

Treball de Fi de Màster

## Màster en Enginyeria de l'Energia

# Design of a Liquid Organic Hydrogen Carrier (LOHC) reactor for X-ray Absorption Spectroscopy (XAS) analysis.

### PROJECT REPORT

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## Resum

Aquest projecte es centra en la tecnologia de l'emmagatzematge i el transport d'hidrogen i en el disseny d'un reactor que permeti que la reacció catalítica de deshidrogenació pugui ser analitzada a través d'X-ray Absorption Spectroscopy (XAS) en *operando*, en aquest cas utilitzant radiació de sincrotró. El projecte repassa tant la tecnologia dels Liquid Organic Hydrogen Carriers (LOHC) com la del mètode XAS i l'utilitza com a referència per entendre les limitacions i els requisits que ha de tenir el disseny del reactor. El disseny i la fabricació del reactor de testeig es mostra pas a pas, explicant els detalls rellevants de tot el procés. S'analitzen els resultats obtinguts en cadascuna de les etapes i les millores a realitzar, tant al reactor com a la manera de procedir a l'experiment. Finalment, els coneixements i conclusions extrets de les versions de testeig s'apliquen al disseny d'una cel·la de deshidrogenació definitiva que s'utilitzarà per estudiar la reacció en *operando* amb XAS a la línia del sincrotró. El testeig de la cel·la de deshidrogenació definitiva no es realitza en aquest treball a causa de les limitacions de temps del projecte, i es deixa tot disposat per a aquesta anàlisi en un futur *beamtime* al sincrotró.

## Resumen

Este proyecto se centra en la tecnología del almacenamiento y transporte de hidrógeno y en el diseño de un reactor que permita que la reacción catalítica de deshidrogenación pueda ser analizada a través de X-ray Absorption Spectroscopy (XAS) en *operando*, en este caso utilizando radiación de sincrotrón. El proyecto repasa tanto la tecnología de los Liquid Organic Hydrogen Carriers (LOHC) como la del método XAS y lo utiliza como referencia para entender las limitaciones y requisitos que debe tener el diseño del reactor. El diseño y fabricación del reactor de testeo se muestra paso a paso, explicando los detalles relevantes de todo el proceso. Se analizan los resultados obtenidos en cada una de las etapas y las mejoras a realizar, tanto en el reactor como en la forma de proceder en el experimento. Por último, los conocimientos y conclusiones extraídos de las versiones de testeo se aplican al diseño de una celda de deshidrogenación definitiva que se utilizará para estudiar la reacción en *operando* con XAS en la línea del sincrotrón. El testeo de la celda de deshidrogenación definitiva no se realiza en este trabajo debido a las limitaciones de tiempo del proyecto, y se deja todo dispuesto para este análisis en un futuro *beamtime* en el sincrotrón.

## Abstract

This project focuses on hydrogen storage and transport technology and the design of a reactor that allows the catalytic dehydrogenation reaction to be analyzed by X-ray Absorption Spectroscopy (XAS) in *operando*, in this case using synchrotron radiation. The project reviews both the Liquid Organic Hydrogen Carrier (LOHC) technology and the XAS method and uses it as a reference to understand the limitations and requirements of the reactor design. The design and fabrication of the testing reactor is shown step by step, explaining the relevant details of the whole process. The results obtained in each of the stages and the improvements to be made, both in the reactor and in the way of proceeding in the experiment, are analyzed. Finally, the knowledge and conclusions drawn from the test versions are applied to the design of a final dehydrogenation cell that will be used to study the reaction in *operando* with XAS in the synchrotron line. The testing of the final dehydrogenation cell is not performed in this work due to the time constraints of the project, and everything is left ready for this analysis in a future *beamtime* at the synchrotron.



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# 1. Introduction

## 1.1. Motivation

The use of hydrogen as energy vector is one of the main pillars towards a sustainable future dependent on renewable energies. Its potential is well known, and its main limitations rely on the difficulties for storing and transporting it. Further research in this field is indispensable for this technology to overtake the market and truly start a period of independence from the fossil fuels. In this regard, innovative technologies could set a milestone in this direction.

The possibility of handling hydrogen by means of a Liquid Organic Hydrogen Carrier (LOHC) is a technology known for several years, which has demonstrated the viability of this method for the storage and transport of hydrogen in a safe and cost-effective way. Even so, there are not many fundamental studies about the processes going on during the reactions, mostly the dehydrogenation reaction. Nevertheless, its potential is huge, and further investment and investigation could optimize the efficiency of the system, already commercialized at this stage. For this reason, this project has been carried out. The analysis of the dehydrogenation reaction by X-ray Absorption Spectroscopy (XAS) method will provide more information for the improvement and development of this technology in the upcoming years.

In order to better understand how the technology works and where there is potential for improvement, the studies in operando, where the measurements are done during the reaction to understand the processes, are very much necessary. The contributions that engineering can make in this aspect are enormous, since the first step in these studies is the development of reactors that allow us to use the different characterization methods under realistic reaction conditions.

## 1.2. Scope

The scope of this project is to design a dehydrogenation reactor according to the requirements of the reaction conditions, as well as the requirements of the XAS technique. In order to do that, some background knowledge is required, which also falls within the scope of the project: the understanding of the requirements of the XAS analysis method, the study of the LOHC technology, and the engineering requirements of a dehydrogenation cell. The testing of the dehydrogenation reactor is not in scope of the project but testing reactors (prototypes) are built and tested to prove the feasibility of the reaction in the required conditions.

### 1.3. Objectives

The main objective of this project is to successfully design a dehydrogenation reactor, necessary to release the hydrogen from the LOHC. The compatibility of the reactor with the requirements to be tested in XAS conditions is a main requirement.

Additional objectives of the project are:

- Analysis of the LOHC technology and how can it become a breakthrough in the hydrogen and energy sector.
- Study and understanding of XAS analysis, which is necessary to understand the requirements needed by the reactor.
- Acquire the knowledge referred to how a synchrotron works and the applications that it can provide.
- Correct assembly of the prototype and experiment preparation.
- Analysis of the de-hydrogenation results.

## 2. Theoretical background

### 2.1. LOHC technology

Liquid Organic Hydrogen Carriers (LOHC) refers to organic compounds that are able to store hydrogen within their atomic bonds by means of a chemical reaction, creating a fuel-like, hydrogen-rich storage liquid [1]. Moreover, the reaction is reversible which allows to reuse the organic compound after the hydrogen is released, as well as the catalyst. In that way, a cycle can be created as transport/storage method for the hydrogen (Fig. 2.1).

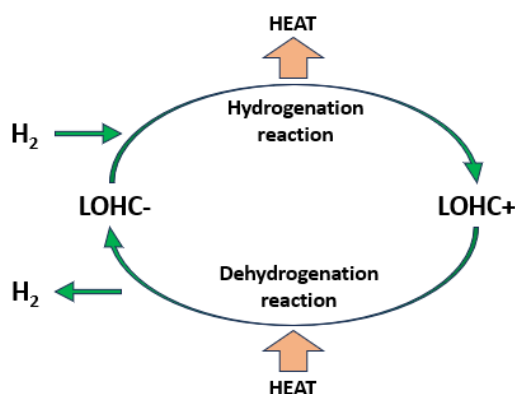


Fig. 2.1. LOHC reaction cycle.

In recent years this innovative technology has been increasingly discussed as an attractive option to store and transport hydrogen. This method is safe, efficient, and cost-effective which are the main demands for a fuel technology to be [2]. LOHC technology allows to manage hydrogen at ambient conditions which represents a huge advantage. Nowadays, most hydrogen technologies rely on increasing the density of the hydrogen to reach a feasible cost-efficiency for the operation, mainly pressurizing and/or cooling down the hydrogen to cryogenic temperatures. This implies expensive processes and infrastructure that LOHC technology avoids.

An energy system based in this kind of technology (Fig. 2.2) would have a hydrogen-lean organic compound (LOHC-), commonly an aromatic compound, ready to use where unpredictable renewable energy is produced such as wind or solar power plants. The excess of electricity on these power plants could be used to produce hydrogen on-site using electrolyzers. That hydrogen could then be bound to the atomic structure of this hydrogen-lean organic compound by means of a catalytic hydrogenation reaction, turning the initial compound into a hydrogen-rich organic compound (LOHC+), commonly an alicyclic compound [3].

The covalent bonds that are formed between the organic compound and the hydrogen are very stable since dehydrogenation enthalpies for the aromatic LOHC systems are typically

at a high level which ensures that the activation energy is not overcome at room temperature [3]. This guarantees safe and efficient storage and transportation of the liquid, at ambient conditions, to any location demanding energy or hydrogen. If the storage of hydrogen is intended, the stable liquid form of the LOHC+ guarantees no energy losses due to self-discharge processes and easy storage conditions [4]. When transportation is needed, it could be done using the existing infrastructure for current liquid fuels such as pipelines, trucks, or vessels, with minor modifications [5], which represents a major advantage compared to the common hydrogen transportation methods.

Once in the site of demand, a catalytic dehydrogenation reaction can be applied to the fuel-like liquid for on-demand hydrogen release. Essentially, the inverse process is done: the hydrogen-rich organic compound (LOHC+) releases its hydrogen to become a hydrogen-lean organic compound (LOHC-) that can be transported to any power plant for its reutilization. Seemingly, the catalysts used in both hydrogenation and dehydrogenation reaction can continue to be used since their lifespan is of thousands of cycles [6]. With the hydrogen released, any conversion technology could be used to produce electrical energy if desired or directly use the hydrogen. It is important to mention that high purity hydrogen (>99%) can be obtained from it [7].

