Development of an efficient LOHC technology

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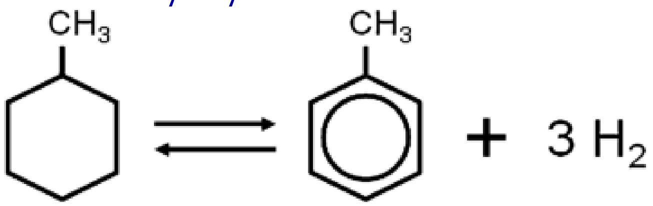
Presentation of the LOHC technology

- Liquid Organic Hydrogen Carriers: an example: methyl cyclohexane



Methyl cyclohexane Toluene

- Density of Methyl cyclohexane (MCH): 771.7 kg/m^3. That is, 1 m^3 of material is 771.7 kg, which, given the molar mass of 98.21 g/mol, corresponds to 7857 mol. This quantity stores 47.1 kg of H_2. The higher heating value of 1 kg of H_2 is 39.7 kWh. That is, the total stored energy in one m^3 MCH is 1873 kWh. The specific energy is therefore 2.43 kWh/kg. Summarizing the numbers:
  - 1873 kWh/m^3
  - 2,43 kWh/kg
- Compared to gasoline:
  - 9500 kWh/m^3
  - 11,1 kWh/kg.
- Hence, more energy can be stored in 1 m^3 of gasoline than in LOHC of the same volume. 1 m^3 of gasoline is enough (at an average consumption of 7 l/100 km) to drive 14,285 km. Using MCH as LOHC, which has 47.1 kg of H_2 in 1 m^3, it is possible to travel 6,730 km with a Toyota Mirai (average consumption of 0.7 kg/100 km).
- A two-axle semi-trailer tanker transports 29 m^3 of MCH, which enables the delivery of 1366 kg of H_2, which can be used to refuel 273 fuel cell vehicles with 5 kg hydrogen tanks.

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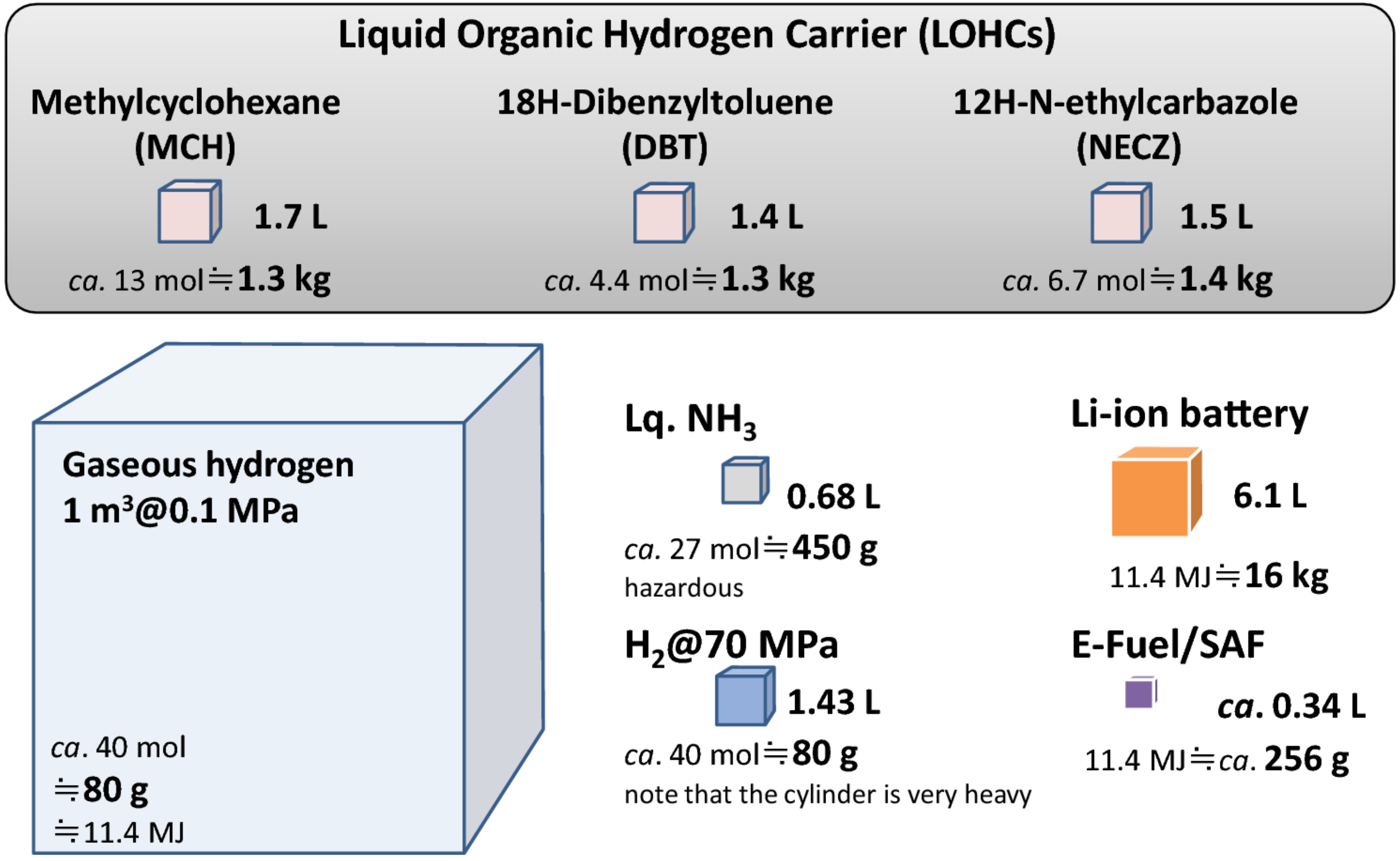
Comparison of LOHC with other energy carriers



