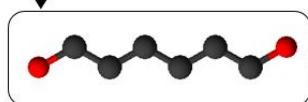
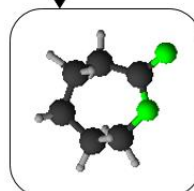




Biomass



1,6-Hexanediol



Caprolactone

Caprolactone from sugar platform chemicals

Conversion of 1,6-hexanediol to caprolactone

Master's thesis in Innovative and Sustainable Chemical Engineering (MPISC)

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Caprolactone from sugar platforms chemicals

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Gothenburg, Sweden 2019

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Abstract

Caprolactone is a chemical of great interest as proves its several applications and derivatives, among them the biodegradable polymer polycaprolactone and the nylon 6 precursor caprolactam. The present industrial production of caprolactone is based on the Baeyer-Villiger oxidation of cyclohexanone, which is a fossil-based source. However, due to the increasing demand for sustainable processes, biomass has attracted a lot of attention. The interest in producing caprolactone from sugar platforms derived from biomass has increased recently; and, so has done the number of publications on the synthesis of this cyclic ester via HMF. The present work focusses on the last step of this process: conversion of 1,6-hexanediol to caprolactone. This reaction can be performed using homogeneous and heterogeneous catalysts. The acceptorless dehydrogenative lactonization of diols is the reaction path used in this study. The reasons for the choice of this route are the easier separation from the product, atom efficiency (an oxidant solvent is not required) and production of hydrogen as a source of energy. Nevertheless, the selection of an effective heterogeneous catalyst for this reaction remains a pending issue in this stage of the process.

The aim of this project is to select and synthesize heterogeneous catalytic materials for the acceptorless dehydrogenation reaction of 1,6-hexanediol. Five different catalysts were selected and a first catalyst screening was performed at 180°C. The products of the reactions were analysed by gas chromatography mass spectrometry (GC-MS). After that, two of the catalysts were selected to study the conditions and the reaction setup effect on the reaction yield.

The results of the analysis showed that the highest conversion of 1,6-hexanediol is achieved with a copper supported on hydrotalcite catalyst; however, it shows poor selectivity towards caprolactone. An increment in the temperature seemed to increase significantly the conversion. Also, the formation of polymeric structures was observed. Finally, the experiments conducted were a source of information for the improvement of the conditions, reactor setups and analysis of the products for this reaction.

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List of abbreviations

1,6 – HDO: 1,6-hexanediol

BSTFA: N,O-Bis(trimethylsilyl)trifluoroacetamide

CSTR: continuous stirred tank reactor

DHMF: 2,5-dihydroxymethylfuran

DHMTFH: 2,5-dihydroxymethyltetrahydrofuran

FID: flame ionisation detector

GC-MS: Gas Chromatography Mass Spectrometry

HMF: 5-hydroxymethylfurfural

HT: hydrotalcite

HTO: 1,2,6-hexanetriol

MIBK: methyl isobutyl ketone

PBR: packed bed reactor

PFR: plug flow reactor

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1. Introduction

1.1. Background and state of the art

In the recent decades, the climate changes and prevision of shortages of fossil-based resources have highlighted the importance of shifting towards more sustainable paths. Society is changing to a bio-based circular economy with a lower environmental impact. In this context, one of the aims to achieve this goal is shifting the source of raw materials, from fossil-based to renewable ones. However, using bio-based feedstock involves using different reaction pathways to produce the same products. Thus, the main challenge of the industry is to develop new bio-based processes as efficient as the fossil-based ones so they can replace the current industrial production.

1.1.1. Biomass as renewable resources

Biomass is a renewable source of raw material and energy originated from plants and animals, which has been formed in a short period of time [1]. Plant-based biomass is one of the most commonly used feedstocks and it is classified in three major groups: first generation (agricultural crops), second generation (lignocellulose, non-food resources) and third generation (algae) biomass resources [2]. Biomass conversion methods can be divided in biochemical (involving bacteria and other microorganisms) and thermochemical (combustion, gasification, pyrolysis and liquefaction) [2].

Typical reactions mechanisms in the biomass processing are similar as the ones used in the synthesis of organic compounds [2, 3]:

- Hydrogenation: hydrogen atoms are added to saturate double or triple bonds.
- Dehydration: a water molecule is removed from the compound in a reaction, which is usually catalysed by an acid.
- Dehydrogenation: a reduction reaction in which hydrogen atoms are remove from the compound.
- Hydrogenolysis: reaction in which a single carbon bond is broken by the presence of hydrogen.
- Ring opening: as the reaction name indicates, this reaction consists in the opening of a cyclic compound to obtain a linear structure.
- Hydrodeoxygenation: a molecule of water is removed with the help of catalytic activity with hydrogen.

Lignocellulosic biomass has a great potential, owing to its diversity, availability and low cost. Moreover, as it belongs to the second-generation biomass there is not competition with the crops destined to food. Lignocellulose materials are composed of cellulose,

hemicellulose and lignin. The two major components are cellulose and hemicellulose (70-90% of lignocellulose). Cellulose and hemicellulose are composed of glucose, fructose, xylose, galactose and other carbohydrates [2, 4]. The hydrolysis of carbohydrates leads to produce several platform chemicals such as: formic acid, lactic acid, levulinic acid, furfurals, sugar alcohols and phenols [3].

Even though the processes using bio-based feedstock have already been the focus of research for many years, some reaction routes are not yet as efficient and economically viable as the conventional processes using fossil-based chemicals [3]. Key factors in these processes are the conversion and selectivity of the reactions, which often involve the presence of a catalyst.

1.1.2. Catalysis

Although catalytic processes have been common in the food preparation industry since history started to be written, it was not until 1835 that catalysts were properly defined and studied by Berzelius [5]. Catalysts are substances that increase the rate of a reaction without being consumed or being part of the reactants [5]. The presence of catalyst does not affect the equilibrium but it makes the reaction faster by promoting a different path of reaction and decreasing the activation energy barrier [5, 6]. Catalysts are widely used nowadays in chemical processes when a reaction does not occur spontaneously due to activation problems, to improve the selectivity of a certain product or to promote another path [6].

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The following factors affect the performance of a catalyst and listed in the following order according to the order of importance [2, 7]:

- Activity: a parameter that gives information on how fast a reaction occurs when the catalyst is present. From a kinetic point of view, it is defined by the reaction rate of the reaction, which is dependent on the rate constant and the activation energy of the reaction. There are several methods for evaluating the activity of a catalyst such as: conversion under constant reaction conditions, space velocity for constant conversion, space-time yield or the temperature required for given conditions [7]. Additionally, the turnover number provides information about the number of times that a catalyst can be used before deactivation occurs.
- Selectivity: the fraction of the reactant that is transformed to the desired product [7].

- Stability: the activity of a catalyst is conditioned by its chemical, thermal and mechanical stability. Stability is related to catalyst deactivation since the lifetime of a catalyst can be measured by its activity in a period of time [7].

- *Catalyst deactivation*

Ideally, a catalyst is not consumed in the reaction, however it can be deactivated due to changes in its structure. The most common reasons for deactivation of a catalyst are:

- Poisoning: absorption of substances such as Hg, Pb or sulphur and phosphorous compounds on the surface of the catalyst that results in the blockage of its active sites [7].
- Coking or fouling: deposit of carbon compounds on the surface of the catalyst, typically in reaction involving hydrocarbons [5].
- Sintering or aging: loss of surface area caused by long exposures to thermal processes which can result in degradation of the catalyst, accumulation of crystals or deposition of metals on the support [5, 7].

- *Classification of catalysts*

Catalysts can be classified in: homogeneous, heterogeneous and biocatalyst (enzymes) [7]. Although, only the first two groups will be explained in this section.

Homogeneous catalysts

These catalysts are characterized by having the same physical state as the one in which the reaction occurs and they are generally in liquid form [6]. Organometallic substances (metal compounds with carbon bonds) are the most common homogeneous catalysts used in industry.

The key factors in the performance of a homogeneous catalyst are the existence of several oxidation states (as many as its coordination number) and the reactivity of organic ligands bonded to the metal. Examples of ligands are: Cl^- , H^- , CH_3CO^- (ionic) and CO , phosphines, phosphites, amines and H_2O [7].

The cycles of reaction of homogeneous catalysts are rather complex as several different reactions can occur. Coordination and exchange of ligands, complex formation, acid/base reactions (interaction between metal cations, which are considered acids, and Lewis/Bronsted acid and bases), redox, insertion and elimination reactions are some of the most common processes taking place in homogeneous catalysis [7, 8].