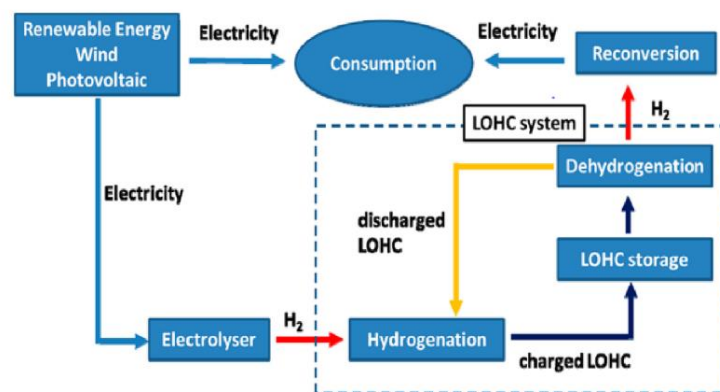


Fig. 2.2. LOHC based energy system [4].

A major important factor to consider is the substances that are used in the system. The LOHC and the catalyst selection imply different reaction conditions as well as different behavior at atomic level when the reaction occurs. In the case of this project, the reactants were provided by *Hydrogenious*, a company involved in the project and experiments within it. The company is developing its own LOHC technology, already proved and being at an early commercial stage. Despite that, there is interest in how the reactants are being modified within the catalytical reactions in order to improve their efficiency and lifespan.

The compound that is being used is benzyltoluene (H0-BT), that when containing hydrogen becomes perhydrobenzyltoluene (H12-BT). This compound is particularly effective for this reaction because of its chemical and structural characteristics [8].

Benzyltoluene (BT) has a gravimetric hydrogen uptake capacity of 6.2 wt% [9][10] giving this compound a decent hydrogen storage capacity. In addition, the technical aspects of the compound are also positive in terms of availability and compatibility with the hydrocarbon-based energy infrastructures [8][10]. BT also presents a low viscosity of  $2.6 \text{ mm}^2 \text{ s}^{-1}$  at  $40^\circ\text{C}$  [9] which compared to other organic compounds suitable for LOHC (not to be discussed) facilitates the handling of the liquid.

Another important data about this compound is that the boiling point is  $270^\circ\text{C}$  [8][10] which is very relevant since the temperature at which the reaction takes place is at  $260^\circ\text{C}$  and above, implying that two phases coexist in the reactor while the dehydrogenation occurs [10].

On the economical aspect, since BT is a product already in use in the industry and the price is relatively low which makes it a feasible option to scale up. Its price is about \$4-5 per kg [9].

The other product required for the reaction is the catalyst. In the case of this project the catalyst used is platinum (Pt) supported on alumina ( $\text{Al}_2\text{O}_3$ ) provided by *Hydrogenious*. It consists of an egg-shell-impregnated spherical alumina support of about 3mm of diameter containing 0.3 wt% of platinum loading in form of nanoparticles on the surface of the sphere.

$\text{Pt}/\text{Al}_2\text{O}_3$  was found one of the most active catalysts among the ones studied in recent investigations [11][12]. Pt is a noble metal frequently used as catalyst, ideal in this case because of its ability to interact with the C-H bond in hydrocarbons. On the other side, alumina is a favorable support for Pt, in this case, because of its thermal and chemical capabilities related to the dehydrogenation reaction.

In addition, it was found that  $\text{Pt}/\text{Al}_2\text{O}_3$  can be used in both hydrogenation and dehydrogenation of the BT. When hydrogenation happens, the catalyst enables the hydrogen uptake at 10-30 bar and  $200\text{-}250^\circ\text{C}$ , while during the dehydrogenation the catalyst enables the hydrogen release at 1-3 bar and  $250\text{-}300^\circ\text{C}$  [13].

Both products to be used in this project were facilitated by *Hydrogenious* since these are the products that are being used by the company, and their effectiveness and efficiency are proved. Despite that, understanding the implicit processes that occur in the reaction can improve the whole process. For that reason, it is important to mention what are the conditions and internal process that the products go through.

## 2.2. BT - $\text{Pt}/\text{Al}_2\text{O}_3$ dehydrogenation reaction

As explained in the previous section, the LOHC used in this system is benzyltoluene (BT), specifically for the dehydrogenation process, the hydrogen-rich version of it is used: perhydrobenzyltoluene (H12-BT).

The dehydrogenation reaction of H12-BT is an endothermic reaction that needs around 63.5 kJ/molH<sub>2</sub> [8]. This is the demanded energy at the reaction conditions that can range from 1 to 3 bar and 260 to 320°. This range in temperature and pressure have important implications in the reaction process.

The boiling point of BT is of 270°C at normal conditions, which is about the same temperature that the dehydrogenation reaction occurs, meaning that two phases will coexist in the reactor during the experiment unless the temperature is kept below 270°C. Despite the reaction being possible in gas phase, the efficiency of the reaction is lower since the density of the BT is lower. On the other hand, below 270°C the reaction is still possible, but the low T will demand more time to complete the reaction, at a lower flow rate and obtaining less efficiency. The range of T and P conditions that allow the reaction can help in this case: at higher P, the boiling point of BT increases, allowing the BT to react only in liquid phase at higher temperatures and therefore reacting faster and more efficiently.

BT is particularly convenient as a LOHC. Its chemical structure allows to take up the hydrogen atoms having only one intermediate during the reaction (H6-BT). The procedure is the same for the dehydrogenation process. Less elementary steps imply a faster reaction which at an industrial level means higher efficiency for the overall process.

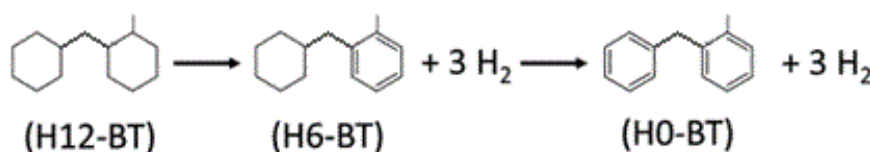


Fig. 2.3. Benzyltoluene to Perhydrobenzyltoluene conversion [10].

On the catalyst side, platinum-based catalyst supported on alumina (Pt/Al<sub>2</sub>O<sub>3</sub>) is used. Pt is one of the most active and effective catalyst to interact with C-H bonds which make it very suitable for the reaction. In addition, the ultra-low loading of Pt in the catalyst results in high productivity of the metal for its purpose while reducing the cost of the material (to consider at industrial scale) [14]. Even so, the efficiency is maintained and the cyclability of the catalyst is considerably high.

The reaction demands of a certain proportion of reactants that have been given by *Hydrogenious*. The proportion used by the company is 9g (10ml) of LOHC+ per 2g of catalyst, in order to achieve a complete dehydrogenation when at the right reaction conditions. To accomplish that, the reactor needs to have a fixed bed of catalyst and the right flow of LOHC+, to be determined in function of the quantities of reactants.

The study using XAS would be carried out focusing on the catalyst present in the reaction and analyzing how the Pt on the surface of the egg-shell would be modified over the course of the reaction. The requirements of the experiment implied the necessity of using X rays in a research environment, only possible in synchrotrons facilities.

## 2.3. Synchrotron

A synchrotron is a type of circular particle accelerator (Fig. 2.4) in which charged particles, mainly electrons, are accelerated to nearly the speed of light producing an extremely bright light up to 10 billion times brighter than the sun light [15]. This synchrotron light travels around a close-loop path governed by magnetic fields and it can be used in different analytical and manufacturing methods in the experimental workstations of the facility. The complexity of the process makes the synchrotrons one of the most advanced facilities, but its principle of operation is well known since the 1950's and have remained the same only changed by improvements in the machinery that allows this performance.

Electrons are initially emitted by an electron gun placed in the middle of the synchrotron rings. This electron gun uses the principle of thermionic emission to liberate and eject electrons from an electrode by heating it up until its work function is overcome and the electron is released. Once the electrons are free, they are packed in 'bunches' and the linear accelerator or LINAC is the responsible to accelerate them gradually. Using alternate magnetic fields, the LINAC accelerates the electrons to 99.99% the speed of light in straight line and move them into the booster ring [16].

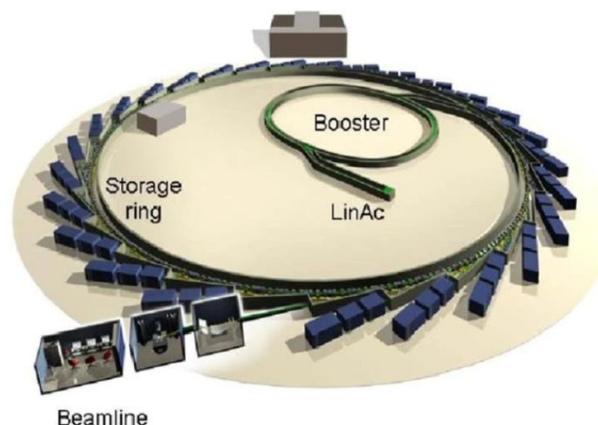


Fig. 2.4. Synchrotron facility scheme [17].

The booster ring is the smaller ring of the synchrotron and is responsible to rise the energy of the electrons to the maximum energy that the synchrotron has. This can be achieved thanks to microwave fields at a specific radio frequency that are present all around the booster ring and are able to increase the energy of the electrons by thousands of MeV, permitting them to achieve 99.99999% the speed of light [18]. The electrons travel around the booster ring over one million times to reach that energy and magnetic fields are used to keep the electrons in a circular path. Then, the electrons are transferred to the storage ring [16].

The storage ring is the largest ring in the synchrotron. High energy electrons coming from the booster ring travel around it producing light for the beamlines. Despite looking circular, the storage ring is composed of small straight sections and dipolar magnets are used to curve the high energy electrons beam. As the electrons are deflected through the magnetic field created by the magnets, they give off energy in form of electromagnetic radiation (also called synchrotron radiation), so that at each bending magnet a beam of synchrotron light is produced. This electromagnetic radiation is emitted in the forward direction, tangent to the electron's orbit. This beam of synchrotron light is precisely directed into the beamlines that are spread around the synchrotron and will be used for the experiments [18][19].