- The smaller the volume of the small cubes, the higher the energy density of the energy-storing material
- Different LOHCs provide storage with ca. three times higher energy density than Li-ion batteries, moreover, the duration of storage is arbitrary (no self-discharge)
- The traditional liquid fuels are by far the best in terms of energy density

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LOHC technology Key performance indicators

In Europe, Hydrogenious and Areva H2Gen are the most important players in the field of LOHC technology. The technology needs to be able to compete with electricity transmission and other hydrogen storage and transport technologies (Key Performance Indicators according to the Clean Hydrogen Europe Joint Undertaking):

- Energy demand
  - The hydrogenation practically does not require energy, because the reaction is exothermic. However, the release of hydrogen is quite energy-intensive and requires 10 kWh/kg of H_2 energy. General objective: The energy requirement of hydrogen storage should optimally reach the value of **6 kWh/kg** of stored H_2, but it should definitely be <10 kWh/kg of H_2.
- Requirements for catalysts:
  - **Inexpensive, noble metal-free or low noble metal catalysts**.
  - Activity of the catalyst: **4 mmol H_2 g_{cat}^{-1} min^{-1}**, corresponding to ca **1,6 g H_2 g_{Pt}^{-1} min^{-1}** when the Pt load is 0.5wt%
  - **The conversion of hydrogen extraction is at least 90%, and its selectivity is at least 99.8%**. The former refers to the extent to which MCH is converted to toluene. The latter means the extent to which MCH is exclusively (selectively) converted back to toluene, without the formation of by-products.

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Our goals

- The creation of LOHC technology with higher energy efficiency than the known, LOHC-based, catalytic hydrogen storage/hydrogen release technologies **by balancing the energy need of catalytic reactions and utilizing heat**. System-integrated heat recovery (heat exchanger) and smart control (reactor state optimization, dynamic operation) enable economical operation and the achievement of an energy demand of **6 kWh/kg H_2**.
- LOHC-based, innovative, highly scalable, stable, hydrogen-pressure-controlled, self-regulating, environment-adaptive, heterogeneous catalytic technology for hydrogen storage and release, including the catalyst, and the **loop reactor**.
- New, **non-noble metal-containing, validated catalyst** for hydrogenation and dehydrogenation of LOHC. integration of the catalyst's active phase into wear-resistant ceramics with favorable mechanical properties: high fracture strength and wear resistance.
- Development, sizing, validation of prototype elements, construction and testing of a **TRL 6 level reactor**.

