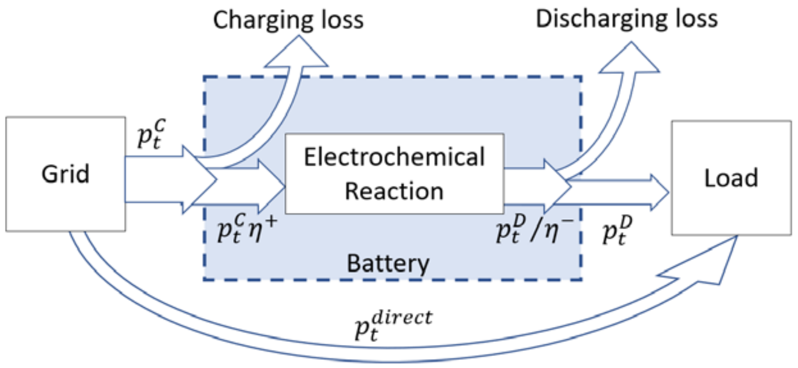
$$c_{rate} = \frac{i}{IC_S^Q}$$

- Battery degradation models
  - Convex approximations appropriate
    (Fortenbacher et al, Proc. IEEE PowerTech, 2017)

$$x_t^{CL} = \Delta t(\alpha_1 (c_{rate,t})^2 + \alpha_2 c_{rate,t})$$

Parameters fitted from experimental data

FORMULATION OF THE OPTIMIZATION PROBLEM



- Main constraints

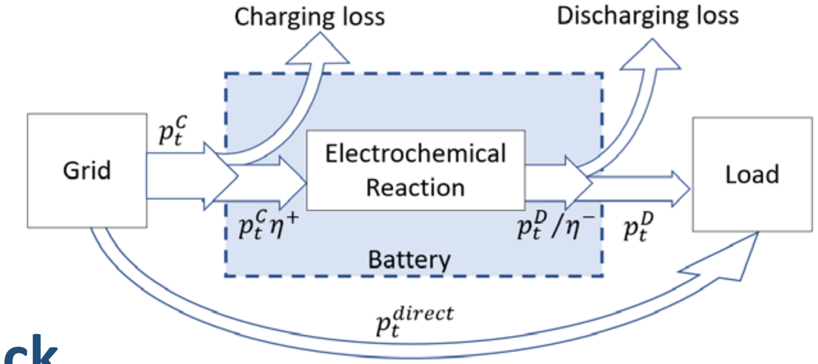
1. Energy balance $SoC_t = SoC_{t-1} + \Delta t p_t^C \eta^+ - \Delta t \frac{p_t^D}{\eta^D}$
2. Non-simultaneous charge/discharge $p_t^C p_t^D = 0$
3. Models for capacity loss

$$x_t^{CL} = \Delta t(\alpha_1 (c_{rate,t})^2 + \alpha_2 c_{rate,t})$$

Introduce non-linearity to the problem

$\Rightarrow$ Limits solving the problem for short time spans

FORMULATION OF THE OPTIMIZATION PROBLEM

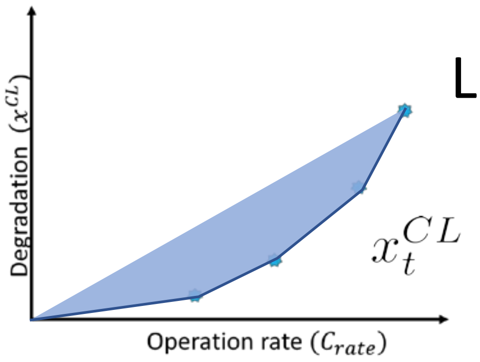


- Convex relaxation

1. Energy balance $SoC_t = SoC_{t-1} + \Delta t p_t^C \eta^+ - \Delta t \frac{p_t^D}{\eta^D}$
2. ~~Non-simultaneous charge/discharge $p_t^C p_t^D = 0$~~ **Drop & check**

   "… simultaneous charge and discharge will not occur if marginal prices are positive"
   (Castillo & Gayme, IEEE Conference on Decision and Control, 2013)

3. Models for capacity loss



Larger x_t^{CL} lower savings

$$x_t^{CL} = \Delta t(\alpha_1(c_{rate,t})^2 + \alpha_2 c_{rate,t})$$

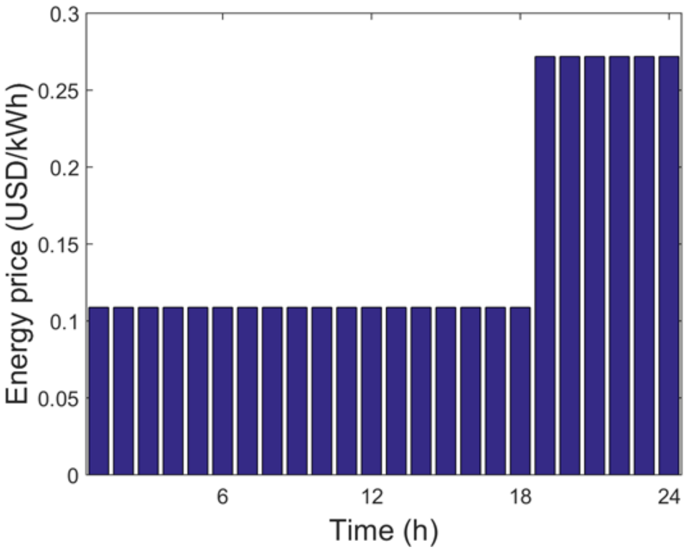
$$\Rightarrow x_t^{CL} \geq \Delta t(\alpha_1(c_{rate,t})^2 + \alpha_2 c_{rate,t})$$

⇒ Equivalent convex problem

✓ global optimum
✓ Also strict => unique

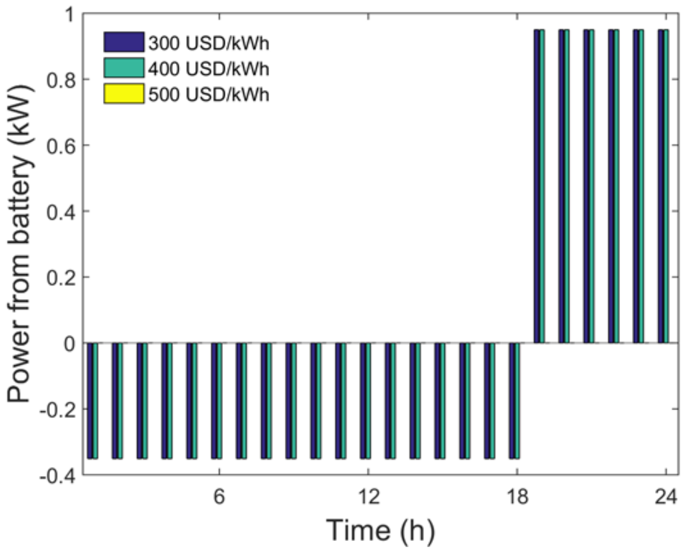
CASE STUDY-SIMPLE SMART TARIFF (Corengia & Torres, *Processes*, 2018)

- Uruguay’s 2H

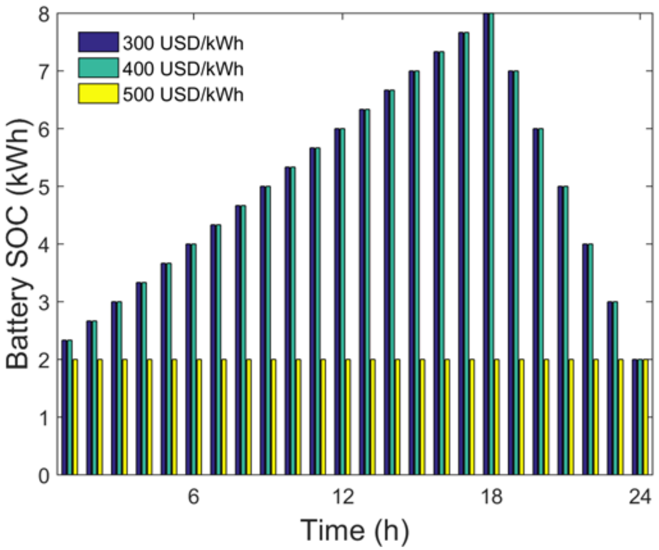


- Charge/discharge schedule

(Li-ion battery, Sarker et al *Power Syst. Res.* 2017)



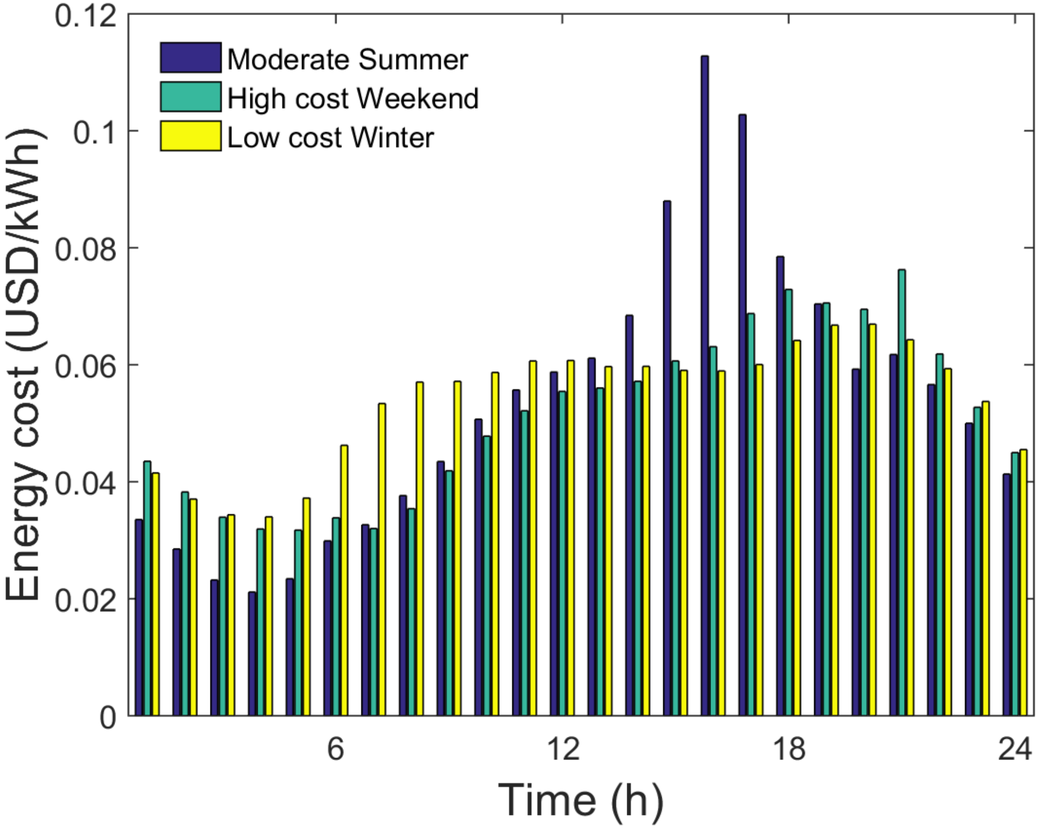
- Battery SoC



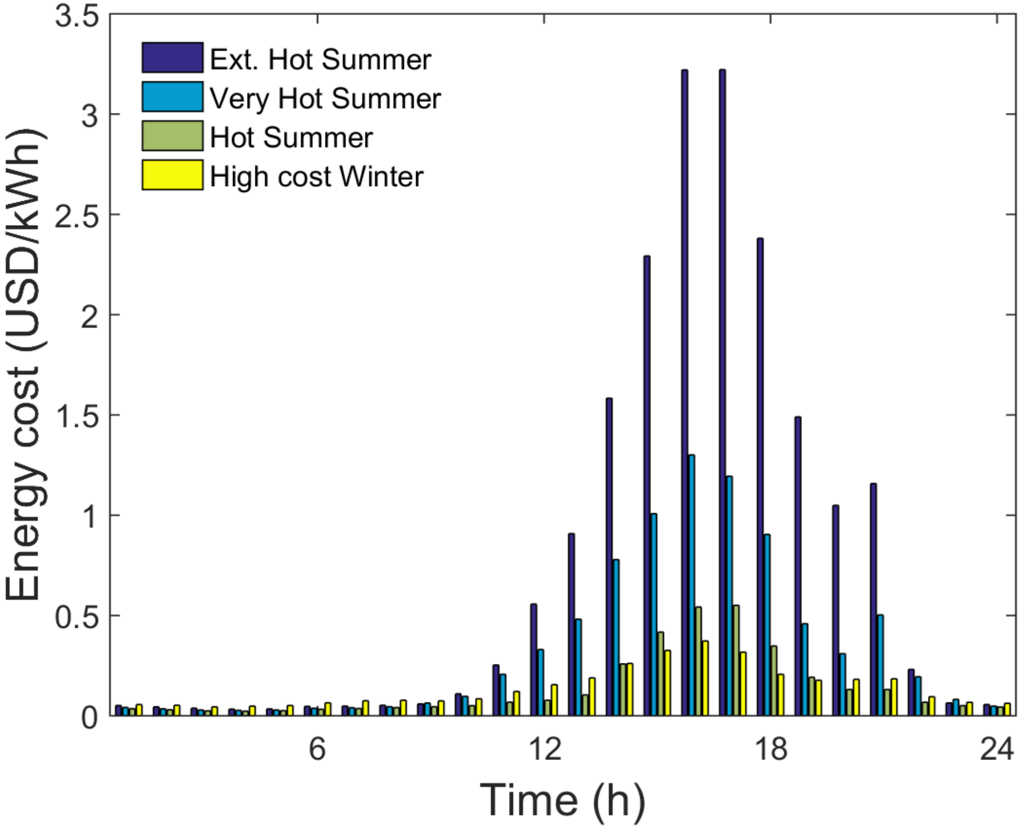
- Optimal solution: charge/discharge the battery as slowly as possible @ constant power
- If battery ≥ 500 USD/kWh => optimal solution never turn on the battery
- GAMS/IPOPT: 1 day analysis is very easy : 96 variables, 24 eq. const., 24 ineq. const.; solved PC i7 in sec

CASE STUDY-COMPLEX SMART TARIFF (Corengia & Torres, *Processes*, 2018)

- Southern California Edison (2018 TOU-GS-2-RTP).