The beamline is the last section of the path of the beam light, also referring to a research station in the synchrotron, since there are tens of beamlines in a synchrotron facility, and they are focus on different fields of study. After the synchrotron light is ejected from the storage ring it enters a cylindrical metallic pipe that conducts it through different optical devices such as monochromators or undulators. Those devices control the light measuring, focusing, and purifying the beam according to the necessity of the experiment of the end user [19]. The experiment takes place in the room at the end of the beamline, known as experimental hutch. It is a safe hutch with walls made of lead that prevent the radiation coming from the beam light to escapee the room. The experimental hutch also contains all devices necessary to set up and conduct the experiment and to collect the data from it. This includes sensible and complex machinery such as X-ray detectors, hexapods, or beam blockers. All this equipment is controlled by the end user of the beamline from the control hutch, placed next to the experimental hutch. In there, the end user disposes of all required hardware and software to control the experiment taking place and can collect and analyze the data that is being obtained [16].

Overall, the whole process and machinery involved is very complex and sensitive, requiring a very precise operation and strict maintenance of the installation. This makes the synchrotrons some of the most advanced facilities in the world and of special interest in research sector. Also, the fact that radiation is being produced requires a security and safety policy according to it.

In total, up to 70 synchrotrons are operating in the present time around the globe [15]. They are usually classified according to the energy that they produced and the technology generation that is being used. They can also differ depending on the purpose of the facility: it can be used for applied science research or synchrotron science improvement. For example, the PETRA III storage ring at the DESY facility in Hamburg, Germany is delivering 6 GeV for applied science research [20]. Same case with SPring-8 at the RIKEN research institute in Japan, delivering 8 GeV [21]. But in terms of generation-wise, the European Synchrotron Radiation Facility (ESRF) in Grenoble, France is the most advanced, being the first to become a 4<sup>th</sup> generation synchrotron, delivering 6 GeV of energy [22] (Fig. 2.5).



Fig. 2.5. Aerial image of the ESRF in Grenoble, France [22].

The ESRF is in fact the facility where this project has taken place between April and July this year. This research center was created and funded by 11 European countries that agreed on the importance of synchrotron science, creating the first 3<sup>rd</sup> generation synchrotron in 1988 [22]. Nowadays, the ESRF is supported by 22 countries: 13 members and 9 associates and have 44 beamlines each of them focused on different fields of investigation such as material physics, structural biology, nanotechnology, medical applications, or cultural heritage, among others [23]. Being biology one of the most successful ones since in 3 occasions users in this field of investigation have been awarded with the Nobel Prize between 2003 and 2012 [22].

Some of the most challenging studies are possible in the ESRF and other synchrotrons thanks to innovative and improved techniques that the installations allow the users to use. One of them is of the interest of this project since the dehydrogenation reactor that has to be built requires compatibility with the usage of this technique: the X-ray Absorption Spectroscopy (XAS).

## 2.4. X-ray Absorption Spectroscopy (XAS)

XAS is a spectroscopy technique that involves measuring the transmission (or fluorescence) of x-rays as a function of incrementing the x-rays energy in small steps at energies close to the absorption edge of an element of interest [24].

Main advantage of this technique is that, since the binding energies of the core-electrons of atoms are well defined, it is possible to select an element to probe by tuning the X-ray energy to the appropriate absorption edge [25]. Therefore, being an element-selective method of study. This allows to focus in one single element of a heterogeneous sample.

The results of XAS analysis give information of the oxidation state as well as the local structure of the element [25]. This are important details for this project since the changes that the catalyst suffer during the chemical reaction can provide crucial information on what is changing, when the changes occur during the reaction, and how the changes occur, obtaining data on how to improve the whole process or the reactants that are involved in the experiment. For that, it is important to understand how the XAS technique works and what are the outputs of it.

As stated before, tuned x-rays according to the element of interest are directed to the sample. These x-rays are basically very energetic photons that can excite the innermost shell electrons (1s level, named K) of the element of interest, also called core-electrons. Those electrons are not valence electrons and are not involved in the chemical bonding of the atom. Instead, they are strongly bonded to the nucleus of the atom, shielding it, and affect the chemical reactivity of it. Core-level electrons can be removed from its core-level upon absorption of electromagnetic radiation (photons). If the energy absorbed is larger than the binding energy, the electron will promote to an empty valence shell of the atom. And, if the kinetic energy is enough to completely free the electron from the atom it will be emitted to the continuum as a photoelectron due to the photoelectric effect (Fig. 2.6a). In this case the atom will become ionized since losing an electron will cause it to be positively charged [26][27].

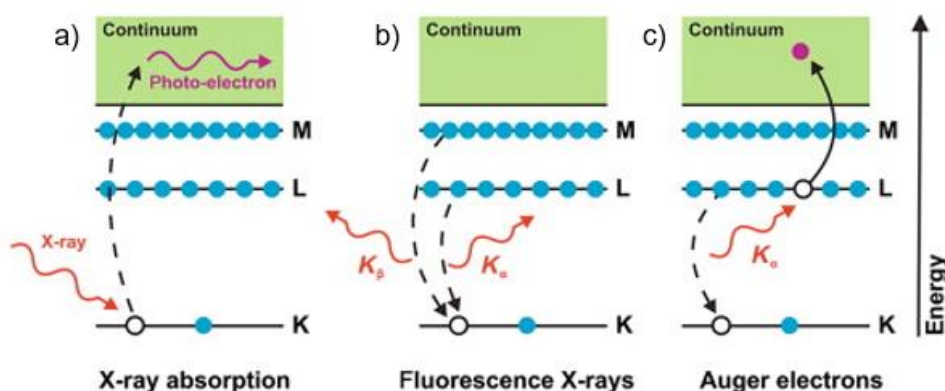


Fig. 2.6. Photoelectron formation and consequence fluorescence x-rays or auger electron formation during XAS method [27].

As a result, the atom will have an empty space in the lower shell, known as core-hole. This needs to be adjusted to regain stability in the atomic structure and 'shield' the nucleus. To do so, in a span of time of few femtoseconds, an electron from the higher neighboring shells will decay to occupy the core-hole in the lower shell. When an electron decays from a higher-energy shell to a lower-energy shell, the excess energy (equal to the difference between the two atomic shells) is released [28]. The detection of the energy emitted in this event, provides useful information on the electronic and local lattice structures of a material. After this, two different scenarios can happen:

On one hand, the energy that is released can be emitted in form of fluorescence x-rays, which is a characteristic x-ray of each element that is analyzed (Fig. 2.6b). This happens for most of the heavy atoms [27][28].

On the other hand, for the light atoms, the released energy from the electron filling the core-hole can also be transferred to a neighbor valence electron, giving it the necessary energy to break its binding and eject from the atom. This electron has enough kinetic energy to escape from the atom and becomes a free electron in the continuum. It is called an Auger electron [27][28] (Fig. 2.6c).

Independently of the case, the atom will have to readjust its electronic structure to regain stability, so a rearrangement of electrons will continue in the span of femtoseconds to picoseconds, including the de-excitation of electrons that were promoted to a higher shell. In this process, the two scenarios that have been exposed before can happen over and over again until the balance within the atomic composition of the atom is stable again. So, at the end the atom goes back to its ground state (initial state).

In resume, energy has been given to the atom of interest, this atom has suffered an alteration of its electronic structure, and the movement of its electrons to restore the initial form gives away energy signals that are collected by a detector. This is valuable data that contains information about the local structure and the oxidation state, most importantly. And when presented as an Energy-Absorption graph, the output can be divided in two regions: XANES and EXAFS [27][29] (Fig. 2.7).

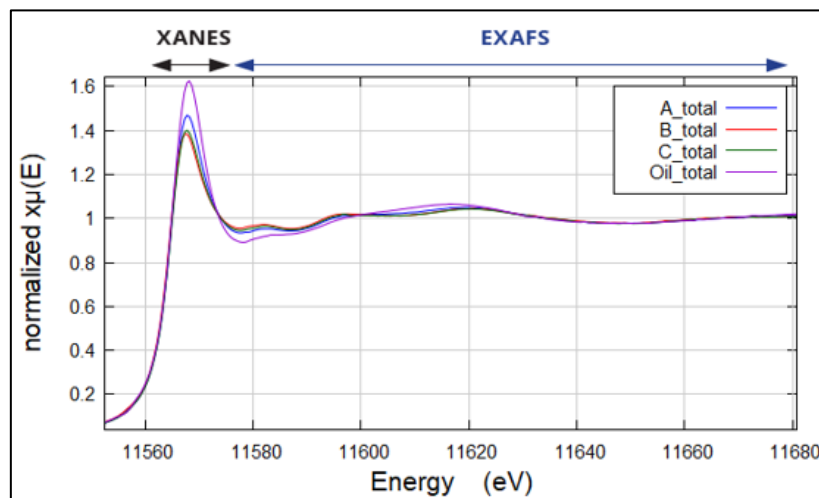


Fig. 2.7. XAS spectrum showing the main regions. This spectrum belongs to a LOHC reactor tested in the ESRF.

As the x-ray radiation scans through the range of energy specific for the element of interest, a sudden increase of absorption appears. That peak corresponds to the absorption of x-ray photon by a specific type of core-electrons. The region containing this main peak or edge is known as XANES and stands for X-ray Absorption Near Edge Spectroscopy. Despite

appearing simple in this figure, XANES region can also contain a pre-edge right before the main edge, originated from core-to-core or core-to-valence transitions which corresponds to, as explained before, a more subtle movement of a core electron to a higher core shell or to a partially occupied valence shell because the energy absorbed by the core-electron is not enough to allow him to escape the atom. This pre-edge can give useful information about the local environment of the absorbing atom. The main edge, on the other hand, corresponds to the energy absorption by a core electron that will eject to the continuum. The edge reveals more relevant information about the electronic structure of the atom and the oxidation state of it since the signal detected is more relevant and stronger [26][28].

The second region of interest that is shown in the spectrum is the so-called EXAFS, meaning Extended X-ray Absorption Fine Structures. This region starts about 50 eV after the main edge and reveals the information relative to the local atomic structure and coordination environment of the absorbing atom. In this way, bond lengths can be very precisely measured. This is revealed by the downwards oscillations that can be observed in the spectrum (Fig. 2.7) and are generated by the wave interactions between the ejected photoelectron and the atoms surrounding the absorbing atom (Fig. 2.8). In most cases, the scattering of the photoelectron with the surrounding atoms will cause it to return to the original (ionized) atom so the atomic balance will be recovered [26][28][30].