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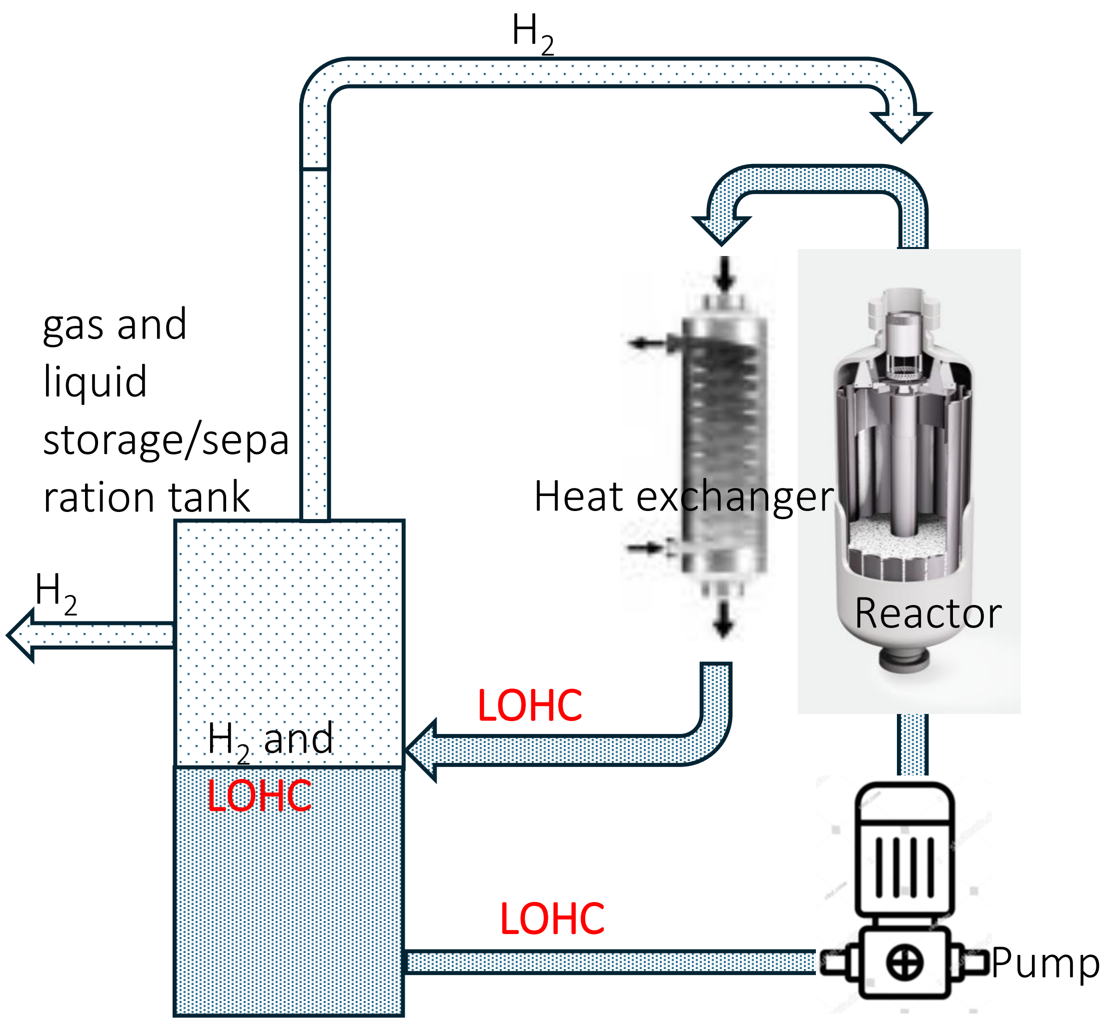
Technology draft
(loop reactor concept)