Heterogeneous catalysts

The catalyst is in a different phase than the one in which the reaction takes place. Generally, solid catalysts are easy to separate from the product after the reaction. Heterogeneous catalysts are usually porous materials that hold active metal catalysts, thus, their performance is governed by diffusion, adsorption and desorption processes [2, 6, 7]. The main advantage of a porous material is its high surface; however, this also makes the catalyst sensitive to limitations of internal mass transfer, which may as well affect the performance of the catalyst.

Catalysis is a complex science and the choice of a catalyst is usually based on experience and experimental studies. A few examples are stated in the following table [5]:

Table 1. Reactions and representative catalyst [5].

| Reaction | Catalyst |
|---------------------------------|---|
| Halogenation – dehalogenation | Pd, AgCl, CuCl ₂ |
| Hydration – Dehydration | Al ₂ O ₃ , MgO |
| Alkylation – Dealkylation | Pd, AlCl ₃ |
| Hydrogenation – dehydrogenation | Co, Pt, Ni, Cr ₂ O ₃ |
| Oxidation | Cu, Ag, Ni, V ₂ O ₅ |
| Isomerization | AlCr ₃ , zeolites, Pt/Al ₂ O ₃ |

Heterogeneous catalysts can be subdivided into bulk catalyst and supported catalyst.

- *Bulk catalysts*

The active phase constitutes the whole catalyst. Examples of this type of catalysts are: metal oxides, zeolites and heteropolyacids. These catalysts can be used directly as a catalyst or as a support for other components [7, 9].

- *Supported catalysts*

Heterogeneous catalysts are often synthesized in a support. The supports are solid porous materials with high surface area, which hold the active metal component [9]. The active metal component is an active phase present in form of nanoparticles of a metal, a metal oxide or a metal sulphide [7]. The support can be inert or it can contribute to the activity of the catalyst. Typical examples of support materials are SiO₂, Al₂O₃, MgO, TiO₂, ZrO₂, zeolites, activated carbon and ceramic materials [7]. In the choice of the support materials the following factors are of importance: fixation and dispersion of the active phase, stabilization of the active component and enlargement of the specific surface area.

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Additionally, other substances can be added to improve the activity of the catalyst. These substances are known as promoters.

- *Promoters*

Promoters are substances that increase the activity of the catalyst without being part of the active phase [10]. In heterogeneous catalysts, the combination of two metals is often used to achieve a better performance of the catalyst. The presence of the second metal can affect the pore size distribution and the surface acidity improving the activity, selectivity and/or stability of the catalyst. Some examples of promoters used in industry are: SiO_2 and ZrO_2 for alumina based catalyst which increase its thermal stability and Sn, Zn or Cu in $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst which are used in the dehydrogenation of alkanes [7, 10].

As stated before, conversion and selectivity of reactions are significantly affected by the presence of a catalyst. These two characteristics are also influenced by the reaction conditions and the reaction mode. In chemical processes, the understanding of the behaviour of a catalyst in a certain reaction is key information for the design of the reactor.

1.1.3. Reaction mode

Chemical reactors can be divided into batch reactors and continuous reactors: continuous stirred tank reactor (CSTR) and plug-flow reactor (PFR).

Batch reactors are characterized by not having any feed or outflow when the reaction is in progress. Generally, this reaction mode is often used for small-scale operations, fine chemistry or process that present difficulties when running in continuous mode [5, 9].

CSTR reactors are mainly used for liquid phase reactions due to the simple control required. Nevertheless, the major drawback of these systems is that the large volume needed to reach a high conversion [5, 7].

Tubular reactors are commonly used in gas phase applications. The name of plug-flow reactor comes from the assumption of perfect axial mixing. High conversion rates are usually obtained with this reactor; moreover, they do not require much maintenance. On the other hand, in exothermic reactions, the generation of hot spots can hinder the performance and the control of these systems [5].

The use of a catalyst in these systems can involve some operational problems. In CSTRs the presence of a solid catalysts difficult the stirring of the reactants and the separation of the catalyst after the reaction. In packed bed reactors (PBR), the inconveniences are in

replacing the catalyst after deactivation and the ineffective use of some part of the reactors due to channelling of the gas flow [5].

In the context of catalytic reactors, the presence of two or more phases during the reaction is usual. These reaction modes are known as multiphase reactors. Slurry reactors, consist of a gas phase reacting in a solid catalyst suspended in a liquid. These reactors can run in batch or continuous modes. Among their advantages are the easy to control temperature and heat recovery. In trickled bed reactor, a gas and a liquid stream are run concurrently through a packed bed with the solid particles of the catalyst. Another example of multiphase reactor are fluidized bed reactors, in which a fluid (gas or liquid) is passed through a bed of solid particles (catalyst) at certain velocity so the catalyst is suspended in the fluid [5, 10].

A good understanding of the reaction mechanisms is required in the design of a reactor. The analysis of internal and external mass transfer in the catalyst is an important step to find the limiting step in the reaction.

1.1.4. Caprolactone

Caprolactone is a cyclic ester from the family of lactones, which are characterized by having the double oxygen bond from the esters and an oxygen atom inside the ring [11].

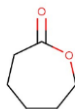


Figure 1. Caprolactone molecular structure [11].

Caprolactone is a versatile compound with several applications. Polycaprolactone can be produced by ring-opening polymerization of caprolactone. This polymer also presents a the ester bond characteristic of the lactone, which is soluble in water, making polycaprolactone a biodegradable polymer with applications in the medicine field [12]. Another important derivative of caprolactone is caprolactam (which can be obtained from the reaction of caprolactone with ammonia) is the precursor monomer for nylon-6 [13]. Moreover, caprolactone can be used as an intermediate for polyurethane, coatings, elastomer and other organic compounds [14, 15]. This molecule is undoubtedly a substance with high potential as it denotes the number of applications obtained from it.

- *Production of caprolactone*

The current production of caprolactone is focus in the Baeyer-Villiger oxidative ring expansion of cyclohexanone. Traditionally, this reaction is performed reacting cyclohexanone with peracetic acid. Although the yield is high, the peracetic acid is a hazardous substance and its use have been restricted [16]. In the recent years, the toxic peracetic acid has been substitute for hydrogen peroxide as oxidant. However, this method has also significant drawbacks. H_2O_2 is a weak oxidant, thus, the reaction needs a catalyst. So far, the yield of this process is not has high as the traditional one. In addition, the water produced as by-product may involve a risk of hydrolysis of the ester group [16-18]. Therefore, these methods have several negative operational aspect. Yet, the major disadvantage is that both processes used a fossil-based feed. Currently, there is a pressing demand for more sustainable processes in the chemical industry. Therefore, the focus of research has shifted for searching a more environmentally friendly production method of caprolactone.

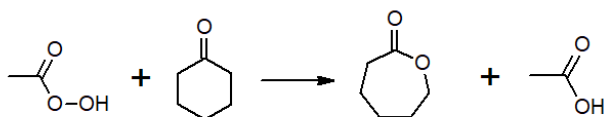


Figure 2. Baeyer-Villiger oxidation of cyclohexanone for production of caprolactone with peracetic acid [19]

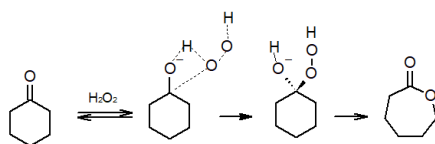


Figure 3. Baeyer-Villiger oxidation of cyclohexanone to produce caprolactone with hydrogen peroxide [18]

The new studies on caprolactone production propose using renewable feedstock. In this context, C_6 sugar platforms present in lignocellulose can be a starting point for the synthesis of 5-hydroxymethylfurfural (HMF) [3]. HMF belongs to the family of furfurals and it is synthesised via glucose or fructose using acids as catalysts [20]. The fructose process has been reported to be more efficient than the glucose due to the higher

selectivity for HMF that is obtained [20]. However, in the current process, both reaction paths are combined so fructose is obtained by isomerization of glucose. Then, fructose goes under dehydration with an acid catalyst to produced HMF [13].

HMF is a platform chemical to produce several derivatives in the manufacturing of biofuels and high-value chemicals such as levulinic acid, 2,5-dihydroxymethylfuran (DHMF), 1,6-hexanediol (1,6-HDO), 2,5-dihydroxymethyltetrahydrofuran (DHMTTHF) and 1,2,6-hexanetriol (HTO), among others. 1,6-hexanediol is especially interesting as it can be used in the production of caprolactone [21, 22]. 1,6-HDO is a diol with a hexane structure with hydroxyl groups at its 1 and 6 positions [23].

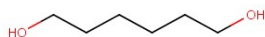


Figure 4. 1,6-Hexanediol molecular structure [23].

