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Alternative fuel production using catalysis

Hydrodeoxygenation of stearic acid on NiMo/Al₂O₃ catalyst

Bachelor Final Project of the Bachelors Degree in Chemical Engineering

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CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2015

BACHELOR FINAL PROJECT 2015

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Cover: Autoclave reactor used in this project.

« Learn from yesterday, live for today, hope for tomorrow. The important thing is not to stop questioning. »

- Albert Einstein -

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Abstract

The high demand of energy and the progressive lack of fossil fuel resources have motivated several researches to find out possible solutions for these issues such as alternative fuels from biomass. Specifically in this project, the black liquor from the paper industry was studied which is a by-product and it contains fatty acids. The hydrodeoxygenation of these fatty acids can produce hydrocarbons that will be utilized for biofuels. Stearic acid is the model compound used to perform all the experiments and NiMo/Al₂O₃ is the catalyst.

Wet impregnation and incipient wetness are the methods applied for catalyst synthesis in order to study which is the most convenient catalyst to remove the oxygen atoms from the acid and obtain as long as possible hydrocarbon chains. Eight different catalysts with the same composition have been synthesized by using one of these methods, adding Mo and Ni in one or two steps and applying different treatments after adding the first metal. These catalyst were characterised by BET and TEM techniques.

In order to perform the experiments a new batch reactor for the division was used and an experimental method developed before to start with activity tests. Referring product analysis, GC and GC-MS were the techniques which enable to quantify and identify the products.

Several interesting results have been obtained from this project. Methods for in situ pre-treatment of the catalyst, sample taking, start up and switch off the reactor have been developed. On the one hand, the results from experimental method development suggests that more development is needed to take samples from the reactor as well as to clean the sample taking line in order to obtain more reliable results. On the other hand, the catalyst preparation takes an important role for stearic acid conversion and selectivity, different concentrations and tendencies of products formation have been reached depending on the catalyst.

Keywords: biofuels, NiMo/Al₂O₃, HDO, decarboxylation, stearic acid and pH influence.

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1

Introduction

1.1 Background

Nowadays, because of the constant demand of fuels as an energy source and the lack of fossil fuel resources, researchers started working with alternative fuels. It is essential to reduce the use of fossil fuels as a nonrenewable energy source in order to avoid further global warming and to achieve this, in the field of the fuels, one of the most potent solutions that has been found is the use of biomass as raw material to yield biofuels [1].

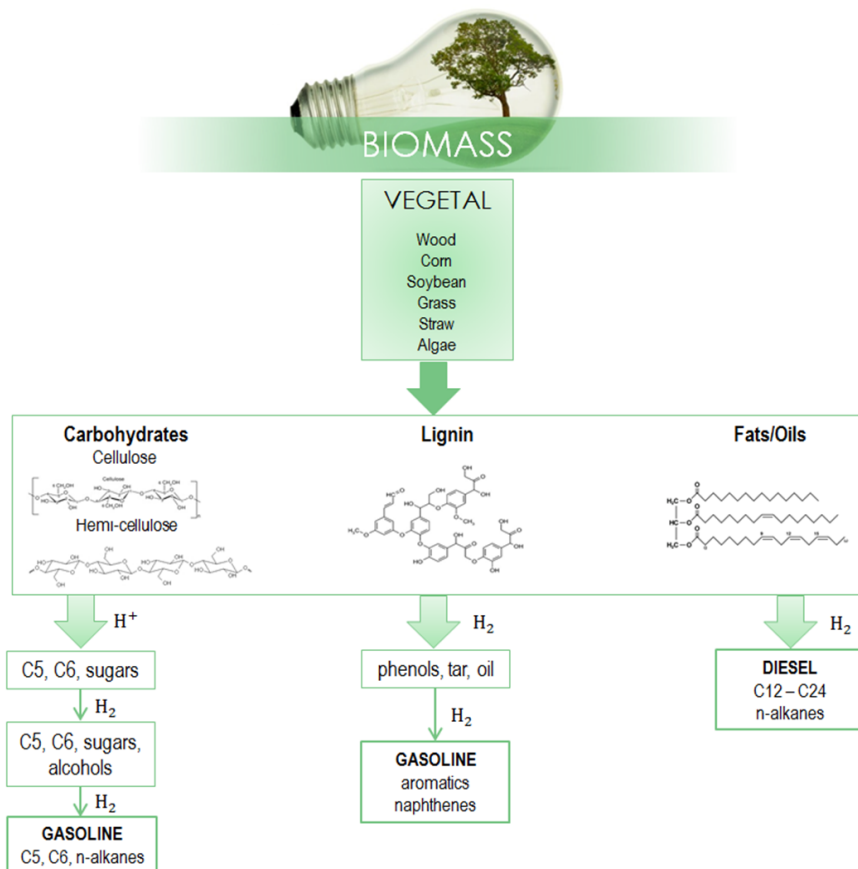


Figure 1.1: Different ways to produce biofuels from biomass [2].

There are different origins of the biomass, it is possible to produce biofuels from animal fats or vegetable biomass and it is possible to split the last ones in three categories (*Figure 1.1*): carbohydrates, lignin and oils [2]. Currently, in order to reduce the emissions of CO₂, biodiesel is used because of the similar characteristics with fossil fuels and as a potential resource for renewable diesel it is interesting to use tall oil [3]. This vegetable oil is a by-product of the paper industry composed of 30-60% fatty acids (TOFAs) mostly unsaturated acids C₁₆ - C₁₈. These fatty acids that stem from the tall oil at the same time, comprise an ideal feedstock for biodiesel yield; it is a cheap raw material extensively used in industrial applications as adhesives and nylon [1, 4].

On the one hand, to replace the fossil fuels by the biofuels offers advantages such as high combustion yields, the sulphur content is lower than in fossil fuels, they are renewable as well as biodegradable and it is possible to replace the fossil fuel raw material in the industry by biomass in order to yield also biofuels. On the other hand, the biofuels show disadvantages. For example regarding the last advantage, it is true that is possible to replace the fossil fuels in the industry by biofuels, but it is essential to study first the viability of these alternative environmental friendly fuels case-to-case, inasmuch as not all raw materials that can be used as biomass fit in the existing refineries [1, 5]. One of the most important factors is the amount of oxygen in the hydrocarbon chain; this oxygen has to be removed from the fatty acids if the objective of the biomass is to become a biofuel using separation sections in a steam cracking already designed for fossil fuels with a lower quantity of oxygen. It could be a serious safety problem when the cracking units are not available to work with these significant amounts of oxygen because of the corrosion in the equipment and the formation of gum as well as fouling in downstream processing [5].

It is relevant to achieve the longest hydrocarbon chain possible because the longer the chain, the higher the energy results will get. The fatty oils are formed by three carboxylic acids, usually as in the *Figure 1.2* is shown, the most common with 18 carbon atoms but it is possible between 14 and 24 as well. Thus, the mechanisms that can be used and are directly related to remove the oxygen atoms and hydrogenate the acids into alkanes are hydrodeoxygenation (HDO) and decarboxylation. The first one allows keeping the whole hydrocarbon chain but the decarboxylation pathway, also called CO₂-elimination, removes one carbon atom from the main chain reducing the number of carbons into the resulting hydrocarbon alkane and consequently decreasing the energy value of the chain. It is possible to understand how the bonds between the oxygen and carbon in the carboxylic group can be broken by different pathways in the *Figure 1.3*. In our case for the tall oil, the reactions will start reacting from the fatty acids already separated from the triglyceride that means it is not necessary to remove the triglyceride oxygen.

In order to increase the H/C ratio and decrease the O/C ratio of hydrocarbons, the hydroprocessing reactions use significant amounts of hydrogen at a high pressure and temperature. For the HDO reaction a catalyst is also needed which is carefully chosen taking into account the conversion of the route that would like to promote, the by-products that could be created, the possible resources for the re-

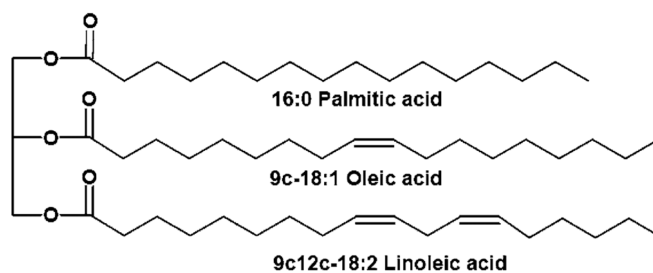


Figure 1.2: Example of hypothetical triglyceride in the fatty oils [6].

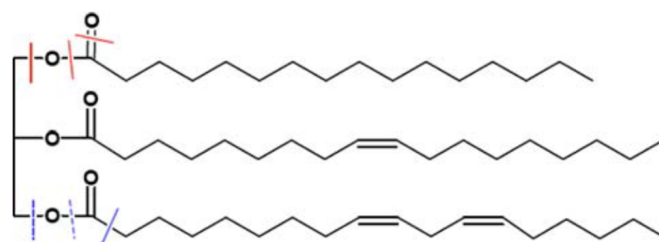


Figure 1.3: Different pathways to remove the oxygen from the fatty acids by hydrotreating. The blue lines relate to decarboxylation pathway and the red ones to hydrodeoxygenation reactions [6].

search amongst other characteristics and it is crucial to allow the multiple effects that can cause changes during the preparation procedure as well. There is a wide range of possibilities to choose the proper catalyst, for deoxygenation reactions it is common to operate with Mo and W sulfided forms promoted with Ni or Co and together with a convenient support, e.g. alumina [7]. For this project, a heterogeneous and tailor-made catalyst known as NiMo/Al₂O₃ will be used where Mo is supported with alumina and promoted with Ni.

For the hydrodeoxygenation process a high pressure and temperature strength will be required so, the bed reactor used will need to endure an extreme working pressure and temperature. In order to keep these properties it is also important to implement a good design and development of the experimental process, this could be a great challenge.

1.2 Objective

This study has two main objectives: The first one is to find good experimental conditions to examine hydrodeoxygenation of oils in a batch reactor, identify the main products and follow their formation. This part includes leak testing of the new reactor, development of a procedure

- for pretreatment of the catalyst in the batch reactor

1. Introduction

- of heating and pressurizing the reactor
- to take samples
- treat the samples
- analyze the samples in a GC

The other objective is to compare in influence of the preparation method on the activity and selectivity of the catalyst. The second part includes also the characterization of the catalysts.

2

Theory

2.1 Reaction mechanism

The hydroprocessing of tall oil is a combination of diverse chemical reactions undertaken simultaneously. This fatty oil contains mostly fatty acids such as palmitic, linoleic and oleic acid [1, 4] but in this project, stearic acid will be used as model compound. Thus, the hydrotreating process will not start with a mixture of triglycerides, that is to say, it is not necessary the saturation and further cracking process with hydrogen, it is possible to start with the free fatty acids.

Transesterification and hydrodeoxygenation are different pathways to produce hydrocarbon based fuels from the fatty acids *Figure 2.1*. The hydrocarbons obtained through the transesterification using methanol as reactive conserve the oxygen atoms because the carboxylic groups are not removed during the reaction. In contrast by the hydrodeoxygenation pathway also called HDO, the fatty acids are converted completely to hydrocarbons that could be used in refineries already designed for fossil fuels through it compatibility with fuel storage, supply system and production plants that need a low O/C ratio in order to avoid problems as materials oxidation and coke formation [8].

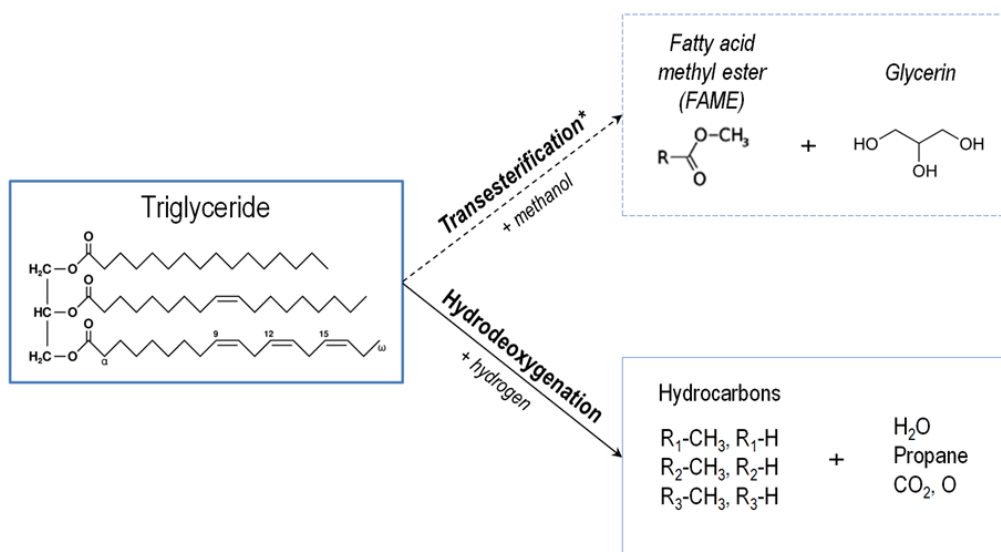


Figure 2.1: Possible pathways in order to produce biofuels from triglycerides [8].

**Hydrodeoxygenation is the pathway chosen for this project.*

By starting the HDO with fatty acids three different chemical reactions could arise: hydrodeoxygenation, decarbonylation and decarboxylation with different products depending on the case. For the HDO *Figure 2.2*, the products are alkanes with the same number of carbon atoms as the original chain and water as a by-product; in case of the decarbonylation reaction is produced alkanes with one carbon atom less than the original chain and the carbon monoxide together with water as a by-products; finally the last one is decarboxylation, where the same elongated chain as by decarbonylation will be obtained but with carbon dioxide as a by-product [8, 9, 10, 11].

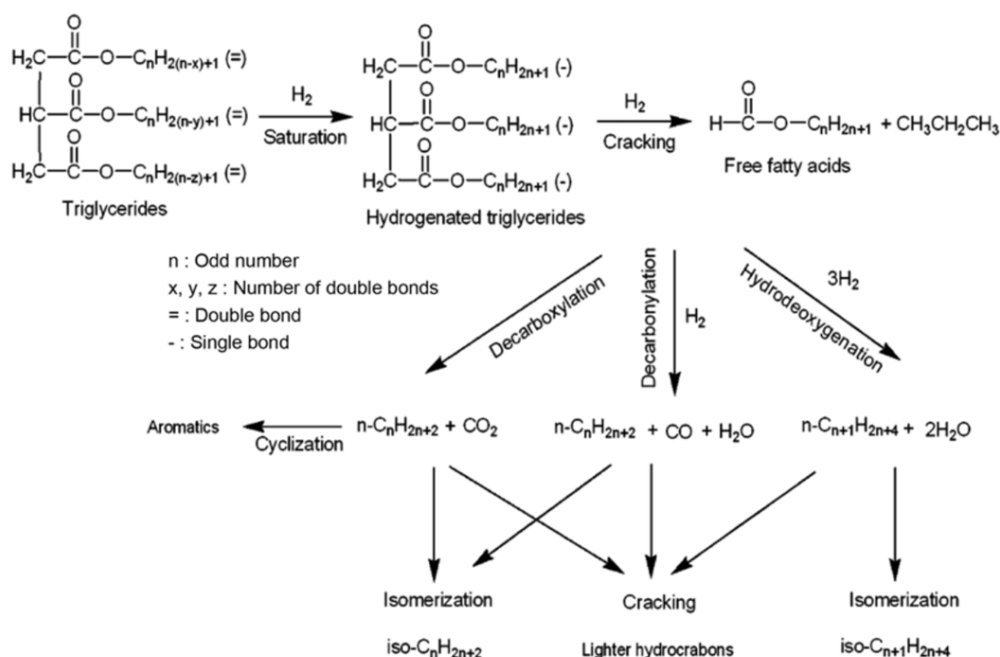


Figure 2.2: Reaction pathways for the hydrogenation of triglycerides [8].