- The LOHC passes from a tank through a catalytic reactor located outside the tank. The concentration of the reactant substance in the tank decreases and the concentration of the product substance increases, while the hydrogen pressure in the system is kept at a constant value by hydrogen storage or release with a pressure regulator.
- *Hydrogenation:* at a temperature of 100 - 250 °C and a pressure of 30 - 40 bar H_2. When the pressure regulator detects a pressure drop, **H_2** flows into the reactor. If the LOHC material is already saturated, there is no loss of H_2 and no detectable pressure drop, the H2 storage ends, the circulation of the LOHC liquid stops.
- *H_2 supply*: the pressure is 3 - 7 bar, the temperature of the reactor > 250 °C. In order to maintain the chosen pressure of the reaction, gas is released from the gas and liquid storage/separation tank through a pressure regulator at a rate corresponding to the formation of H_2.



Reactor operation

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Partnership

- We offer
  - Research expertise and infrastructure in the field LOHC technologies
  - We are open both for research contracts and partnership in granted projects
- Research activities
  - Highly durable, selective catalysts with low Pt content for reversible LOHC conversion.
  - Development of the loop reactor.
- Our technical expertise
  - High throughput tests of catalysts in a 6-channel flow-through tubular reactor system.
  - Combination of optimization algorithms, with machine learning tools such as PLS and ANNs, RF, XGBoost
  - Research service in the field of design, preparation and testing of heterogeneous catalysts.
  - Characterization techniques (XRD, TG-DSC, FTIR, TPR and TPO, RAMAN, UV-VIS, particle size analyses, quantification of the number of acid and redox sites, SEM-EDX, TEM-EDX, XPS, electrochemical techniques)
- **We need industrial partners**
  - In the field of catalyst formulation
  - Scaling up catalyst production
  - Safety-related operational balance of plant components
  - Providing demonstration sites in EU for deployment of the technology

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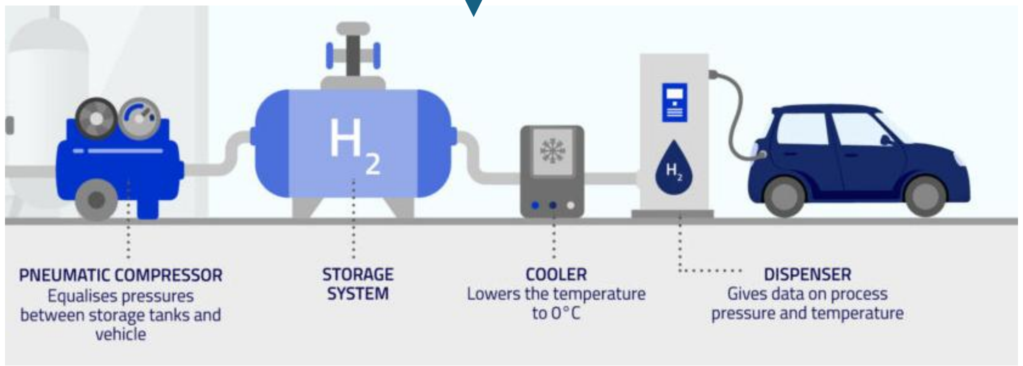
Market opportunity 1: Connection to a hydrogen refuelling station

- The LOHC liquid (MCH) is transported to the station by a two-axle semi-trailer tanker (29 m^3 MCH) and fills the LOHC storage container.
- The system detects when the pressure in the hydrogen storage system at the HRS decreases and then the LOHC material flow starts to the reactor and H_2 release begins. The evolved hydrogen is pumped into the storage system by a compressor to the desired pressure, and from there it reaches the dispenser through the gas cooler.

LOHC container

LOHC reactor



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Market opportunity 2: Battery-like operation

- It is necessary to build energy storage capacity next to a 500 kW photovoltaic unit (e.g. in an energy community). To do this, we install a 500 kW electrolyzer, which converts the excess electricity into H_2.
- The H_2 produced by the electrolyzer during the day is stored in LOHC. 7.35 tons/year, i.e. an average of about 20 kg (800 kWh) of H_2 per day, can be stored in this way if the electrolyzer efficiency is 70% and the annual operating hours are half that of the PV power plant.
- In LOHC, energy can be stored in the long term without loss: periods of several days or weeks without sunlight can be bridged.
- The technology is modular and scalable.