The synthesis of caprolactone from HMF was proposed by Buntara et al.[21]. This group suggested up to four reaction pathways. First, they reported hydrogenation of HMF to 1,6-HDO, using Pd/C and CuCr as catalysts; however, this direct reaction led to low conversion and undesired by-product (1,5-pentanediol). A two-steps reaction via 2,5-THF-dimethanol (THFDM) was also developed: hydrogenation with a Ni based catalyst and further ring opening of THFDM with Rh-Re/SiO₂ as catalysts. This pathway can also lead to another intermediate 1,2,6-hexanetriol (1,2,6-HT) by selective hydrogenolysis with Rh-Re/SiO₂ and water as catalyst agents [24]. Hydrogenation of 1,2,6-HT with the same catalyst produces 1,6-hexanediol and 1,5-hexanediol, the presence of the latest results in separation problem (three-steps route). A solution to this problem is adding a Brønsted acid to the hydrogenation reaction to obtain tetrahydro-2H-pyran-2-ylmethanol (2-THPM). Then 1,6-HDO is produced by hydrogenation of 2-THPM in presence of the Rh-Re/SiO₂ catalyst used in previous steps. Once 1,6-hexanediol is produced, the last reaction of the process is the lactonization of 1,6-hexanediol to caprolactone.

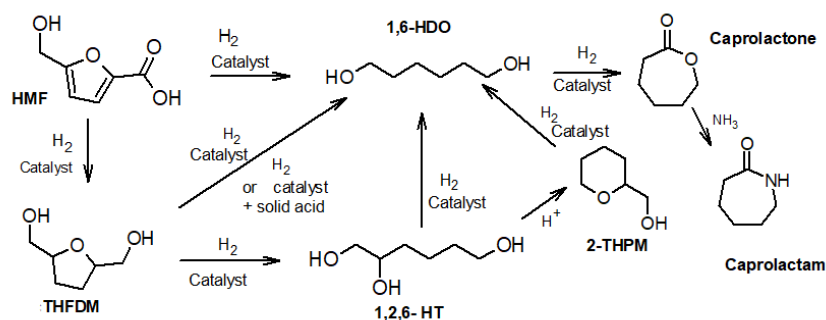


Figure 5. Different routes of synthesis of caprolactone from HMF, reprinted from reference [21].

- Catalysts for conversion of 1,6-hexanediol to caprolactone

The conversion of 1,6-hexanediol to caprolactone is a one-pot and two steps reaction. First, 1,6-hexanediol is dehydrogenated to a monoaldehyde, which spontaneously cyclates into a hemitacetal; and a second dehydrogenation to caprolactone [13, 21].

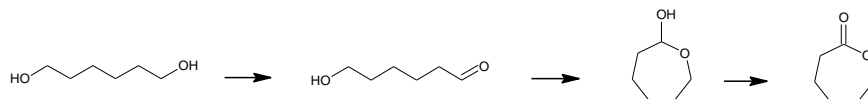


Figure 6. Mechanism of reaction for the acceptorless dehydrogenative lactonization of 1,6-hexanediol to form caprolactone [13].

An oxidant is needed when using homogeneous catalyst for the lactonization of diols, as it acts as acceptor of hydrogen [25]. Niklaus et al. [26] studied the Oppenauer oxidation and lactonization of 1,6-hexanediol with a catalyst based on ruthenium/1,1'-bis(diphenylphosphino)ferrocene and using methyl isobutyl ketone (MIBK) as oxidant, obtaining a good yield for the lactone production. Other authors had suggested ruthenium or iridium complex catalysts for the lactonization of diols [27, 28]. However, despite of the good selectivity obtained, the use of homogeneous catalysts is not economical due to difficulties in separation of the reaction products from the solvents and catalyst and non-recyclability of the catalyst. Moreover, the need of promoters and other additives can

result in separation problems and toxic waste streams [25, 29]. For these reasons, the interest in heterogeneous catalyst for this process has increased. Additionally, heterogeneous catalysts are easy to separate after the reaction.

When using heterogeneous catalysts, the lactonization of diols can be performed in two ways. If the reaction is carried out in presence of an oxidant, the hydrogen produced reacts with such oxidant to form water. Mitsudome et al. [30] developed as gold nanoparticle-based catalyst and performed the reaction with molecular oxygen.

Conversely, if there is no hydrogen receptor, then the reaction is defined as acceptorless dehydrogenation and molecular hydrogen is produced instead. The absence of oxidant avoids the production of waste streams or other by-product that required further separation from the product stream. Moreover, this reaction maximizes atom efficiency and the hydrogen produced is pure enough to be use as an energy source [25, 31]. Therefore, the dehydrogenation of diols to produce lactones without an acceptor oxidant is a more efficient and sustainable method.

The acceptorless dehydrogenative lactonization of diols was investigated by Touchy and co-workers [31] who reported high selectivity results for such reaction (82%) using Pt/SnO₂ as catalyst. Previous publications [32, 33] have described the lactonization of diols using copper-based catalysts. Mikami et al. [34] investigated a copper catalyst supported with hydrotalcite, obtaining a yield of 1,4-butanediol to butyrolactone higher than 99% and 1,5-pentanediol with a yield to the correspondent lactone of 83%. Ichikawa et al. [32] studied the influence of several metal oxides in a copper catalyst obtaining a selectivity of 97.7% of 1,4-butanediol to γ -butyrolactone with a combination of metal oxides (CuO:ZnO:ZrO₂:Al₂O₃). Later, Miura and co-workers [35] reported high yield in the conversion of 1,4-butanediol and 1,5-pentanediol to their respective lactones with a Cu/ZrO₂ catalyst. A photoactivated Pt-TiO₂ catalyst was developed by Wada et al. [36]. Such catalyst improved the photocatalytic lactonization of diols and its performance was better when adding Al₂O₃. Nevertheless, most of these publications do not report directly the lactonization of 1,6-hexanediol; thus, there is still room for improvement in the performance of this reaction.

The synthesis of caprolactone from 1,6-HDO using heterogeneous catalysts is definitely a process with great potential. However, the catalytic alternatives for such reaction are not yet well defined or ready to use at industrial scale in which a high selectivity (over 90%) is required for a process to be efficient.

1.2. Objectives of the thesis

The aim of this project is to study the synthesis of caprolactone from biomass resources. The experimental work will focus on the last step of this process: the conversion of 1,6-hexanediol to caprolactone. Three main objectives are proposed for this study:

1. Understanding the mechanisms of reaction of oxygen free dehydrogenation of 1,6-hexanediol to caprolactone. This involves a literature review of the work published on this reaction, as well as the explanation of the mechanisms for formation of the products obtained in the experimental part of the project.
2. Catalyst screening, which is the initial part of the experimental work and includes selection and synthesis of heterogeneous catalytic materials. Additionally, reaction experiments with these catalysts are to be performed to study their conversion and selectivity. A method for the analysis of the reaction products will be developed.
3. Study the effect of some reaction parameters such as temperature and pressure. The dehydrogenation reaction of 1,6-hexanediol will be run in two reactor setups.

2. Experimental

This section covers the experimental part of the project. Starting with selection and synthesis of catalysts, following by the reaction setup and conditions of the reaction to finish with the analysis of products of the reaction.

2.1. Equipment and methods

2.1.1. Screening of catalyst

The catalysts selected for this project were copper on hydrotalcite, platinum on alumina, platinum on tin oxide and tin oxide. The motivation to use these catalysts was a result of the literature review.

- *Tin (IV) oxide*

Metastannic acid ($\text{H}_2\text{O}_3\text{Sn}$, purchased from Keeling & Walker) was calcined at 500°C for 3 hours, which is treatment with heat in an oxidizing environment. During this process, a water molecule is removed from the compound and results in formation of SnO_2 support [31].

- *Copper on hydrotalcite (Cu/HT)*

The support used for this catalyst is hydrotalcite, which contains MgO and Al in proportion 70:30 respectively and it was purchase from CONDEA Chemie GmbH. The hydrotalcite support was first calcined at 520°C for 4h. Then, the active metal in this catalyst is copper which was added to the support from copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Sigma-Aldrich) precursor.

The synthesis of the catalyst was done via an impregnation method. In this method, the volume of impregnating solution of the active metal exceeds the volume of the pore of the support [10]. First, the support was impregnated with deionized water and heated at 60°C under continuous stirring. Then, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was diluted in deionized water and added to the hydrotalcite solution, drop wise. The amount of copper nitrate added was calculated so the concentration of Cu in the catalyst is 4.5 wt.%. The resulting solutions was left under stirring at 60°C so the water added can evaporate. Once all the water was evaporated, the catalyst was dried at 80°C in an oven for 20h under air atmosphere. After that, the catalyst was sieved to achieve a homogeneous particle size; the sieve size was $300\text{ }\mu\text{m}$. Finally, the catalyst was calcined again at 520°C for 4h.

