



## **FACULTY OF CHEMISTRY**

**DEPARTMENT OF ORGANIC CHEMISTRY,  
BIOCHEMISTRY AND CATALYSIS**

### **MSc Thesis - literature report**

**From humin wastes to carbon quantum dots  
(CQDs) based photocatalytic nanocomposites**

**MASTER: CHEMISTRY OF ADVANCED MATERIALS**

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## Introduction

In this literature report there are summarized the main theoretical aspects that are going to be the background of the following work. The purpose of the thesis is the valorization of humins into Carbon Quantum Dots (CQDs)-TiO<sub>2</sub> nanocomposites with acid and photocatalytic properties. As to be able to bring this idea to life, first of all it is important to understand its importance. Secondly it is crucial to have a good understanding of the structure and properties of the humins. Lastly, the properties of the CQDs have to be known in order to tune them with the necessary features.

Biomass is defined as any renewable organic matter and has become one of the most studied fields in today's world of green chemistry research. Bio-refinery started to develop very fast because mankind needs new alternatives to the fossil fuels that are going to be depleted in the next 50 years. This alternative is seen as a very promising one due to the fact that it is capable of supplying a great diversity of platform molecules which researchers can transform into the desired products.

Humins are known for a quite long time, and since their discovery, the applications were very different. They went on from useless wastes to fuel for heating in the industrial processes where they were first obtained. However, in the recent time researchers started studying humins as to make them more useful for the industry. Thus, there were studied different possibilities of transforming humins to other products.

The appearance of quantum dots has been a revolution in the perception of chemistry. It is not a secret that the properties of quantum dots are considerably different from the ones of the elements or substances in bulk form. In fact, the properties are outstanding and open new opportunities for creating new substances with different purposes. Carbon Quantum Dots for instance can be applied in chemical or biochemical sensing, bioimaging, drug delivery, as supports in catalysis and even as catalysts themselves. This is indeed a very interesting possibility for developing new catalysts with interesting applications in a wide range of processes.

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# **Chapter 1. Sustainable catalytic systems for biomass valorization.**

## **1.1 Introduction – Biomass**

It is no secret that the fossil fuel reservoirs will be drained at some point. Taking into consideration the fact that humanity demands more and more every year, mankind needs to focus on finding new sources of energy and chemicals in order to sustain the production processes all over the world. In the case of electricity, the problem was heavily studied and at present there are different kinds of alternatives to fossil fuels in order to provide energy, some examples being the solar panels, wind turbines, hydroelectric plants and even nuclear plants. Regarding chemicals, the problem is more complex, a perfect source of chemicals being a renewable one. Moreover, such source should be able to provide more complex molecules that can still be shaped in the need way. In order to fulfill these conditions, there were many studies performed and one of the most promising sources of renewable chemicals is the biomass.

The biomass is a very abundant source of carbon, which is also renewable, and which provides different kinds of molecules that can be further transformed into complex molecules. Several biomass resources, such as animal waste, agricultural crops, wood, and aquatic plants are available for the production of sustainable chemicals [1]. As to materialize the biomass there were developed many processes based on the necessities for the production of the desired chemicals and on the structure of the specific biomass that was chosen for a given process. In order to refer to all the processes which involve transforming the biomass into value-added products, the term of biorefinery was introduced. Typically it consists of three main steps. The first one supposes the separation of biomass into its components. The second step implies thermochemical processes, such as gasification, or biochemical processes (e.g., fermentation). The third step represents the catalytic conversion of the previously processed biomass into value-added products. In fact, this is the step which requires the most attention because of the complexity of the procedure. The difficulty lies not only in the conversion itself, but also in finding sustainable catalytic systems that can work in this field without being very expensive, having a short lifetime or a reduced selectivity in the desired products. These facts lead to the problem of having sustainable catalytic systems for biomass valorization. [1]