	Rated power MW	Yearly operating hours h	Yearly power consumption/production MWh	Efficiency %	Yearly hydrogen production/comsumption MWh	tonna	thousand m^3
PV plant	0.50	1,300	650				
Electrolyser	0.50	700	350	70	245	7.35	89.86

The size of the LOHC container (if we implement a maximum storage requirement of 1 week): 2.99 m^3, in which we store 2.3 tons of LOHC, which corresponds to 5.6 MWh of energy.

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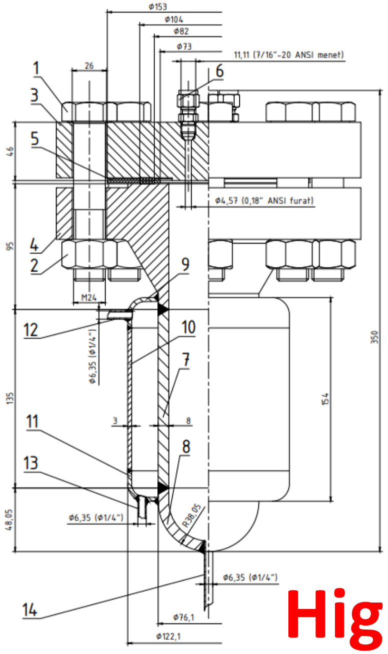
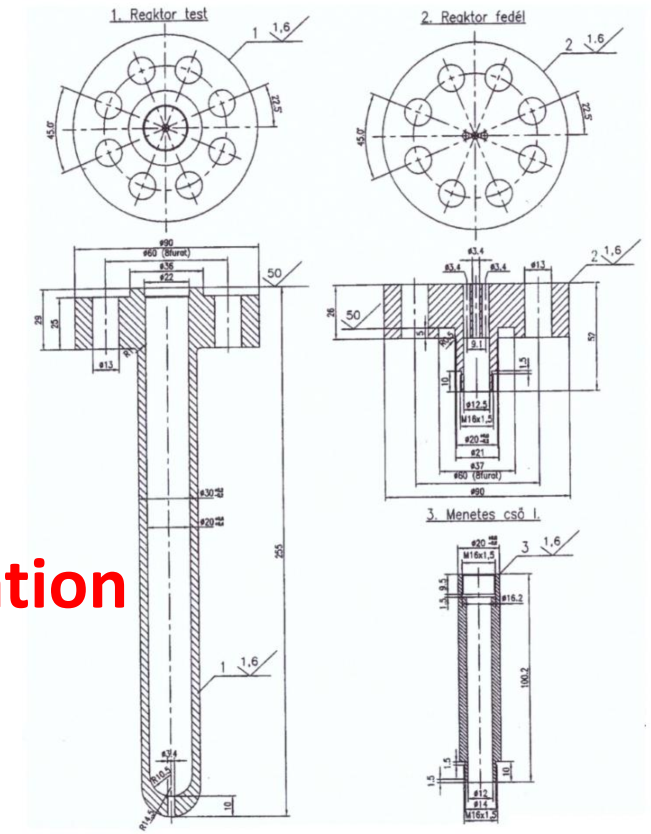
Summary

- By implementing the heat management of the LOHC, we achieve the energy demand of 6 kWh/kg H_2, for which we implement a loop reactor concept. We implement system-integrated heat recovery (heat exchanger) and intelligent control (reactor state optimization, dynamic operation), which enables economical, modularly scalable, LOHC-based H_2 storage and release operation.
- We are installing a TRL6 level reactor that operates autonomously in its application environment.
- We develop long-life technology (over 99% selectivity) and develop low-cost, noble metal-free and durable catalysts.