Other studies have proven that the consumption of hydrogen in reactions where the decarbonylation and decarboxylation were advantaged is lower compared to other cases where the HDO was promoted [8, 11] even so, the most relevant factor referring to these pathways and that could enhance one of these is the catalyst. Several researches have been carried out on the effect of different catalysts in fatty acids hydroprocessed, such as a relevant study Kim et al., which has investigated the catalyst effects during the hydroprocessing of soybean oil as model compound demonstrating how CO and CO₂ ratios are higher with Pd/Al₃O₂ and Ni/Al₃O₂ than with NiMo/Al₃O₂ or CoMo/Al₃O₂. Consequently, this means that decarboxylation and decarbonylation are promoted with this catalyst [11, 12]. Referring stearic acid as model compound, the possible expected HDO pathways could be mostly the reactions in *Figure 2.3*, where methanation reactions are included using the excess of hydrogen to remove CO gas formed during decarbonylation reaction [9]. This reaction is undesired due to extra consumption of hydrogen.

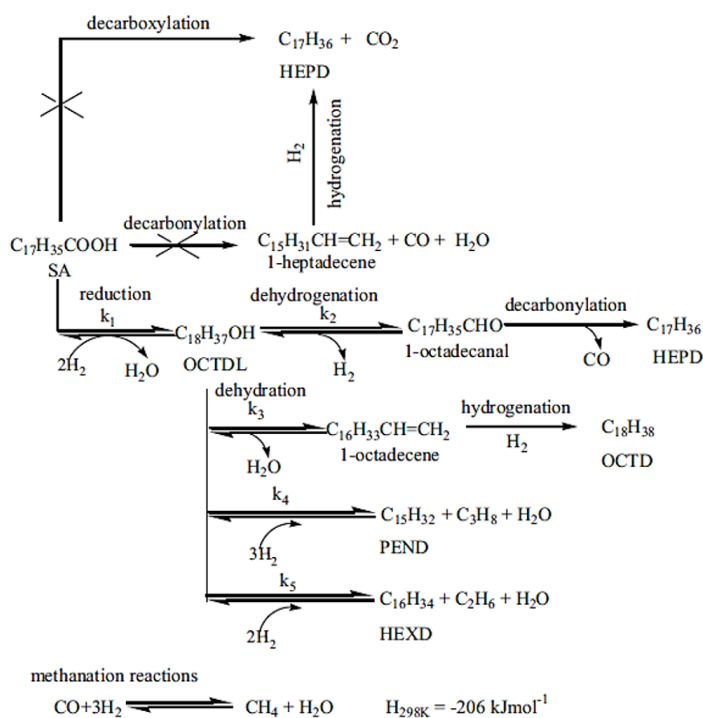


Figure 2.3: Possible stearic acid reaction mechanism for HDO [9]. Nomenclature: HEPD - heptadecane, OCTD - octadecane, OCTDL - octadecanol, PEND - pentadecane and HEXD - hexadecane.

The temperature favorable for hydrodeoxygenation with the kind of catalyst used for this project would be around 250 - 400 °C. It is possible to compare between some catalysts at which temperature these catalysts get reduced as shown in the *Figure 2.4*. In this figure is shown the H₂-TPR (Temperature-programmed reduction) which is a technique often used for the characterization of heterogeneous catalysts and it is possible to perceive that for NiMo/Al₃O₂ and Ni/Al₃O₂ the temperature where an H₂ uptake occurs and, thus, the samples are reduced is between 400 and 500 °C, so 400°C could be suitable temperature for the pre-treatment [10].

2.2 Catalysts

Heterogeneous catalyst is the most common kind of catalyst used in order to produce biofuels by hydrotreating pathway. It is considered that a heterogeneous catalyst is effective when its total surface area is as large as possible, otherwise, the reaction area would not be efficient enough to achieve high yields. Small particles are required in order to obtain acceptable results and the support as well as its porosity for the catalysts, usually take an important role [13].

There are several advantages of heterogeneous catalysts such as complete and simple

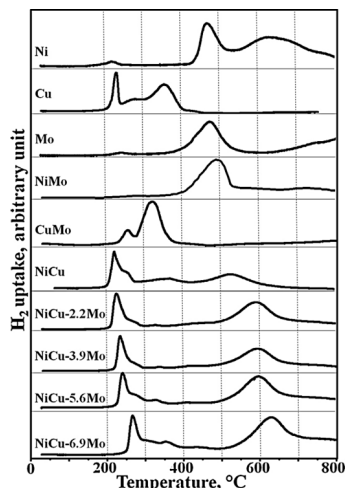


Figure 2.4: H₂-TPR profile of different catalysts [10].

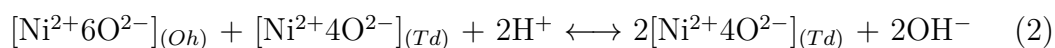
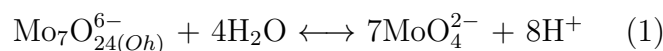
separation of the solid catalyst from the fluid phase, the catalyst recuperation is not required, it has a high temperature stability and long catalyst life, but it is important to take into account the disadvantages as well. The sintering of the particles of the active metal on catalysts forming a big one could be a problem for the catalytic activity because of the smaller surface area and in order to avoid that, small amounts of promotor are required [13, 14]. Another common inconvenience for all the catalysts is the poisoning that could be caused by impurities or even products from the reaction.

For the propose producing biofuels from tall oil, several studies have been investigating which catalysts are suitable for these kind of reactions and wide range of possibilities are applicable but NiMo and CoMo supported on alumina are the most common catalysts for hydrodeoxygenation reactions. Actually, Elliot and Baker were pioneers in conducting a study where the reduction of the oxygen by different catalyst where reported in 1984 [7, 15] and before this study, both catalysts were used for hydrodesulfurization with fossil fuels called HDS as well. Usually Ni and Co promoters have high activities and therefore great results, but there are some drawbacks that should be controlled because NiMo/Al₃O₂ and CoMo/Al₃O₂ need to be sulfurized producing thus an extra small amount of sulfur atoms to the sample. Another factor to consider is coke formation since it could poison the catalyst as well as water or other by-products also can do.

However, even the formation of coke, it is necessary trying to choose among all the possibilities for organosulfide agents the correct one. The first experiments were performed by H₂S in order to activate the catalyst, but nowadays, other kind of activating agents are being used, mainly because of the easy handling and control of the gradual sulphur delivery to the catalyst affecting its kinetics of decomposition [16]. Other important reason is that the organosulfide agents such as DMDS and polysulfides (also called “spiking” agents) had shown better results than H₂S during the activation procedure at specific temperatures [17]. Even NiMo catalyst should be activated by organosulfide agents, will not be in this project due to safety issues.

2.2.1 pH effect

For this research one of the most relevant parts is the synthesis of catalysts in order to achieve as small metal particles as possible on alumina support. Small particles are more suitable referring the metal dispersion and consequently the pH has an essential effect during the catalyst preparation. With $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2\cdot\text{H}_2\text{O}$ at different pH values it is possible to obtain different species in solution, so in order to obtain the desired MoO_4^{2-} and $[\text{Ni}^{2+}\text{O}^{2-}]$ respectively, the control of pH in this solution is required. Contributions as Guevara-Lara, Bacaud et al. 2007 [18] have reported that a basic pH (*Eqs.(1)* and *Eqs.(2)*) describes the equilibrium at pH 9) is possible to perform a satisfactory NiMo/Al₃O₂.



(Oh: octahedral Ni specie, Td: tetrahedral Ni specie)

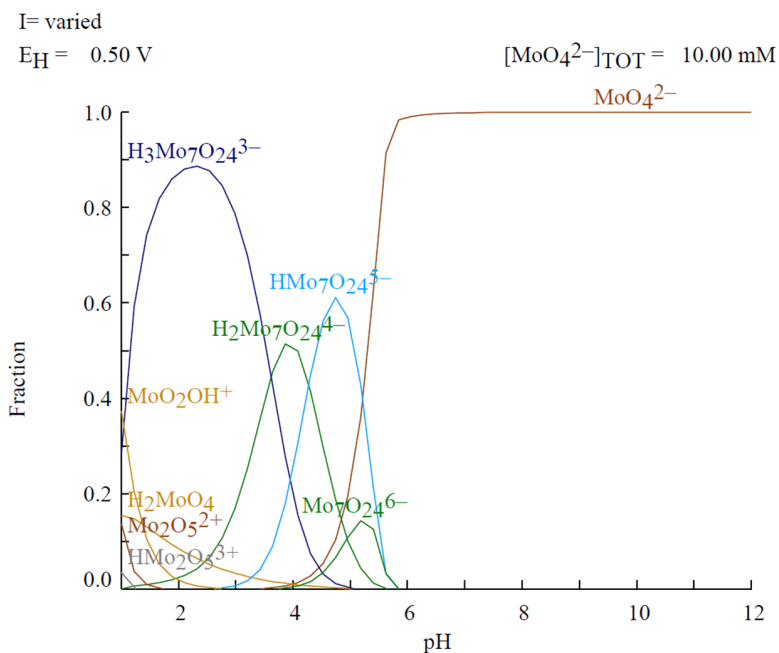


Figure 2.5: Fraction vs pH of different molybdenum complex species dissolved in a water solution and 10mM MoO_4^{2-} .

Moreover, this catalyst is synthesized on alumina which is positively charged at $\text{pH} \leq 8.4$ [19, 20]. So, to achieve acceptable interaction of catalyst metals on support surface, the metal species should be negatively charged to avoid repulsion due to charge. In order to ease the interaction between positively charged alumina and

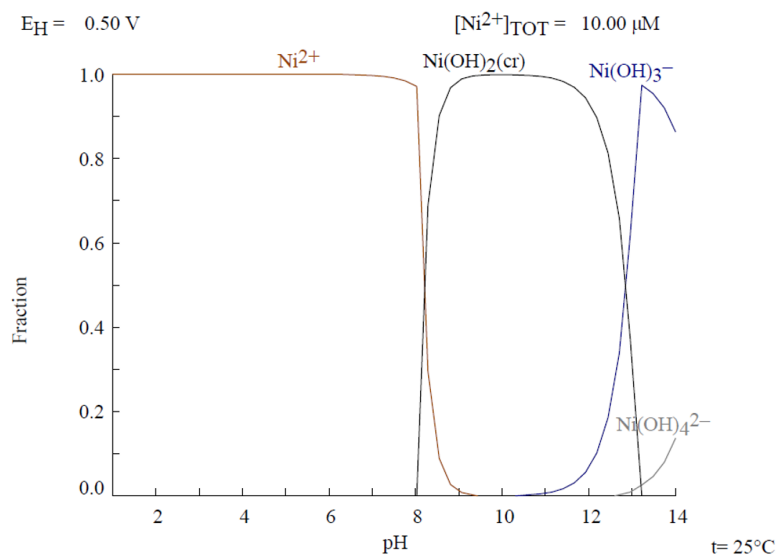


Figure 2.6: Fraction vs pH of nickel complex species dissolved in a water solution and 10mM Ni^{2+} .

these species, pH adjustment case-by-case is required. As in *Figure 2.5*, molybdenum species can be negatively charged between pH 2 and 12 even though, the pH desired for MoO_4^{2-} with number of oxidation 6+ will be higher than 6. On the other hand, as shown in *Figure 2.6*, basic pH is needed in order to get negatively charged nickel species. Due to the fact that is necessary to be absorbed by alumina support, in this case and as the molybdenum as well, working at pH higher than 11 will be convenient because as more basic is the pH, more negatively charged nickel species will obtain.

Another factor to take into account is alumina stability; at pH higher than 10, its chains start stretching and the adsorption of the Mo and Ni on Al_3O_2 surface could be inhibited as well as the viscosity increased [21] even so, previous research has demonstrated that at pH 11, the catalyst surface area is bigger than at pH 6 where alumina and molybdenum have an acceptable adsorption [22]. Therefore, as pH adjustment is highly important, a thorough study about catalyst preparation is necessary and a wide range of options should be evaluated.

3

Experimental

3.1 Catalyst preparation

The catalyst preparation methods could be very divers and it is possible to prepare the same kind of catalyst following different steps. The chosen catalyst for this research is considered as supported metal and oxide catalyst; therefore, it is common to prepare it by the succession of impregnation for the metal preparations, drying by freeze dryer or at room temperature, calcination or not and finally activating the precursor in order to obtain an active catalyst.

The catalyst synthesis involves two different kind of impregnation methods: wet impregnation and incipient wetness. The objective of impregnation connects the solid support with a liquid solution containing the precursor in order to obtain a dispersion as high as possible combined with thermal stability [23].

As has been mentioned earlier, the pH of these catalyst is an important parameter and it is necessary to study different sequences in order to control it in specific values. Consequently, NiMo/Al₂O₃ synthesis will be prepared and tested afterwards with pH control at different values or without it.

The reactive components were 15% by weight (NH₄)₆Mo₇O₂₄·4H₂O, 5% Ni(NO₃)₂·H₂O and 80% Al₂O₃. Because of these crystalline structures with nitrogen compound, the basic solution chosen for pH adjustment is NH₄OH 2M. The main reason is subsequent nitrogen forms removal by pre-treatment with hydrogen before activity tests, otherwise this procedure would be longer.

3.1.1 Wet impregnation (W)

This method, also known as soaking, consists of using liquid excess to perform solid-liquid contact. For this research, a non-quantitative amount of water has been used to dissolve nickel and molybdenum complexes. The reason for this is because of the pH adjustment; significant amounts of base and acid solutions were used and consequently the liquid volume increased [23, 24]. In *Figure 3.1* it is possible to observe the appearance of the solution and disposition of the experimental pH adjustment.