## 1.2 The Biorefinery Concept

As stated in 2004: “chemists learn from the very beginning to think in terms of petrochemical product lines.” However, while they “continue to prefer simple petrochemical molecules as feedstock to develop catalysts and reactions, the growing trend among the newly forming green chemistry community is to develop green catalysts, green solvents, and green reactions around renewable source materials”. This is in accordance with the seventh principle of Green Chemistry, “A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.” Fuel (accounting for the largest amount), commodities and fine chemicals are to be obtained from a cheap, renewable feedstock alternative to fossil fuels, a change of perspective that involves huge amounts of materials. What is required is a source of carbon analogous to petrol, where a complex mixture of chemicals can be converted in several high-value molecules, through the development of efficient refinement procedure including cracking, chemical modification and separation in the so-called *bio-refineries* defined as “a facility or a network of facilities that converts biomass including waste into a variety of chemicals, biomaterials and energy, maximizing the value of the biomass and minimizing waste” (National Renewable Energy Laboratory (NREL)). Advanced biorefineries are analogous in many ways to today’s petrorefineries [2]. A comparison between these 2 types of refineries is presented in Figure 1.

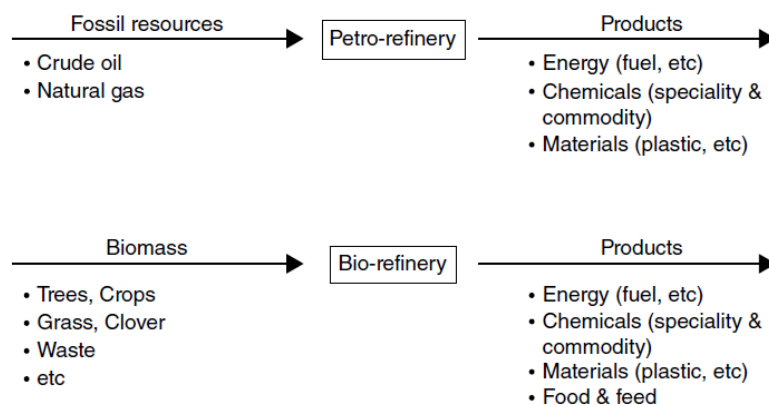


Figure 1. Comparison between petrorefinery and biorefinery [2].

Similarly to oil-based refineries, where many energy and chemical products are produced from crude oil, biorefineries produce many different industrial products from biomass. These include low-value high-volume products such as transportation fuels (e.g. biodiesel, bioethanol), commodity chemicals and materials and high-value low-volume

products or specialty chemicals such as cosmetics or nutraceuticals (ie, food containing health-giving additives and having medicinal benefit).

Energy is the driver for developments in this area, but as biorefineries become more and more sophisticated with time, other products will be developed. In some types of biorefinery, food and feed production may also be incorporated.

According to the Joint European Biorefinery Vision for 2028, a significant proportion of the overall European demand for chemicals, energy and materials will be met using biomass as a feedstock by 2028:

- 28% of overall chemical production is expected to be bio-based in nature by this date (for high-added-value chemicals and polymers, the proportion might even be >50%);
- 25% of Europe's transport energy needs will be supplied by biofuels, with advanced fuels (and in particular bio-based jet fuels) taking an increasing share; and
- 28% of Europe's heat and power generation will be derived from biomass.

The obvious alternative to fossils is biological material (biomass) from living or recently living organisms, not metabolized for thousands of years into petrol and coal, thus not concurring to CO<sub>2</sub> emissions.

As already specified, in principle, the biorefining concept has similar objectives as today's petroleum refineries, but the feedstocks are totally different. The feedstock in a conventional refinery is oil which is mostly a mixture of hydrocarbons (including alkanes, cycloalkanes and aromatic hydrocarbons). To produce fuels, this is a positive feature because they release more energy per gram than, for example, an alcohol. However, to produce chemicals for the chemical industry, functional groups have to be added.

"Biomass" term is, therefore, defined as any renewable organic matter including agricultural food and feed crop residues, energy crops and trees, wood and wood residues, aquatic plants and animal wastes (Figure 2).