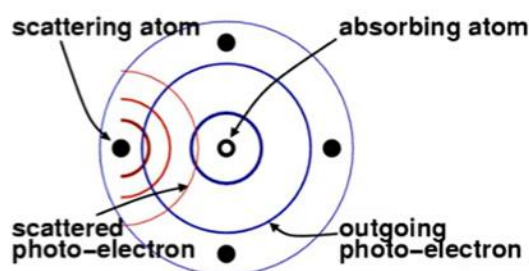


Fig. 2.8. The outgoing photoelectron will interact with the neighbor atoms scattering it back to the former initial atom [30].

The interference between the outgoing waves and the incoming waves leads to constructive and destructive interferences that are represented as oscillations in the EXAFS region of the spectrum. At the end, the equilibrium is found within the atomic structure of the sample and the spectrum will appear flat meaning the interactions have very much ended [28].

For this project, the XAS procedure in *operando* conditions will bring the opportunity to understand how the atomic structure of platinum in the catalyst is being modified in real time by the interaction with the benzyltoluene based LOHC under the reaction conditions. The knowledge of the technique is definitely a must to ensure that the reactor will be an effective and efficient platform, and that the requirements to make it suitable for the XAS are met.

### 3. Methodology, experimentation, and results

A reactor suitable for XAS analysis requires some specific characteristics that need to be taken into account when designing it. These characteristics need to be tested before making an investment for a more advanced and high-ended reactor. For this reason, a simpler reactor needs to be manufactured in the first phase, one reactor that can be easily modified, and does not imply a costly investment, but still can recreate the required characteristics of the final design of a dehydrogenation reactor.

As explained above in section 2.4, XAS method is sensible to the elements that the X-ray goes through. For this reason, one of the main demands is to ensure that the beam penetrates through as few matter as possible and that the elements that compose the materials used are as light as possible to minimize the energy lost and the undesired noise in the output signal.

It is also important to ensure that the catalyst is fixed. The vibrations or flow of LOHC can cause the catalyst to move from the initial position. During XAS analysis, the beam needs to be focused on the same spot continuously, an area of few micrometers. A change in the position might cause the beam to aim to a different area where the composition is not exactly the same, giving inconsistent results.

The requirements as a whole suggest that the reactor needs to be of a reduced size and rather thin, so the material used is minimized as well as the energy lost by the beam when going through. By extension, this means that volume of the reactants will be small. It is important to consider that this is the first time that this experiment is done. Never before the dehydrogenation reaction of LOHC with a catalyst have been studied in such small volumes.

This section reviews the design and testing of a dehydrogenation reactor made to test the characteristics that are needed to accomplish the final objective of it, that is to be analyzed in-situ, operando, under XAS method.

The methodology followed is repetitive for each of the versions of the reactors tested and the conditions are equal ensuring a common ground for subsequent data analysis. These conditions are specified in the background theory expressed in a range of temperature and pressure suitable for the reaction to happen. For this experiment it was found a better approach to determine a feasible and practical reaction conditions: 260 °C and atmospheric pressure (1 bar). Once this conditions were reached, the reaction should go on for 4 hours at constants conditions to ensure a complete reaction.

In each version, the designing and manufacturing process is explained, then the reactor is tested, and a review is done on the reactor to evaluate the performance of it and consider further improvements.

### 3.1. Testing reactor v0.0

Initially, the reactor was thought to be a continuous flow reactor with the catalyst placed in the central cylindrical container acting as reactor made of thin glass in a vertical position, and the LOHC+ flowing through it reacting at the right temperature (Fig. 3.9). The pressure would not be a concern since the reaction is determined to occur at atmospheric pressure, so no pressurization is needed. The heat transferred to the reactor's cylinder, where the catalyst is, would produce the dehydrogenation. Once the hydrogen is released, the LOHC- would follow its path leaving the reactor and it would be deposited in an outlet vessel, providing the ability to do the density check of the organic compound from time to time during the experiment. On the other hand, hydrogen would be released to the fume hood ventilation system. The only requirement would be to check is that hydrogen is being released, which can be controlled with a flow meter on the outlet tube for hydrogen.

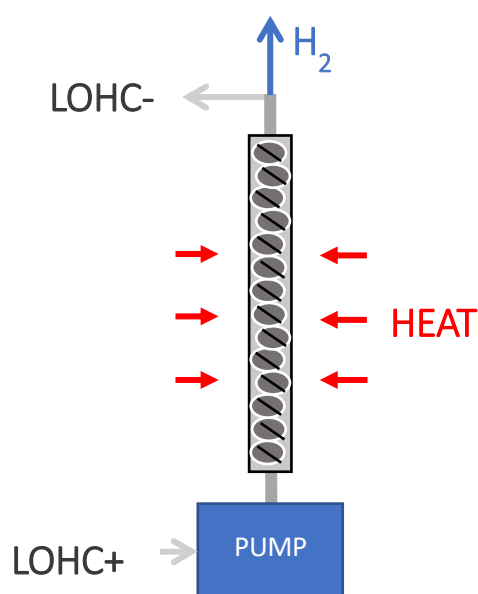


Fig. 3.9. Flow reactor scheme.

But many unsolved issues arose. The main part of the reactor, the cylindrical glass, had to be made of thin glass, as thin as possible to avoid having too much noise in the XAS results and thus not obtaining favorable results from the experiment in the beamline. Manipulating such a delicate piece of glass in addition to finding a way to make the connection with the tubing could be a problem. That cylindrical glass piece also had to contain and prevent any movement by the catalyst since this was a main demand. To finish, if the LOHC needed to flow, a pump would be needed, which can create some internal pressure with uncertain consequences for the glass piece. Seemed like an expensive and complicated reactor just for the tryout of the reduced volume reaction. It was clear that another approach was needed.

### 3.2. Testing reactor v1.0

The reactor needed to be simplified, so the design needed to change. The best option was a batch reactor type where all reactants were already in the mix and no flow was needed. This more simplified reactor needed to prove that the reaction could happen in such conditions of volume and temperature and still achieve a proper dehydrogenation, so it was not that important if the reactor type was changed or modified.

This new reactor would consist of a main central piece of thin glass containing all reactants that would be heated up to the specified temperature, and a tube connected on the top part of the glass to evacuate the hydrogen and also help condensate the LOHC in case it changed to gas phase (Fig. 3.10). Since the boiling point of the LOHC is similar to the reaction temperature it is important that the gas phased LOHC condenses back to the batch and continues to react to ensure full conversion.

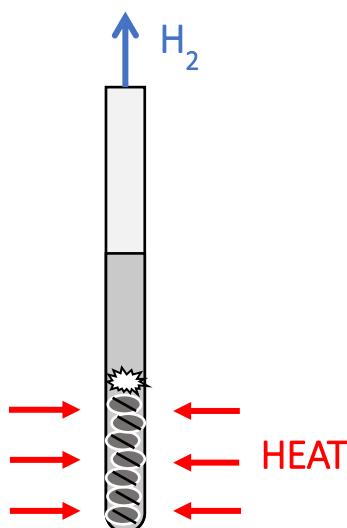


Fig. 3.10. Static reactor scheme.

Following this idea, the materials needed to be chosen. As for the thin glass cylindrical part, the main piece in the reactor, the best option was to use a capillary made of quartz glass of 10  $\mu\text{m}$  thickness. Quartz glass capillaries are able to sustain up to 450°C with nearly null physical expansion, has high purity, its surface is smooth, has high tensile strength, and is chemically stable. In our facilities this kind of capillary was available in 2.5 mm of diameter, which forced to fragmentate the catalyst of 3mm of diameter in smaller pieces to make sure it could fit inside the capillary (Fig. 3.11). This could entail a problem because the active surface of the catalyst is on the outside surface of the spheres. This implies a lower efficiency in conversion terms: same active surface but more surface in contact with the LOHC overall. It was yet to be checked how it could affect the results.

In addition, to ensure the stability of the catalyst, glass wool was proposed. This material

would be placed above the reactants inside of the capillary to avoid the catalyst to rise in case some bubble was created under it and pushed it. This material is chemically and thermally stable and would not interfere in the reaction.



Fig. 3.11. Grounded  $\text{Al}_2\text{O}_3$  catalyst was achieved with an agate mortar and then introduced in the capillary.

Similar to the capillary, the tubing also needed to be chemically stable to be able to sustain the reaction. The tubing used was a 3mm outer diameter PTFE tube that needed to be connected to the capillary. For that purpose, an adaptor made with a cut-out piece of a pipette plastic tip was improvised. This was the weakest part of the reactor since the material quality was lower and the connection with the glass piece was delicate. Despite that, the piece was small, and the sealing was made using high strength glue and epoxy that completely covered the piece and all union spots, making the reactor a whole unique piece (Fig. 3.12). In the assembly process, the small diameter of the capillary required the reactor to be filled with the reactants when the pieces were not united yet. Then all pieces could be assembled.



Fig. 3.12. Handmade connection for the PTFE tubing and the capillary.

In terms of reactants, the right proportion of LOHC+ and catalyst is key to make sure the reaction is done efficiently and the whole quantity of reactants are used. This proportion was given by *Hydrogenious*, the company involved in the investigation about this dehydrogenation procedure. For this experiment, the volume of LOHC+ and amount of catalyst was limited by the volume of the capillary, which was around 0.3ml. Taking into account the proportion of the reactants of 9g (10ml) of LOHC+ per 2g of catalyst, a suitable amount was considered so all reactants could fit properly in the capillary. That amount was 0.045g of catalyst and 0.2ml of LOHC+.

At this point, the sample was prepared and the reactor ready to be tested. In order to heat the reactor in a homogeneous way, an aluminum block was used and placed on top of a heating plate. The aluminum block had several holes that could be used to fit in the capillary as well as the thermocouples to control the heating system and the temperature in the reactor. The aluminum block was also covered with carton to work as an isolator. The whole setup was prepared in the fume hood of the lab due to the safety requirements of the experiment (Fig. 3.13).



Fig. 3.13. First experiment setup in the fume hood.