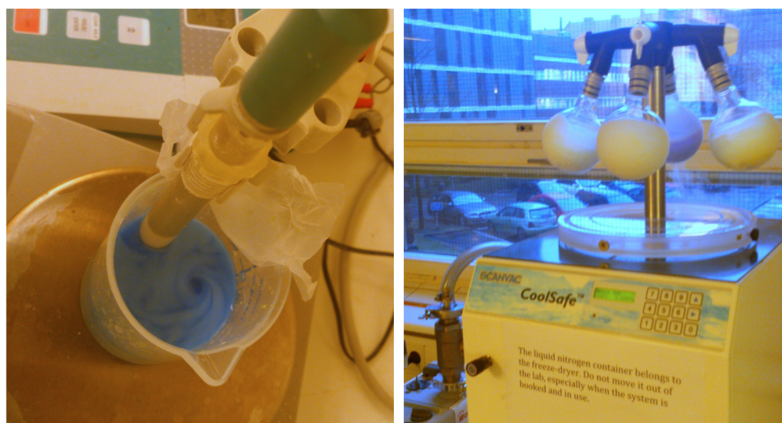


Figure 3.1: In the picture on the right it is possible to observe the appearance of the solution while the pH adjustment was performing. On the left, it is possible to observe the freeze dryer experimental design.

The drying procedure for the wet impregnation method was performed by freeze drying which consists of sublimation of water. The steps that need to be followed are: sample freezing by liquid nitrogen, connecting the round-bottom flask to the equipment as shown in *Figure 3.1* prepare the vacuum system at $-110\text{ }^{\circ}\text{C}$ and leave it overnight. The result is a completely solid sample without water.

All the catalysts that were synthesized by wet impregnation involve pH control at 10.5 or 9. For the pH 9 catalyst, Ni and Mo complexes were dissolved and pH adjusted at the same time but for the pH 10.5, only the Mo complex was added to the support. The first one was used as dried powder after freeze dryer but the second one was split into three samples to apply subsequent treatments. These treatments are: calcination at 400°C during 2h, reduction with 5 bar of hydrogen at 400°C during 18h and the third one is only dried.

3.1.2 Incipient wetness (I)

Unlike the previous method, for this preparation method a specific amount of water previously determined is required [23]. The amount of water needed in order for the powder to become wet is calculated empirically before the catalyst performing. For this quantity of water solubility in water of Ni and Co complexes was considered and afterwards, enough wet appearance of alumina and dissolution. It is not involve pH adjustment for wet impregnation method otherwise, this would require a considerable amount of liquid (basic and acid solutions or water).

In order to dry it, the samples were left drying overnight at a room temperature as extended as possible to improve the drying procedure. Finally, the catalyst that was obtained through Ni and Mo complexes dissolved together was not split but the other one, where the Ni complex was added after subsequent treatments was split into three samples. These called treatments are the same as those used in the

wet impregnation method: calcination at 400°C during 2h, reduction with 5 bar of hydrogen at 400°C during 18h and the third one is only dried.

3.1.3 Catalyst identification

CATALYST	Treatment I	pH controlled	Succession of Ni and Mo complexes addition		Treatment II			Catalyst NAME
			1 step	2 step*	Calcined	Reduced	Dried	
1	W	x	x	-	-	-	x	Wd9
2	I	-	x	-	-	-	x	Id1
3	I	-	-	x	x	-	-	Ic
4	I	-	-	x	-	-	x	Id2
5	W	x	-	x	-	-	x	Wd10.5
6	W	x	-	x	-	x	-	Wr
7	W	x	-	x	x	-	-	Wc
8	I	-	-	x	-	x	-	Ir

**First addition with Mo complex and after treatment II, second addition with Ni complex.*

NOMENCLATURE. W: wet impregnation / I: incipient wetness / c: calcined / r: reduced / d: dried / 9: pH 9 / 10.5: pH 10.5 / 1: 1 step / 2: 2 steps

Figure 3.2: Catalyst identification according the synthesis procedure.

3.2 BET

The BET (Brunauer-Emmett-Teller) theory published by S. Brunauer, P. H. Emmet and E. Teller [25] is applied to measure the specific surface area of different materials. The basis of this theory is focused on the physical adsorption of adsorbates in gas phase on a solid surface area [26] and for this research, it was calculated focusing on the surface roughness and open pores size distribution of different catalysts used.

BET theory is based on Langmuir theory (monolayer molecular adsorption) and considering several hypothesis it is possible to calculate the surface area using the equation in *Figure 3.3*. The hypothesis are: there is inexistent interaction between adsorption layers, gas molecules can be adsorbed infinitely on a solid and Langmuir theory is individually used in every layer [25].

Therefore, this unknown surface area is determined using known size gas molecules that will condense onto that. It is possible to achieve this because every pore and irregularities of the catalyst surface area of the adsorbate will be properly covered (*Figure 3.4 .A*) but internal porous are not covered, this method is completely on the surface area of the solid (*Figure 3.4 .B*). Nitrogen e.g. could be a proper inert candidate as an adsorbate because of its availability and stability and it is also used in this study.

$$\frac{p}{v(p_o - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \frac{p}{p_o} \quad \text{where } c \text{ is } c = \exp\left(\frac{E_1 - E_L}{RT}\right)$$

Figure 3.3: Equation of BET theory and definition of c , BET constant [25].

Nomenclature: p and p_o are the equilibrium and the saturation pressure of adsorbates at determined temperature; v is the quantity of adsorbed gas; v_m is the quantity of monolayer adsorbed gas; E_1 is the necessary heat for the first layer; E_L corresponds to heat of liquefaction and it is applicable for second and following layers.

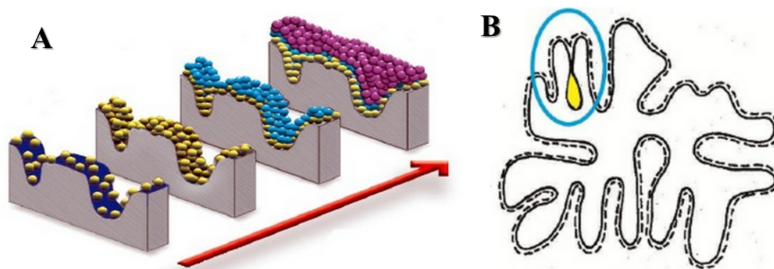


Figure 3.4: A: Progression of nitrogen adsorption on a solid surface area [27]. B: Area coloured in yellow is an internal porous that is not covered by BET method [27].

The followed procedure in order to analyse all of the catalyst surface area was a succession of previous pre-treatment to clean the samples, it was subsequently weighed and three of them connected to the BET. For the pre-treatment, SmartPrep equipment was used to dry the samples during 3h with nitrogen at 225°C. Afterwards, all the already dried catalysts were weighed and connected properly to the BET to proceed with the leak test. If the connection is not tight enough, the whole procedure needs to be repeated from the beginning. For this system that works with nitrogen, pressures around its saturation pressure are required.

3.3 TEM

TEM (Transmission electron microscopy) is a powerful and advanced microscopy technique. It consists of an assembly of lenses as shown in *Figure 3.5* crossed by a beam of electrons. This beam of electrons is transmitted through a specimen and after this interaction, the transmission is detected by a viewing screen. The image obtained is improved by an imaging device until it reaches enough resolution and enlargement as needed [28].

The thin specimen of the resulting picture is magnified and its details are then used in this research in order to analyse how molybdenum and nickel atoms are

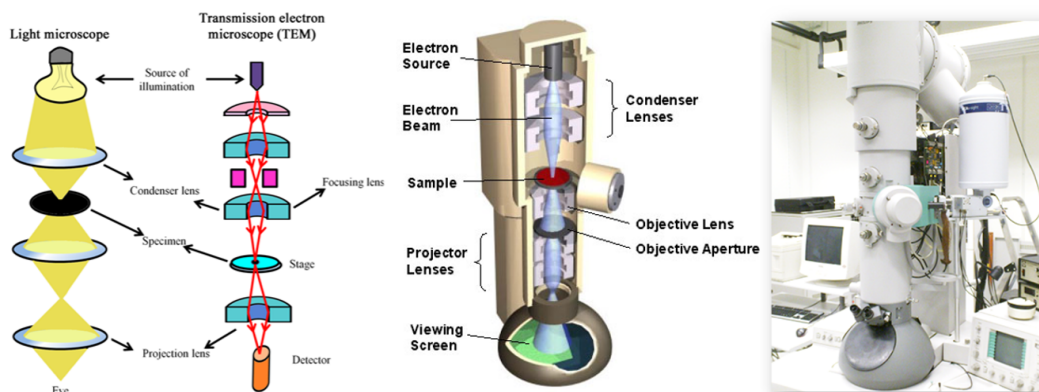


Figure 3.5: Left to right: Structure comparison between light microscope and TEM microscope [29]; Simplified disposition of lenses, sample and detector from a TEM microscope [30]; Philip CM200 [31].

distributed on alumina support. This interpretation could be difficult and confusing because a 2D image is shown of a 3D specimen so, sometimes these images could be overlapped. Nowadays, if we would like to analyse a 3D structure of a specimen, it could work due to new technology advances on TEM. For this research, Philips CM200 is used as shown in *Figure 3.5*.

TEM technique needs to have the samples carefully prepared before analysing them. It is really important to prepare the samples meticulously because an insignificant mistake could destroy the sample or create undesired shadows in TEM pictures. First step is grinding a very small amount of catalyst powder and mixing it with ethanol. Afterwards, TEM grids have to be extracted carefully from the TEM grid-storage box trying not to bend or crumple the grids. Next step is to permeate the darker side of the grids with 7 or 8 drops of the solution already prepared and finally, the grids can be analysed or saved again into their box.

3.4 Activity tests

In order to reach the goal of this research, some experiments testing catalyst activities were performed. This was achieved by carrying out activity tests in a batch reactor described below. For these tests, the reactor conditions and raw materials were always the same, only parameters around catalyst synthesis were varied and tested.

The experimental device e.g. reactor start up and taking of samples was used for the first time so an important design of experimental procedure was needed. Several previous tests were performed in order to resolve different experimental inconveniences and find the most relevant; to achieve the most safe and efficient final procedures.

3.4.1 Description of the reactor

In order to perform the experiments a batch autoclave reactor system as shown in *Figure 3.6* was used. This stirred autoclave reactor is the most common reactor utilized for heterogeneous catalytic reactions as HDO. This is due to the requirement to withstand high pressures and temperatures that are known to occur from hydrogenation reactions. Therefore this system is composed of an empty vessel (5) well tightened on the top to a base with several connections, a heater (3), a cooling water system (4), a gas bottle (1), a sample taking line (2) and a set of manometers and valves (6).

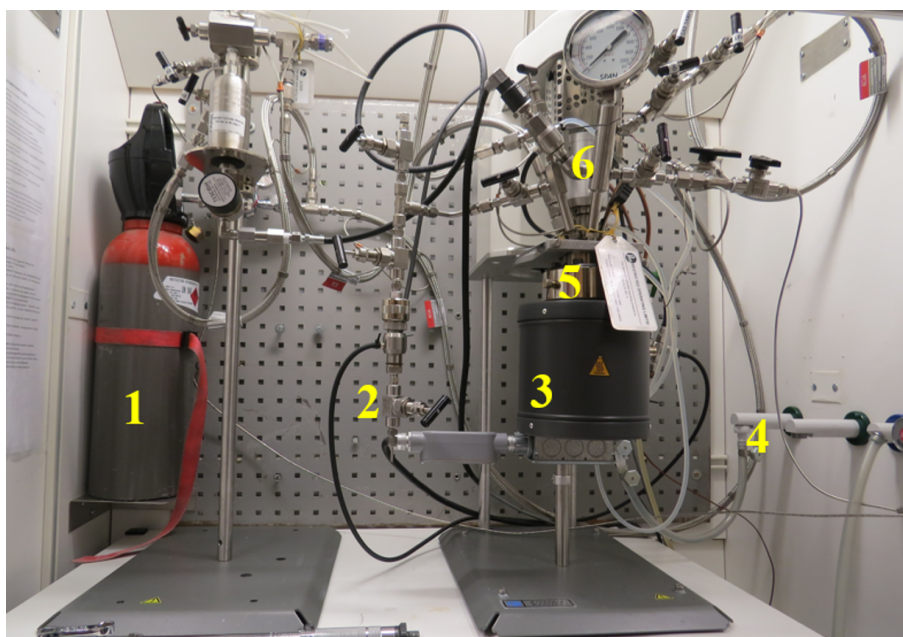


Figure 3.6: View of the autoclave reactor and experimental device.

This kind of reactor is considered to be a mini-reactor performing small-scale experiments at high pressures and temperatures. Although it is possible to achieve up to 500°C and 100 bar (not necessarily at the same time) with this 300 mL reactor, a generous safety margin was taken in order not to exceed 415°C around 40 bar.

Different fluid phases (gas and liquid) together with catalyst powder in liquid suspension were mixed inside the vessel so, for this multiphase system an effective stir is required in order to keep the reagents as well mixed as possible. Therefore this empty vessel has a stirrer formed by a propeller (4) together with a sample taking line (1), a thermometer (2) and cooling coil (3). It is possible to see the details in *Figure 3.7 .A*.

Another important block of connections is on the top of the vessel (shown in *Figure 3.7 .B*) where all the lines that charge reagents into the reactor are connected. The

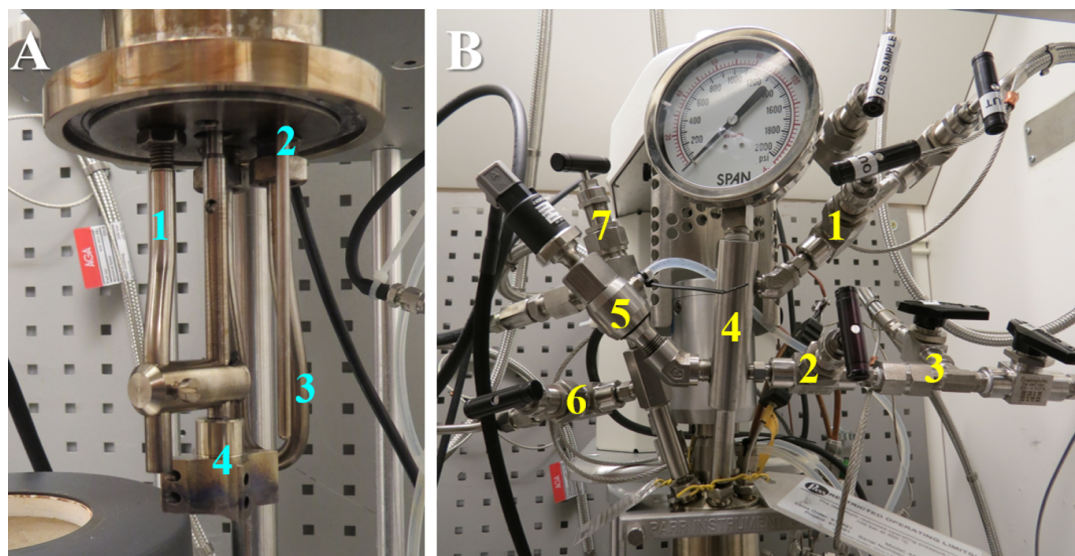


Figure 3.7: A: Instruments in the reactor. B: Connections on top of the reactor.

main lines are the outlet (1) and the inlet (2) where gases e.g. hydrogen and nitrogen are coming out from the inside of the reactor and also going in, respectively. It is possible to decide which gas we would like to introduce in the reactor using the valves in the intersection (3); the valve on the right side is to introduce nitrogen and the other valve on the top is used for hydrogen. Number (4) is a line connected directly from the inside of the reactor in contact with it atmosphere in order to control pressures so number (5), shows the bursting disk which is a safety measure, in case overpressures in this system will break and consequently reduce the pressure sending it to the exhaust gas discharge. To take samples is the valve (6) is used which connects the sample line with the bottom of the reactor (number (1) in A). Finally valve (7) connects the reactor with another part of the system not used for this research.