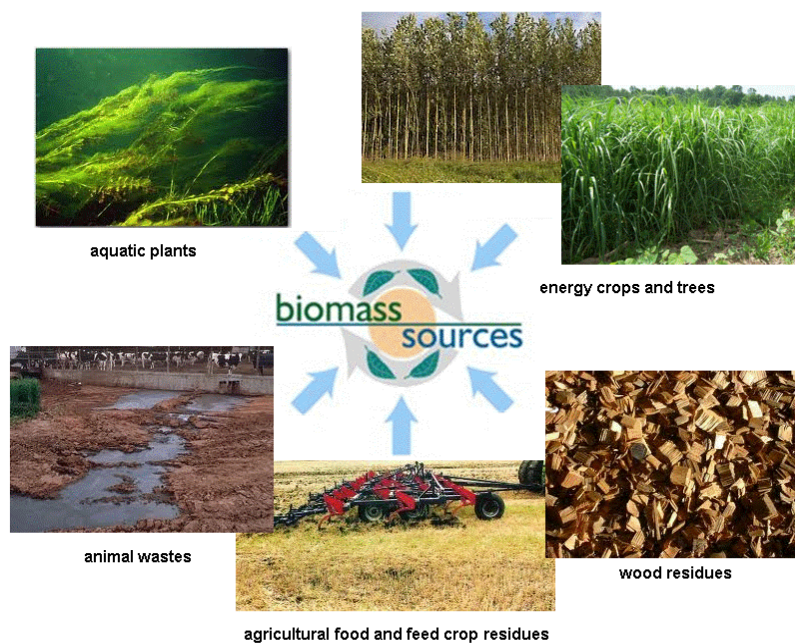


Figure 2. Biomass sources [3].

Biomass is a very valuable feedstock, both for the production of chemicals and of novel fuels, which in the future could replace crude oil and gas as the current major raw materials. A controlled de-functionalization is necessary rather than the functionalization used in the chemical industry. Unfortunately, this means that most of the developed processes in petrochemical and chemical industry are not suitable for converting biomass and alternative pathways for the production of fuels and chemicals should be developed. Moreover, from sustainable development and environment protection reasons, an efficient biorefinery unit should provide a complete valorization of the biomass source by performing the overall processes with a minimum loss of energy and mass and should maximize the overall value of the production chain with the minimum formation of wastes. For the efficient utilization of biomass, it will be crucial to create a similar comprehensive network of process chains.

However, the dynamics of this process are dictated rather by the market prices and political decisions than by purely chemical reasoning. For instance, the glycerol market faces downward pricing pressure due to the low demand growth and the abundant supply created by the massive increase of biodiesel production worldwide over the last five years. New outlets for glycerol are thus mandatory to improve the profitability of biodiesel market and the competitiveness of this sector.

### 1.3. Biomass composition

Lignocellulose is the most abundant biomass feedstock, with an annual growth of 170 billion tons and it does not directly compete with food supplies because of its non-edible nature. [1] Lignocellulose is mainly composed of three biopolymers: cellulose (28–50%, polymer of glucose), hemicellulose (20–35%, polymer of C5 and C6 carbohydrates), and lignin (15–28%, aromatic polymer), along with smaller amounts of pectin (generic term for a polymer comprising galacturonic acid units of at least 65%), protein, extractives (triglycerides, terpenes, pigments, waxes, etc.) and ash (Figure 3). Lignin is acting as glue, holding together the cellulose microfibrils and hemicellulose fibres, imparting structural support, impermeability, and resistance against microbial attack.