- Days with moderate variation in prices

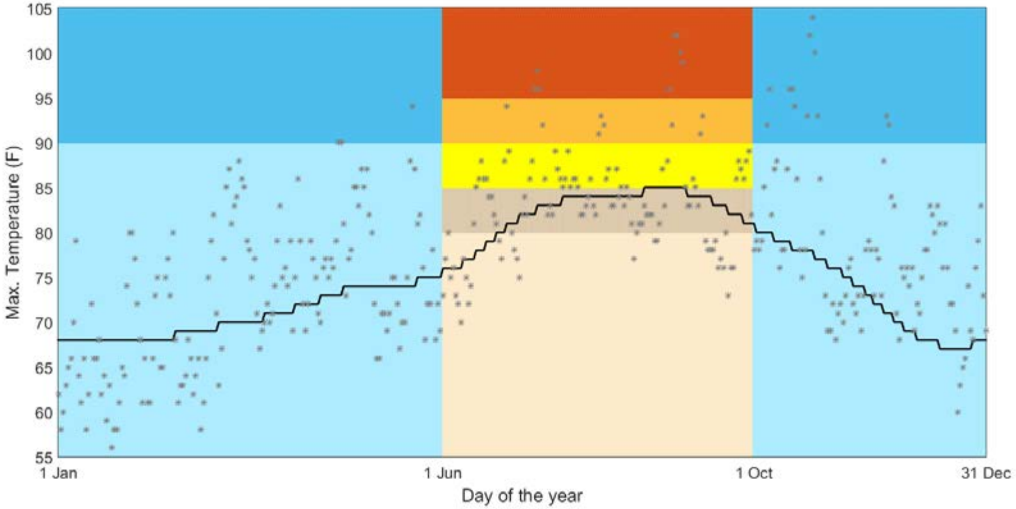


- Days with large variation in prices

CASE STUDY-COMPLEX SMART TARIFF (Corengia & Torres, *Processes*, 2018)

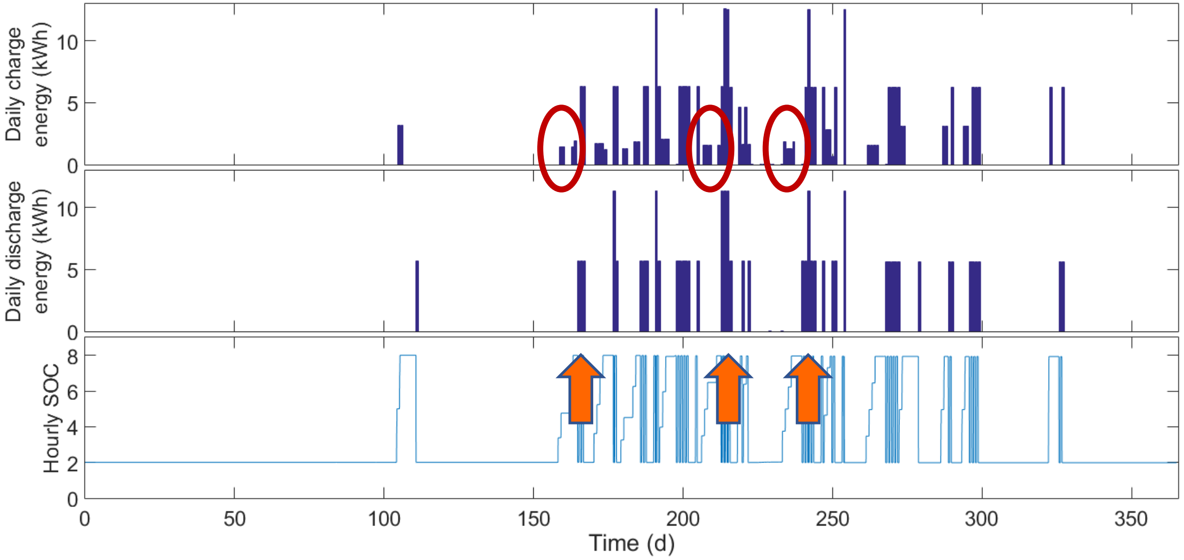
- Long term behaviour

LA- Maximum temperatures 2017



Background colors => limits for tariffs

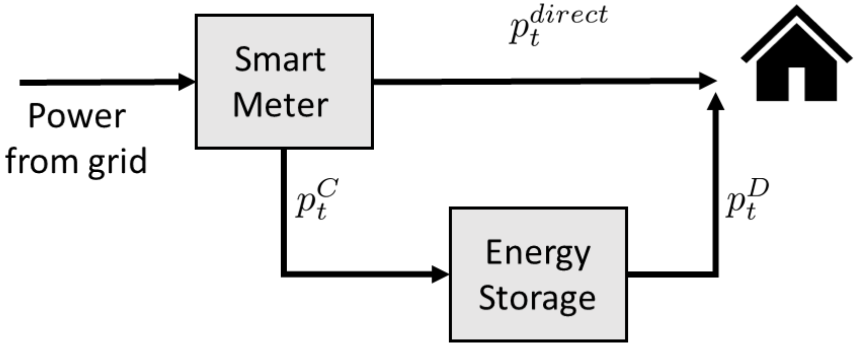
$\Rightarrow$



- Strategy: use the battery in days with large differences between peak/ off-peak prices
- Start charging slowly the battery even days before to preserve battery => add constraint to limit this behavior
- 1 yr analysis 35405 variables, 9125 eq. const., 8760 ineq. constr., 26280 DOF; solved PC i7 in ~1h
- 5 yr analysis 177k variables, 45k eq. const., 219k ineq. constr., 131k DOF; solved PC i7 in hours , not solved before

CASE STUDY-MATCH CONSUMPTION PROFILES

(Corengia & Torres, *ENERLAC*, 2020)



Direct Power to users

p_t^{direct}

Smart Meter

Power from grid

p_t^C

Energy Storage

p_t^D

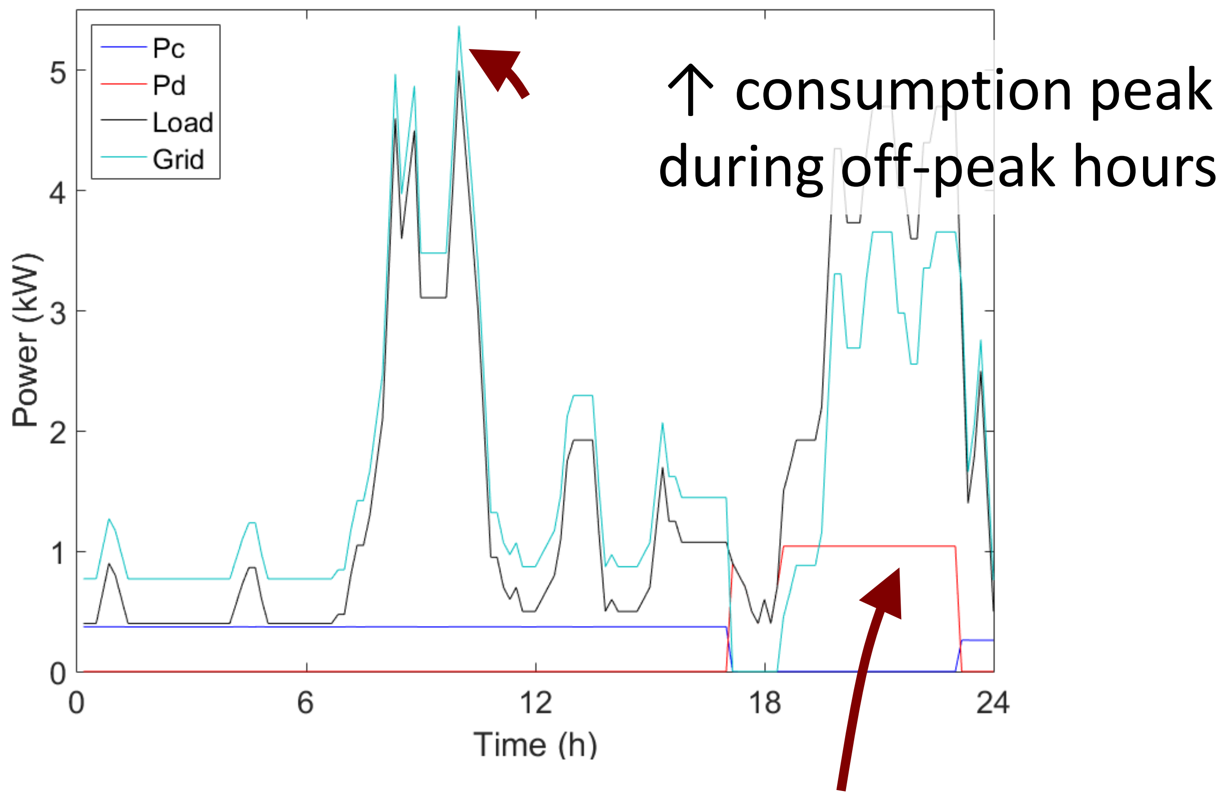
- Add constraint: always satisfy demand

$$p_t^{load} = p_t^{direct} + p_t^D$$

- Cap maximum power from the grid

$$p_t^{direct} \leq p^{contract}$$

Student residency- TOU Uruguay 2H

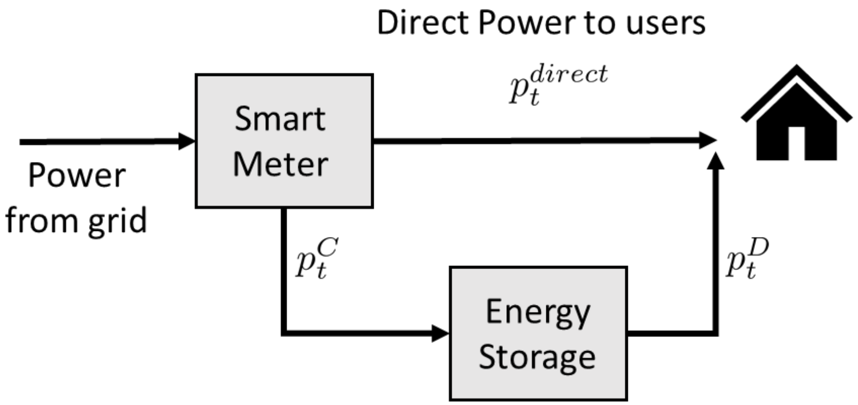


↑ consumption peak during off-peak hours

- Discharge concentrated in part of the high price region

CASE STUDY-MATCH CONSUMPTION PROFILES

(Corengia & Torres, *ENERLAC*, 2020)


Direct Power to users

p_t^{direct}

Smart Meter

Power from grid

p_t^C

Energy Storage

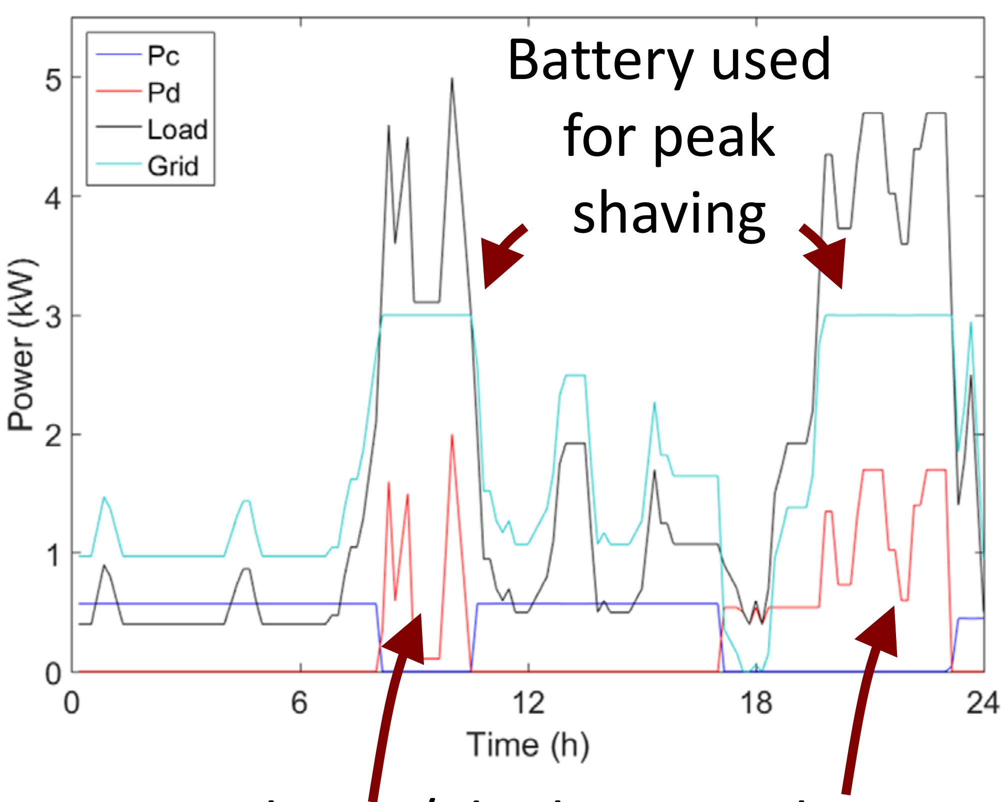
p_t^D

- Add constraint: always satisfy demand

$$p_t^{load} = p_t^{direct} + p_t^D$$

- Cap maximum power from the grid
  - $p_t^{direct} + p_t^C \leq p^{contract}$
  - Include penalty for consuming over contract