- *Platinum on tin (IV) oxide (Pt/SnO₂)*

Tin (IV) oxide previously obtained from calcination of metastannic acid (H₂O₃Sn) at 500°C for 3 hours was used as support for this catalyst. Pt (NO₃)₂ is used as precursor and the amount of this solution was added so the final concentration of Pt in the catalyst is 5 wt.%. Platinum nitrate was added drop-wise after the support had been wetted with deionized water. The next steps were the same as in case of the Cu/HT catalyst: drying the catalyst at 80° C, sieving and calcination of the catalyst at 500° C for 3 hours. Regarding the mechanisms of reaction of this catalyst, Sn⁴⁺ acts as a Lewis acid that attracts the oxygen in the C=O bond and the metal extract the hydrogen promoting the formation of an aldehyde. Such aldehyde spontaneously cyclates into a lactone [21, 25].

- *Pt/SnO₂ acidic-1*

The effect of the pH of the impregnating solution during the catalyst synthesis on the activity and selectivity of the Pt/SnO₂ catalyst was studied. For this, the acidity of the support solution was altered by adding 30µL of 10% HNO₃. The following steps were performed in the same way as done with previous catalysts.

- *Pt/SnO₂ acidic-2*

Another platinum-based catalyst was synthesised using tin (IV) oxide as support and the synthesis method was incipient wetness impregnation. This method differs from the wet impregnation in that the volume of the precursor solution is lower than the volume of the pores of the support. In this case, the acidity was modified by adding the 30µL of 10% HNO₃ to the precursor solution (platinum (II) nitrate). The final loading of platinum in the catalyst was 5 wt.% of platinum. The mixture was dried in an oven at 80°C, sieved and calcined at 500°C for 3 hours.

- *Alumina supported platinum (Pt/Al₂O₃)*

A commercial catalyst of platinum on alumina was used to study the effect of a different support in the reaction. The catalyst, with a loading of 5 wt.% of platinum, was purchased from Sigma-Aldrich.

Table 2 presents the catalysts used in this study, as well as the synthesis method and the calcination procedure used in each catalyst.

Table 2. Summary of catalysts

| Catalyst | Calcination procedure | Synthesis method |
|-----------------------------------|-----------------------|---|
| SnO ₂ | 500 ⁰ C 3h | Calcination of H ₂ O ₃ Sn |
| Pt/SnO ₂ | 500 ⁰ C 3h | Impregnation |
| Cu/HT | 520 ⁰ C 4h | Impregnation |
| Pt/SnO ₂ acidic-1 | 500 ⁰ C 3h | Impregnation |
| Pt/SnO ₂ acidic-2 | 500 ⁰ C 3h | Incipient wetness impregnation |
| Pt/Al ₂ O ₃ | Calcined | Commercial catalyst |

2.1.2. Reflux reactor

- *Reactor setup*

The reaction was carried out in a reflux reactor operating under atmospheric conditions. The reactor consisted of two main parts: the reaction vessel and the condenser. Figure 7 shows a schematic representation of the reflux reaction. A 25 mL round bottom flask was used as the reaction vessel. The reaction vessel was surrounded by sand (used as a heating jacket) and heated by a magnetic hot plate. The heating device was covered in aluminium foil to prevent heat losses. To maintain an inert atmosphere during the experiments, a nitrogen line was continuously purging the system. Two temperature sensors were set in the heating media to control the temperature during the reaction. The condenser consisted of a 50 mL glass tubular condenser which had an outlet on the top part so the produced hydrogen in the reaction could exist the system safely. The reason for removing the H₂ was to avoid a possible reaction between hydrogen and products. The flow of nitrogen and/or hydrogen is controlled by a rotameter kit (float material: sapphire; float density: 3.98 g/mL). The main function of the condenser was to prevent evaporation of the reactant. Water at 20⁰ C was used as cooling media.

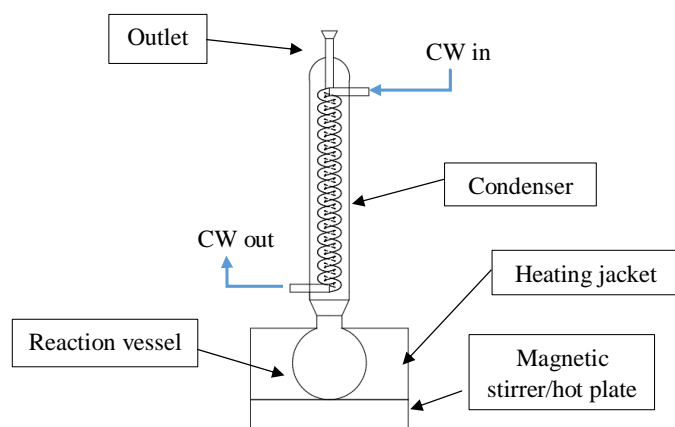


Figure 7. Schematic representation of the reflux reactor

- *Catalyst activation treatment*

All catalyst were activated via a reduction treatment. This reduction treatment was performed to convert the inactive metal oxides into their active metallic phases.

Prior to the reaction, 1g of each catalyst was reduced in the reactor with a flow of 3% H₂ in N₂ (24.4 mL/min) at 260°C for 6h. Then, the catalyst was left in an inert atmosphere under a nitrogen flow of 15.9 mL/min to avoid oxidation of the metal phase.

- *Dehydrogenation experiments*

After the reduction, 5 g of 1,6-HDO (99 wt.% , Sigma-Aldrich) were warmed up to 60°C (liquefied) and then injected to the reduced catalyst. Then, the reactor was heated to 180⁰ C and cooling water was circulating through the condenser tube to prevent evaporation of 1,6-HDO (which evaporates at over 60⁰ C [23]). Once the temperature reached 180⁰ C, stirring was started at 1000 rpm, then the reaction begun and run for 15h. The flow rate of N₂ was maintained at 15.9 mL/min throughout the reaction. This was done partly to remove the produced hydrogen from the reaction vessel, and partly to maintain an oxygen free atmosphere. For safety reasons, the reaction was not carried out in continuum for 15 hours, but instead this time was divided into two days: 7 hours the first day and 8 hours the second day. When stopping the reaction between the first and second day the heating media was removed, the stirring was stopped and the reactor was cooled down to room temperature.

2.1.3. Batch reactor

- *Reaction setup*

A 300 mL stainless steel autoclave (Parr instrument) was used. A schematic of this reactor setup is presented in Figure 8. The heating system consisted of a heating jacket and a thermocouple to control the temperature, which can reach a maximum of 500⁰ C. After a reaction, the reactor needed to be cooled down and the cooling media was water. There were two gas inlets at the top part of the reactor (one for hydrogen and the other for nitrogen) and a gas outlet to depressurize the vessel. The reactor was also equipped with a sampling line that allowed the collection of samples during the reaction.

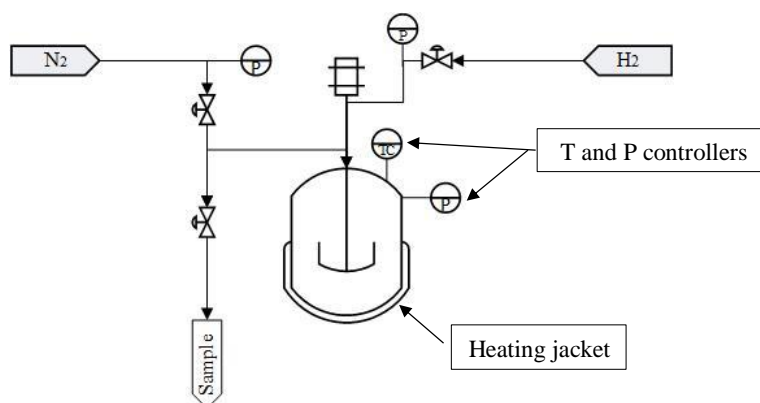


Figure 8. Schematic representation of the batch reactor

- *Catalyst activation*

2g of catalyst were introduced to the reactor and reduced with 20 bars hydrogen, at 460°C for 4h. After the reduction procedure, the reactor was flushed with nitrogen and left in an inert atmosphere until the reactants were added.

- *Reaction procedure*

10g of 1,6-hexanediol were mixed with 80g of xylene (solvent, Sigma-Aldrich) and added to the reduced catalyst. The reactor was purged three times with N₂ and, then, the reactor was pressurised by 6 bars of N₂. The reason for the initial pressure of nitrogen was to keep the feed in liquid state. After this, the temperature increased to a desired reaction temperature. When temperature stabilised, stirring started and maintained at 1000 rpm. At the end of reactions, three liquid samples were taken.