The sample taking line is shown in *Figure 3.8* and it is used for taking liquid samples depending on the time. At the moment of use it, the filler plug (1) and the valve (2) must be closed, otherwise an accident could occur; the reactor is working at 40 bar and 350 °C. It is essential to take the sample carefully because gases could come out and even they are in small quantities, are toxics. When we would like to proceed taking samples, all the valves will be closed so the correct opening-closing order is: valve (3), valve (4) and valve (5) but in order to push down possible stacked solids, it is recommended to open and close again valves (4) and (5) in this order.

3.4.2 Testing procedures

Several procedures needed to be modified, readjusted and tested before starting catalyst activity tests in order to define a sequence of steps case-by-case and set

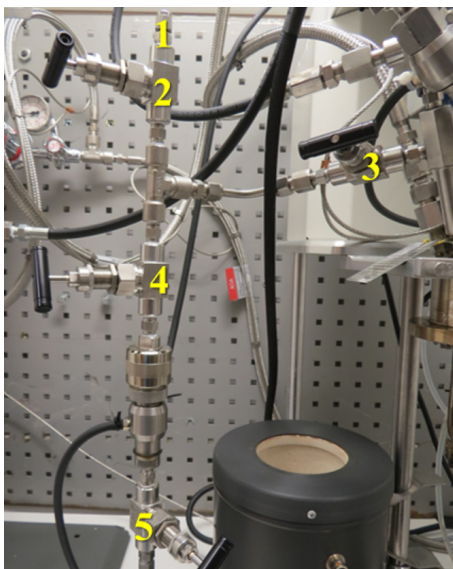


Figure 3.8: Sample taking line.

parameters, so that it is possible to test all the catalysts in the same way.

3.4.2.1 Pre-treatment

The activation of the catalyst requires a previous reduction with hydrogen at the most efficient reduction conditions. In the literature a reducing gas on oxidized catalyst precursor but for this project, the reactor is loaded with hydrogen one time so it is not a continuous flow of hydrogen. On one hand, 400°C is the temperature chosen (as shown in *Figure 2.4* in Theory section) and on the other hand, 5 bar of hydrogen are used for this catalyst reduction.

There is not already created experimental device for these reactor and chemical reaction so a sequence of steps will be developed and shown in Results section.

3.4.2.2 Start up

Reagent quantities were: 90 % wt dodecane as solvent and 10 % wt stearic acid as model compound. The catalyst amount of 0.5 g was added into the vessel as well. It is important to take in account that safety measures are the same in every procedure.

For hydrodeoxygenation reaction the working temperature and pressure are 350 °C and 40 bar respectively. It is necessary to increase first the temperature until 350 °C and when the system is stabilised (it means that the temperature is more or less constant, without relevant fluctuations), it is possible going up to 40 bar. In order to pressurize, the external hydrogen gas bottle is used and with the help of

valves, the pressure of the system can reach the desired set point. Several tests were developed with the purpose of creating a safe and an efficient sequence of steps to be followed.

When this process described in Results section finishes, several samples will be taken; the first sample is taken before to start pressurizing; the second one is taken after 30 minutes starting to count time after first sample; the third sample is after another half an hour; finally, the rest samples are taken every hour until decide to finalize the reaction.

Three more procedures need to be developed: sample taking, switch off the reactor and cleaning sample taking line. All of them are based from the experience and comparisons of similar proceedings.

3.5 Product analysis

A really complex mixture of substances is obtained as a result of the hydrodeoxygenation reaction. Therefore, in this project, the sample analysing process will be focused on identifying and quantifying the main products in order to determinate conversions, defining different scenarios for subsequent discussion and drawing conclusions.

Gas chromatography (GC) and gas chromatography - mass spectrometry (GC-MS) are the analytical techniques chosen to analyse the samples. This is because the substances that we could obtain in this experiments are sufficiently volatile, properly separated from contaminants or residues and finally, they are thermally stable enough and will not degrade at high temperatures.

3.5.1 Gas chromatography, GC

By using gas chromatography the components will be distributed into two phases: stationary and mobile phase. This distribution depends on the affinity of the components with the stationary phase thus according to this, every compound will elute depending on the time. This means that by comparing different retention times, it will be possible determining the time at which each component appears. In order to quantify the concentrations of every compound, a calibration has to be carried out because depending on the area of every appearing peak, different concentrations can be determined and consequently, to quantify them depending on the time.

In these experiments, the mobile phase was pure nitrogen as carrier gas and this carries the sample through the column. This liquid sample that needs to be analysed is 1 μL of our resulting sample already prepared to be analysed including the standard (3 μL of heptane per 0,6mL of sample).

3. Experimental

The injection is a manual process; it means that the syringe is filled manually and the injection of the sample is done manually as well. In this step, it is important to take into account a few considerations: while the syringe is filled, the sample should be warm in order to keep the sample in liquid phase (some compounds at room temperature can be in solid phase and it is an inconvenience for the equipment), it is not dissolved by any dissolvent; the injection needs to be done as fast as possible in order to avoid peak broadening or time offset and after every injection, the syringe should be cleaned with dodecane (solvent) and three times with the next sample. In *Figure 3.9 .A* it is possible to see briefly which components form the injector.

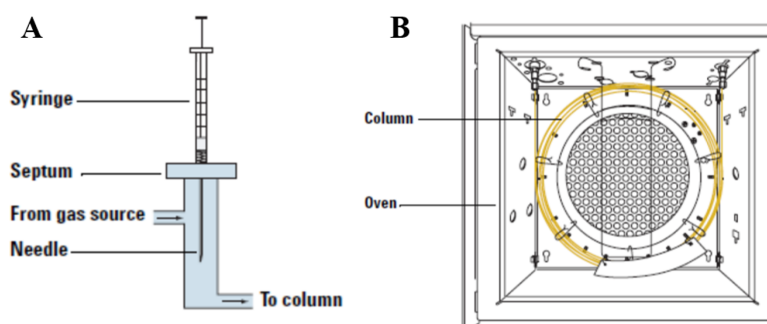


Figure 3.9: A: Parts of GC injector [32]. B: Oven and column of GC [32].

The column adjusted into the oven (shown in *Figure 3.9 .B*) is where every compound is separated at different retention times depending on the attraction between the gas phase and stationary phase. Every compound is flowing slower than the gas phase through the column and according to its attraction (property intrinsic of each compound), they will be separated in the stationary phase at different times. High efficiency will be guaranteed if the resulting peaks are narrow and separated, otherwise the results may not be reliable.

The separation of the compounds depends mainly on the column temperature. The working temperature has to be between a minimum and a maximum temperature which respectively means: lower, the compounds will change to solid phase and higher, the compounds will boil or degrade. Nearly always, temperature ramps will be programmed creating different kind of methods in order to accelerate the analysis. The method shown in *Figure 3.10* is used for this study, after several oven setting changes, the best option is to split ratio 20 and use 15 minutes for each injection dividing this time as in the temperature ramp.

The gas detector used is a photoionization detector (PID) that through ultraviolet light (UV) can ionize the gas molecules and thereby detect its concentrations. A lot of interesting information can be extracted from GC but in order to interpret it, a calibration is required. Different calibrations were performed: the first one consists of finding out in which order the compounds appear and at what retention time.

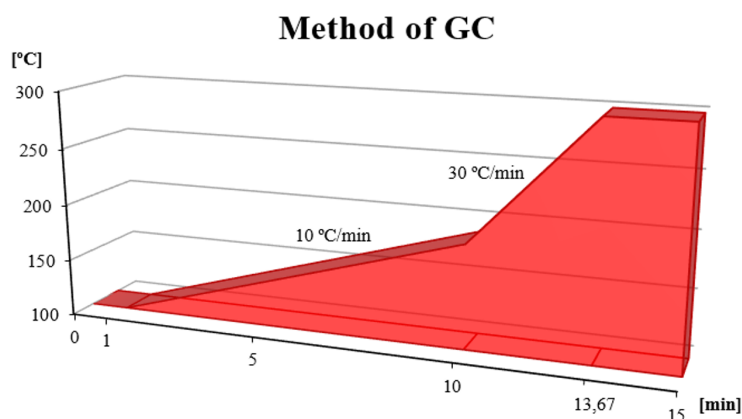


Figure 3.10: Gas chromatography method used in this project.

These tested compounds were chosen from the bibliography and deduced from the reaction mechanisms. The substances used are: dodecane (solvent), stearic acid (model compound), heptane (standard), heptadecane, 1-heptadecene, octadecane, 1-octadecene and 1-octadecanol. The second one is the ordinary calibration; from known concentrations of the compounds already identified, add heptane as standard and find several concentration values dissolving the mixture with more dodecane (solvent) thus, the concentration of all the substances will be quantified.

3.5.2 Gas chromatography - mass spectrometry, GC-MS

An important amount of unknown substances were obtained during the first experiments and that led to the use of another more powerful analytical technique: gas chromatography - mass spectrometry (GC-MS). This technique will be useful in order to identify new and unknown compounds.

This method uses a gas chromatographer and a mass spectrometer together and this combination allows an identification much more powerful than if both methods were working separately. The gas chromatographer works as the GC method described above and the mass spectrometer breaks every molecule ionising them and using mass-to-charge ratio.

Unlike GC, for GC-MS all the samples need to be properly dissolved in order to avoid huge peaks and assure the liquid phase for the samples. The solvent that could dissolve the samples at room temperature is dicloromethane (DCM).

4

Results and discussion

4.1 Method development

4.1.1 Pre-treatment

A sequence of steps needs to be followed during pre-treatment start-ups and switching off. The following flow charts show how to proceed:

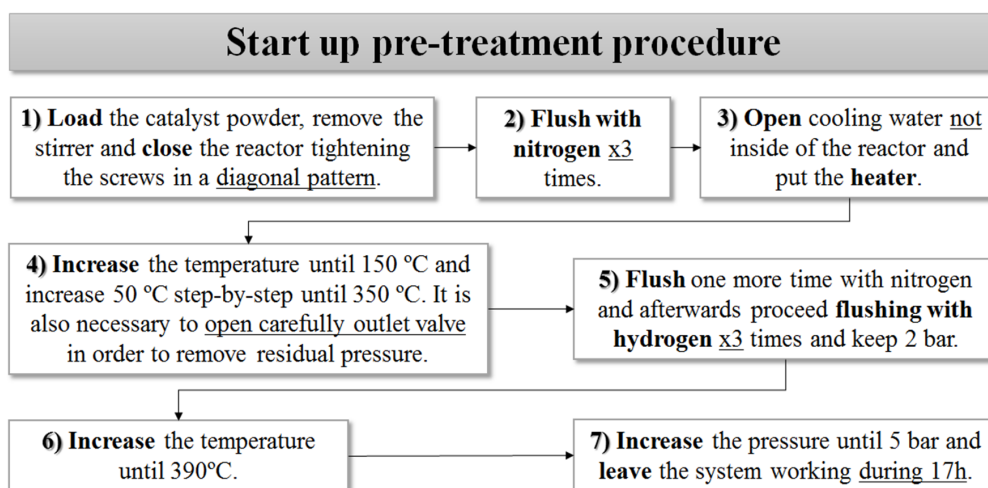


Figure 4.1: Flow chart to start the reactor up for the pre-treatment.

These flow charts are made according to previous test experiments and some steps have been decided according to these experiments. Reviewing the start-up procedure: 1) it is important to tighten the bolts in a diagonal pattern to ensure a proper fit; 2) it is flushed with nitrogen 3 times to guarantee that the atmosphere inside the reactor is inert; 3) the cooling water has to be open during the whole procedure because it is used to cool some parts of the system as well as inside the reactor when it is needed; 4) The reactor is not designed for gas phase use. Therefore, temperature control is difficult so it is necessary to increase the temperature step-by-step until it is stable enough and meanwhile, residual gases formed by the decomposition of the metal precursors coming out can be removed by opening the outlet valve; 5)

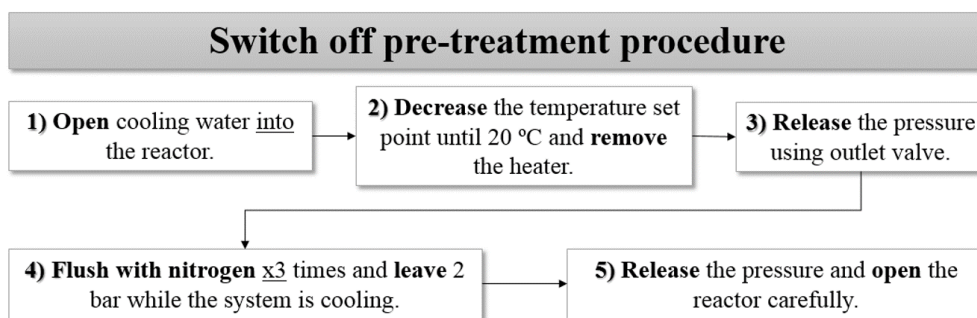


Figure 4.2: Flow chart to switch the reactor off for the pre-treatment.

it is at this point of the procedure more needs to be taken because the temperature can start fluctuating again; 6) this reaction was previously carried out at 400°C but the set point has to be 390 °C because of the instability of this reaction and it is not recommended to activate the high limit temperature button which completely disables the heater as a safety measure at 410 °C; 7) finally, it is possible to reach 5 bar of hydrogen and leave it overnight. The start-up procedure until arrive to 5 bar of hydrogen takes approximately 2 hours.

Now reviewing the switch off procedure: 1) in order to decrease the temperature as fast as possible, cooling water should circulate inside the reactor through cooling coil; 2) another step to refrigerate rapidly the system is by changing the heater settings and removing the heater because the heater wall is much thicker so it is an efficient heat maintainer; 3) and 4) release the hydrogen and keep an inert atmosphere; 5) while the reactor is cooling it is important to leave 2 bar of nitrogen because decreasing temperatures involve decreasing pressures as well.

4.1.2 Start up

This procedure is different than the pre-treatment start-up; more instruments are built into the reactor and extra accessories are used improving the experimental conditions.

When the reagents are already loaded, to enhance contact between different phases, it is important to mix all of them as good as possible together with hydrogen. In order to guarantee a proper mixture, a stirrer with propeller is used and a baffle that, while the stirrer is rotating, creates a turbulence thus it increases the interaction between all the compounds. The following steps different than the pre-treatment procedure are going up temperature and pressurizing in this specific order. The reason to increase first the temperature and then the pressure is because while the temperature is increasing (keeping a constant volume), the pressure is increasing as well due to the vapour pressure of the solvent. For this reaction, the pressure reaches around 10 bar while the temperature is going up to 350 °C so, during the pressurizing procedure it is possible to start at 15 bar.