Student residency- TOU Uruguay 2H- cap peak

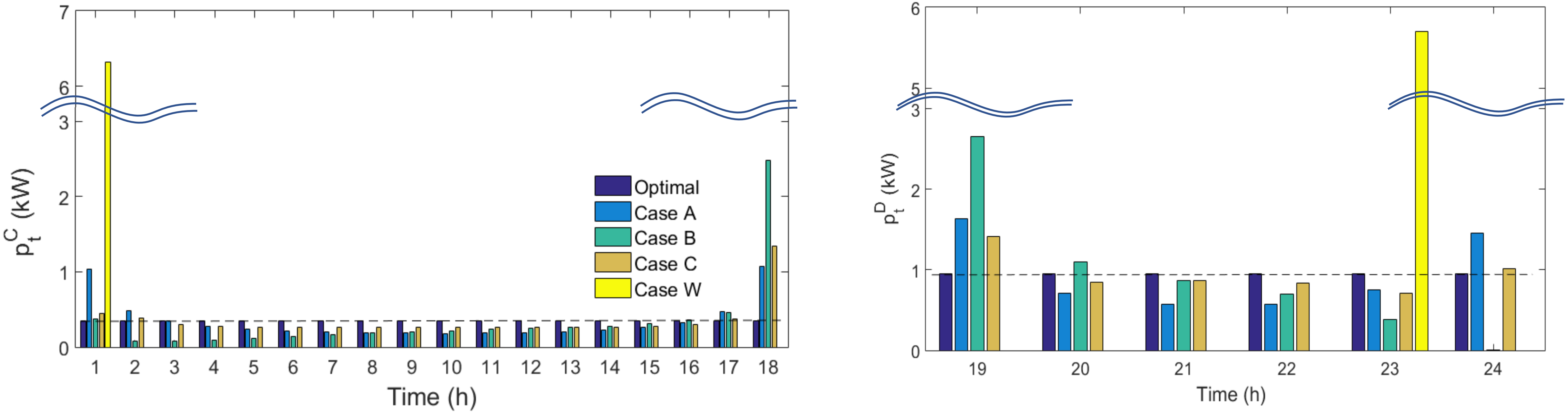


Battery used for peak shaving

- Two charge/ discharge cycles- nonuniform discharge
- Use ES to contract less power

IS IT WORTH COMPLICATING OURSELVES WITH DEGRADATION TERMS? (Corengia & Torres, *FOCAPD*, 2019)

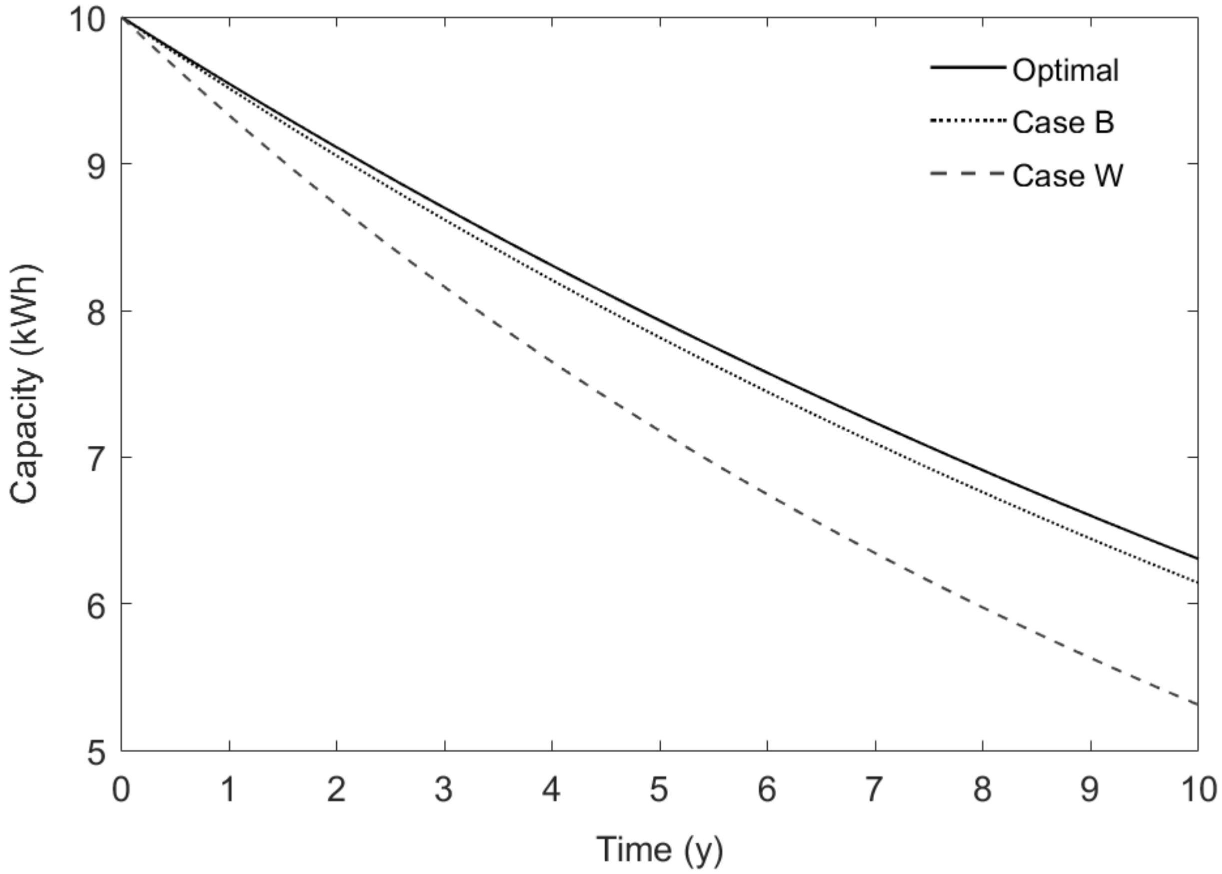
- Compare solutions to penalized and non-penalized problems



- Non-penalized problem not strictly convex ⇒ global optimum not unique
- Cases A, B, C, W several possible schedules, W =worst (single charge/discharge)

IS IT WORTH COMPLICATING OURSELVES WITH DEGRADATION TERMS? (Corengia & Torres, *FOCAPD*, 2019)

- Consequences of sub-optimal operation (for Li-ion battery, Sarker et al *Power Syst. Res.* 2017)



- What if degradation occurs but was not considered in optimization problem?
  - Algorithm stops at case B: not that different ⇒ Lucky case
  - Algorithm stops at case W ⇒ increased capacity loss

SUMMARY: BEHIND THE METER STORAGE IN BATTERIES

- Take advantage of TOU strategies w/o disruptive changes in habits
- Mostly studied outside ChemE

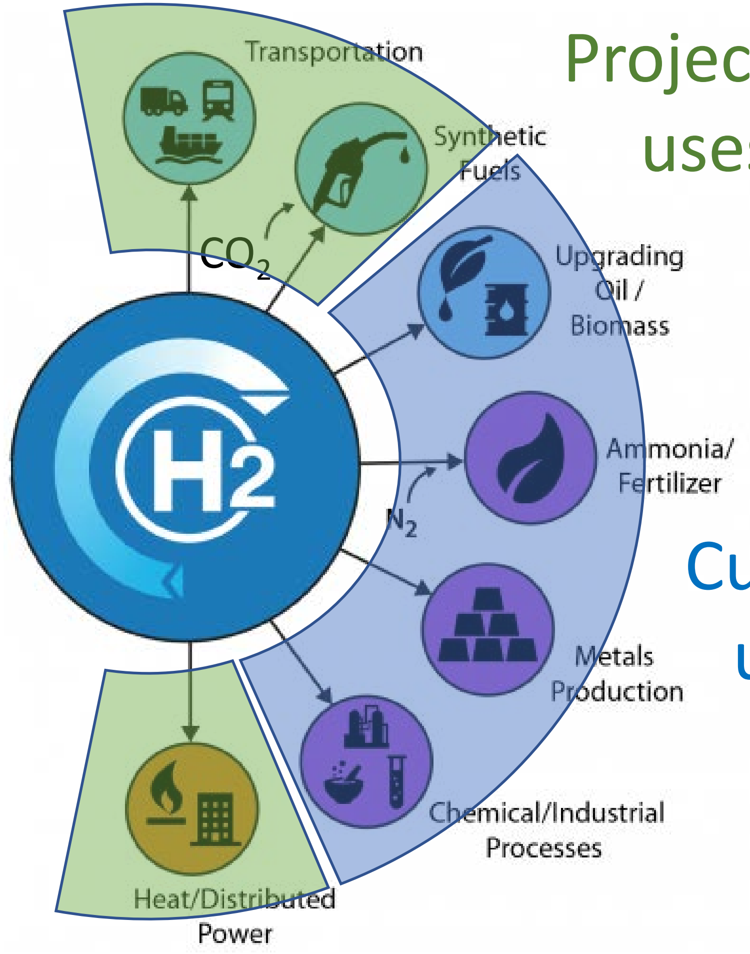
  $\Rightarrow$ include degradation effects in formulation of optimization problems

  $\Rightarrow$ convex formulations allows for solving for years vs day

- Case study new Li-ion batteries:
  - Only worth if large price differences in smart tariff $\Rightarrow$ second life batteries?
  - Not considering degradation may lead to significant premature loss of capacity