2.1.4. Experiments

Table 3, presents a summary of the performed reaction experiments. The first set of experiments (1-6) contained the catalyst screening study. Experiments 7-10 were tests with the Cu/HT catalyst at different temperatures and reaction setups. Finally, the last set of experiments (11-12) were done using the Pt/SnO₂ acidic-1 in different reactor.

Table 3. Summary of reaction experiments and conditions

| Nº | Catalyst | Reaction set-up | Reduction conditions | Reaction conditions | Feed/Catalyst |
|----|-----------------------------------|-----------------|--|----------------------------------|-----------------------------|
| 1 | SnO ₂ | Reflux reactor | 250 ⁰ C 6h H ₂ : 3% | 180°C 15h 1000 rpm | 5:1 |
| 2 | Pt/SnO ₂ | | | | |
| 3 | Cu/HT | | | | |
| 4 | Pt/Al ₂ O ₃ | | | | |
| 5 | Pt/SnO ₂ acidic-1 | | | 200°C 15h 1000 rpm | |
| 6 | Pt/SnO ₂ acidic-2 | | | | |
| 7 | Cu/HT | Reflux reactor | 250 ⁰ C 6h H ₂ 3% | 190°C 8h 1000 rpm | 5:1 |
| 8 | | | | 200°C 15h 1000 rpm | |
| 9 | | | | 210°C 15h 1000 rpm | |
| 10 | | | Batch reactor | 460°C 4h H ₂ 100% | 200°C 12 bar 20h 600 rpm |
| 11 | Pt/SnO ₂ acidic-1 | Reflux reactor | 250 ⁰ C 6h H ₂ 3% | 210°C 15h 1000 rpm | 5:1 |
| 12 | | Batch reactor | 460°C 3h H ₂ 100% | 210°C 12 bar 20h 600 rpm | 5:1, solvent = xylene |

2.1.5. Analysis of reaction products

- *Gas Chromatography-Mass Spectrometry (GC-MS)*

The liquid samples were analysed by a mass selective detector (Agilent 5977A) and quantified by gas chromatography (Agilent 7890B).

The preparation of the samples was done according to the following procedure:

- The reaction products were heated until 55⁰ C and under stirring; 100 mg of sample were taken for analysis.
- Then 1 mL of xylene was added.
- 200 µL of pyridine were added
- The sample was centrifuge for 2 minutes at 1500 rpm (in a WIFUG Lab Centrifuges, 500E)
- 200 µL were taken from the centrifuged sample and 50 µL of derivatization agent N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA).
- The samples were left to react with the BSTFA for 20h at room temperature.
- The samples were filtered with a 0.45µm filter.

Afterwards, the samples were analysed with a temperature ramp (20⁰ C-300⁰ C), injection 0.2 µL and split ratio of 80. The xylene is a non-polar component used as a solvent. Pyridine is a polar solution which was added so 1,6-HDO can be separated from the catalyst. The main function of BSTFA is to silylate the OH⁻ groups of 1,6-HDO, so the elution of it in the column will be enhanced.

Before the analysis, the equipment was calibrated for 1,6-hexanediol and caprolactone. The results of such calibration are shown in the appendix.

3. Results and discussion

The aim of this study was to investigate the catalytic dehydrogenation of 1,6-hexanediol to produce caprolactone. Six different catalysts were studied for such reaction. In the light of these results, two of the catalysts were selected to be further studied in a different conditions and reaction setups.

3.1. Catalysts screening

3.1.1. SnO_2 catalyst

Figure 9 shows a flame ionisation detector (FID) chromatogram of a sample from the reaction product with the tin (IV) oxide catalyst. In such graph, there are three peaks with retention times of 2.3, 2.6 and 3.5 min that correspond to BSTFA derivatives and the solvent (xylene), respectively. The later peak (7.2 min) represents 1,6-hexanediol.

Figure 9, clearly shows zero percent conversion of 1,6-HDO when SnO_2 used as a catalyst. The same result was also reported elsewhere [31].

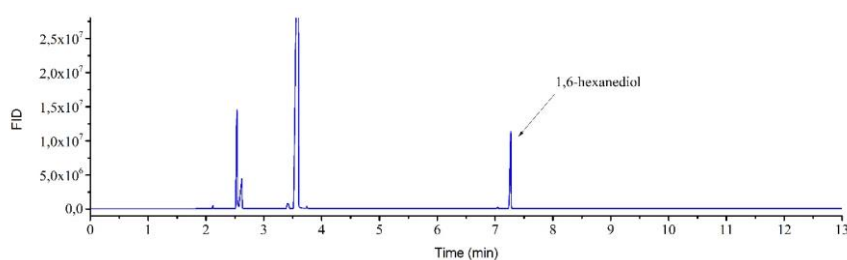


Figure 9. FID chromatogram of reaction products using SnO_2 catalyst. Reaction conditions 180°C , atmospheric pressure under flow of N_2 with stirring rate of 1000 rpm.

3.1.2. Pt/SnO_2 catalyst

The conversion for the reaction of 1,6-hexanediol in presence of Pt/SnO_2 catalyst is calculated to be approximately 29 mol%. Figure 10 shows formation of at least two products. The first product, with a peak at 6.6 min, identified to be cyclohexanediol. The second product, at 11.4 min, identified to be 6-hydrohexanoic acid. 6-hydroxyhexanoic acid (also known as 6-hydroxycaproic acid) is a six-carbon acid, which contains a

hydroxyl group connected to the sixth carbon. The appearance of this compound in the chromatogram is interesting because it is used as a precursor in the production of polycaprolactone [37]. A possible reaction mechanism for production of 6-hydroxyhexanoic acid will be presented in section 3.4. 1,4-cyclohexanediol is a six-carbon ring molecules with two OH⁻ groups attached in the para position of the ring. 1,4-cyclohexanediol is possibly formed from a dehydrogenation reaction [38].

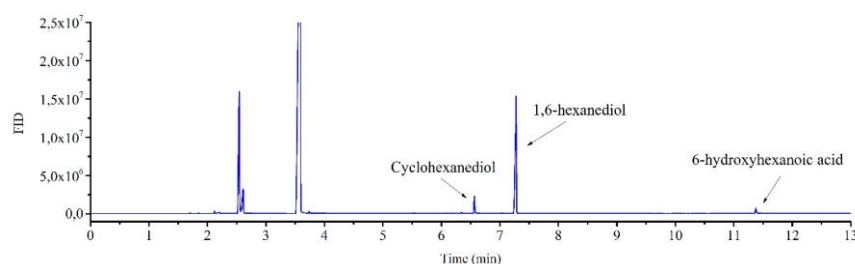


Figure 10. FID chromatogram of reaction products using Pt/SnO₂ catalyst. Reaction conditions 180°C, atmospheric pressure under flow of N₂ with stirring rate of 1000 rpm.

3.1.3. Pt/Al₂O₃ catalyst

When using a Pt/Al₂O₃ commercial catalyst, after 15h, nearly 44% of the 1,6-HDO was converted. The results (Figure 11) shows only that 1,4-cyclohexanediol was formed. Therefore, the selectivity was towards 1,4-cyclohexanediol.

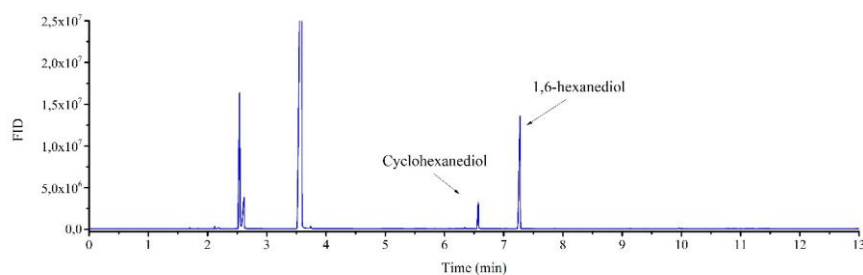


Figure 11. FID chromatogram of reaction products using Pt/Al₂O₃ catalyst. Reaction conditions 180°C, atmospheric pressure under flow of N₂ with stirring rate of 1000 rpm.

3.1.4. Cu/HT catalyst

For the reaction of 1,6-HDO in presence of the copper supported on hydrotalcite catalyst, the conversion of 1,6-hexanediol, calculated to be nearly 69 mol.%, significantly higher than the observed conversions of previous experiments. The main product is 6-hydroxyhexanoic acid (see Figure 12).