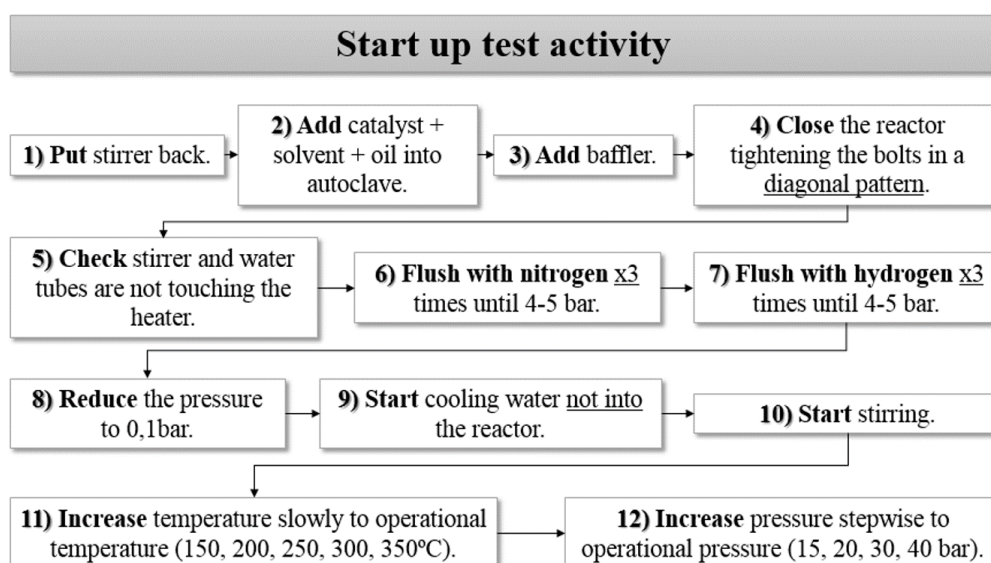


Figure 4.3: Flow chart to start the reactor up.

4.1.3 Sample taking

To take samples there is not an experimental device already designed so a sequence of steps is created according to the timing of this project. After several attempts, the best procedure is shown in the flow chart below.

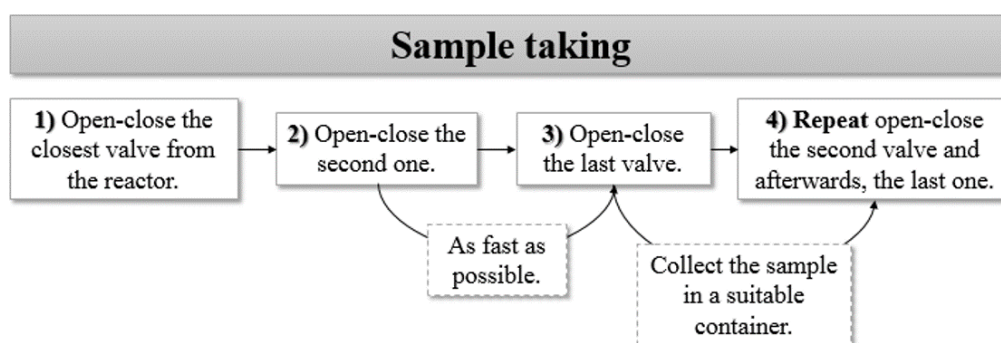


Figure 4.4: Flow chart to take samples during every experiment.

In this flow chart additional notes are highlighted because first of all, it is really important to take samples as fast as possible. The substances that could appear in this project change quickly from liquid phase to solid phase so, the timing while opening-closing the valves should be fast to avoid the possibility of stack formations and it is also relevant to do step 4 in order to obtain enough amount of sample.

Last but not least, a suitable container will be necessary to collect the sample and analyse it efficiently afterwards.

It is recommended to take sample following this procedure two times in a row. The first time will be used to purge remnants of the previous sample (the sample should throw it away in a proper waste container) and the second one will be analysed.

4.1.4 Switch off

After taking all the required samples, the reactor needs to be switched off properly. Reviewing the procedure several considerations should be taken into account. The first step is refrigerating the reactor slowly at the beginning because it is interesting to decrease the temperature until 200 °C and indispensably above 180 °C; the reason for this crucial step is not to form nickel carbonyl ($\text{Ni}(\text{CO})_4$), one of the most toxic substances found in the industry. This reaction between nickel from the catalyst and carbon monoxide as a secondary product from the decarbonylation reaction arises around 130 °C and at 180 °C a thermal decomposition starts. Consequently, the resulting gases will be evacuated from the reactor around 200 °C. The temperature is chosen as cold as possible but higher than 180 °C to have as low vapour pressure as possible from the products and loose as little as possible.

Continuing with the switch off procedure, after flushing three times with nitrogen to remove all formed CO, it is important to keep 3 bar of nitrogen more or less because while the temperature is decreasing, the pressure is also decreasing and pressures near vacuum can be problematic. Proceeding to step 7, the stirrer is still working to allow for a good heat transfer and to cool the system as fast as possible.

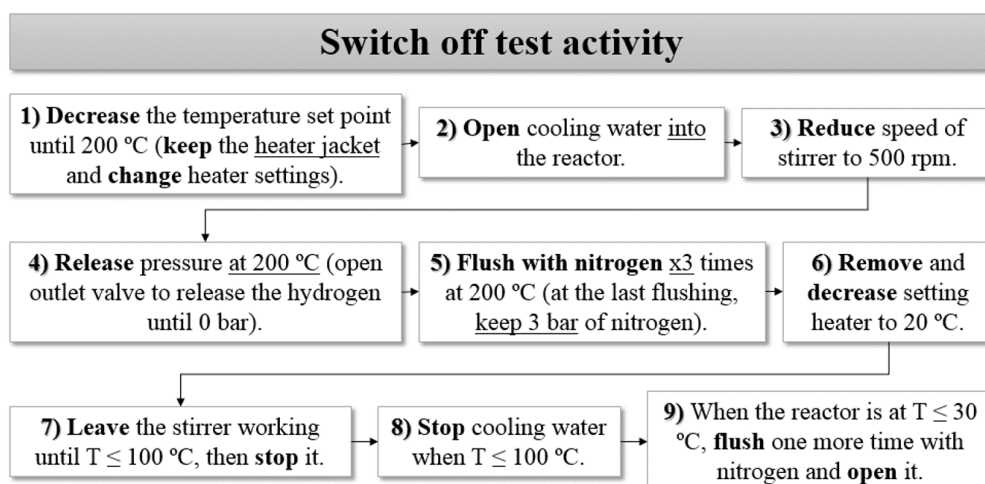


Figure 4.5: Flow chart to switch the reactor off after every experiment.

After leaving the reactor to cool, another nitrogen flushing is recommended to ensure

that no toxic gas comes out and they are already directed to exhaust gas discharge. Finally, after opening the reactor, the whole system should be cleaned properly. For the reactor and all the instruments that have been in contact with chemicals, soap and water is used for the first cleaning and ethanol is used for the second one. Ethanol can help mainly to clean difficult parts of the propeller and dry it quickly. It is also important in order to avoid future problems with material oxidation.

4.1.5 Cleaning procedure

After cleaning the reactor, it is also necessary to clean the sample taking line because otherwise, future experiments results could be affected for residual products from the last experiment. Ethanol is the polar cleaning solvent used to dissolute possible stack formations and heptane is the non-polar solvent. Both substances are used because of their availability and adaptability to the process; heptane is used as standard to analyse the results in the gas chromatograph.

The detailed procedure shown in this flow chart is the most efficient cleaning process used while doing this project but it still seems not to be the most appropriate, because not all the solids stacked in this line can be perfectly removed.

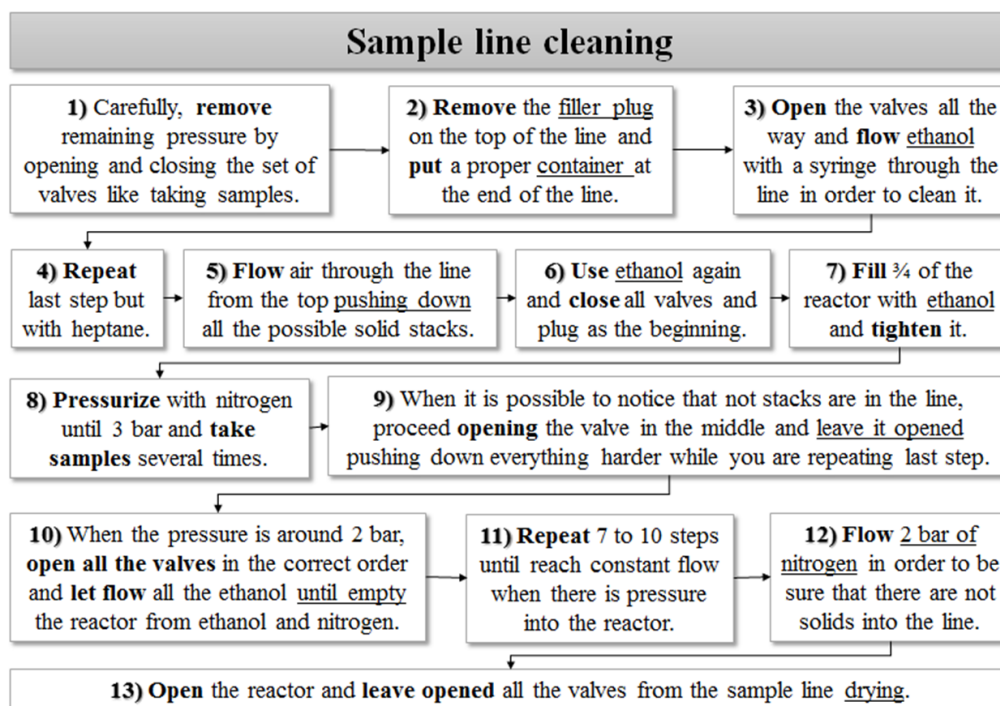


Figure 4.6: Flow chart to clean the reactor and sample taking line off after every experiment.

4.2 Sample preparation

The resulting samples are not ready to be directly analysed. All of them are divided into two phases: liquid and solid. These samples will be analysed by gas chromatography so, all the solid products as catalyst and coke formations should be removed.

The samples are collected directly in centrifuge tubes because the first step is to warm up slightly the sample with warm water and centrifuge the samples at 1500 rpm during 3 minutes. After repeating this process twice, the liquid part is separated from the solid part while the sample is still warm.

These samples need to be filtered by a syringe with a thick filter at the end. From the resulting liquid sample, 0.6 mL is split and mixed with 3 μL of heptane as standard. This mixture will be analysed by the gas chromatograph.

The procedure with the gas chromatograph is based on a few simple steps. First of all, cleaning several times the syringe with dodecane and with the sample to analyse. Secondly, it is important to keep the samples warm and the syringe as well because otherwise, the compounds could change quickly to solid phase creating thus an obstruction in the thin syringe. Finally, the last step is to introduce the syringe into the septum and start the injection as fast as possible.

In contrast to the GC, with GC-MS it is required to dissolve the sample with a suitable solvent that helps keeping the sample in liquid phase and less concentrated. In order to dissolve the samples, different solvents were tested and the most successful is DCM.

4.3 BET

Due to the adsorption of nitrogen on the catalyst surface, it was possible to determine the surface area of all of synthesized catalysts. For this kind of non-structured mesoporous solid, the experimental isotherm of adsorption-desorption of nitrogen obtained is shown in *Figure 4.7 .A*. Compared with different types of adsorption-desorption functions, it is viable to find similarities between experimental and theoretical curves and finally, the best adjustment corresponds to type IV *Figure 4.7 .B*. Although the different slopes, looking more closely and starting the comparisons in point A, it is possible to follow a tendency: at starting point A with low relative pressures, the pathway ABC shows the beginning of the isotherm type IV shared with type II; secondly, following CDE the function presents a noticeable ascendant change in the slope; when the pressures are near to saturation (EFG), this slope decreases; finally, at FGH the function is stabilized.

The isotherms type IV are characteristic of mesoporous solids and this means that

while the isotherm is increasing, an adsorption of multi-layers is produced on the solid surface. Another characteristic property is the formation of a hysteresis loop. This is the explanation for non-identical adsorption-desorption curves; the condensation of the adsorbate in capillaries is irregular and consequently the desorption curve is different than the adsorption curve.

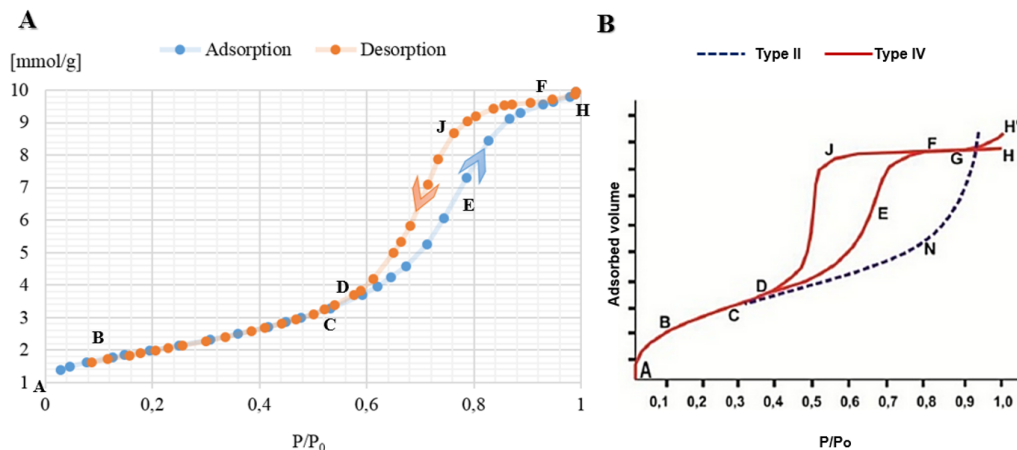


Figure 4.7: A: Experimental adsorption-desorption isotherms of nitrogen on catalyst surface area. B: Theoretical adsorption-desorption isotherms of nitrogen type IV [27].

Moreover, the most interesting information to be obtained from BET analysis for this project is the surface area of all the samples *Figure 4.8*. A varied range of results according to different catalyst synthesis is exposed. The smallest surface area ($152.3 \text{ m}^2/\text{g}$) is for *Wr* catalyst and consequently it should have the worst activity, yet *Ik* catalyst is following it closely ($153.4 \text{ m}^2/\text{g}$). On the opposite side, the biggest surface area ($168.2 \text{ m}^2/\text{g}$) is *Id1* catalyst so, considering only BET results and comparing them with the other catalysts, it may expect the best catalyst activity because of the high available area to react. The next biggest surface area ($162.7 \text{ m}^2/\text{g}$ *Id2* catalyst) is closer to the average ($160 \text{ m}^2/\text{g}$) than *Id1*, therefore the highest surface areas are between 168.2 and $160 \text{ m}^2/\text{g}$. Finally, the rest of the catalysts (*Wd9*, *Wd10.5*, *Wc* and *Ir*) have approximately the same surface area: $160 \text{ m}^2/\text{g}$. As expected the surface area is smaller than that of pure alumina ($197 \text{ m}^2/\text{g}$) because during the synthesis of the catalyst, the metallic particles may be positioned such that they clog some of the alumina pores and consequently the total surface area decreases.