PRODUCTION OF GREEN-HYDROGEN

- The hydrogen economy

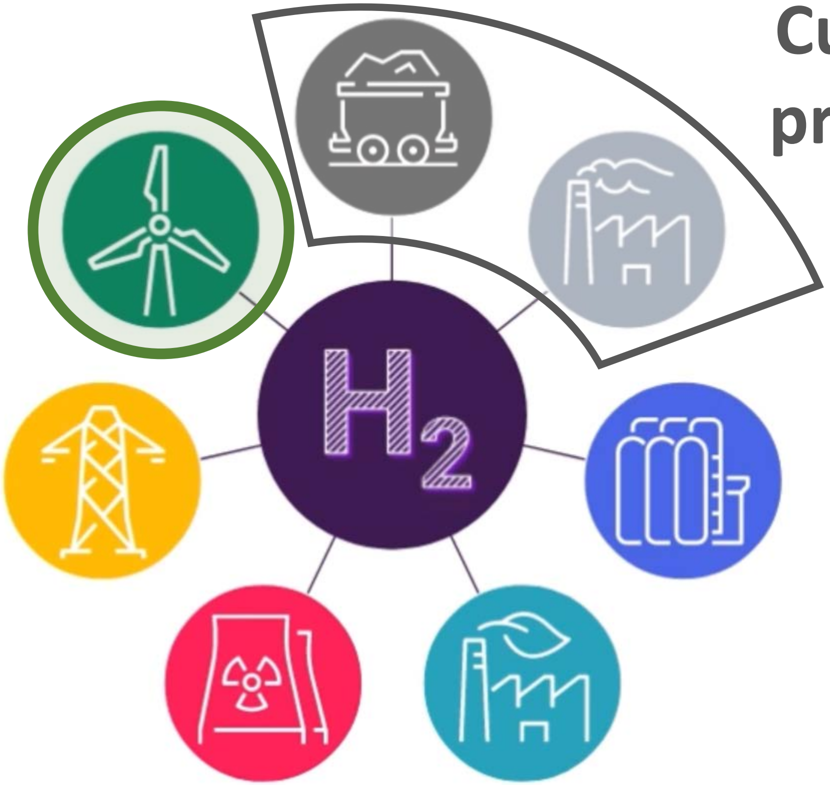


Projected uses

Current uses

Figure made on the basis of https://www.energy.gov/eere/fuelcells/h2scale

- The colors of Hydrogen

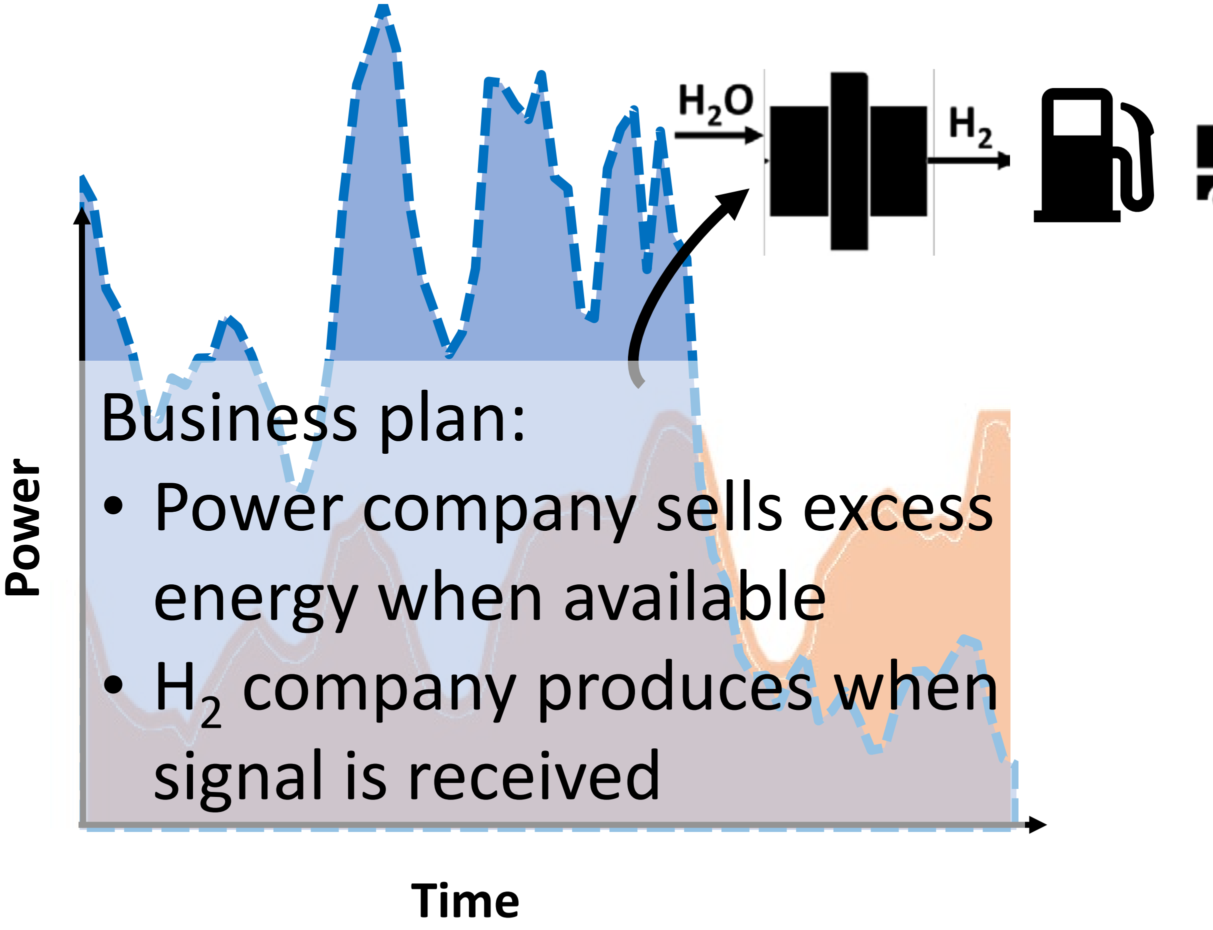


Current practice

- Green H2: Water electrolysis powered by renewable sources

Image from “**Simulating the Hydrogen Transition**” AVEVA

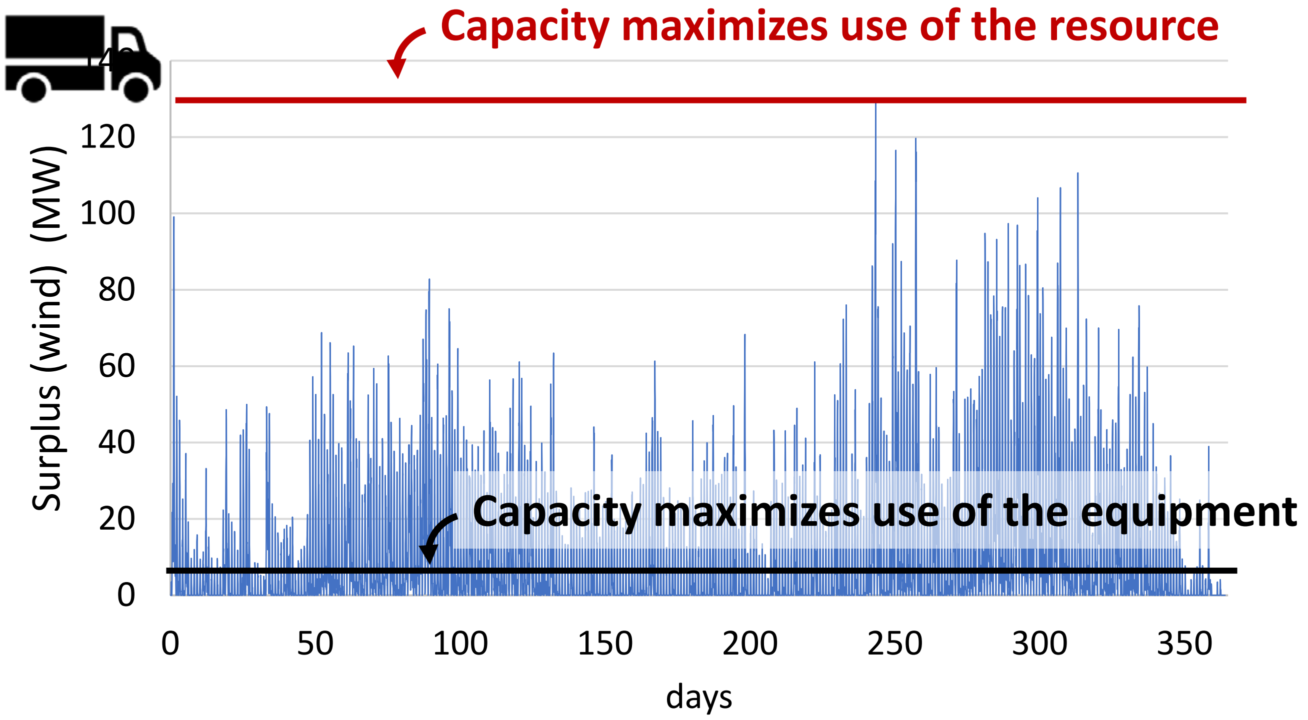
THE VERNE PROJECT URUGUAY-PILOT FUEL STATION



Business plan:

- Power company sells excess energy when available
- H_2 company produces when signal is received

- H_2 production capacity?

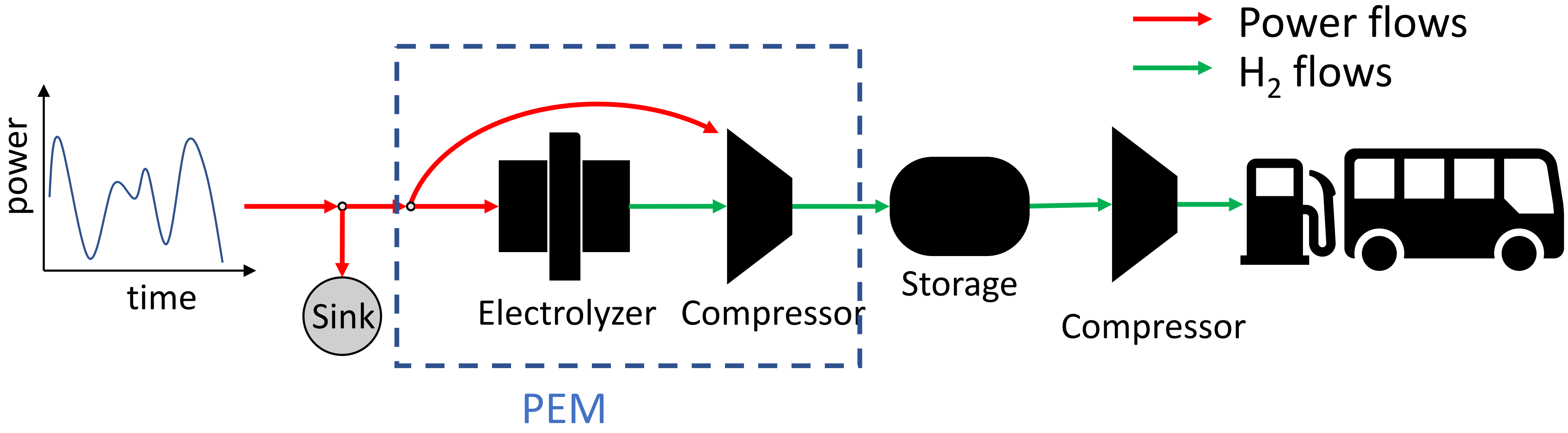


Capacity maximizes use of the resource

Capacity maximizes use of the equipment

- Surpluses → fuel H_2
- Trade-off => optimization

GREEN-H_2 CASE STUDY 1: SURPLUSES→ PEM → Fuel H_2 ⁽¹⁾



- PEME:
  - low temperature (80-100ºC)
  - fast on-off dynamics (startups ~2-3 min ⁽²⁾)
  - work at any partial load

- Compression system:
  - designed and costed offline (Aspen Plus/APEA)

(1) Corengia & Torres, *ESCAPE 30,* 2020 (2) Corengia & Torres, *PSE,* 2018

GREEN-H_2 CASE STUDY 1: SURPLUSES→ PEM → Fuel H_2 (1)

Optimization Problems:

- **Objective functions**

1. max NPV for target $\$H_2$
2. max surplus usage for target $\$H_2$ (NPV≥0)
3. min $\$H_2$ for target H_2 production

- **Constraints:**

- $\dot{m}_{H_2,t} \leq IC_{H_2}$
- $\dot{p}_{H_2,t} + \dot{p}_{comp,t} \leq \dot{p}_{surplus,t}$
- $CAPEX(IC_{H_2})\ \&\ OPEX(IC_{H_2})$ (1)

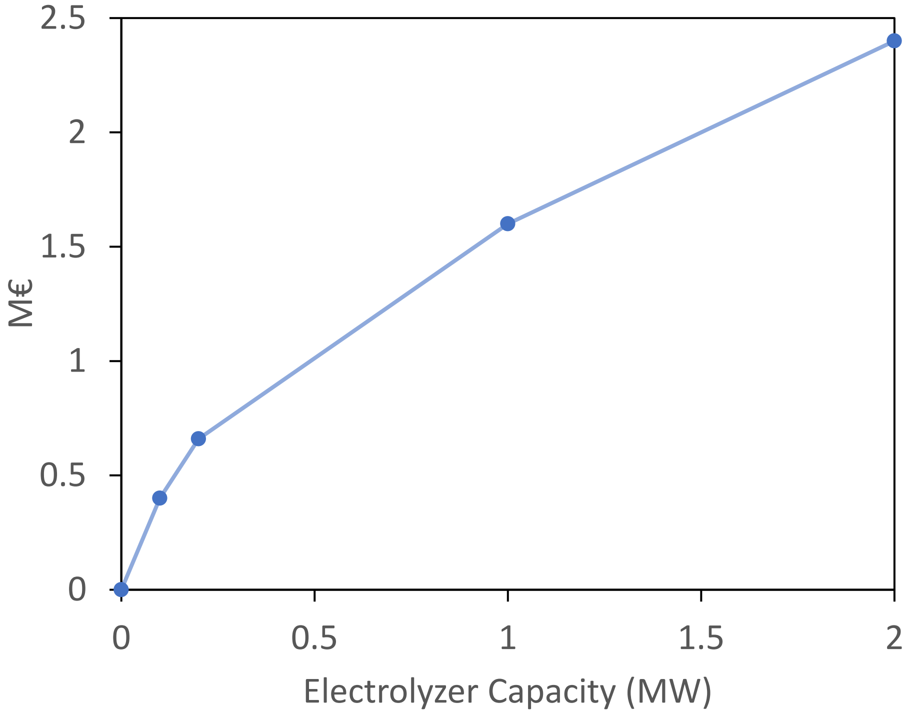
- **DV:** IC_{H_2}, operation mode
- LP problems, GAMS-CPLEX
- (MILP IC_{H_2} < 2MW)

---

(1) Electrolyzer costs J. Proost, 2019. *International Journal of Hydrogen Energy* 44 (9), 4406–4413

PEM ELECTROLYZER COSTS

- J. Proost, *International Journal of Hydrogen Energy* 44 (9), 4406–4413, 2019



- Equipments: stacks of cells up to 2 MW
- Beyond 2 MW: multiple stacks

=> Composite curve approximated by linear fitting: 1257 euros/kw

(costs include demineralizer, gas separators, vessesls, puryfying system, peripherals)

GREEN-H_2 CASE STUDY 1: SURPLUSES→ PEM → Fuel H_2 ⁽¹⁾

Optimization Problems:

- **Objective functions**

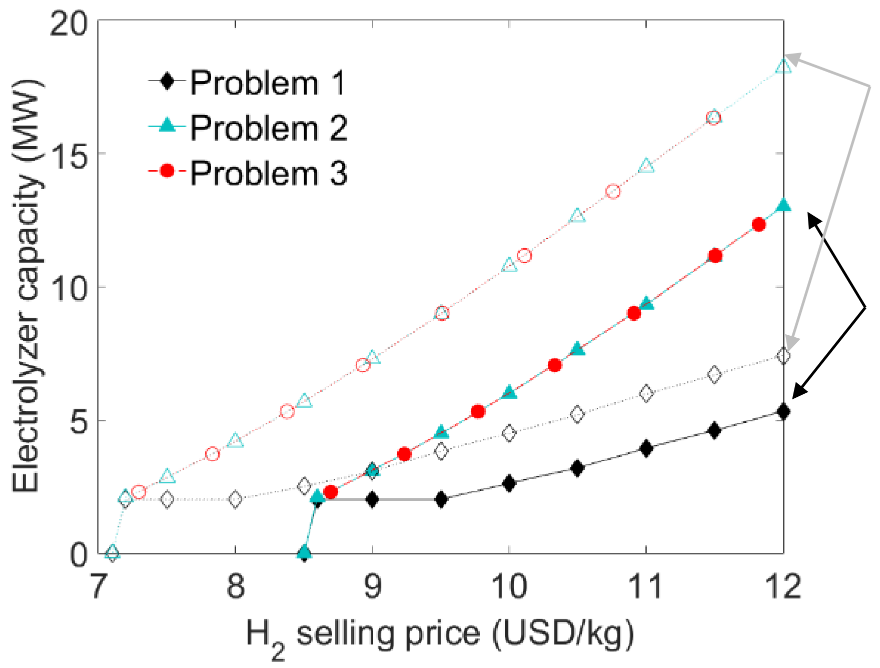
1. max NPV for target $\$H_2$
2. max surplus usage for target $\$H_2$ (NPV≥0)
3. min $\$H_2$ for target H_2 production

- **Constraints:**

- $\dot{m}_{H_2,t} \leq IC_{H_2}$
- $\dot{p}_{H_2,t} + \dot{p}_{comp,t} \leq \dot{p}_{surplus,t}$
- $CAPEX(IC_{H_2})\ \&\ OPEX(IC_{H_2})$ (1)

- **DV:** IC_{H_2}, operation mode
- LP problems, GAMS-CPLEX
- (MILP IC_{H_2} < 2MW)

- **Results**



0 cost for energy

lowest day ahead UTE tariffs large consumer

- Install only if $\$H_2$ > 7 USD/kg
- Threshold capacity 2 MW: largest single electrolyzer cost in Ref. (1)

---

(1) Electrolyzer costs J. Proost, 2019. *International Journal of Hydrogen Energy* 44 (9), 4406–4413

GREEN-H_2 CASE STUDY 1: SURPLUSES→ PEM → Fuel H_2 (1)

Optimization Problems:

- **Objective functions**

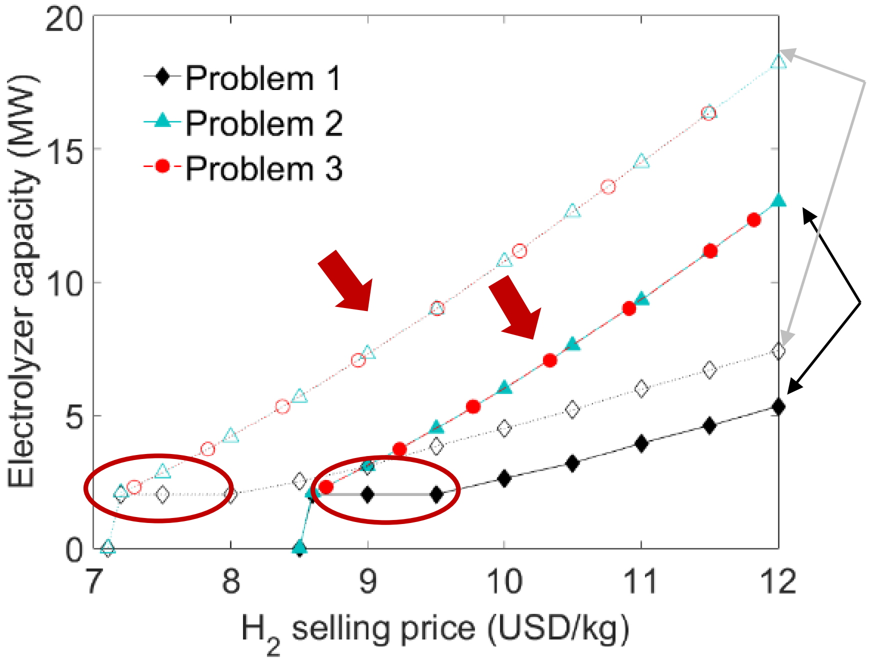
1. max NPV for target $\$H_2$
2. max surplus usage for target $\$H_2$ (NPV≥0)
3. min $\$H_2$ for target H_2 production

- **Constraints:**

- $\dot{m}_{H_2,t} \leq IC_{H_2}$
- $\dot{p}_{H_2,t} + \dot{p}_{comp,t} \leq \dot{p}_{surplus,t}$
- $CAPEX(IC_{H_2})$ & $OPEX(IC_{H_2})$ (1)

- **DV**: IC_{H_2}, operation
- LP problems, GAMS-CPLEX

- **Results**



0 cost for energy

lowest day ahead UTE tariffs large consumer

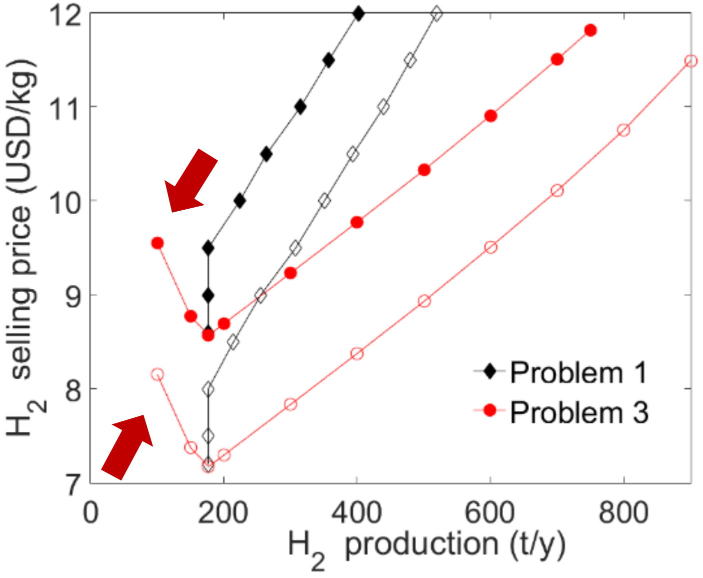
- NPV ↑wo ↑ IC
- Both optimize @ NPV= 0

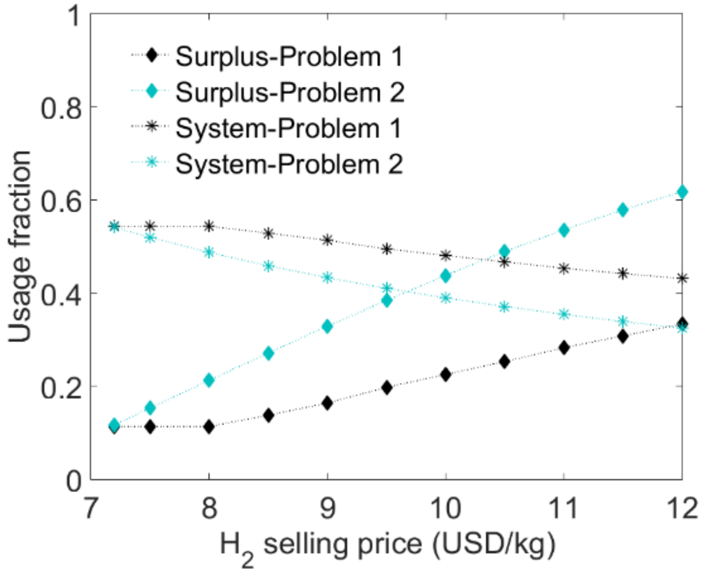
(1) Electrolyzer costs J. Proost, 2019. *International Journal of Hydrogen Energy* 44 (9), 4406–4413

GREEN-H_2 CASE STUDY 1: SURPLUSES→ PEM → Fuel H_2 (1)

- **Results**

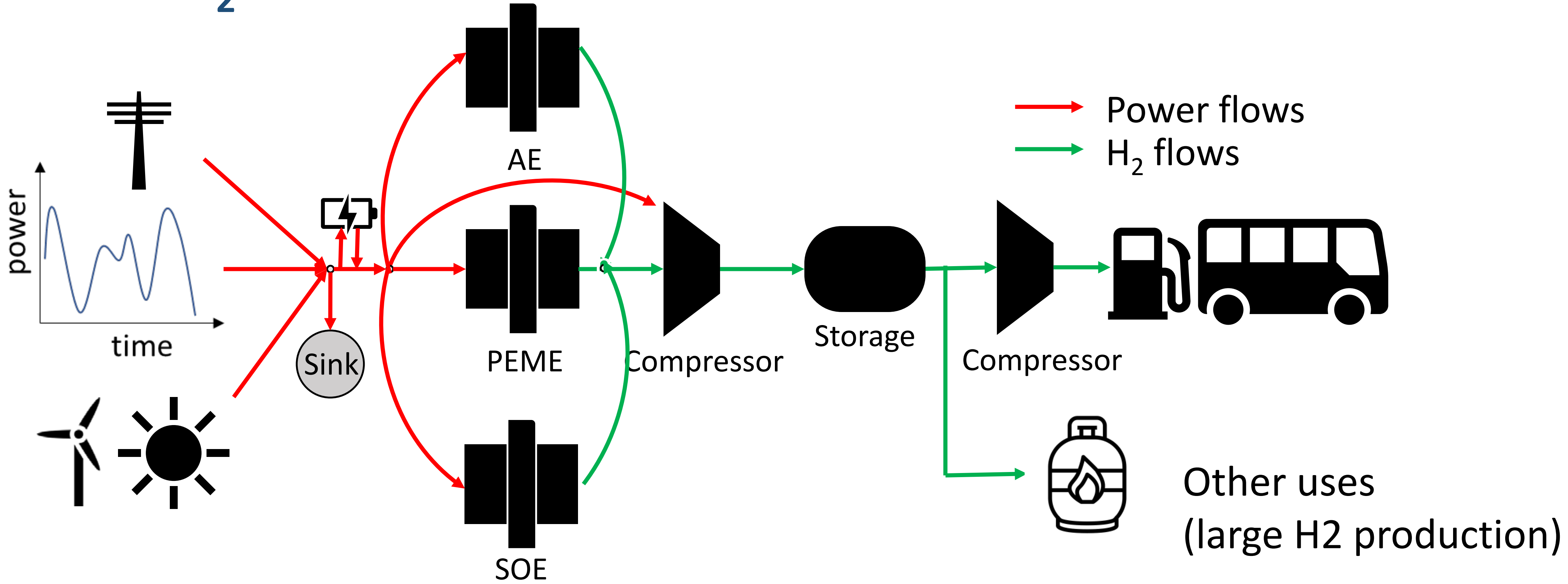
(P1) max NPV for target \$$H_2$ (P2) max surplus usage for target \$$H_2$ (NPV≥0) (P3) min \$$H_2$ for target H_2 production





- Forced IC<2MW => small and costly equipments => ↑ H_2 prices
- ↑ H_2 prices favors ↑ IC to capture resource at the expense of not fully using IC

GREEN-H_2: ADD FLEXIBILITY



- PEME flexible but too expensive => combine (cheaper) AE for base operation + PEME peaks
- AE not at partial load => grid (not only surpluses) or install generator
- Also considered SOE: newer (not in the market) technology

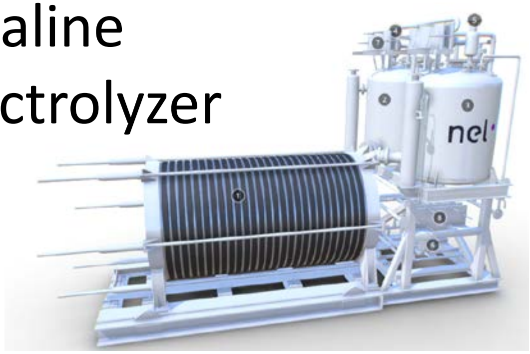
Corengia & Torres, Ìn preparation 2022

GREEN-H_2: TECHNOLOGY COMPARISON (1)

- PEME

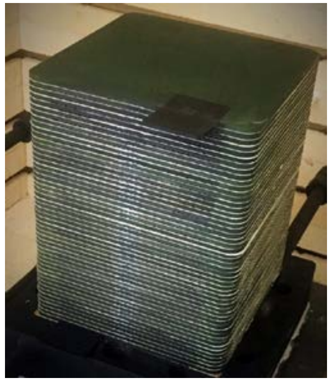
- Low temperature (80-100 °C)
- Work at partial load
- In the market (NEL, Siemens)

- Alkaline Electrolyzer



- Low temperature, but lower current densities
- Efficiency ~PEME but low flexibility: minimum partial load for each stack 15-40% (safety)
- Old mature technology

- Solid Oxide Electrolyzer

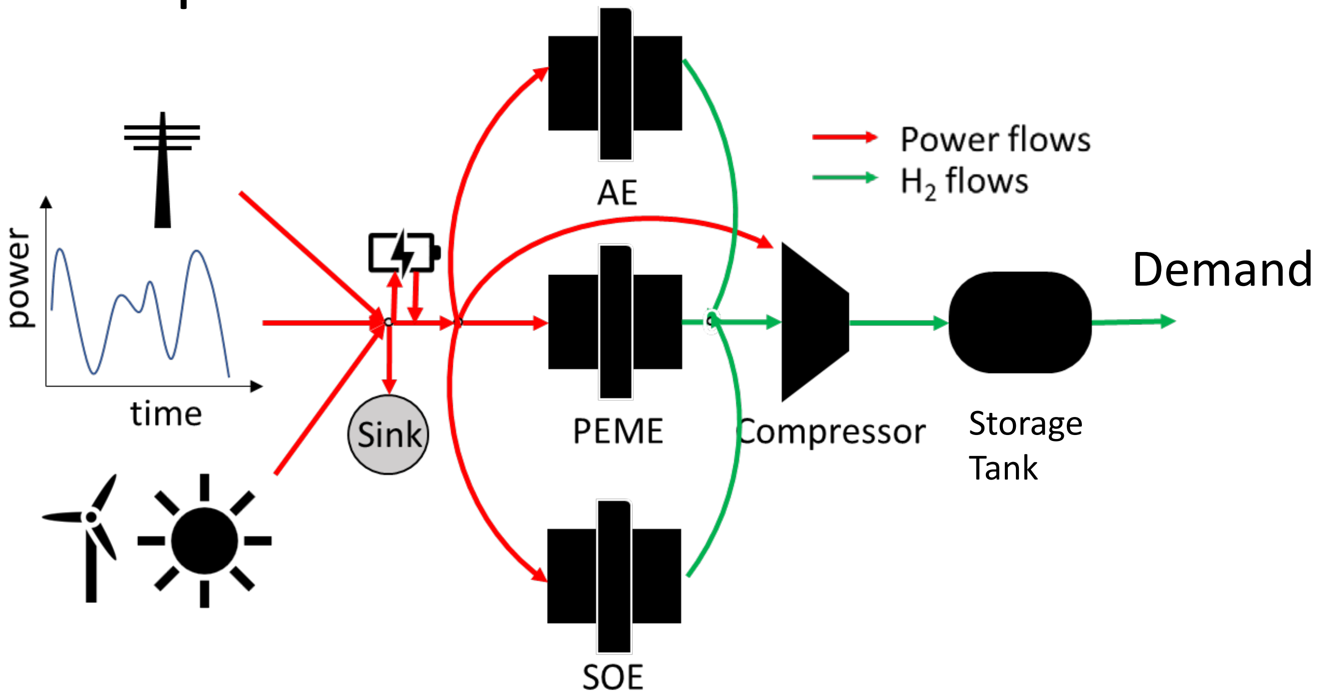


- High temperature (500-850 °C) => on-off not easy
- More efficient than AE and PEME, partial load > 60% does not require external heat
- Current densities comparable to PEME
- Market: lab scale

Figures: Siemens, NEL Technology, Oxoenergy
(1) Schmidt, *Int. J. Hyd. En,* 42, 2017