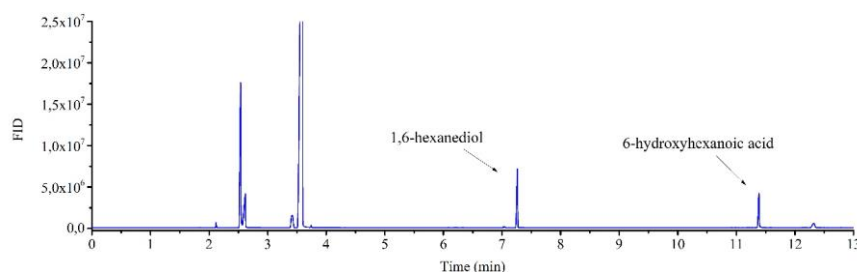


Figure 12. FID chromatogram of reaction products using Cu/HT catalyst. Reaction conditions 180°C, atmospheric pressure under flow of N₂ with stirring rate of 1000 rpm.

3.1.5. Pt/SnO₂ acidic-1 catalyst

In this case, the catalyst was prepared in a more acidic condition, which according to the results (Figure 13) changes the selectivity of the reaction. When comparing Figure 10 and Figure 13, the peak corresponding to 1,4-cyclohexanediol is no longer present whereas the one for 6-hydroxyhexanediol shows a more intense response. However, the conversion of 1,6-hexanediol is still low (20.8 mol.%).

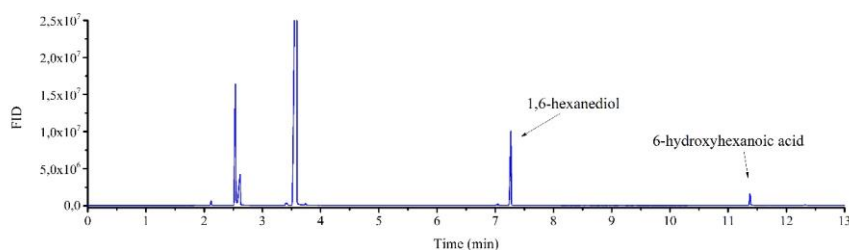


Figure 13. FID chromatogram of reaction products using *Pt/SnO₂ acidic-1* catalyst. Reaction conditions 180°C, atmospheric pressure under flow of N₂ with stirring rate of 1000 rpm.

3.1.6. *Pt/SnO₂ acidic-2* catalyst

In this case, the platinum on tin oxide catalyst is synthesised with a different method (incipient wet impregnation instead of wet impregnation) and the reaction is performed at 200°C. The main difference with the other acidic catalysts is that the conversion of the reactants is higher 44.5 mol%. The higher rate of conversion may partially be because of higher temperature of reaction. Nevertheless, the selectivity does not change. As shown in Figure 14, the main product detected by the GC-MS is 6-hydroxyhexanoic acid.

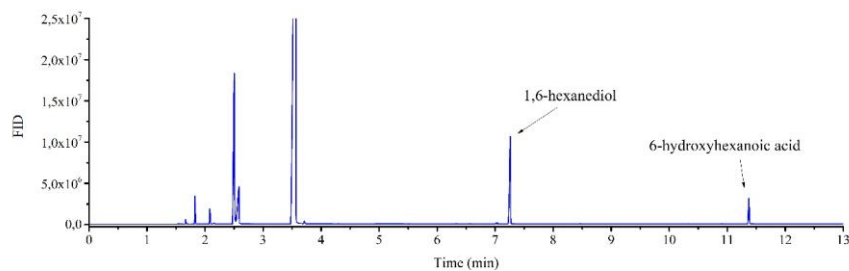


Figure 14. FID chromatogram of reaction products using *Pt/SnO₂ acidic-2* catalyst. Reaction conditions 180°C, atmospheric pressure under flow of N₂ with stirring rate of 1000 rpm.

3.1.7. Summary of the catalyst screening

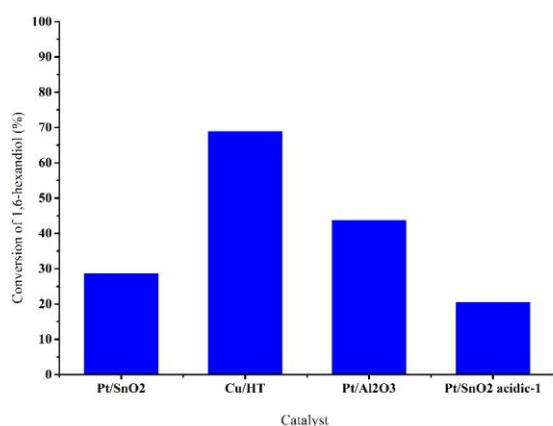


Figure 16. Results of the catalyst screening at 180°C, unit are in percentage of mole conversion of 1,6-hexanediol

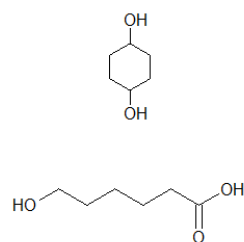


Figure 15. Molecular structures of 1,4-cyclohexanediol (top) and 6-hydroxyhexanoic acid (bottom)

The results of the catalyst screening at 180°C shows that Cu/HT is the most effective catalyst in terms of mole conversion of 1,6-HDO. With the rest of the catalysts, the conversion is lower than 50%. Regarding selectivity, the major products obtained were 1,4-cyclohexanediol and 6-hydroxyhexanoic acid. The first one might be obtained because was introduced as an impurity of the feed or as a derivative from 1,6-hexanediol. The acid product formed is more interesting due to its relation with polycaprolactone. Apart from the experiment with Cu/HT, this acid was obtained in the experiments with Pt-SnO₂, Pt-SnO₂ acidic-1. Due to the low conversion reach in the reactions at 180°C, it was decided to increase the temperature from 180°C to 200°C.

The increase in temperature resulted in increment in the conversion rate of 1,6-HDO. Although, the change in the synthesis method or increase of acidity does not offer any significant changes in selectivity. Therefore, the Cu/HT and Pt-SnO₂ acidic-1 catalyst were selected to perform more experiments in different conditions.

3.2. Experiments with Cu/HT catalyst

The experiment with the copper on hydrotalcite catalyst in the catalyst screening at 180°C showed a high conversion of 1,6-hexanediol after 15 hours. Thus, a set of experiments in different temperatures is performed.



Figure 17. Solid polymer obtained as a product of the reaction of 1,6-hexanediol on Cu/HT catalyst at 210°C

First, the reaction was carried out at a higher temperature. The selected temperature was 210°C. With the same reaction time (15 hours), the product of the reaction was a solid substance (see Figure 17) that presented a certain elasticity when removed from the reaction vessel. This polymer did not melt when heating it at 80°C or dissolving in ethanol. It seemed like all the 1,6-HDO had been converted to this polymer; however, since it is a solid substance, it cannot be analysed with the GC-MS. Therefore, the conversion cannot be quantified.

Another experiment was run at a lower temperature (200°C), this time the sample was in liquid state so it was possible to analyse. Figure 18 shows three major peaks that correspond to 1,6-HDO (time = 7.3 min), 6-hydroxyhexanoic acid (time = 11.4 min) and 2-hydroxyoctanoic acid (time = 12.3 min). The latest, is an acid similar to 6-hydroxyhexanoic acid but with an extra hydroxyl group. In this case, the mole conversion of 1,6-HDO was 94.89%. Taking a closer look at the chromatogram, there is a small peak at time 5.87 min that corresponds to caprolactone. Although, the intensity of such peak is not enough to be quantified, its presence indicates that this is a better temperature to perform the experiment. For this reason, it was decided to run the reaction at 190°C. Nevertheless, after 8 hours of reaction the GC-MS did not register any caprolactone and the main product was again 6-hydroxyhexanoic acid (see Figure 20). It would be interesting to check whether caprolactone is being produced in small quantities or if it is reacting to give 6-hydroxyhexanoic acid. This can be verified by repeating the reaction at 200°C, also taking samples of the reaction mixture during the reaction. However, with the current setup, this is not possible because there is no sampling line and once the reactor is opened the reaction conditions would change, thus the reaction could not be continued.

This catalyst was also tested in a batch reactor setup (Figure 19 shows the results of the analysis of the samples). This experiment can be compared to the one done at the same temperature in the glass reactor. In the batch reactor, the conversion of 1,6-HDO is significantly lower (62.57%), even though the reaction time was longer. A possible explanation for this is that the produced hydrogen was not removed and interacted with the feed and products. Another difference was noticed at the end of the experiment, when

removing the products from the reactor, at the bottom there was a thicker layer of products mixed with the catalyst. However, the GC/MS analysis of a sample of this layer did not show a clear conclusion of what product was formed.