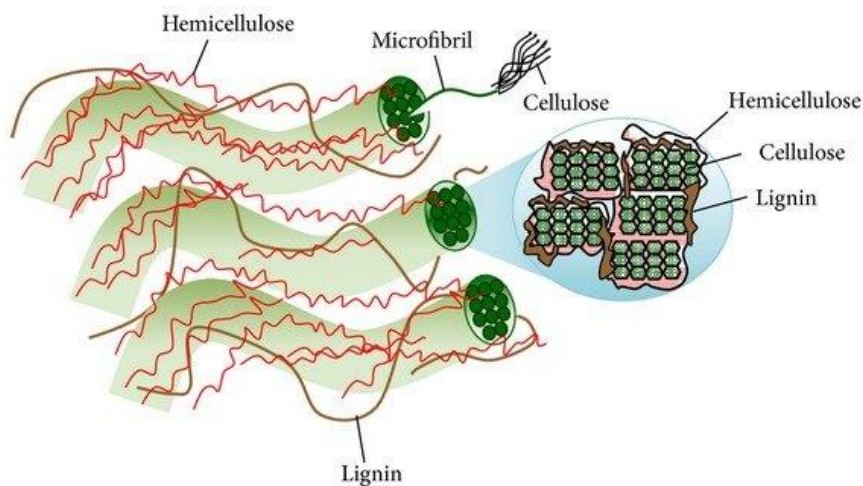


Figure 3. Composition of lignocellulose [4]

Hence, the efficient fractionation of lignocellulose into separated streams of these three polymers is often the entry point for a fruitful bio-refinery as it opens the possibility of subsequent transformations to high-value chemicals and fuels. In this context, reductive catalytic fractionation (RCF) of lignocellulose has received tremendous attention, providing stable lignin oil containing high-value phenolic mono-, di- and oligomers as well as a vaporizable solid carbohydrate pulp that can be used for the production of paper, fine chemicals, or biofuels. [5]

From the chemically point of view, *cellulose* is a non-branched long chain water-insoluble polysaccharide consisting of several hundred up to tens of thousands of D-glucose units linked to each other by  $\beta$ -(1,4)-glycosidic bonds. These long-chain cellulose polymers



are linked together by physical (i.e., hydrogen and van der Waals) bonds, which cause the cellulose to be packed into microfibrils (Figure 4).

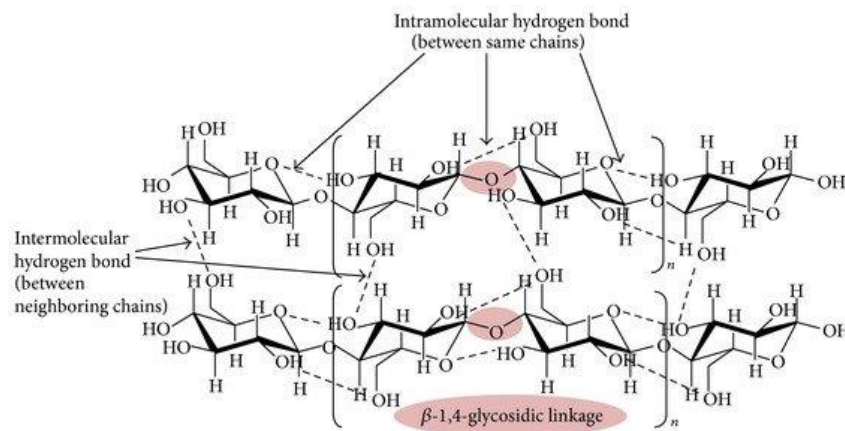


Figure 4. Cellulose packing structure [4]

Unlike cellulose, *hemicellulose* has easily hydrolysable branches with short lateral chains consisting of C6-sugars (glucose, mannose and galactose), C5-sugars (mainly arabinose and xylose) and uronic acids (e.g., 4-*o*-methylglucuronic, D-glucuronic, and D-galactouronic acids), linked each other by  $\beta$ -(1,4)-glycosidic bonds (predominantly) and by  $\alpha$ -(1,3)-glycosidic bonds (occasionally). The structure of the hemicellulose and its main monomer units is shown in Figures 5 and 6.