GREEN-H_2: OPTIMIZATION PROBLEM$^{(1)}$

- Superstructure



- Family of problems
- MILP (AE), Some LP
- All GAMS/CPLEX with SolnPool

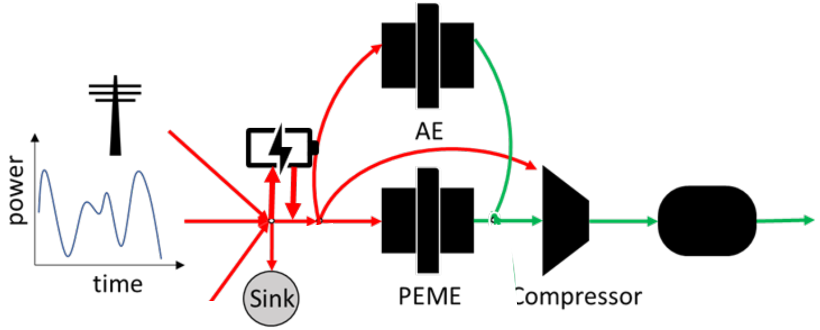
- Allow all technologies and power combinations
- Objective function: Annualized cost
  - CAPEX: Wind, Solar generators, AE, PEME, SOE, Compressor, Tank, Battery
  - OPEX: Electrolyzers, Compressor, penalty for using the battery
- Restrictions for the equipment loads:
  - SOE if selected always on: min. load ≥ 60%
  - AE: may turn on/off; min load 40%
- Costs: AE, PEM literature; SOE estimates^2 => worst case SOE~AE, then sensitivity analysis
- Demand curve: substitution of NG imports
- Wind/Sun availability, energy prices: real curves Uruguay

(1) Corengia & Torres, Ìn preparation 2022

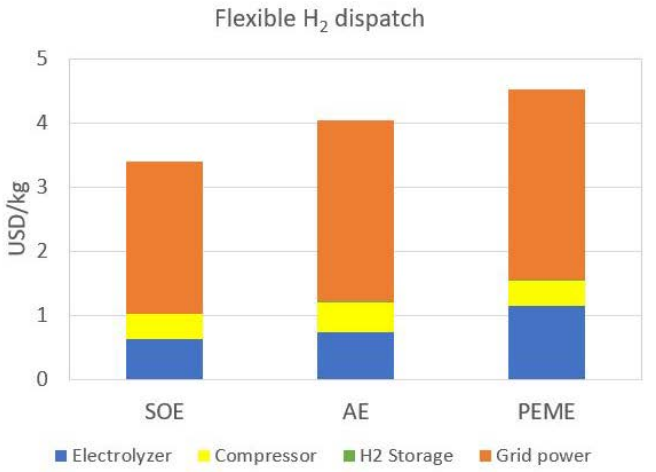
(2) Anghilante et al, *International Journal of Hydrogen Energy*, 43, 2018

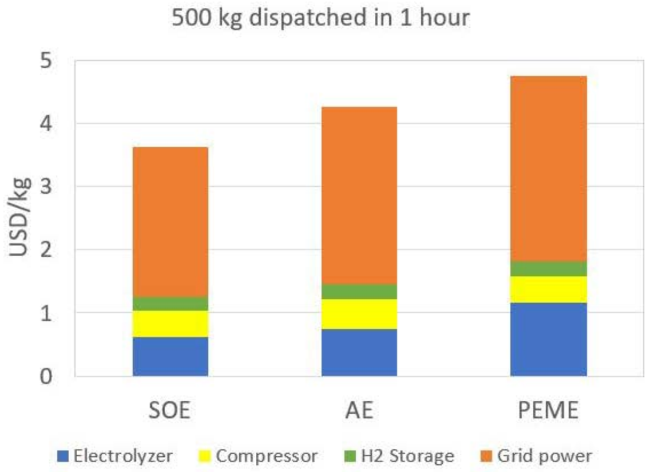
GREEN-H_2: RESULTS LOW H_2 PRODUCTION (JUST GRID)

- SOE are preferred over AE, PEME
- Optimal solutions do not install batteries
  - pay large prices for electricity from the grid
  - Average usage factor SOE: ~90%
- Trend is valid until Cost SOE~2 Cost AE



- If SOE not considered AE always preferred over PEME

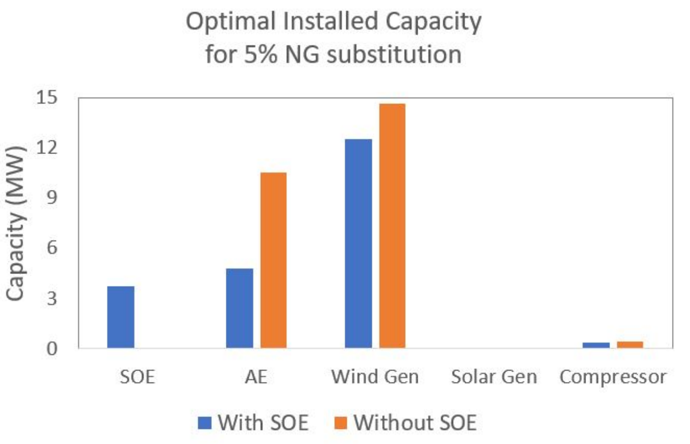


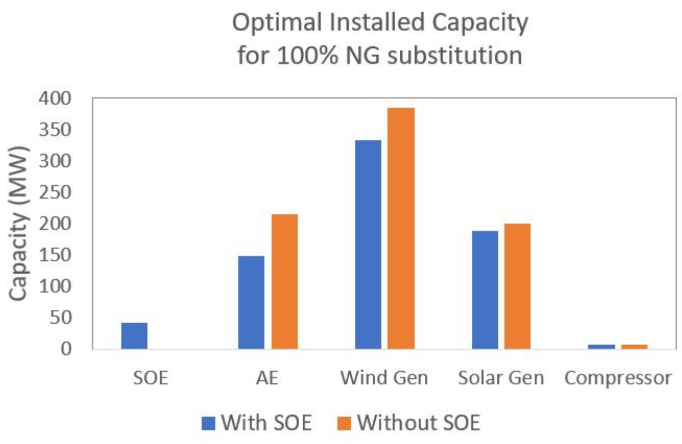


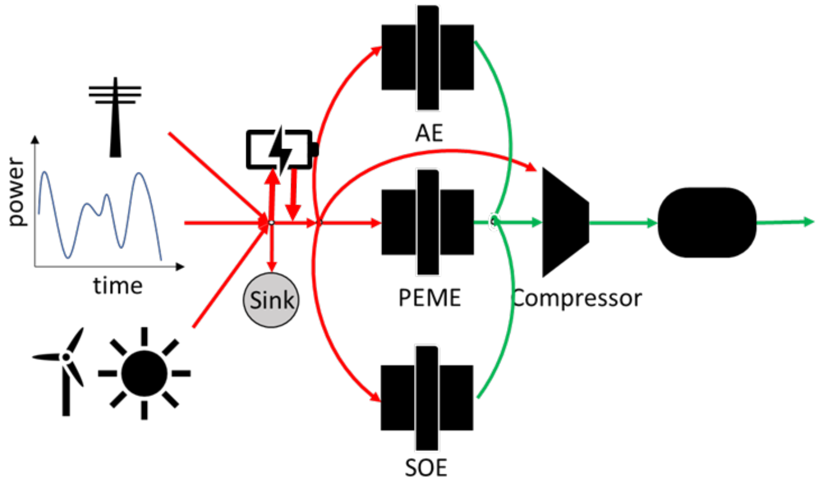
- 1h dispatch considers bad case scenario for storage

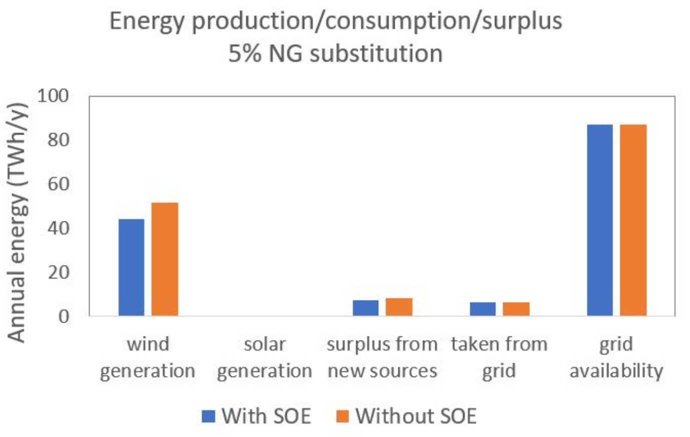
GREEN-H_2: RESULTS LARGE H2 PRODUCTION

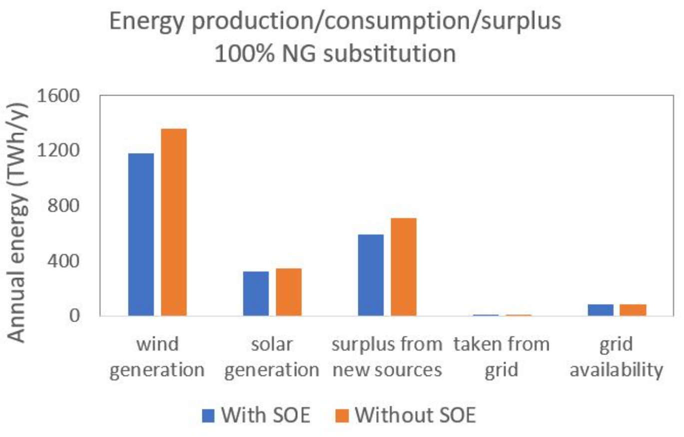
- AE preferred; combines AE & SOE & storage in batteries (if batteries < 300 USD/kWh)


Optimal Installed Capacity
for 5% NG substitution


Optimal Installed Capacity
for 100% NG substitution




Energy production/consumption/surplus
5% NG substitution


Energy production/consumption/surplus
100% NG substitution

- Installation of wind generators is preferred over consuming from the grid
- Installation of solar => complementarity of the resource

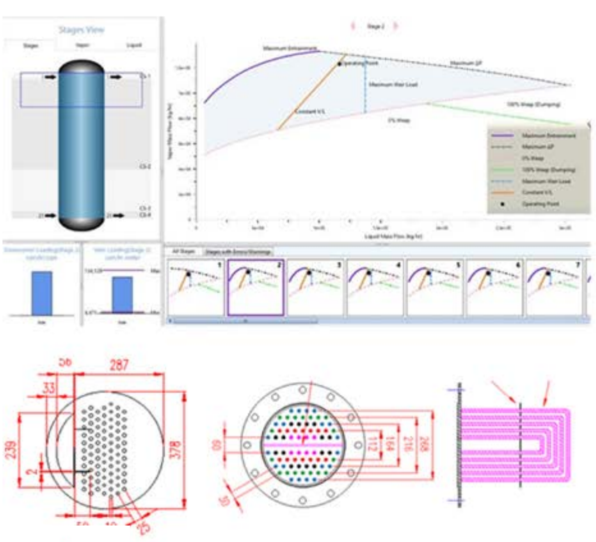
(Figures: batteries 100 USD/kWh—Tesla's target)

SUMMARY: GREEN H_2

- Case study Uruguay: ~100 % renewable electricity
- Surplus → H_2 : not an option for current settings
- Options electricity : - (large) up to 50 tonH_2/day install wind generators
  - beyond 50H_2/day ton install wind + solar
  - consider batteries
- Electrolyzer technologies:
  - PEM's flexibility is not compensating its current cost => AE
  - SOE not yet in the market but look very promising

CO_2 CAPTURE & UTILIZATION-MOTIVATION

- Increasing pressure to lower CO_2 emissions
- Many capture & storage solutions: displace but not solve the problem



Development CO_2 capture process for a cement industry

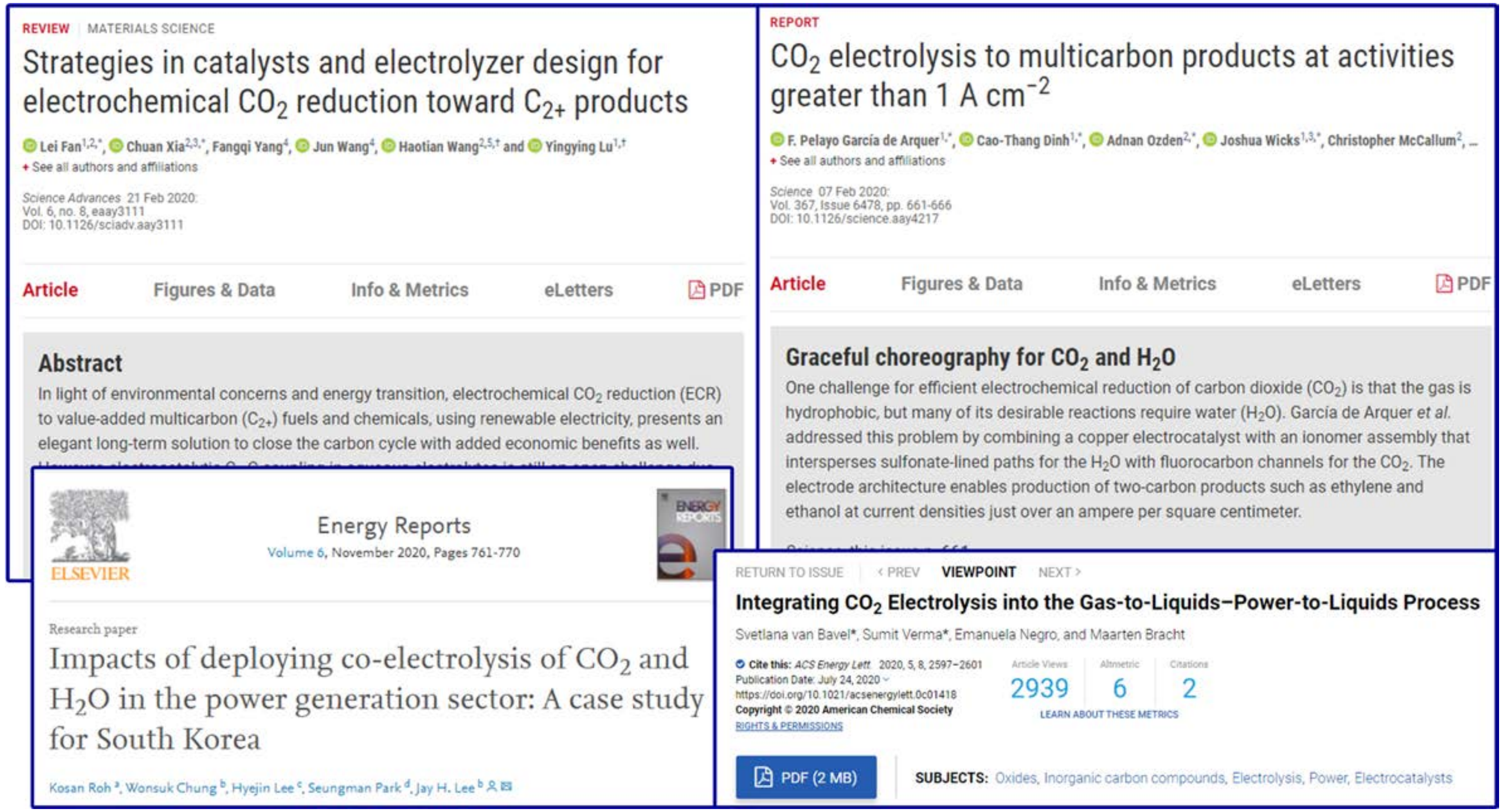
- Tower directly connected to exhaust of clinker oven
- KEY: A *marketable* product that can be sold by the industry
- Solution is not universal
- Heat is required