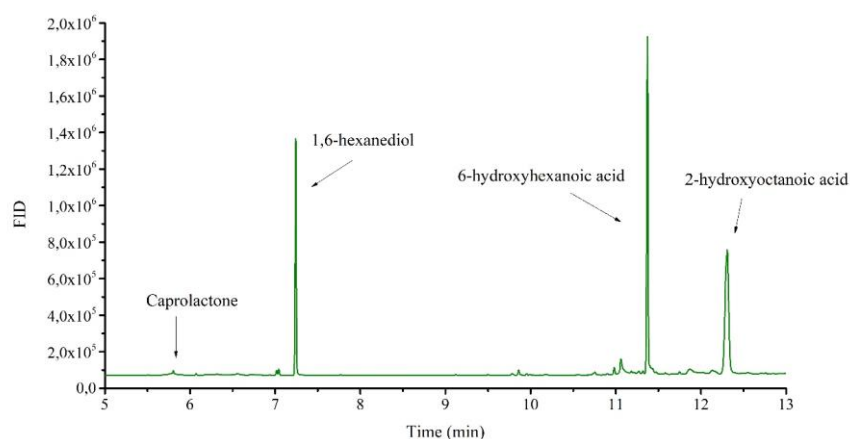


Figure 18. FID chromatogram of reaction products using Cu/HT catalyst. Reaction conditions 200°C, atmospheric pressure under flow of N₂ with stirring rate of 1000 rpm.

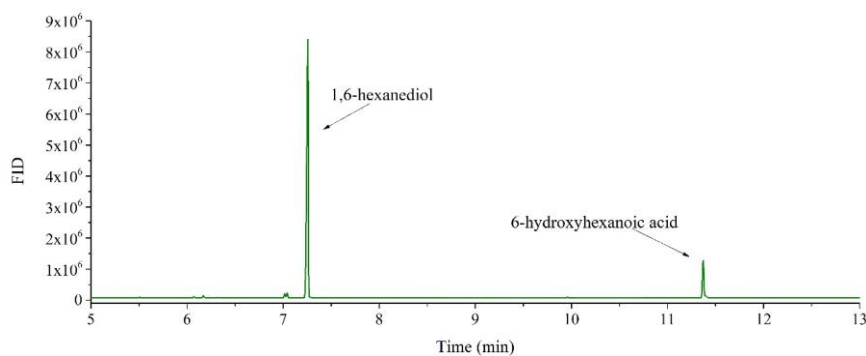


Figure 19. FID Chromatogram of the reaction product of the reaction with the Cu/HT catalyst run in the batch reactor for 20h at 200°C and 12 bars of N₂ pressure.

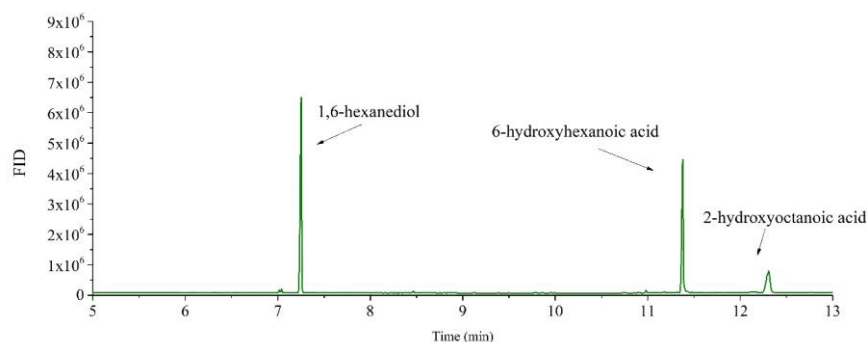


Figure 20. FID chromatogram of reaction products using Cu/HT catalyst. Reaction conditions 180°C, atmospheric pressure under flow of N₂ with stirring rate of 1000 rpm.

3.3. Experiments with Pt/SnO₂ acidic-1 catalyst

A conversion of nearly 80 mol.% was achieved from a dehydrogenation reaction of 1,6-HDO by using Pt/SnO₂ (Pt/SnO₂ acidic-1) catalyst at 210°C. This experiment was performed in the reflux reactor setup. The reaction products from this experiment are similar to those reported previously such as: 6-hydroxyhexanoic acid and 2-hydroxyoctanoic acid (Figure 21). The conversion in this case is lower than in other experiments at the same or lower temperature. Thus, Pt/SnO₂ is a less active catalyst compared to Cu/HT.

The acidic Pt/SnO₂ catalyst was also used in the batch setup. In this reaction, temperature was set at 200°C for 20h. At the end of the experiment, it was observed that a polymeric layer was formed at the bottom of the reactor vessel that contained the catalyst. The GC-MS analysis of the samples (Figure 22) did not show formation of any products. Only 1,6-hexanediol was detected in the samples. Based on the 1,6-HDO peak, the concentration of 1,6-hexanediol in the samples was calculated to be nearly 37 mol.%, which may indicate a 63 mol.% conversion. However, it seems that the reactant and product remained in the polymeric layer.

Such polymeric substance also was observed in the other experiment done in the batch reactor with the Cu/HT, although in that case layer was more liquid. Thus, both experiments done in this reaction setup result in the formation of a polymeric structure surrounding the catalyst that hinders the yield of the reaction.

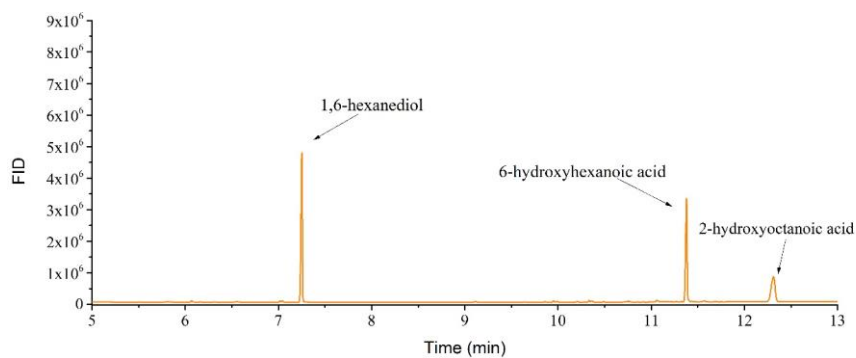


Figure 21. FID chromatogram of reaction products using Pt/SnO_2 catalyst. Reaction conditions $210^\circ C$, atmospheric pressure under flow of N_2 with stirring rate of 1000 rpm.

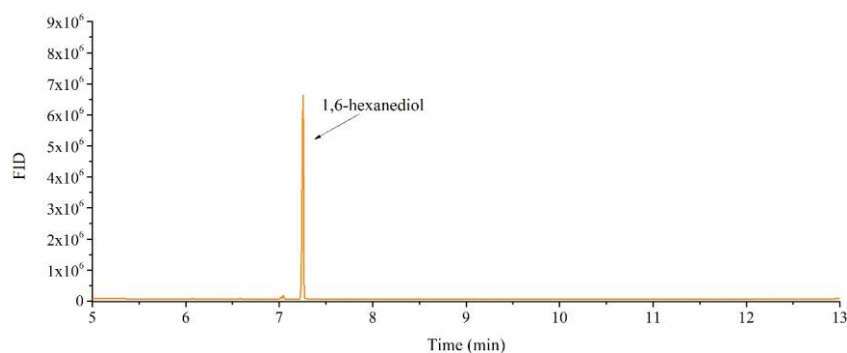


Figure 22. FID chromatogram of the products from the reaction with the Pt/SnO_2 acidic-1 catalyst in the batch reactor at $200^\circ C$ for 20h.

3.4. Possible reaction pathways

This section describes possible reaction pathways for formation of the products detected during the analysis of the samples by GC-MS. As mention in previous sections, the major product detected was 6-hydroxyhexanoic acid. The mechanism of formation of 6-

hydrohexanoic acid from 1,6-HDO feed, in an oxygen free environment, may not be very straightforward to explain. However, several possibilities can be considered (Figure 23).