6-channel reactor system for high pressure reactions





High-throughput experimentation

- Catalyst (+ diluent) load – ca. 5 ml
  - Inner diameter of reaction tubes: 8 mm
  - Length of the catalyst bed: 10 cm
- Total flow rate: not limited
- Reaction temperature up to 600 °C – the heating and cooling rates can be adjusted independently in each reaction tube. Standard deviation: 0.5 °C.
- Operating pressure: up to 80 bars

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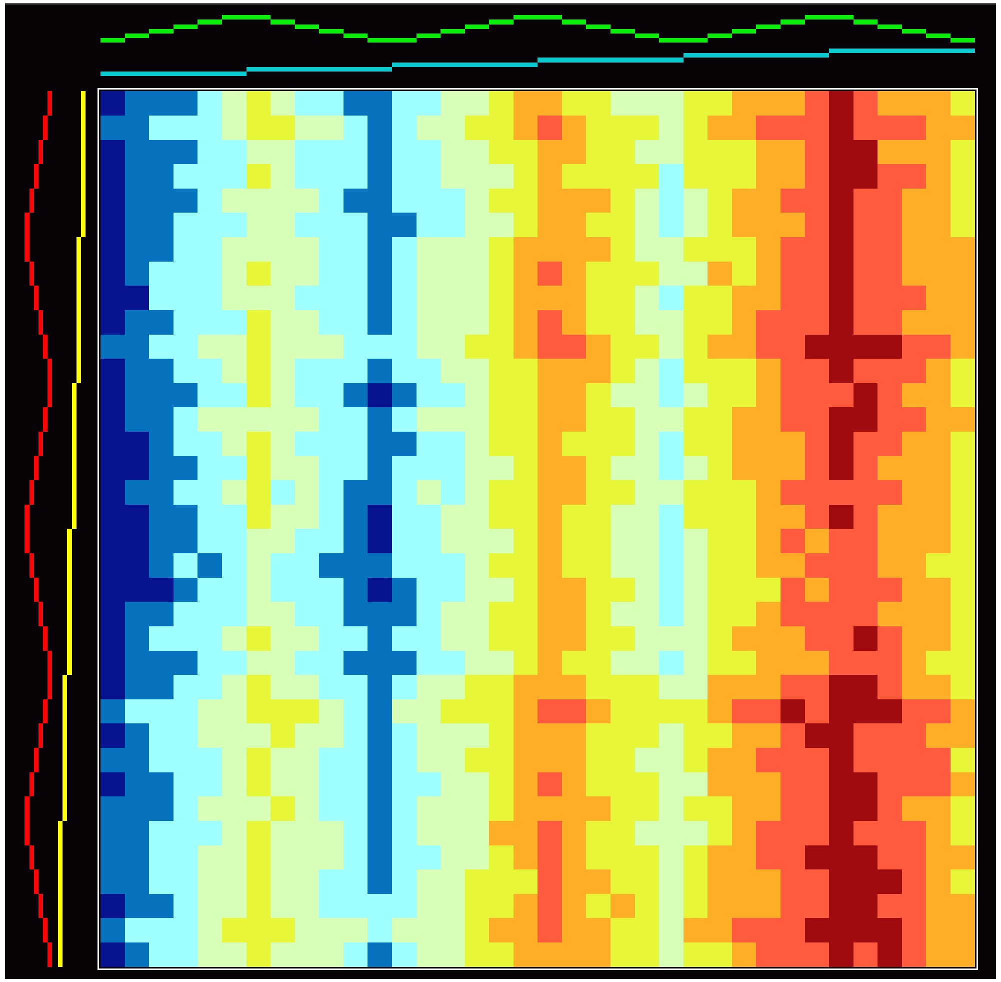
2D visualisation of multidimensional experimental spaces



- A 4 dimensional example can be seen: 2-2 variables along the X and Y axis, respectively.
- Objective function is shown by a color code leading to a “heat map”.
- Variables can be placed optionally along the axes.
- The levels of the experimental variables are arranged to form waves.
- Moving along any axis from one experimental point to the next one only one level of one variable changes.
- Therefore, the two-dimensional transformation of the experimental space is continuous.