- Design and evaluation in Aspen Plus
- A view of the pilot plant in operation

(Project ANII-HPI 147304, PI-Udelar: AI Torres, PI-Cementos Artigas: F. Gutiérrez)

ELECTROCATALYTIC REDUCTION OF $CO_2 \rightarrow$ CHEMICALS

- **Very recent advances in chemistry**



REVIEW | MATERIALS SCIENCE

Strategies in catalysts and electrolyzer design for electrochemical CO_2 reduction toward C_{2+} products

Lei Fan[1,2,*], Chuan Xia[2,3,*], Fangqi Yang[4], Jun Wang[4], Haotian Wang[2,5,†] and Yingying Lu[1,†]

+ See all authors and affiliations

Science Advances 21 Feb 2020:
Vol. 6, no. 8, eaay3111
DOI: 10.1126/sciadv.aay3111

Abstract

In light of environmental concerns and energy transition, electrochemical CO_2 reduction (ECR) to value-added multicarbon (C_{2+}) fuels and chemicals, using renewable electricity, presents an elegant long-term solution to close the carbon cycle with added economic benefits as well.

REPORT

CO_2 electrolysis to multicarbon products at activities greater than 1 A cm^{-2}

F. Pelayo García de Arquer[1,*], Cao-Thang Dinh[1,*], Adnan Ozden[2,*], Joshua Wicks[1,3,*], Christopher McCallum[2], ...

+ See all authors and affiliations

Science 07 Feb 2020:
Vol. 367, Issue 6478, pp. 661-666
DOI: 10.1126/science.aay4217

Graceful choreography for CO_2 and H_2O

One challenge for efficient electrochemical reduction of carbon dioxide (CO_2) is that the gas is hydrophobic, but many of its desirable reactions require water (H_2O). García de Arquer *et al.* addressed this problem by combining a copper electrocatalyst with an ionomer assembly that intersperses sulfonate-lined paths for the H_2O with fluorocarbon channels for the CO_2. The electrode architecture enables production of two-carbon products such as ethylene and ethanol at current densities just over an ampere per square centimeter.

Energy Reports
Volume 6, November 2020, Pages 761-770

Research paper

Impacts of deploying co-electrolysis of CO_2 and H_2O in the power generation sector: A case study for South Korea

Kosan Roh[a], Wonsuk Chung[b], Hyejin Lee[c], Seungman Park[d], Jay H. Lee[b]

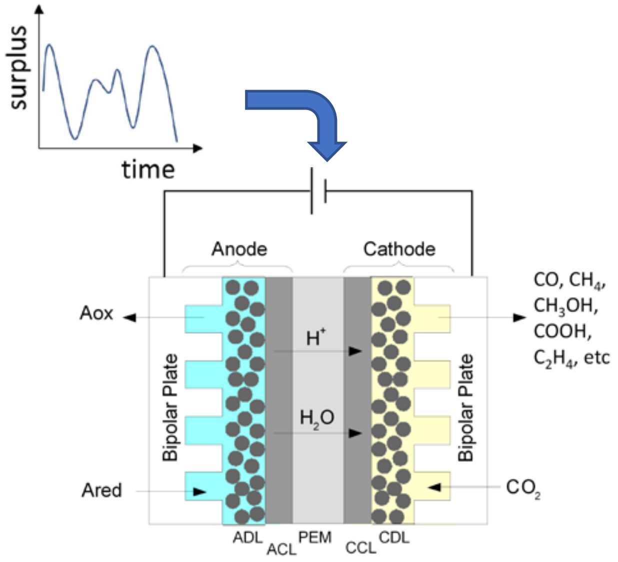
Integrating CO_2 Electrolysis into the Gas-to-Liquids–Power-to-Liquids Process

Svetlana van Bavel*, Sumit Verma*, Emanuela Negro, and Maarten Bracht

Cite this: *ACS Energy Lett.* 2020, 5, 8, 2597−2601
Publication Date: July 24, 2020
https://doi.org/10.1021/acsenergylett.0c01418
Copyright © 2020 American Chemical Society

Article Views	Altmetric	Citations
2939	6	2

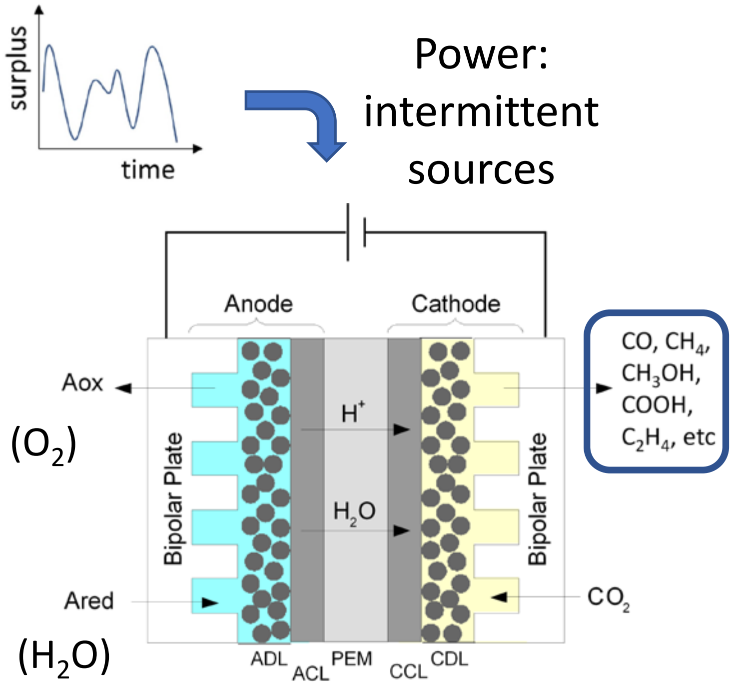
SUBJECTS: Oxides, Inorganic carbon compounds, Electrolysis, Power, Electrocatalysts



- Reactor can be coupled to intermittent energy sources => *carbon negative chemicals*

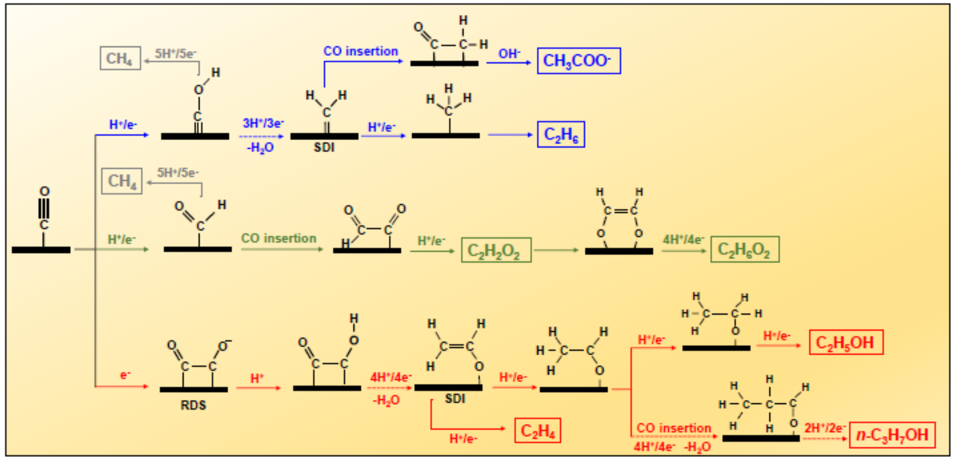
ELECTROCATALYTIC REDUCTION OF CO_2 (Work in Progress)

- Main challenge: Selectivity

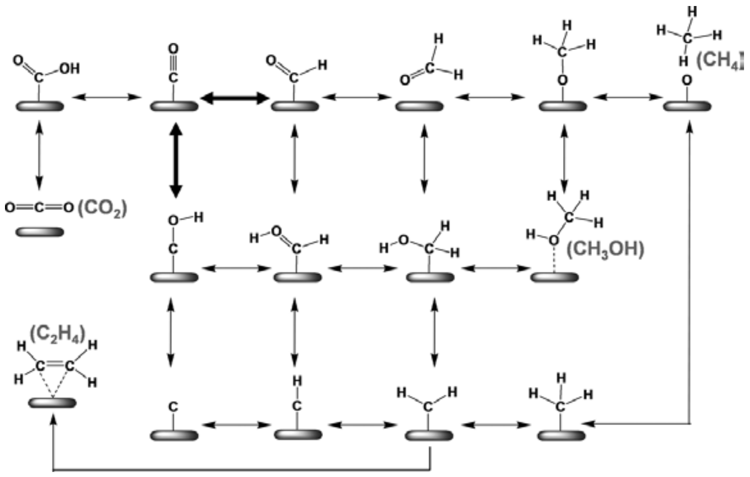


Electro-catalysis:

- Catalytic surface promotes a series of elemental reactions
- Pathways on Cu surfaces



(Zheng et al, JACS, 2019)



(Nie et al, Angew. Chemie, 2013)

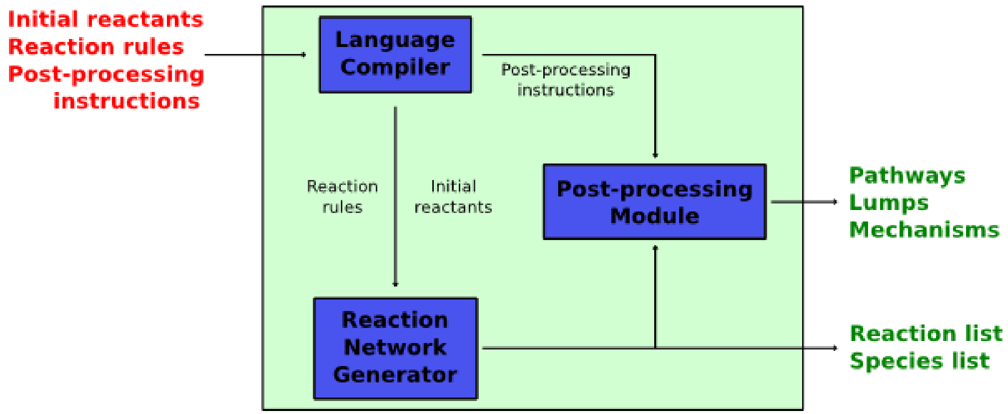
- Products and their distribution depend on catalyst, voltage, current density

=> Not a clear agreement on pathways/products

ELECTROCATALYTIC REDUCTION OF CO_2- BUILDING THE NETWORK

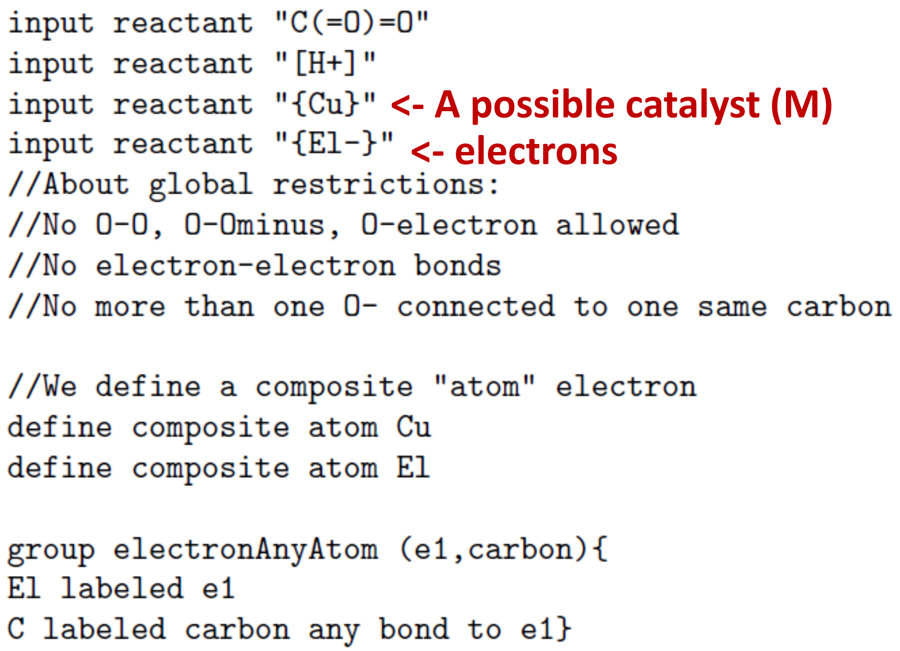
- Idea: use Rule Input Network Generator (RING[1]) to build reaction network

RING (daoutidis.cems.umn.edu/software)



- Apply all reaction rules to all reactants, and species formed to generate all possible reaction pathways

- Screenshot of our code



```
input reactant "C(=O)=O"
input reactant "[H+]"
input reactant "{Cu}"
input reactant "{El-}"
//About global restrictions:
//No O-O, O-Ominus, O-electron allowed
//No electron-electron bonds
//No more than one O- connected to one same carbon

//We define a composite "atom" electron
define composite atom Cu
define composite atom El

group electronAnyAtom (e1,carbon){
El labeled e1
C labeled carbon any bond to e1}
```

<- A possible catalyst (M)

<- electrons

Some allowed reactions:

- Capture of an e-
- Form C-Metal bond
- Form C=Metal bond
- Form C≡Metal bond
- M-C-OH dehydration to form $M-C^-$ bond
- Form M-C-H bond (from $M-C^-$)
- Desorption: breakage of C-M bond and formation of C-H bond
- etc

[1] Rangarajan & Daoutidis Rule Input Network Generator https://daoutidis.cems.umn.edu/software

ELECTROCATALYTIC REDUCTION OF CO_2- BUILDING THE NETWORK

- Partial view of the generated CO_2 -> chemicals network
- Compounds in squares show final stable products (>70)

- Number of routes to different products:

Methanol	12	Oxalic acid	30	Propane	70
Formic acid	2	Ethylene	45	1-Propanol	67
Methane	12	Ethylenglycol	45	Acetic Acid	20
Ethane	40	Ethanol	40	glyoxal	32

- These products appear in the previous mechanisms and have been reported in different experimental contributions

ELECTROCATALYTIC REDUCTION OF CO_2

- Next: assess which of these routes are thermodynamically feasible
- Classical approach prediction using DFT calculations
  - DFT databases for a number of species/ surfaces
  - Can we use these databases to learn a model and predict for other species ?