### 3.2.1. Experiment and reactor review

The reactor heated up for one hour until the reaction temperature was reached. The thermal conductivity of the materials involved was unclear so the temperature on the heating plate was adjusted during the heating up process to reach the right temperature and then sustain

it. At that point the reaction is considered to start, and the countdown of 4 hours is set. Bubbles were visible which gave a sign that the reaction was occurring. But, after 20 minutes into the reaction, LOHC was escaping the tube. Only hydrogen was supposed to escape, so the experiment was stopped.

The LOHC was not condensing fast enough, and it was escaping the tube, condensing at the end of it and falling down the outer part of the tube. The tube had a length of 30 cm which reached the top part of the fume hood, so the best option was to add a cooling system to accelerate the condensation process.

### 3.3. Testing reactor v2.0

In this second version the basic characteristics of the first reactor were maintained. In this case the improved part was a water-based cooling system consisting of a handmade co-current flow heat exchanger (Fig. 3.14) that was added to the outlet tube of the reactor to increase and improve the condensation rate of the LOHC.



Fig. 3.14. Handmade co-current flow heat exchanger.

The heat exchanger was made with different tubing sizes and different types of connections. Since the only tube that the LOHC could go through was the inner tube, that was the only PTFE tube. In this heat exchanger the outlet tubing of the reactor enters through one side of a T type connection and goes through the middle section of the heat exchanger where the heat convection between gas (hydrogen mixed with gaseous LOHC) and water happens. After that, the outlet tube leaves through another T connection on the other side.

On the other hand, water flows through the other side of the T connections and stays on the outer tubing of the heat exchanger. Thanks to this addition, the LOHC condensation rate was supposed to be improved and the remaining hydrogen in the outlet tube would escape the system freely.



Fig. 3.15. Second experiment setup in the fume hood.

The setup was prepared in the fume hood (Fig. 3.15) similarly to the previous reactor. A new sample was made with a new capillary with the same amount of reactants. There was an additional layer of isolation for the aluminum block made with aluminum foil and paper as visible in the figure above. Main difference, as explained, was the addition of the heat exchanger in the outlet tube. The experiment was ready to start.

### 3.3.1. Experiment and reactor review

The reaction temperature was set in the temperature controller and the heat up process went well. After approximately one hour, 260°C were reached and the reaction was considered to start. Countdown from 4 hours was set. Bubbles were visible on the top of the capillary which meant that the reaction was happening. But 45 minutes into the reaction period the experiment needed to be stopped. The condensation of the LOHC was occurring but the gas coming up from the reactor was not letting the condensed LOHC to come back down to the reaction. This was due to the small section of the tube, which was not large enough for the superficial tension of the liquid to be broken, and the gas was pushing the liquid up through the tube and out of it.

The only feasible option to overcome this problem was to increase the diameter of the section of the tube or capillary.

### 3.4. Testing reactor v3.0

In this third version, similarly to the second version, the basic characteristics of the reactor were maintained. The heat exchanger was also maintained to improve the condensation of the LOHC in the outlet tube.

The objective in this version was to ensure that the condensing LOHC was able to go back down to the reactor to continue reacting with the catalyst and make sure all hydrogen was released. The best option was to increase the section of the reactor or tube. Increasing the tube diameter was not an option since the initial tube was already incorporated into the heat exchanger system and changing it would suppose having to redo the whole system with bigger parts that were not available in the lab, which meant buying them. Increasing the capillary diameter was also not an option since the 2.5 mm diameter capillaries were the largest available in the lab.

Finally, the best option was to add a middle piece between the capillary and the tube. That part consisted of a glass pipette that was carefully cut to fit into the top part of the capillary and epoxy and high-strength glue was used to fix it and seal the union (Fig. 3.16). On the other end of the pipette piece, a PTFE tube was also fixed using the same products. This tube was then connected to the outlet tube used in the previous reactor, the one that has the heat exchanger incorporated.



Fig. 3.16. On the left, capillary attached to the bottom part of a cut pipette with epoxy. On the right, compressed air is directed to the pipette in the new setup.

In addition, a new cooling system was proposed, based on compressed air. This cooling system would project a compressed air flow directly to the glass pipette part in order to cool down and condensate the LOHC, minimizing the amount of LOHC in gas phase that can escape through the exit tube (Fig. 3.16). Taking advantage of the increased section, the impact of this cooling system would be even greater.

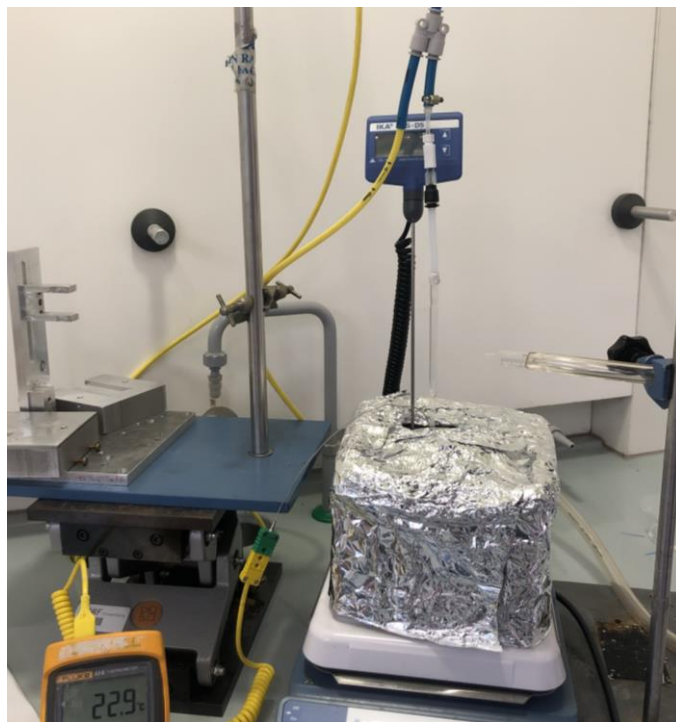


Fig. 3.17. Third experiment setup in the fume hood.

Once again, after these improvements were added to the reactor design and to the set-up of the experiment, everything was ready for another tryout in the fume hood (Fig. 3.17). As in the previous experiments, same conditions and procedures were employed.

#### 3.4.1. Experiment and reactor review

The experiment was initiated, and after one hour and 20 minutes the target temperature of 260°C was reached. At this point, the 4 hours countdown is set. This time the reaction was occurring with no problem, gas bubbles were visible and were escaping without pushing the LOHC through the tube. Also, some condensation was visible in the walls of the pipette, which means that the purpose of the pipette section and the compressed air were working perfectly, preventing the LOHC in gas phase escape the reaction and condensing it to force the liquid back to the reactor.

The entire 4 hours passed without incidences. The reaction seemed to have worked fine, but when the reactor was disconnected from the outlet tube and was taken out of the hole in the aluminum block, it was broken. Despite still having some LOHC inside, the capillary was broken. It is unclear how it broke and if it happened during the reactor disconnection

once the reaction was finished or it happened during the reaction. Anyway, the remaining LOHC was mixed with extremely small glass fragments from the capillary. Also, the amount of it remaining was not enough to check what was the density. This is a key step because the density of the LOHC allows to determine the hydrogenation degree and thus, the effectivity of the reactor to extract the hydrogen and perform the reaction.

Despite the reason for the capillary to broke was not clear, another tryout with the same design should be done, expecting a better result.

### 3.4.2. Experiment and reactor review (2)

With a new sample and the reactor assembled, a new experiment started. After one hour and 20 minutes, the temperature of 260°C was reached and the reaction started. Again, 4 hours from now the experiment would be stopped.

During this 4 hours the reaction went on without any problem. Like in the previous experiment, the pipette and the compressed air were key to prevent the LOHC to escape the reaction. Condensation was visible in the pipette part but never reached the tubing, meaning that the liquid was going back to the reactor effectively, not blocking the outlet tube to the hydrogen released. After 4 hour, the experiment was stopped, and it was time to let the reactor cool down in order to disassemble and manipulate the sample.

Once the capillary was disconnected of the tubing, it was carefully cut right below the epoxy that connects with the pipette part. This was necessary to extract the liquid inside and the rest of components, such as the glass wool or the catalyst. This was done very delicately with a needle and then using a syringe the liquid could be extracted. At this point a problem arose: the amount of liquid that could be extracted was very poor.

Once the density checks were made, the result indicated that the dehydrogenation degree exceeded 100% which is impossible. After this finding some reasoning was needed.

The main problem was the quantity that could be extracted: the proportion of reactants used was chosen to ensure that there was enough material in the capillary for the reaction and to analyze it, but also limited by the capacity of the capillary. Out of 0.3 ml capacity of the capillary, the LOHC filled 0.2 ml, thought to be enough. Certainly, the reaction happened, but some elements in the reactor diminished the quantity of LOHC. The catalyst is a porous element which absorbed part of the liquid in the capillary. Also, the glass wool did so. This reduced the quantity considerably and the density checks could not be repeated. Dead volumes were also a big inconvenient considering the already limited quantity of LOHC.

On the other hand, residues of catalyst or glass wool could have ended in the liquid extracted, increasing the density of the LOHC, and resulting in an unexpected high density associated with a higher degree of dehydrogenation. In this case to an impossible degree.

In order to solve this, modifications in the main part of the reactor were needed since the problem was the capacity of the capillary and the residues that the fragmented catalyst and glass wool caused.

### 3.5. Testing reactor v4.0

The key to increase the volume of LOHC in the reactor was to have a larger capillary or to substitute it for an equivalent piece. At the same time, this gave the possibility to increase the diameter of the reactor, allowing the catalyst to be used without the need to ground it. This would also increase the effectivity of the reactor since all the surfaces of the catalyst in contact with the LOHC would be active.

The best option was to use a pipette to substitute the capillary. Despite the glass being of a lower quality and the thickness being around 0.5 mm, the volume increased considerably, and the catalyst could fit perfectly inside. Now the quality of the signal if it was used in a XAS experiment would be worst since the noise would be greater than before, but for the testing of the reactor, it would allow to check the density of the LOHC at the end of the experiment and thus, verify the effectivity of the reactor and the reaction efficiency at this low volume and reduced space environment.