Végvári L , Tompos A , Gőbölös S , Margitfalvi JL: Holographic research strategy for catalyst library design. Description of a new powerful optimisation method. ***CATALYSIS TODAY*** 81:(3) pp. 517-527. (2003)

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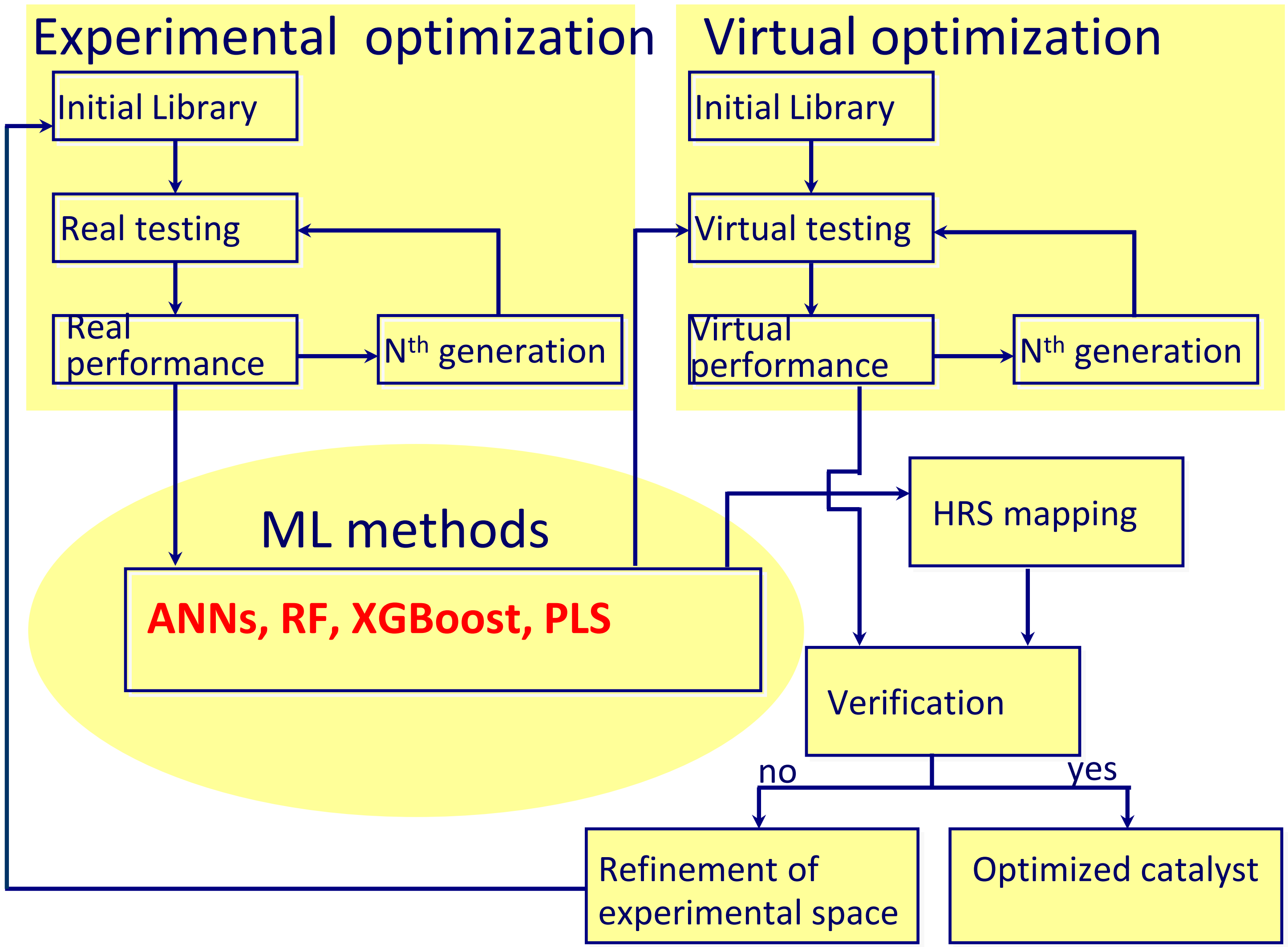
Machine learning models



- Artificial Neural Networks (ANNs), Random Forest (RF), Extreme Gradient Boosting (XGBoost) and PLS are used to build models providing correlation between composition and catalytic performance (conversion, loss).

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