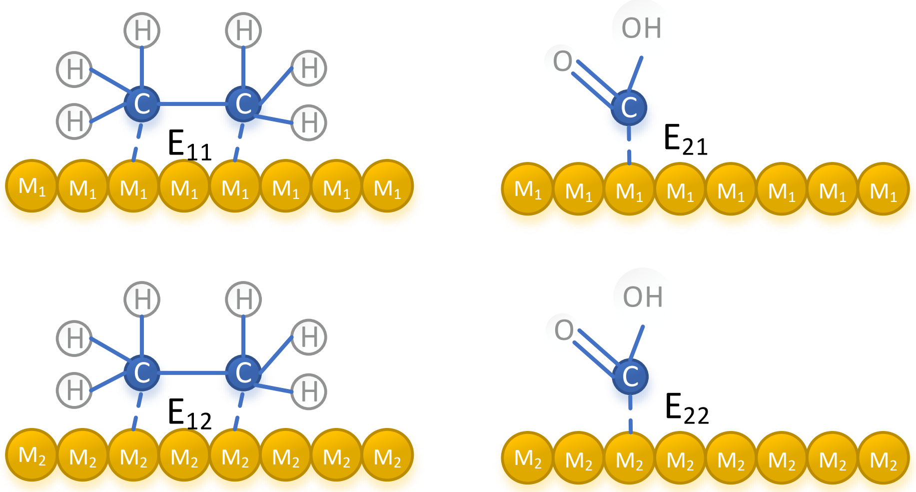
=> Original idea Chowdury et al., Journal of Physical Chemistry, 2018

- Limitation just one DFT database

ELECTROCATALYTIC REDUCTION OF CO_2 – LEARNING A MODEL TO ESTIMATE ADSORPTION ENERGIES

- Model: $E_{ads} = f(\text{descriptors molecule}, \text{descriptors surface})$

Type and number of atoms, bonds, including atom-bond-metal, etc.



Step 2: learn & validate model

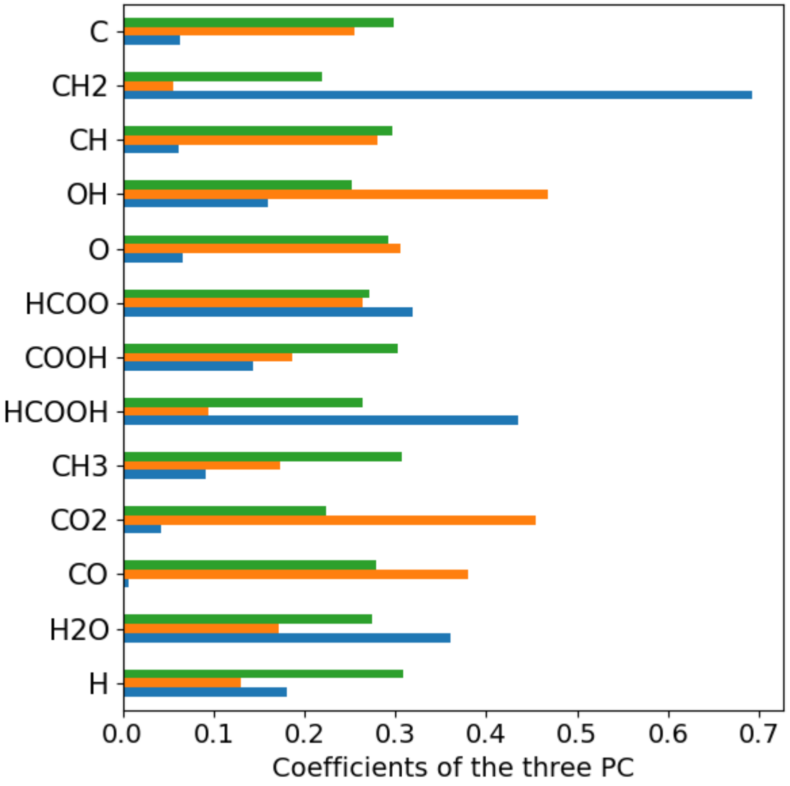
Step 0: Build database

Step 1: find the descriptors

- Idea: Find the adsorbates whose Eads vary the most for different surface
- Use those adsorbates as the descriptors

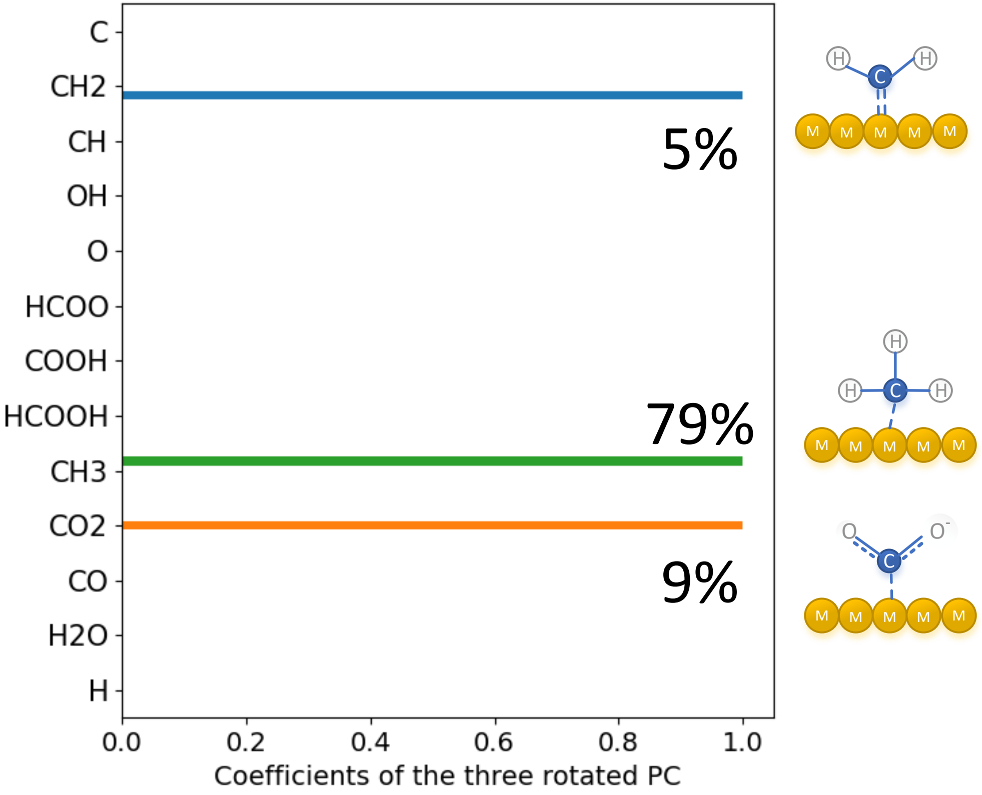
ELECTROCATALYTIC REDUCTION OF CO_2

- Step 1: Descriptors PCA 3 principal components 93% variation in data



Change of coordinates

(Varimax Rotation)



Surfaces: Cu, Pt, Pd, Rh, Re, Ru, Ag, Au, Fe, Ir, Os, Co, Ni

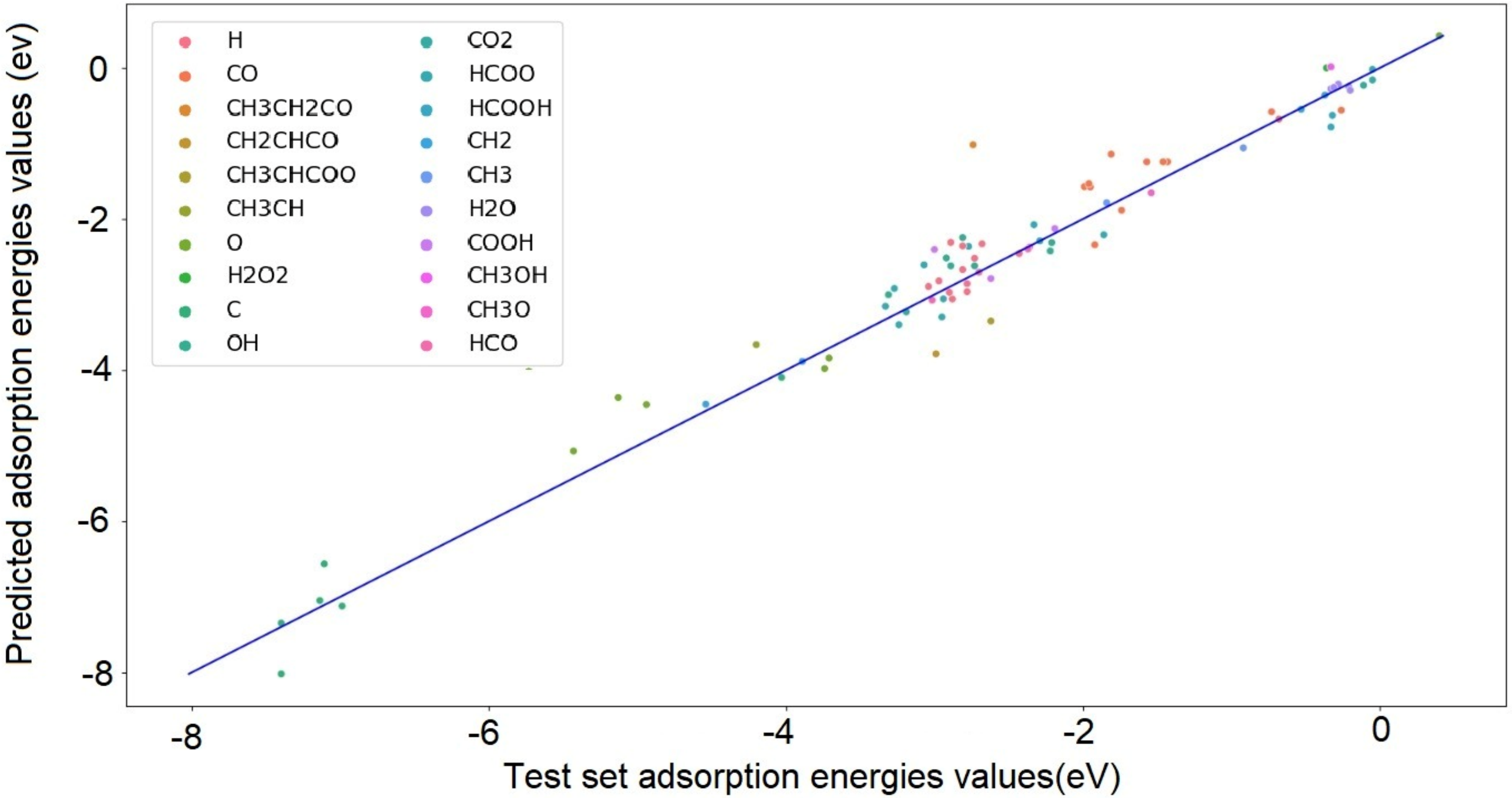
- If we want to test new surfaces, we need Eads from these 3 adsorbates

Arsuaga & Torres, submitted to ESCAPE 2022

ELECTROCATALYTIC REDUCTION OF CO_2

- Step 2: Regression: tested several techniques; similar & good results

Predicted vs DFT data; validation set, KRR (radial basis functions)



- Expanded set of databases
- Next: combine model and CO_2 network

Arsuaga & Torres, submitted to ESCAPE 2022

SUMMARY: ELECTROREDUCTION OF CO_2

- Very promising route to capture CO_2 and produce green chemicals

- Electrocatalytic processes not well understood:
  - many products
  - many pathways
  - many possible cell geometries

=> lots of research opportunities, collaboration with experimentalists

- Initial work (in progress)
  - Building reaction network at metallic electrode
    => Find most favorable species and pathways

ACKNOWLEDGMENTS

- Students & Researchers


M. Corengia

J. Ferreira

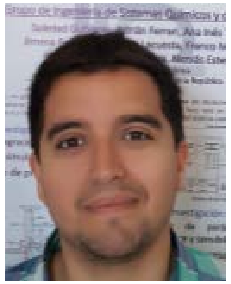

V. González


M. De Armas


J. Arsuaga


A. Porley


A. Helal


N. Estefan


M. Tejera


C. Phillipi


P. Ures


F. Mangone

- Funding

PROYECTO ANII
FSE 1 2018 1 152900
HPI X 2018 1 147304

SNI SISTEMA NACIONAL DE INVESTIGADORES

CSIC COMISIÓN SECTORIAL DE INVESTIGACIÓN CIENTÍFICA

ANCAP

UNIVERSIDAD DE LA REPÚBLICA COMISIÓN CENTRAL DE DEDICACIÓN TOTAL

THANK YOU VERY MUCH FOR YOUR ATTENTION!!!