The manufacture of the reactor started with two pipettes that needed to be cut very carefully to keep the top part of them (Fig. 3.18). In one of them, a blowtorch was used to melt the lower part of it so it could be used as the bottom part of the new reactor and contain the reactants in it. After this, both parts could be assembled using high strength glue and epoxy. Similarly to the older version of the reactor, a PTFE tube was needed to connect the reactor with the outlet tube, so a new PTFE tube was adjusted to fit in and assembled at the top of the pipettes with high strength glue and epoxy (Fig. 3.18).

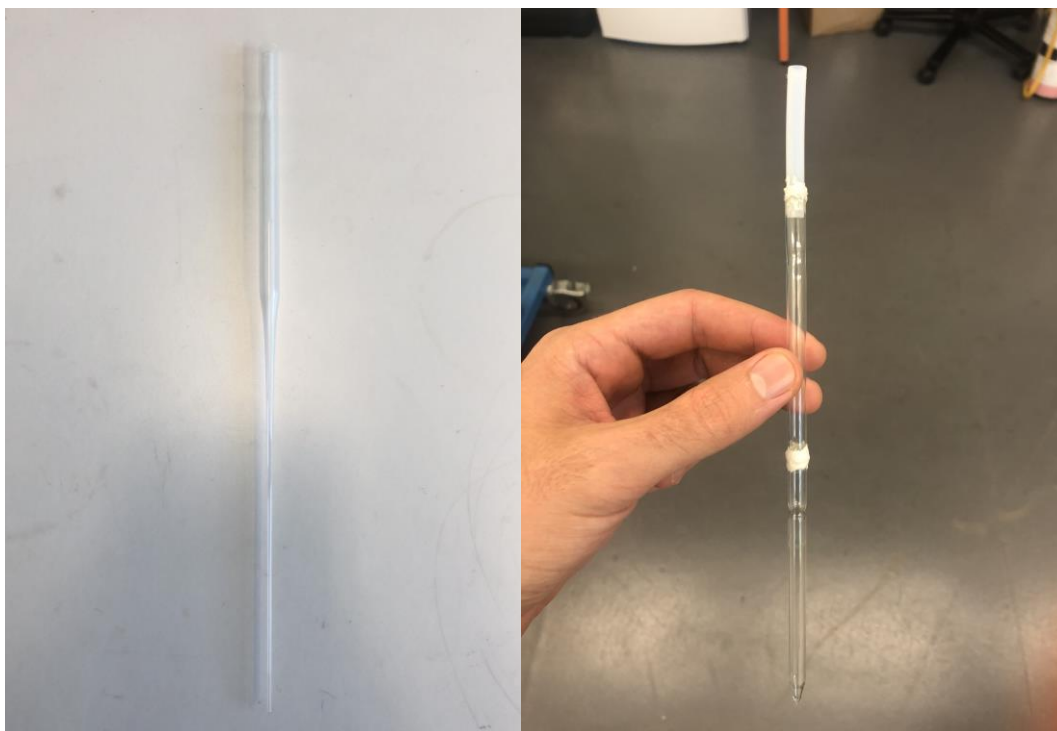


Fig. 3.18. The top part of the pipette (left) was used for the testing reactor, made of two of them (right).

One advantage of this design was that the reactants could be placed inside after the assembly because the diameter allowed it. Also, the extraction of the products would be easier at the end of the experiment: since the glass was thicker, it was easier to cut precisely without breaking the pipette.

Once the design was assembled, the products were introduced. The proportion of LOHC and catalyst was maintained but the amount was increased. This time, 0.30g of catalyst and 1.33ml of LOHC were used, with the catalyst in its original shape. A small piece of glass wool was placed on top of the catalyst to ensure no movement during the reaction. The sample was ready to be used.

On the other hand, the heating method needed to be changed. The pipette diameter could not fit in any of the holes of the aluminum block, which was key to heat up the capillary in a uniform way in the past experiments. The alternative was to use gas blowers: they could sustain the temperature perfectly for hours and were much more precise with the temperature selection, despite not allowing an even distribution of the heat all around the pipette. The rest of the systems that were used around the reactor remained the same: the compressed air and the co-current heat exchanger in the outlet tube. This time the fume hood was not high enough to fit in the installation, so the experiment was conducted outside the fume hood and using a fume extractor on top of the reactor (Fig. 3.19). At this point the experiment was set up and ready to start.



Fig. 3.19. Fourth experiment setup.

### 3.5.1. Experiment and reactor review

The gas blowers were set at 350°C in order to reach the 260°C in the reactor. Temperature was continuously checked with the thermocouple and adjusted if necessary. The cooling systems were also running since the beginning. After one hour and 10 minutes the target temperature was reached, and the reaction was considered to start.

During the experiment, no incidents were noticed, and the reaction seemed to run perfectly. The compressed air and having a larger diameter worked perfectly to avoid the condensation of LOHC on the outlet tube and all the LOHC remained in the reactor at all times. This was also supported by the water heat exchanger in the outlet tube. Bubbles were visible during all the reaction which gave another good sign of the reaction happening and the LOHC being at the boiling point. In this case, the new design allowed to observe the pipette during all the experiment unlike previous reactors where the aluminum block prevented this. Four hours later the experiment was stopped. One hour was given for cooling and then the pipette was disassembled.

The lower pipette was cut right below the epoxy to extract the products of the reaction. This time the extraction of the catalyst and glass wool was much easier compared to previous reactors and minimum residue was left in the LOHC. After this, the liquid was extracted and introduced in a glass flask for the density checking.

The density checking was conducted with an analytical balance by adding 0.1ml at the time and checking the proportionality of the correspondent mass up to 0.8ml. With this method it was determined that the average density of the LOHC extracted from the reactor had a density of 954.5 kg/m<sup>3</sup> equivalent to a 25.32% of hydrogenation degree.

This was an exceptional result since compared to the 100% hydrogenation degree of the LOHC+, nearly 75% of the hydrogen had been released. This showed similar results to the ones obtained by *Hydrogenious* converting the LOHC at industrial scale at their facility. This was the prove that the reaction was perfectly able to occur in such reduced volumes and space, and with great effectivity. This allowed to move on and design a high-end reactor able to conduct the experiment in the beamline using XAS method in in-situ/operando conditions.

### 3.6. Reactor design

For the new reactor the design needed to be changed completely since now the LOHC needed to flow through the reactor instead of staying in it. The same volume being converted all the time means that the catalyst deteriorates faster because the hydrogen that is left to release in the LOHC is decreasing with the time. This are not the real conditions for a reactor at industrial scale. An industrial approach is to flow the LOHC+ through the reactor to extract the hydrogen and obtain the dehydrogenated LOHC at the other end with a conversion as higher as possible. Following this approach, the design was based on a similar low volume reactor built in another beamline in the ESRF. It was used for other purposes but some of its characteristics could help in the design of the dehydrogenation reactor.

#### 3.6.1. V1.0

The design would consist of a rectangular stainless-steel reactor with 2 main holes (Fig. 3.20). The first hole would be vertical and go through the whole reactor. This hole would contain the catalyst fixed within the reactor and the LOHC would flow through it and being converted at the same time since the whole piece would be heated up. The size of the hole would be of about the same size of the catalyst to ensure permanent contact between the LOHC and the catalyst along the reactor.

The second hole would be perpendicular to the first one and would also go through the whole reactor. This hole would be a window for the beam light to pass through the catalyst at that position and extract data from it. All that data would be then collected by the detector placed behind the reactor. This window would be a bit larger than the first one to ease the beam light positioning and manipulate the catalyst if necessary. The window would be covered with a thin layer of Kapton which is a high-performance polyimide film that can sustain the temperature of the reaction and the small pressure inside caused by the pump.

It is also chemically stable and have low X ray absorption which is very desirable for XAS technique. In order to effectively seal the hole, specially designed FFKM O-rings would be used. FFKM is a high-performance synthetic rubber able to sustain high temperatures while being chemically stable and resistant to oil, such as the LOHC, making it very suitable for this project.

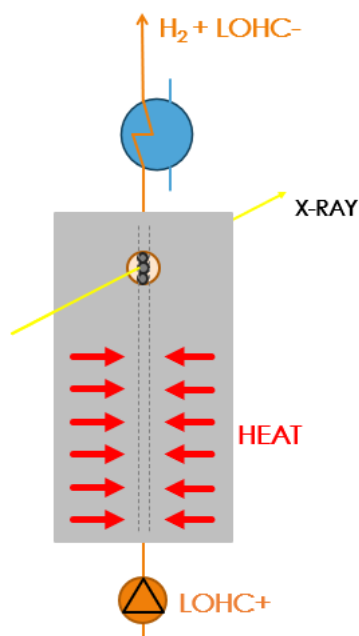


Fig. 3.20. Reactor scheme.

In addition, resistances would be used to heat up the reactor so the target temperature for the reaction could be reached and thermocouples would be placed close to the points of interest in the reactor to check the temperature during the experiment.

To finish, a peristaltic pump would pump the LOHC+ into the reactor and a heat exchanger would be needed at the outlet to condense the LOHC- that changed phases to gas state. In that way, in the outlet, the hydrogen would be released in gas state and the LOHC- could be collected in liquid state, making it easier to separate both products of the reaction.

An important part of the process was to ensure a high degree of dehydrogenation which simulates the real process in the industry and proves an effective reaction. In order to achieve a good result, it was important to know the ideal flow rate for the conversion to happen in such a small volume that the reactor represented. The volume was not defined either and was also dependent on this subject. Based on previous dehydrogenation reactors built for other experiments and the recommendations from *Hydrogenious*, it was determined that the proportion to be used was 0.7ml/h of LOHC per 1g of catalyst. This was the minimum proportion feasible for the reaction to happen, and it would be the determining factor for dimensioning the reactor volume. It is important to consider that 0.7ml/h is an incredibly low flow rate that not many pumps can assume, and having a pump able to satisfy

that was key to allow the design of a considerably small reactor. The syringe pump that would be used would have 0.5ml syringes that would be bought for this experiment. This syringe pump could then work at a flow rate of 0.5ml/h which gave the possibility to limit the dimensions of the reactor.