Even with the notable differences between these catalysts, there is not a clear conclusion referring to catalyst synthesis that can be drawn so far. Catalyst *Ik* and *Wr* have the lowest surface areas but their synthesis is completely different: the first one is an impregnation wetness without control of pH where Mo and Ni are added in two steps and finally calcined; the second catalyst is a wet impregnation adjusting the pH until 7.5 for addition of Mo and 10.5 for addition of Ni in two separate steps

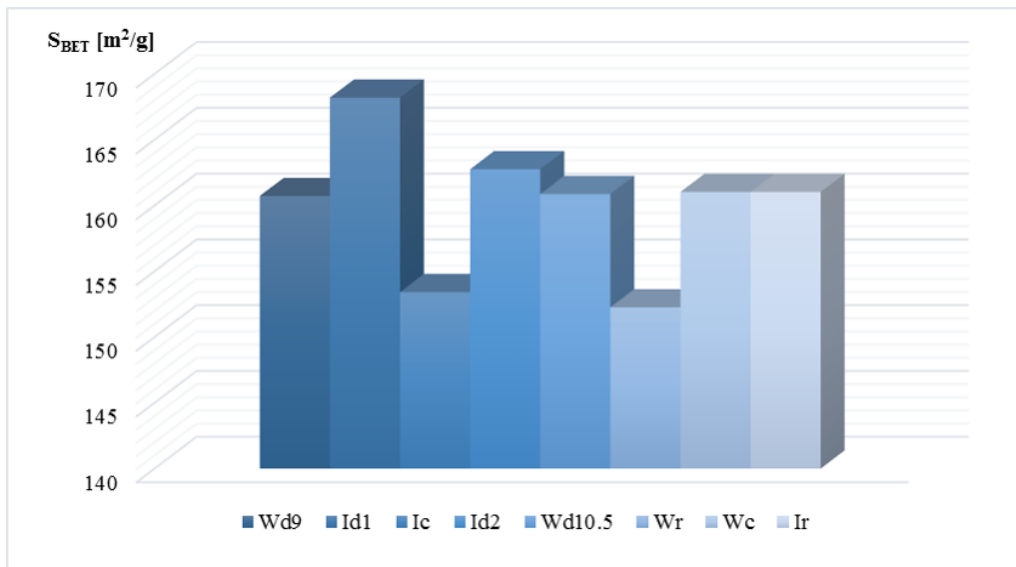


Figure 4.8: Surface areas of every catalyst calculated by BET method.

and a reduction process between. Moreover, on the opposite side the *Id1* catalyst with the highest surface area, the synthesis procedure has no similarities with them, the only difference with the second highest is that for *Id1* synthesis Mo and Ni were added in one step and for *Id2* in two steps. The rest of the process is the same: impregnation wetness without pH adjustment and dried at room temperature.

After all these discussions it would seem that incipient wetness (excluding incipient wetness followed by calcination, *Ic*) is slightly more convenient than wet impregnation but more data is needed before a final conclusion.

4.4 TEM

Some catalysts were analysed by TEM technique and after different attempts of rotating the sample and improving the resolution of the images, the pictures shown in *Figure 4.9* and *4.10* were achieved. These type of images with a dark background and bright zones are called Dark Field TEM so it is useful to recognize how crystalline particles are distributed in amorphous materials. In this project, it is interesting to examine the size of these particles.

Giving a general glance to the photographs, it is not possible to recognise a clearly defined structure so the interpretation of them cannot be completely accurate, but the same criteria will be followed. On the one hand, the light grey disperse particles that usually occupy a large area are identified as alumina particles and on the other hand, the densest bright particles with defined straight edges are identified as metallic particles.

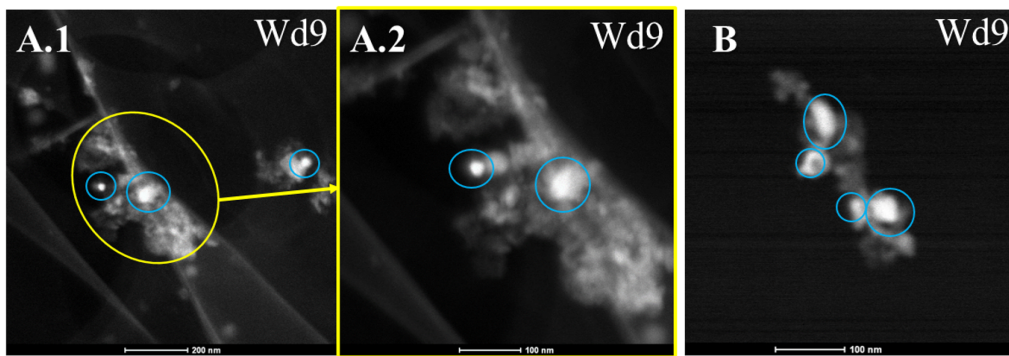


Figure 4.9: TEM images for *Wd9* catalyst. Resolution: A.1 (200 nm), A.2 (100 nm) and B (100 nm).

In *Figures 4.9 A.1., A.2. and B.*, the *Wd9* catalyst is shown. In these images it is possible to identify several points (blue circles) where the bright areas are quite dense so all of them could be metallic particles.

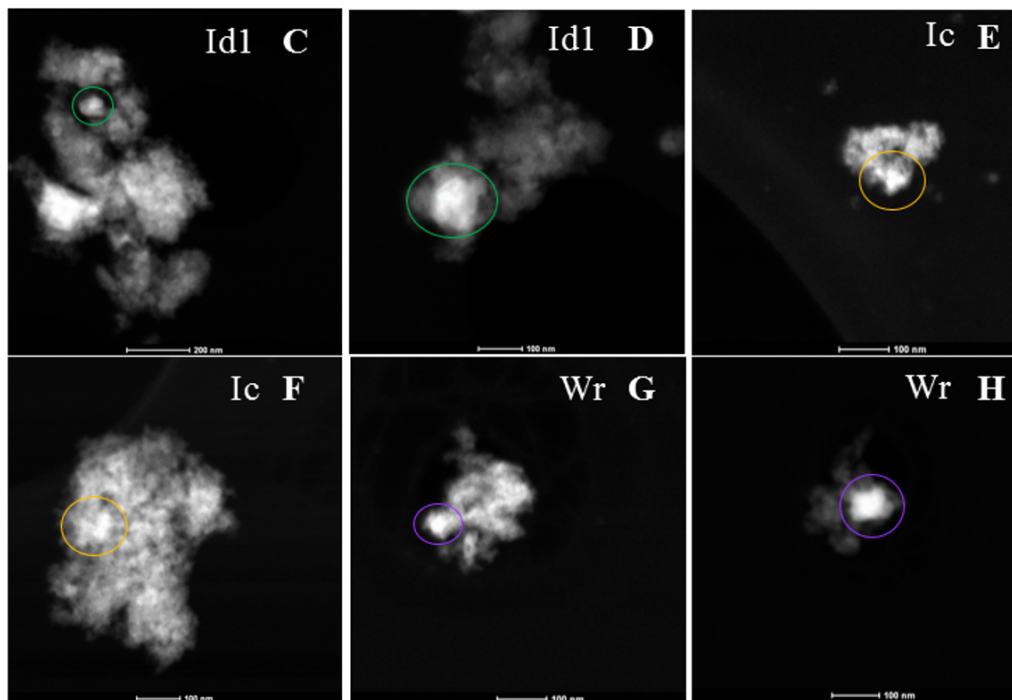


Figure 4.10: TEM images for *Id1* (C,D), *Ic* (E,F) and *Wr* (G,H) catalysts. Resolution: C (200 nm) and D, E, F, G, H (100 nm).

Continuing with the following *Figure 4.10*, catalysts *Id1* (C,D), *Ic* (E,F) and *Wr* (G,H) are exposed and compared with *Figure 4.9*, less defined particles have been achieved. For *Id1* catalyst is very hard to identify the particles, because they are probably all highly dispersed, although the orange circles could be some particles. The next one, *Ic* catalyst is similar as the previous case and in picture F, instead

of a particle, it could be an agglomeration of alumina powder. Finally, with *Wr* catalyst a clearer particle identification can be carried out. Both images (G, H) are taken in high magnification (100 nm) and in spite of the small sample areas, proper defined particles can be recognized between 50 and 100 nm.

In addition, comparing all the catalysts characterized by TEM technique, it can be said that a larger number of metallic particles on alumina support is more clearly identified in *Wd9* and *Wr* catalysts than in the other ones. Moreover, for a less ambiguous interpretation of the results an instrument with a higher resolution or more experience with interpretation of TEM images is needed. Some steps from the preparation of these samples can interfere during the interpretation of these images: if the sample mixed with ethanol is not impregnated enough on TEM grid, it is difficult or even impossible to find relevant particles in the images and last but not least, another consideration to take in account is the identified particles in these pictures could be an agglomeration of alumina powder seen from the wrong angle and it could seem a particle, different compound densities can create confusions so, different interpretation criteria have been considered.

Finally, comparing BET and TEM results, on one hand it is possible to differentiate how the *Id1* catalyst with the highest surface area in the TEM pictures has not clearly shown defined particles and *Ic* catalyst with the second lowest surface area shows a similar result; a non-clearly distribution and identification of particles. On the other hand, *Wr* catalyst that presents the lowest surface area, shows several isolated dense bright areas and this could mean that there are well defined metallic particles. Another possibility could be that these considered areas are an agglomeration of alumina powder seen from another angle but, taking into account the satisfactory surface definition, the odds are low for this last situation.

4.5 Activity tests

4.5.1 Calibration and compounds identification

The first step in order to quantify the concentration of the products is according to the GC method is to find out in which order the possible products appear. In *Figure 4.11* the order of all the expected products and reagents is determined: 1) heptane (standard), 2) dodecane impurities, 3) dodecane (solvent), 4) dodecane impurities, 5) 1-heptadecene, 6) heptadecane, 7) 1-octadecene, 8) octadecane, 9) 1-octadecanol, 10) stearic acid and 11) oleic acid.

Thereupon, a calibration is performed to find out different concentration points by using as standard 3 μL heptane. The results are shown in *Figure A.1* where it is possible to observe several calculations of reliable regression lines with a respective equation for each compound. Starting at the intercept, almost all of them were

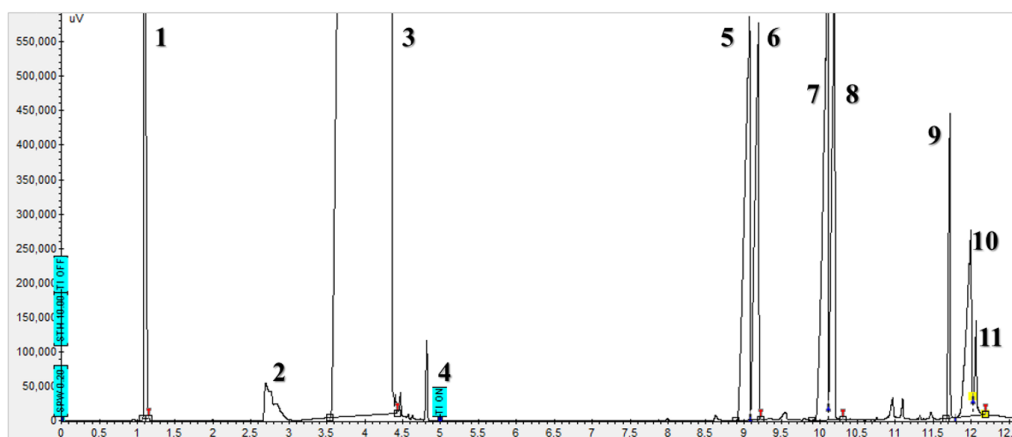


Figure 4.11: Identification of the expected products for HDO and decarboxylation reactions. 1) heptane, 2) dodecane impurities, 3) dodecane, 4) dodecane impurities, 5) 1-heptadecene, 6) heptadecane, 7) 1-octadecene, 8) octadecane, 9) 1-octadecanol, 10) stearic acid and 11) oleic acid.

obtained correlation factors between 0.99 and 1. The only compound that is not within this range is stearic acid. It could be explained because of its melting point which is around 69 °C and consequently it causes difficulties at the time of handle. This is solved by warming up cautiously the mixture but even so, the best resulting correlation factor is 0.79.

4.5.2 Conversions and quantification of the expected products

4.5.2.1 Stearic acid conversion

It has not been possible to reliably determine the conversion of stearic acid with the applied methods. Stearic acid is a compound difficult to analyse because its melting point is quite high, around 69 °C thus at room temperature its appearance is solid. This property impacts directly on the sample taking procedure; during this process an obstruction of solids is easily formed in the tube used for taking the sample and this can contaminate future samples and, thus, vary significantly the results of the concerned sample. Therefore, the obstruction of solids has a strong impact on the results hindering us to determine the conversion of stearic acid.

In *Figure A.2* it is possible to see how these difficulties can affect to the conversion. In order to see how the conversions are strongly varied, for example, in the last two points of experiment 5, the conversion arrives at 90% but it suddenly decreases until 40%. It can mean that for the penultimate sample, a solid obstruction was formed appearing that less amount of stearic acid than should be in this sample and for the last sample, these solids could be des obstructed obtaining more stearic acid than

should be obtained for the last sample.

4.5.2.2 Experiments

1. Experiment 3 (*Wd9*)

1-octadecene (0.4%) is the main product in experiment 3 and it is closely followed by heptadecane, octadecane and 1-octadecanol (*Figure 4.12*).

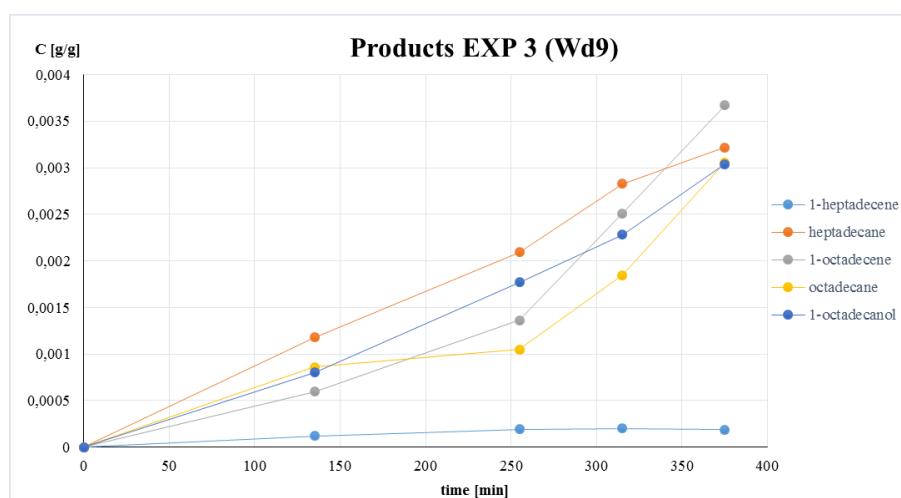


Figure 4.12: Products from the reaction performed with *Wd9* catalyst.