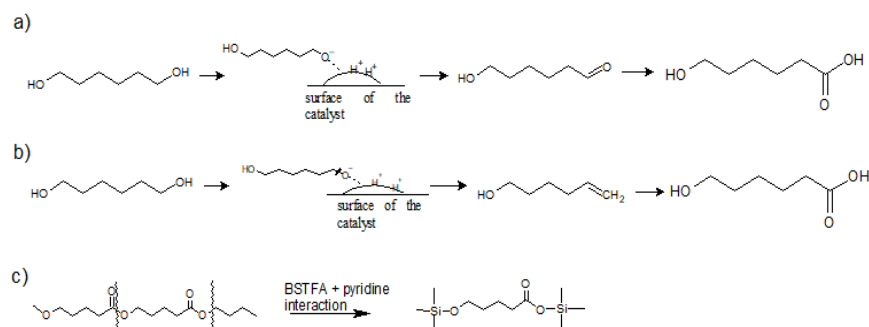


Figure 23. Possible reactions pathways of formation of 6-hydroxyhexanoic acid

The first possibility is the formation of an aldehyde as an intermediate via a dehydrogenation reaction. This means that 1,6-HDO is dehydrogenated and two hydrogens atoms are removed. Such hydrogen can form a molecule and exist the reactor as incondensable product or remain dissociated as two hydrogens on the surface of the catalyst. If the second option occurred, then, the aldehyde can be hydrolysed 6-hydroxyhexanoic acid. However, this possibility seems unlikely since the acid has three oxygens but there is no other source of oxygen.

The second route is that one hydroxyl group is cleaved and a C_6 olefin is formed. In order to form 6-hydroxyhexanoic acid, methanol would have to be present in the system which would only be possible if it comes from another molecule of 1,6-HDO that may have been cleaved in the first carbon. However, presence of a C_5 structure was not observed in the GC-MS results. The olefin would have had to be oxidized in an oxidant free environment. Thus, this hypothesis is not credible.

Another possibility is that what really is being formed is a longer chain and that this chain is not being detected in the analysis due to its length. Then, BSTFA and pyridine would interact with this chain breaking it into shorter products such as 6-hydroxyhexanoic acid. In order to verify this theory, instead of using pyridine and BSTFA, liquid samples were dissolved in methanol only. The FID signal showed, in fact, a peak for caprolactone and 1,6-hexanediol. However, there was no sign of 6-hydroxyhexanoic acid but instead another acid with a longer chain was detected (cyclopentanecarboxylic acid, $C_{14}H_{26}O_2$). Therefore, this result confirms the theory of the formation of a long chain. However, this possibility needs to be further evaluated by using other characterization methods.

4. Conclusions

In this project the acceptorless dehydrogenative lactonization of 1,6-hexanediol was investigated. Supported Cu and Pt catalyst such as Cu/HT, Pt/SnO₂ and Pt/Al₂O₃ were tested. The reactions were performed in two different reaction setups: a reflux reactor and a batch reactor. The reaction products were analysed by GC-MS. The most significant findings are the following:

- At 180°C, the results indicated low activities for most of the catalyst. After 15h of reaction in the reflux setup, only Cu/HT showed a conversion of nearly 69 mol.%. Therefore, to see a higher conversion of 1,6-HDO either time or temperature needs to be increased. In later experiments, it was observed that running the reaction at 200°C shows better results in terms of conversion of 1,6-HDO.
- Experiments showed that Cu/HT is the most active catalyst. Although the main product obtained from this reaction was 6-hydroxyhexanoic acid, a small amount of caprolactone was produced at 200°C. However, modifications should be made on the reflux reactor to extract samples during the reaction, without disturbing the reaction conditions to draw a clearer conclusion.
- The results reveal that the produced hydrogen must be removed from the reaction vessel due to its adverse effect on the selectivity towards caprolactone. Caprolactone can react with hydrogen to produce other products. The present of a small amount of caprolactone in the samples from the experiment using the reflux reactor validates this possibility. Thus, the batch reactor setup is not a suitable system to perform the dehydrogenative lactonization reactions. Moreover, at higher temperatures, the formation of a polymeric layer on the catalyst was observed. If the polymer sticks to any part of the reactor, for example the stirrer, it may result in damages to its structure.
- Other analytical methods should be used to validate the products that were identified by GC-MS in this study. Nevertheless, the method used in this project is useful for a qualitative analysis.

5. Suggestions for future work

Some ideas for the continuation of this work can be suggested based the conclusions extracted from this project:

- Improvement of the glass reactor setup to a system that allows taking samples during the reaction.
- Use of $\text{Pt}(\text{NH}_3)_2(\text{NO}_3)_2$ precursor for the synthesis of the Pt/SnO_2 catalyst as it was proposed by Touchy et al. [31]
- Use a different technique for the analysis of the reaction products or gas chromatography with a polar column.

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7. Appendix

7.1. GC-MS calibration

A first calibration was done with samples of known concentration of caprolactone and 1,6-hexanediol using methanol as solvent.

However, the result of the calibration for this method shows that the peaks for caprolactone and 1,6-HDO come at times very close to each other (as shown in Figure 1Figure 24). Additionally, the chromatography column is non-polar whereas the compounds to analyse are all polar. Several parameters can be altered in a calibration method (split ratio, introduction of isotherms, injected volume), still none of these variation produce any better results. Thus, this calibration method cannot be used for analysing caprolactone as the reaction product.

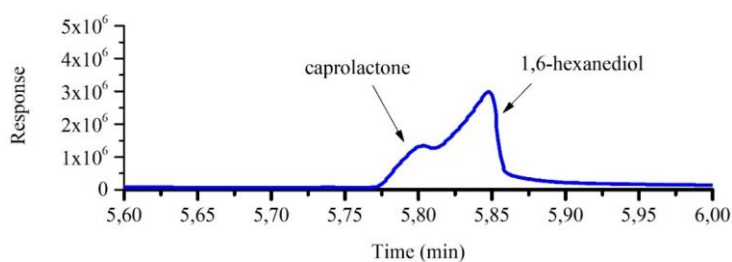


Figure 24. Extract of chromatogram of calibration procedure of 1,6-hexanediol and caprolactone with methanol as solvent

A second method is designed for analysing the results.

The samples are analysed with a temperature ramp (20⁰ C-300⁰ C), injection 0.2 µL and split ratio of 80.

With this new method the peaks of caprolactone and 1,6-hexanediol are separated (see Figure 25). This calibration method is used with different compositions of caprolactone and 1,6-hexanediol and the respective calibration curves are obtained for the range of compositions stated in Table 4.

Table 4. Calibration compositions for 1,6-hexanediol, caprolactone and xylene

| HDO | | Caprolactone (mg) | | Xylene (mg) | |
|-----------|-------|-------------------|-------|-------------|-------|
| Mass (mg) | % mol | Mass (mg) | % mol | Mass (mg) | % mol |
| 94 | 8.16 | 103 | 9.25 | 855 | 82.59 |
| 62 | 5.71 | 68 | 6.49 | 856 | 87.80 |
| 30 | 2.95 | 33 | 3.36 | 856 | 93.69 |

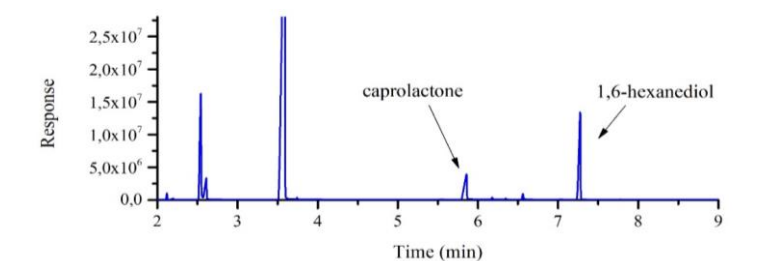


Figure 25. FID chromatogram of calibration procedure of 1,6-hexanediol and caprolactone with xylene and pyridine as solvents and BSTFA as derivation agent

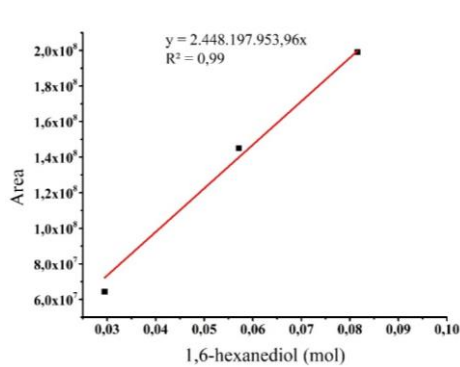


Figure 27. Calibration curve for 1,6-hexanediol

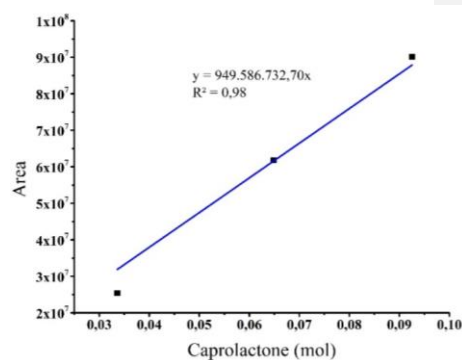


Figure 26. Calibration curve for caprolactone