Following the established proportion, at 0.5ml/h, 0.71g of catalyst were needed, equivalent to 48-50 pellets of catalyst. Since the size of each of them was on average 3mm, the space required in the vertical channel, to place the balls in contact with the LOHC, was about 150mm. This was the main dimension to consider affecting the height of the reactor. In terms of width and depth, the reactor needed to be wide enough to fit the resistances and thermocouples, but the depth could be narrow.

Taking into account all the requirements specified, a first 3D design was produced using SolidWorks (Fig. 3.21).

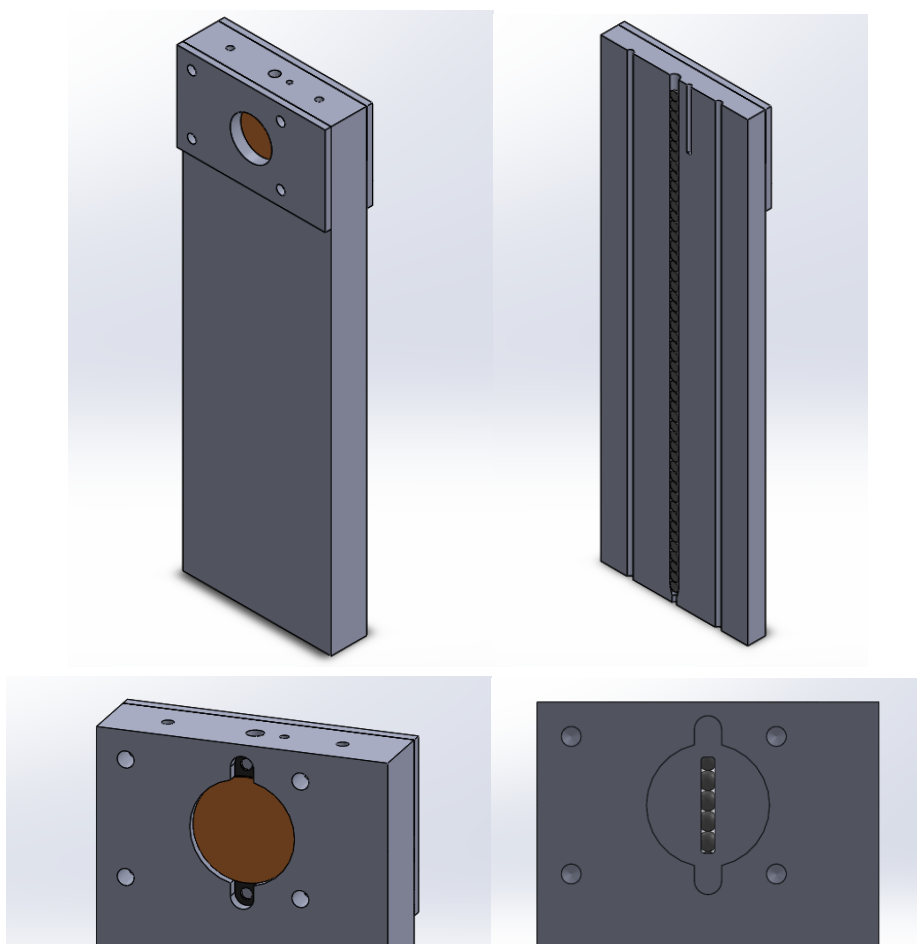


Fig. 3.21. 3D design of the reactor made with SolidWorks.

In this prototype, it is visible that the vertical channel could fit the right number of pellets of catalyst for the reaction to happen entirely. On both sides of the main channel, two vertical holes were drawn to fit the resistances that would heat up the reactor, and an additional

holes to fit the thermocouple close to the window of measurement, the main point of interest. It is also visible that the window was drawn with a specific shape to allow the placement of the FFKM sealing and the Kapton foil on top, both of them pressed together with a stainless-steel plate screwed to the central piece. This design was to be discussed with the supervisors and the sample environment team, responsible for the manufacturing and assembly of it.

### 3.6.2. V2.0

After the first design was discussed, some doubts arose, and new considerations needed to be assessed. The reactor needed to be longer than 150mm in order to heat up the liquid to the target temperature before making contact with the catalyst. If not, the first section of reactor full of catalyst would not serve as a reactor but as a heater, and the catalyst placed in that part would not be used for the reaction. For that reason, the reactor length needed to be increased in the entrance to a total of 180mm, using those first centimeters to heat up the LOHC flowing.

Secondly, the holes for the resistances needed to be shorter since the resistances that were available could not heat properly and homogeneously being this thin (the holes were 2mm in diameter). So, the only option was to change the vertical holes for shorter and wider horizontal holes on both sides. Similarly, the hole for the thermocouple was changed, and now three new horizontal holes would be intended for thermocouples so more points of interest could be monitored during the experiment.

Additionally, it was found that the stainless-steel covers were unnecessarily large, and the same job could be done by smaller plates just covering the surrounding part of the windows on both sides. This would imply the modification of the shape of the window, affecting the shape of the sealing and the Kapton foil.

Considering all this new modifications, a new 3D design was produced using SolidWorks (Fig. 3.22).

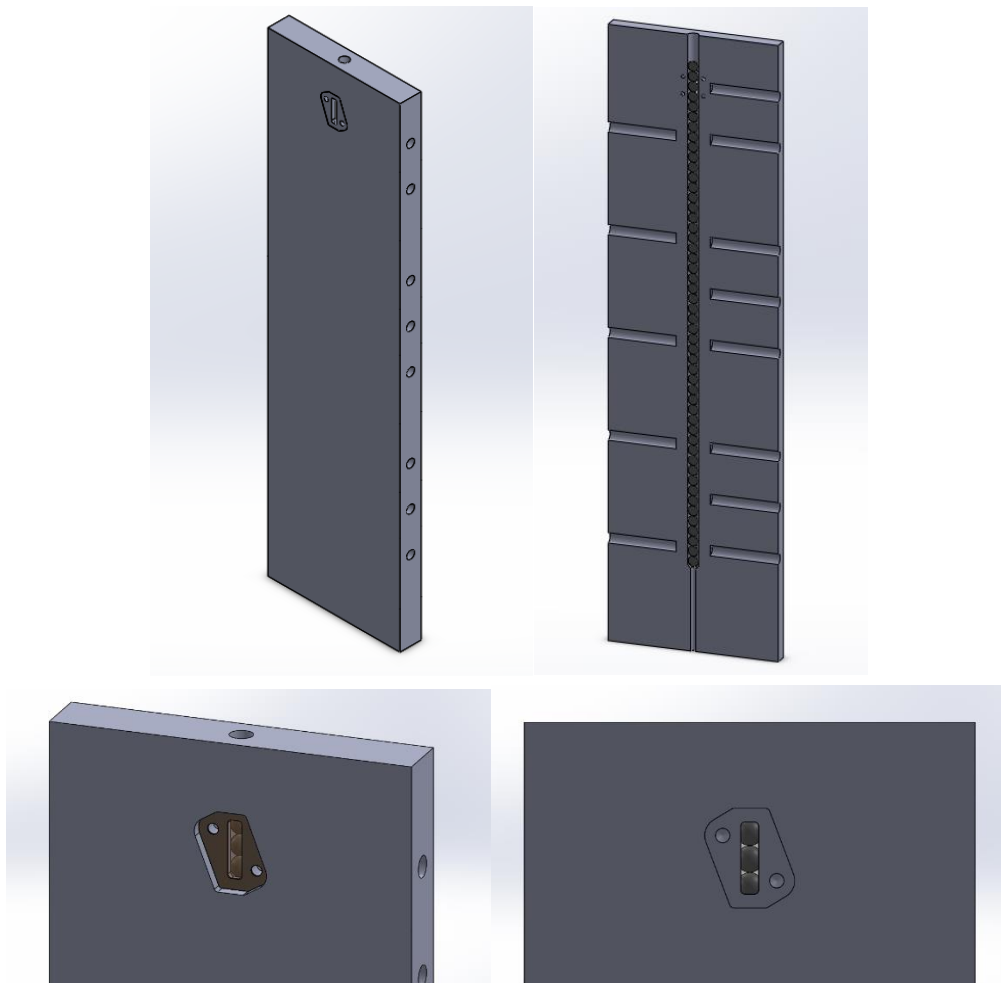


Fig. 3.22. New 3D design of the reactor made with SolidWorks.

But the main change was the idea of adding a spacer inside the vertical channel containing the pellets, when desired. The spacer would be placed between the bottom part of the channel and the pellets placed inside, rising them. The purpose would be to limit the number of pellets inside the catalyst while keeping them always at the height of the window (Fig. 3.23). This variations would allow to study the catalyst representing three different position in the reactor: the catalyst at the inlet of the reactor, when the LOHC is not converted at all; the catalyst at the middle of the reactor, when the conversion is half-way through; and the catalyst at the outlet of the reactor, when the LOHC is converted to the maximum possible. This scenarios would imply different circumstances for the catalyst that might perform differently and deteriorate at different rate.