If these results are compared with the proposed mechanisms, catalyst *Wd9* seems to favour a hydrodeoxygenation pathway (*Figure 4.13*), as the first step. Specifically, after the reduction of stearic acid to 1-octadecanol two cases are possible but according to the concentration of these products, dehydration of 1-octadecanol to 1-octadecanal with following decarbonylation to heptane is majoritarian more frequent than dehydrogenation of 1-octadecanol to 1-octadecene and hydrogenation to octadecane. Therefore, all products showing relevant concentrations are explained by this mechanism because even if 1-octadecene is the most relevant and the other reactions are not totally completed, the rest of the products can still be formed.

Several new compounds have appeared in this reaction GC analysis and according to the proposed mechanism, 1-octadecanal could be one of them.

2. Experiment 4 (*Id1*)

The interpretation of experiment 4, where catalyst *Id1* is used (*Figure 4.14*), is analogous to experiment 3 with the difference that in this case, higher total

carried out until 180 min. Despite this variation in experimental development, it is possible to observe a similar tendency with previous experiments 3 and 4 where dehydrogenation pathway is enhanced.

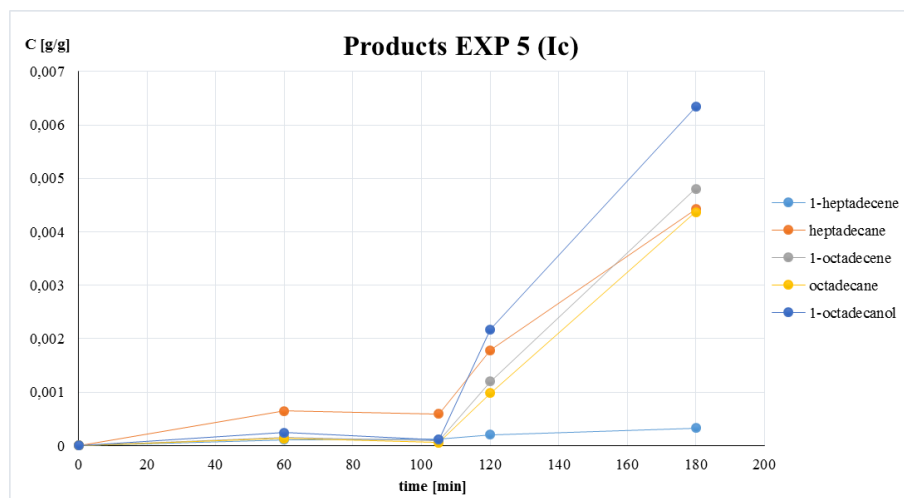


Figure 4.15: Products from the reaction performed with *Ic* catalyst.

Such as experiment 3, *Ic* catalyst promotes the formation of 1-octadecanol in the first place and followed by 1-octadecene, heptadecane and octadecane showing nearly identical concentrations. The highest concentration achieved by 1-octadecanol is 0.6% and in the chart it seems that the chemical reaction starts to show activity around 120 min, before this time the activity is quite weak. The mechanism is properly explained in *Figure 4.13* and in this case, the first reduction of stearic acid to 1-octadecanol takes more weight than the following succession of reactions. If the experimental time had been longer, maybe other reaction products could appear afterwards because of the intermediate concentration behaviours which are increasing more than final products such as octadecane and heptadecane. According to the observed products, dehydration is more favourable than dehydrogenation.

4. Experiment 6 (*Id2*)

This is the first experiment where the results (*Figure 4.16*) are quite different than the previous ones. For experiment 6, where catalyst *Id2* is used, 0.6% of heptadecane is obtained as dominant compound. This means that a different mechanism needs to be proposed as an explanation to these results so, the mechanism in *Figure 4.17* is used in order to interpret the heptadecane formation.

Decarboxylation pathway is one of the most probable explanation for heptadecane formation as principal product. Decarbonylation pathway has not

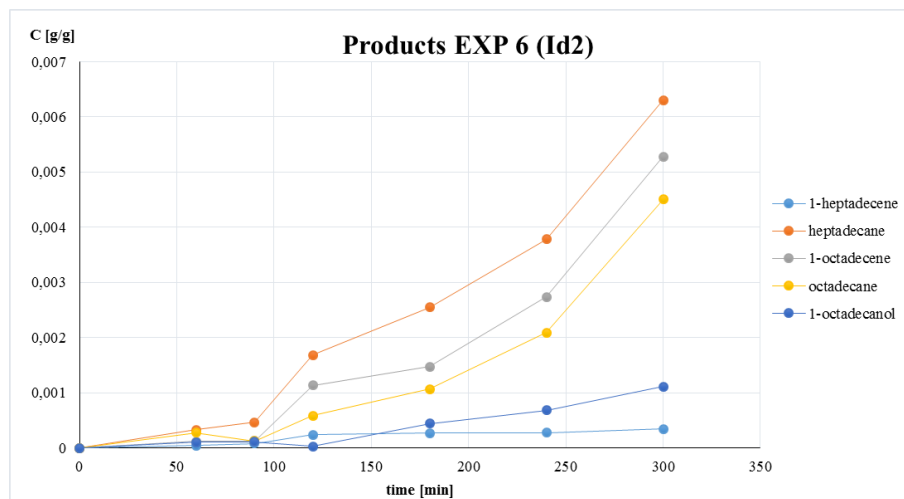


Figure 4.16: Products from the reaction performed with *Id2* catalyst.

been chosen as a convincing solution because there is not a significant 1-heptadecene formation. Even so, both reactions may occur simultaneously. Moreover, mechanisms from *Figure 4.13* could occur in the background as well and, consequently, the 0.5% of 1-octadecene and 0.45% of octadecane could be explained.

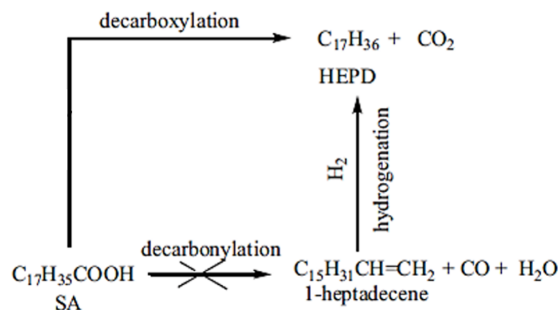


Figure 4.17: Mechanism of decarboxylation and decarbonylation of stearic acid [9].

5. Experiment 7 (*Wd10.5*)

Several similarities have been observed between experiment 6 and 7 (*Figure 4.18*) The main products are the same and the tendency of all of them is almost identical. One of the most important differences is after 250 min when the concentrations of experiment 7 seem to start stabilising. In experiment 6, concentrations keep increasing after 250 min. The other difference is quantifying products; the highest concentration of heptadecane is less than 0.6

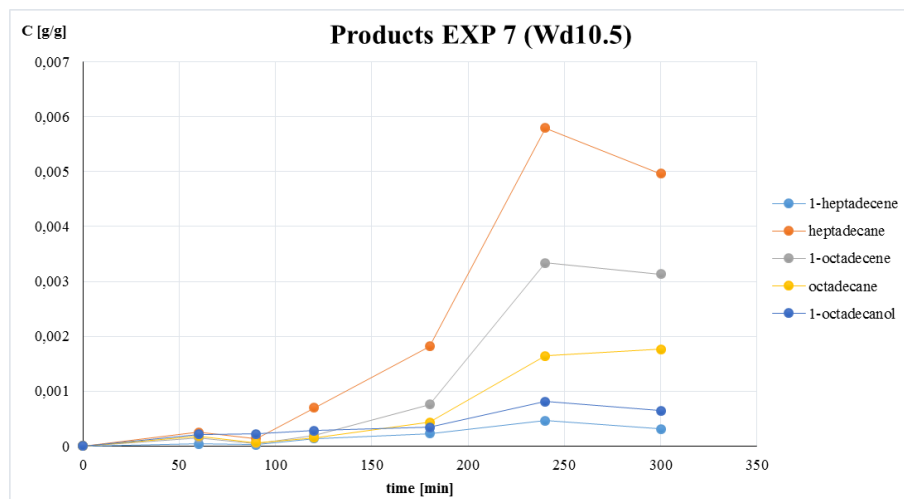


Figure 4.18: Products from the reaction performed with $Wd10.5$ catalyst.

6. Experiment 8 (Wr)

Decarboxylation reaction is enhanced in experiment 8. It is concluded that because heptadecane is the most abundant product (concentration of 1.1%) and despite the two possible pathways to achieve this product, there is not a high concentration of 1-octadecanol which is the intermediate that makes way to dehydrogenation and decarbonylation one after the other (mechanism shown in *Figure 4.13*). In addition, heptadecane starts its formation before 1-octadecanol, therefore it is possible to appreciate a pronounced slope at the beginning of the experiment (*Figure 4.19*) even before hydrogen pressurization (40 bar of hydrogen achieved at 60 min).

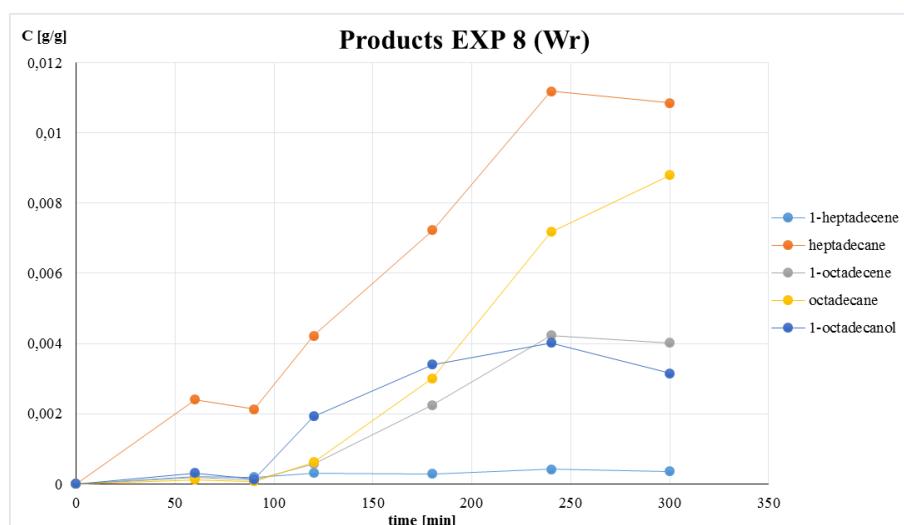


Figure 4.19: Products from the reaction performed with Wr catalyst.

Sticking to the original project goals, this catalyst may be one of the best because, the main compounds that want to be obtained at higher concentrations are heptadecane (1.1%) and octadecane (0.9%). Although, as long hydrocarbon chains as possible would like to be achieved in this project and even if heptadecane has one carbon less, both concentrations will be considered as successful results.

At the end of the experiment (after 250 min), it seems to show how 1-octadecanol is decreasing at the same time as octadecane is notably increasing. This may reinforce the theory that octadecane is produced by following orderly this succession: stearic acid reduction, dehydration of 1-octadecanol and hydrogenation of 1-octadecene.

7. Experiment 9 (*Wc*)

Catalyst *Wc* has enhanced the decarboxylation pathway more than dehydroxygenation but it is possible that both occur simultaneously as discussed in experiment 8. In contrast with experiment 8, 1-octadecene achieves the same concentration as octadecane around 0.58% and heptadecane concentration for experiment 9 is 0.8%, less that the 1.1% in experiment 8.

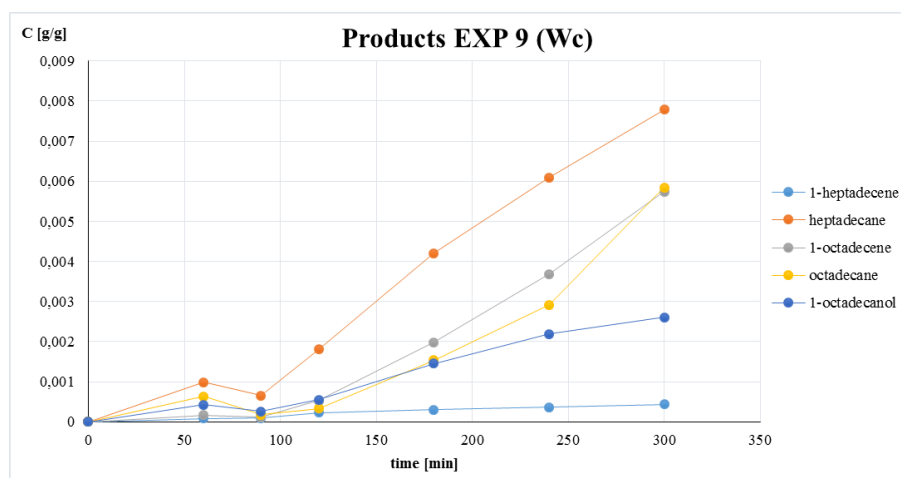


Figure 4.20: Products from the reaction performed with *Wc* catalyst.

4.5.2.3 Summary of expected products obtained

Figure 4.21 is the final summary of the activity tests where the most relevant information is included. New unexpected products are not included and 1-hepadecene neither. 1-heptadecene is not a major product and if it appears in these results it

is because several chemical reactions are occurring simultaneously e. g. decarboxylation, which is the reason for 1-heptadecene formation but for all experiments, the concentration was really low compared with the other products.

EXP	CAT	Saturated products		Intermediates			C ₁₇ /C ₁₈ ratio
		heptadecane	octadecane	1-octadecene	1-octadecanol	1-heptadecene	
3	Wd9	0.32%	0.31%	0.37%	0.30%	0.02%	0.5
4	Id1	0.62%	0.70%	1.14%	0.32%	0.04%	0.35
5	Ic	0.44%	0.45%	0.48%	0.63%	0.03%	0.51
6	Id2	0.63%	0.45%	0.53%	0.11%	0.03%	0.67
7	Wd10.5	0.58%	0.18%	0.33%	0.08%	0.05%	1.23
8	Wr	1.11%	0.88%	0.42%	0.40%	0.04%	0.88
9	Wc	0.78%	0.59%	0.57%	0.26%	0.04%	0.71

**It is considered C₁₇: heptadecane and 1-heptadecene and C₁₈: octadecane and 1-octadecene.*

Figure 4.21: Summary of the activity tests.

Heptadecane is the main product for experiments 6-9 and consequently it means that this mechanism is strongly involved with decarboxylation and decarbonylation. Hydrodeoxygenation and decarboxylation are probably reacting at the same time in all of them; for experiments 8 and 9, where heptadecane concentrations are the highest: 1.11% and 0.78% respectively, octadecane is the second main product so, at least for these, HDO pathway has an important role, too.

For almost all of these experiments (7 to 9), 2 step wet impregnation is used as catalyst preparation method at a pH of 7.5 for Mo and a pH of 10.5 for Ni. The highest concentrations of heptadecane and octadecane are achieved with the catalyst Wr that it is prepared by wet impregnation at a pH of 7.5 and 10.5 adding Mo and Ni complexes in two steps, respectively and drying it by sublimation, it was reduced at 400 °C and 5 bar of hydrogen between Mo and Ni additions. These results show that this preparation method, enhances the formation of desired saturated hydrocarbons regarding other product formation possibilities.

The catalysts of this group of experiments (7 to 9) are all prepared by wet impregnation with 2 steps. For all these catalyst the formation of heptadecane is favoured thus, decarboxylation becomes increasingly important. Now including in this group experiment 6, even the values of concentrations are quite different, it is possible to identify the same order of main products from the highest concentration to the lowest: heptadecane, octadecane, 1-octadecene, 1-octadecanol and 1-heptadecene. An explanation that could fit in this group of mechanisms is: decarboxylation is the main pathway but closely followed by the hydrodeoxygenation pathway where the intermediates can finish the reaction until the unsaturated hydrocarbon or can stop in secondary or intermediate reactions. When the 1-octadecene concentration

is quite high, it could mean that after stearic acid reduction to 1-octadecanol and dehydration to 1-octadecene, the sequence of reaction stops or proceeds slowly.

Contrasting the group of experiments 3 to 5 with the last group, the selectivity is worst regarding saturated hydrocarbons. For this group the main products are intermediates: 1-octadecanol for experiment 5 and 1-octadecene for experiments 3 and 4. Especially for experiment 4 where the highest product concentration of all activity test has been achieved, 1-octadecene is the main product so it is possible that the reaction stops at the dehydration step instead of continuing until the end by hydrogenation pathway.

Another important intermediate product was found in experiment 5; the main product for catalyst Ic is 1-octadecanol. It is explained by stearic acid reduction, the first step of HDO in order to produce hydrocarbons such as octadecane and heptadecane. The evolution of 1-octadecanol as an intermediate is well represented in experiment 8 *Figure 4.19* where the 1-octadecanol curve has the shape of an intermediate; increasing at the beginning and decreasing at the end while derived products of this intermediate appear. Finally, comparing both experiments, it is conceivable that if the duration of experiment 5 had been longer, this intermediate behaviour could be shown too.

Regarding C_{17}/C_{18} ratio, it shows that on the one hand, wet impregnation method enhances the formation of C_{17} because its ratios are the highest between 0.7 and 1.2 so consequently, as higher the ratio, the more the formation of C_{17} will be promoted. On the other hand in general, incipient wetness favours the formation of C_{18} hydrocarbons. It is possible to appreciate how the C_{17}/C_{18} ratios for this method are lower than for wet impregnation.

4.5.3 Identification of unexpected species formation

With the aim of identifying all the main products including unknown peaks, GC-MS has been used in order to find out which products could appear and compare the experimental data with literature. The already identified products are named in *Figure 4.22* in such way that the untagged peaks are the unknown products.

The analysis by GC-MS is configured to start identifying peaks after dodecane so, the previous peaks situated mainly around heptane, it is possible to guess that there are small chain hydrocarbons resulting from cracking reactions. This is an unproved theory. So, in order to reach a more certain conclusion, another GC-MS analysis should be performed including the first peaks.

After inspecting case-by-case and removing possible contaminant species from previous analysis, *Figure 4.23* shows which compounds could be in the sample. Substances in green are the already identified during the calibration; the blue species are the substances that GC-MS has detected and appear in the mechanism proposed in

4. Results and discussion

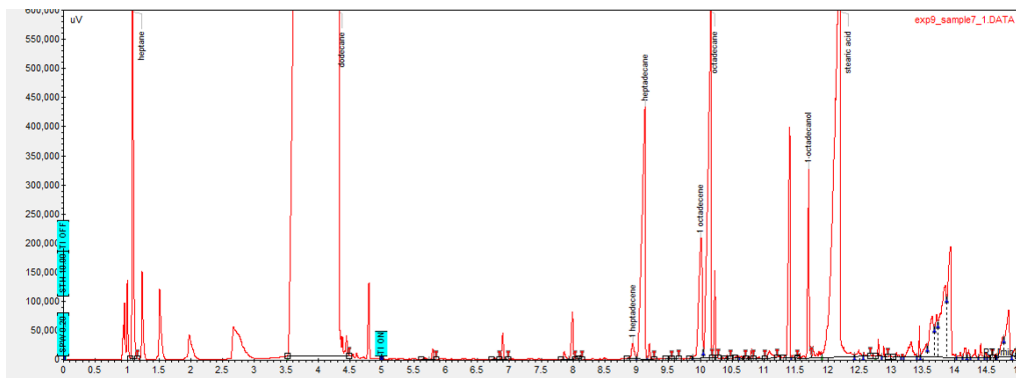


Figure 4.22: The resulting peaks of experiment 9 sample 7 where the peaks which are named are already identified and quantified products. The peaks without identification are other compounds that have not been identified yet in this project.

Theoretical part (*Figure 2.3*); finally, substances in red are compounds identified by GC-MS but they are not proposed in the mechanism and they do not help removing oxygen. The formation of these esters can occur because of reactions from alcohols with acids and this formation of by-products is often not included in reaction mechanisms.

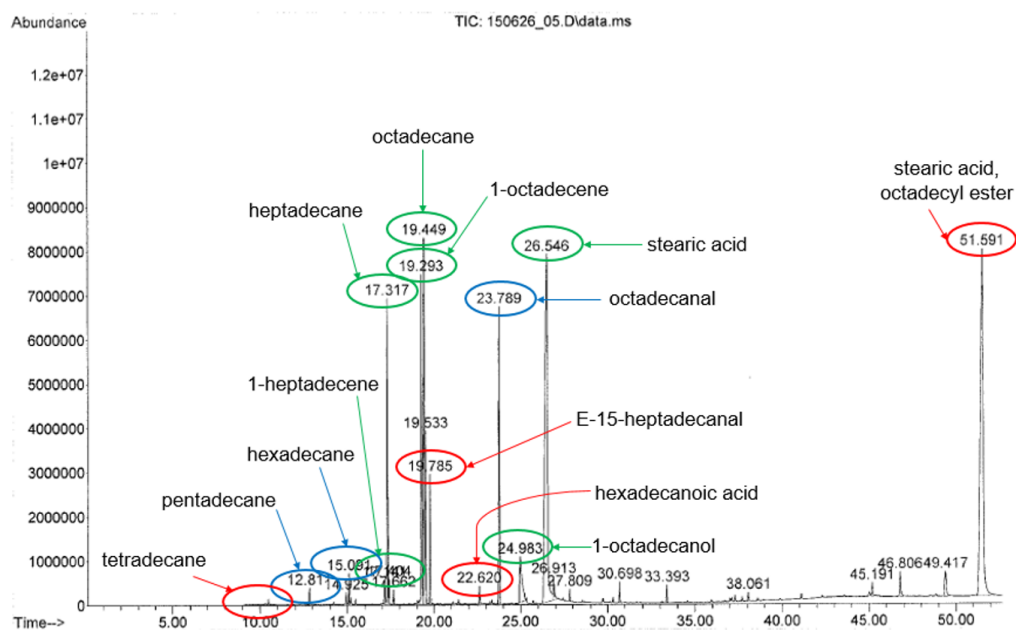


Figure 4.23: GC-MS results including the identification of some compounds. The green substances are products already identified and quantified; the compounds in blue are the products identified in the proposed mechanism but have not been quantified; finally, the compounds in red are products identified by GC-MS but not included in the proposed mechanism.

Referring to the red substances, maybe they are not very reliable but at least they

offer a better and more accurate explanation of the results. Stearic acid octadecyl ester is an example of the ester formations named above. This information is useful in order to explain which kinds of products are possible to obtain after running the reactor for 4 hours. Usually after this time and just after stearic acid appearing, similar peaks as in *Figure 4.22* appear in all the experiments which are suspected to be a recombination of long hydrocarbon chains connected by an ester or ketone. Another theory could be that they are species trapped in the column contaminating it because if there are heavy compounds e. g. really long hydrocarbon chains, they could be improperly decomposed afterwards so, it is recommended to perform regular conditioning of the column.

Finally, the identification of pentadecane, hexadecane and 1-octadecanal needs to be considered a successful result because all of them are in the proposed mechanism and show a reliable comparison between experimental and theoretical data. Despite this fortunate identification, these compounds cannot be quantified, yet because they are not calibrated.

5

Conclusions

5.1 Method development

The method development for the experimental device was performed in order to create a sequence of steps for different procedures of sample preparation and activity tests such as start up for the pre-treatment, start up for activity test, consequently switch off for both procedures, sample taking procedure and cleaning the sample taking line. Despite these new procedures, more development is needed in sample taking and cleaning in order to get more reliable results.

GC-MS is an important technique to use for some samples because it is possible to identify a higher amount of products that can appear during HDO reactions and it can help to complete the mass balance of the reaction.

5.2 Comparison of different catalysts

In order to increase the H/C ratio and decrease the O/C ratio of stearic acid, in this project a NiMo/Al₂O₃ catalyst has been used and which has shown different results for HDO and decarboxylation pathways. These results have helped to find the first conclusion in this project; despite some products have been enhanced more than others, in all the experiments it is shown how HDO, decarboxylation and decarbonylation pathways are reacting simultaneously.

According the first conclusion, the different catalyst preparation methods take an important role for the formation of unsaturated hydrocarbons such as 1-octadecene or 1-heptadecene; saturated hydrocarbons, e. g. heptadecane and octadecane; or intermediates. In general, wet impregnation at pH of 10.5 enhances the formation of saturated hydrocarbons (orderly *Wr*, *Wc* and *Wd10.5*, mostly heptadecane and incipient wetness method favours the formation of intermediates: 1-octadecene and 1-octadecanol. Furthermore, completing this with C₁₇/C₁₈ ratio results, it is possible to conclude that using wet impregnation higher amount of C₁₇ will be obtained and using impregnation wetness more C₁₈.

The mechanism proposed for these reactions is well proved in this project but more species have appeared during the product analysis. These by-products from secondary reactions can be explained by cracking reactions or formation of esters which

5. Conclusions

were started reacting at the latest reaction times. Concluding, during these experiments, more secondary reactions as shown in the proposed reaction mechanism have been occurred simultaneously with HDO, decarbonylation and decarboxylation thus, more compounds have been obtained.

Finally, in connection with the formation of new compounds and its identification, some species have been determined: octadecanal, hexadecane and pentadecane. There are also other products identified but they are not a very reliable such as the lasts. For octadecanal, hexadecane and pentadecane, the probabilities of to be obtained as products were higher than others and they appear in the proposed reaction mechanism.

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A

Appendix

A.1 Calibration

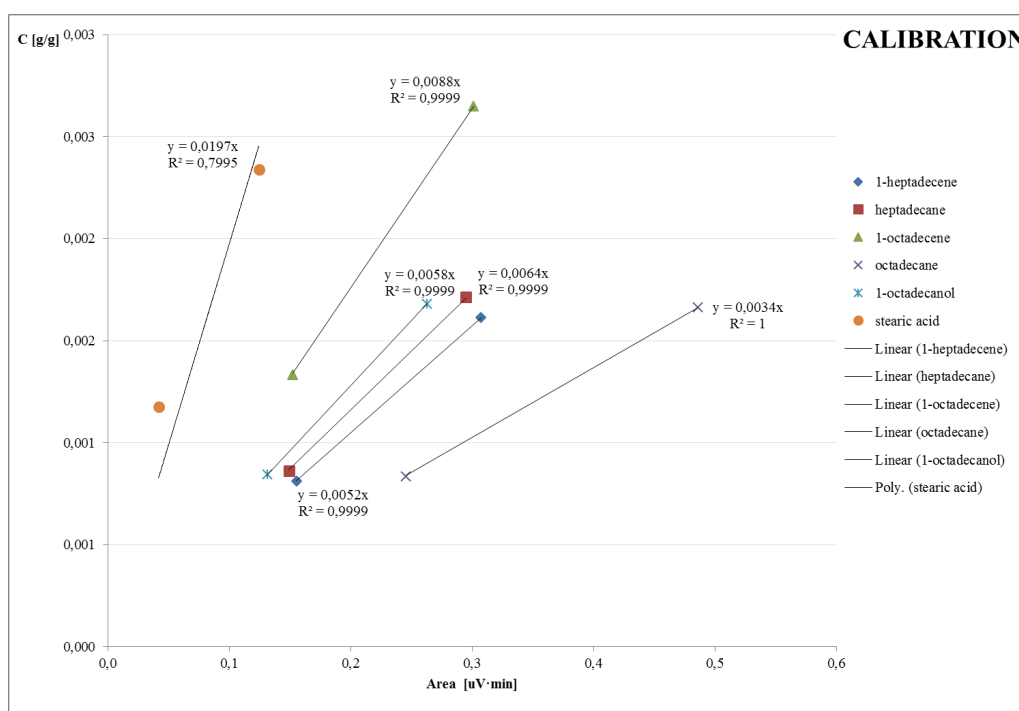


Figure A.1: Calibration of all the expected products.

A.2 Stearic acid conversion

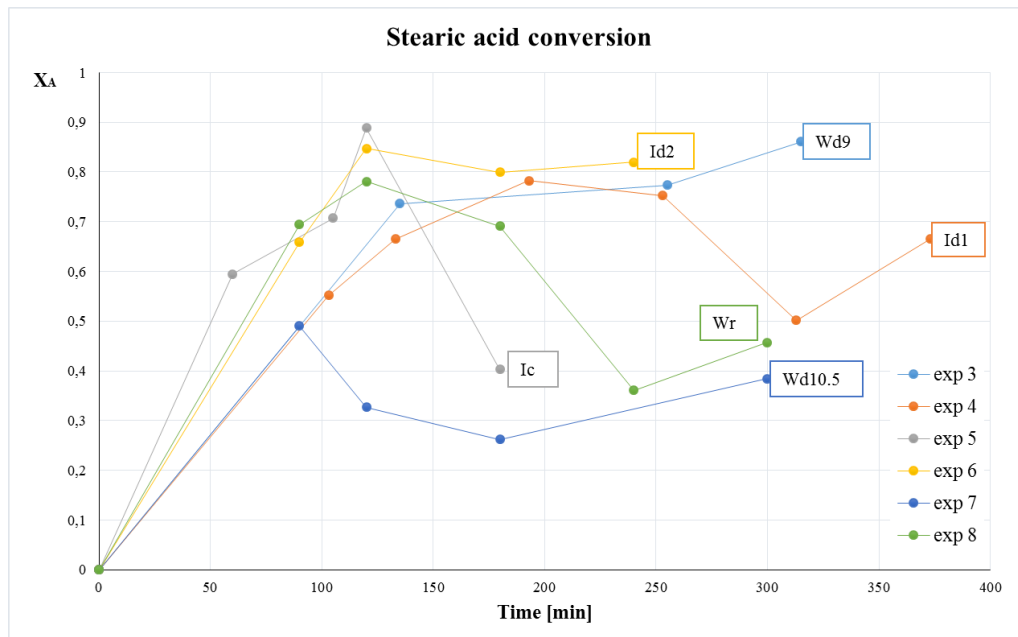


Figure A.2: Conversion of stearic acid including all the experimental points.