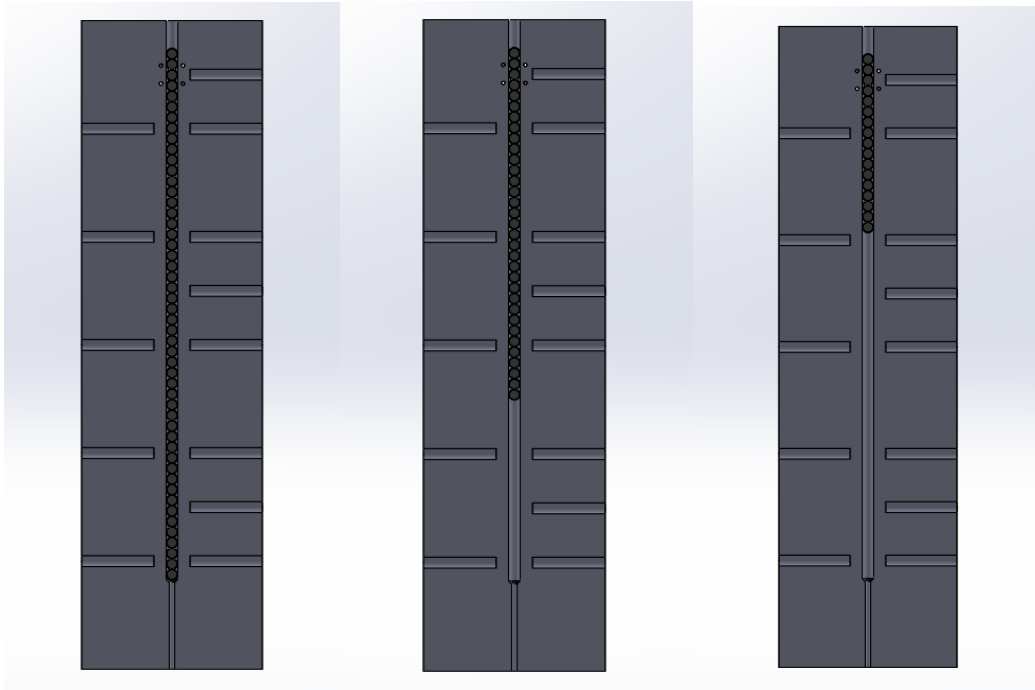


Fig. 3.23. This new design would allow 3 different positions for the catalyst.

After this new design was presented to the beamline supervisor and the sample environment team, it was agreed that it complied with all the requirements for the reaction and provided the requested solution for the study of the system with the XAS technique.

The engineering sample environment team also confirmed the viability of the execution of the reactor by the use of additive manufacturing (3D printers) in stainless steel. This would allow an easier and faster manufacturing process.

Although the construction and testing of this final version are out of the scope of this project, the design is being pursued and will be in operation in the upcoming months in order to be proved in experimentation and then used in future, still to plan, *beamtime*.

## 4. Discussion of results

The results obtained in this work are not just numerical. The design of the reactor and the testing reactors to prove that the reaction is feasible in reduced volumes and the further manufacturing of the definitive design are result of research, practices, and collaborations within the ESRF and the ID31 beamline.

For the testing reactors, initial research and how-to techniques were needed to learn in order to build and test the prototypes. As explained initially, this is a first timer, meaning that there is no other experiment to compare at this volume of reactants and space, so the expectations were uncertain on the output. The most challenging part was to deal with the fragility of the first designs, resulting in many failed attempts during the built up of testing reactors. Despite that, the versions detailed in the previous section gave an output on how to improve not only the testing reactors but also the building process of them.

Another challenging part of the process was the LOHC collection when the experiment was finished. The low volume of reactants, the absorption of liquid by the catalyst or the glass wool and the dead volumes from removing the LOHC when the experiment was finished, diminished the available volume to analyze, resulting in the impossibility to measure the results or inaccurate measurements. This forced to modify the reactor and in consequence the reactor environment as a whole.

Finally, in the final testing reactor, a decent volume of LOHC could be collected and the measurements results were successful: nearly 75% of conversion. An outstanding result comparable to the results obtained by *Hydrogeniuos* at industrial scale in the commercial reactors. Since there is no other similar reactors, this is the only meaningful and possible comparison.

For simplicity, the experimentation with the reactors have been carried out at ambient pressure, having phase change, and needing the heat exchanger on top of the reactor to condense the LOHC. With the final design for the reactor (flow reactor), this might be able to change allowing some pressure inside the reactor and therefore being able to keep the LOHC in liquid phase. This would be done by using a pressure valve at the outlet, containing the gasses, and increasing the pressure inside the reactor. This would make the reaction faster, more efficient, and maybe obtaining a higher conversion.

For the definitive design to be built in a near future, all lessons learned from the testing reactors were implemented, also considering the XAS requirements. The design was discussed and improved and is now to be built and proved effective for its purpose. It is expected to have an opportunity for this experimentation in the beamline during the 2024.

## 5. Conclusions

The results of this work support that the construction of a dehydrogenation reactor that permits the reaction and its monitoring is feasible. The results obtained in the testing reactor were clear and depicted a high conversion in the limitations of the volume at the low part of the range of temperatures and pressure for the dehydrogenation reaction.

The design of the dehydrogenation reactor has been successful and is now approved by the supervisors of the beamline for its manufacture and further utilization in future *beamtime*. Despite the dimensions and shape of the reactor can still be adjusted according to the necessities of the fabrication, the design is finished. The requirements for the XAS analysis in the conditions of *in situ* and *operando* will be met thanks to the characteristics of the reactor, allowing a comprehensive, in-depth study of the modifications that the catalyst suffers. This information might be revealing for future improvements on the catalyst composition to improve the efficiency and effectivity of the process.

To conclude, this technology can be a key player for the storage and transportation of hydrogen in the near future and become one of the best options for this purposes. Hydrogen is meant to become one of the main vectors for the green energy and this technology has the potential to ease this process. Definitely, more research and investment in this topic can bring better and improved techniques to help in this transition.

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## 8. Annex

### 8.1. Economical assessment

The cost of this project is included in the budget of the ID31 beamline where it was carried out at the ESRF, Grenoble. Despite that, the exact amount destined to this specific project is unknown, since is part of the budget earmarked for internship projects without specifying each project.

Due to the availability of technology and resources at the research center, the costs of the project can be reduced to the hours spent on my part, the material used for the tests, and the approximate cost of the material in the fabrication of the final reactor. The manufacturing and analysis costs are not contemplated since all of it is done in the ESRF with own technology and are difficult to quantify.

Table 8.1. Costs breakdown table.

	Cost (€)	Units/Hours/Meters	Total cost (€)
<b><u>PERSONNEL COSTS</u></b>			
Trainee	8,22	420	3452,4
<b><u>TESTING REACTOR COSTS</u></b>			
Quartz Capillary 10 um 2.5 mm	15	12	180
Borosilicate Pipette	0,35	5	1,75
High strength Epoxy	117	0,5	58,5
Syringes/plastic pipettes	0,2	5	1
PTFE tubing	0,8	4	3,2
Tubing connections	3	6	18
Plastic tubing	0,15	4	0,6
Lab material (gloves, paper...)			20
<b><u>FINAL REACTOR COSTS</u></b>			
Stainless steel pieces			To determine
FFKM customized O-rings	50	2	100
Kapton foil 25 um	15	1	15
0.5 ml syringes for pump	120	2	240
<b>TOTAL COST</b>			<b>4090,45 €</b>

As can be seen, the stainless-steel pieces cost is still to determine. The stainless-steel pieces will be 3D printed in the ESRF, but the process or material cost is unknown to me, and I am unable to do an approximation. The rest of the costs are based on references or actual prices of the products.

The profit of this investment is uncertain since the goal for this project is to advance in this specific research field and topic. For this exact same reason, it is difficult to analyze whether the cost of the project is high or low. The answer will depend on the results that will be obtained from the experiment in the beamline once the reactor is done.

## 8.2. Environmental assessment

The environmental impact of the project is minimal. Despite implying the utilization of benzyltoluene and pellets catalyst of Pt-Al<sub>2</sub>O<sub>3</sub>, the amount used in the project was very small: around 20 ml of BT and 60 pellets of catalyst. The production of pollutant gases or wastes is managed in an extremely cautious and concise manner at ESRF due to the substances that some of the experiments conducted at the research center contain. Therefore, the BT either in its hydrogenated and dehydrogenated form are treated cautiously and contained in product-specific containers, mainly because of the toxicity of the product. The catalyst is also carefully stored in the dedicated containers, before and after its utilization in the experiment. Both products are sent by *Hydrogenious* in small quantities, just for the purpose of the projects related to LOHC.

In the operating process, the necessary and settled measures are taken to ensure a safety management of the reactants. According to the safety sheet, it is extremely important to prevent further spillage or leakage, avoid the chemical to enter drains or discharge into the environment.

Hazard statements associated to BT:

- H304: May be fatal if swallowed and enters airways.
- H315: Causes skin irritation.
- H360FD: May damage fertility. May damage the unborn child.
- H411: Toxic to aquatic life with long lasting effects.

Precaution statements associated to BT:

- P201: Obtain special instructions before use.
- P273: Avoid release to the environment.
- P280: Wear protective gloves/protective clothing/eye protection/face protection/hearing protection/...
- P301+P310: If swallowed: Immediately call a poison center/doctor/...
- P308+P313: If exposed or concerned: Get medical advice/attention.
- P331: Do NOT induce vomiting.
- P405: Store locked up.
- P501: Dispose of contents/container to an appropriate treatment and disposal facility in accordance with applicable laws and regulations, and product

characteristics at time of disposal.

Another environmental repercussion that the experiment has is water consumption. The heat exchanger depends on flowing water to evacuate the heat and ensure that the BT condensates and falls back in the reactor. The water flow needs to be constant and continuous during the whole reaction, meaning that for 4 hours there will be water consumption. The flow has not been calculated but can be estimated between 180L and 220L per experiment. This means that the project implied the consumption of about 2400L of water. This is a huge amount of water considering the size of the experiment and is a main point to improve, either by substituting the heat exchanger or creating a closed circuit. This was not possible during the project because there was not a pump available at the moment that could flow the water in a loop to cool it down.

Another aspect to evaluate is the energy consumption for the project. Since the dehydrogenation reaction demands of heat, the energy consumption cannot be avoided, only more efficiently managed. But for this project, at very low scale, the simplest option was to use heaters or gas blowers. According to the data sheet of the heating plate (IKA C-MAG HS 7) the power consumed is 1020W. Multiplied by the duration of the experiment (5 hours in total) we obtain that the energy consumption during the experiment is of 5.1kWh. Considering that during the project the experiment have been tested 10 times, this gives a total energy consumption of 51kWh. This might seem a lot, but the process requires heat to enable the reaction, and the experiment time is 5 hours in total, so despite it could be possible to heat up the reactor more efficiently, the consumption of energy needs to be done inevitably.