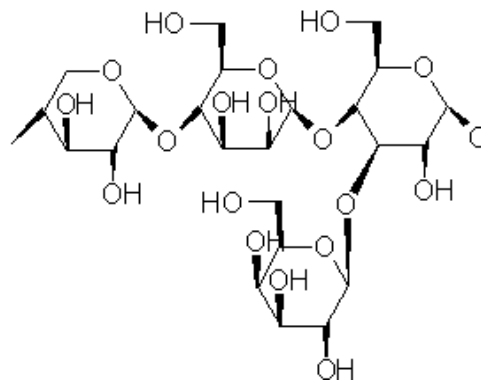


Figure 5. Structure of hemicellulose [4]

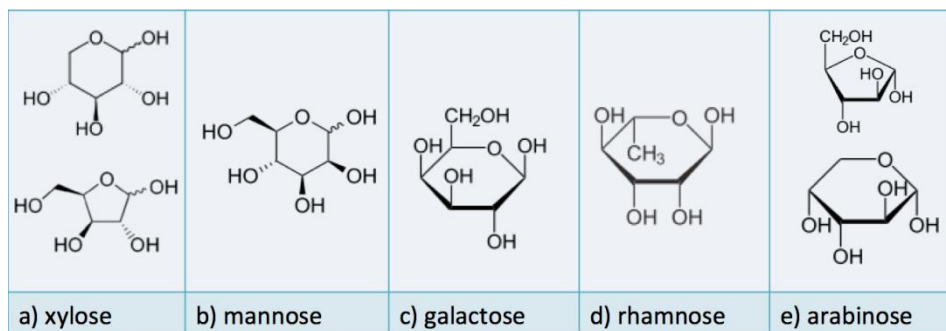


Figure 6. The main units found in hemicellulose [4]

Lignin comprises 15–28% of lignocellulosic biomass and is the only scalable renewable resource, consisting of abundant aromatic chemicals derived from p-coumaryl, coniferyl, and sinapyl alcohols (Figure 7). [6]

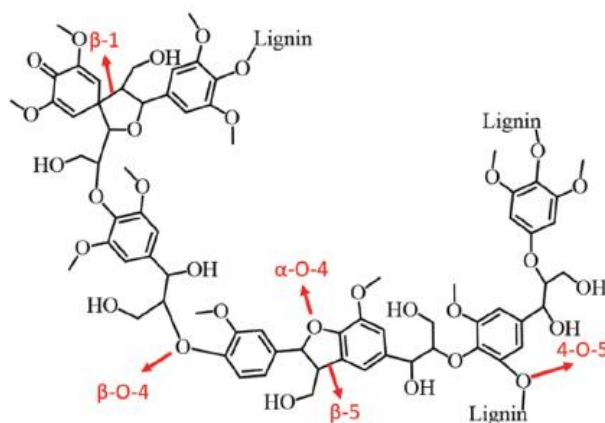


Figure 7. The structure of lignin polymer [7]

#### 1.4. Platform molecules and added-value products

A prime objective in the catalytic conversion of lignocellulosic feedstocks is the improving of the catalysts efficiency and selectivity towards value-added products. However, the incorporation of compatible catalytic processes in the actual infrastructure of petrochemical industry plants requires as biomass feedstocks to be converted to building block chemicals with fewer oxygenated groups. These building block chemicals (also known as “platform molecules”) are molecules with multiple functional groups that possess the potential to be transformed into new families of useful chemicals. The most important 15 platform molecules that can be produced from sugars via biological or chemical conversions and can be subsequently converted to a number of high-value bio-based chemicals or materials are given in Table 1.

Table 1. Building blocks obtained from biomass [8]

Building Blocks
1,4 succinic, fumaric and malic acids
2,5 furan dicarboxylic acid
3 hydroxy propionic acid
aspartic acid
glucaric acid
glutamic acid
itaconic acid
levulinic acid
3-hydroxybutyrolactone
glycerol
sorbitol
xylitol/arabinitol

Some of building blocks were the subject of intense research and development during the past few years (such as 5-hydroxymethylfurfural, furfural, levulinic, lactic and succinic acids, as well as new industrial derivatives from sorbitol) while there was a comparatively modest interest for organic acids (such as aspartic, malic, fumaric, glutamic and itaconic acids).

### 1.5. The design of solid catalysts for biomass conversion

Cellulose becomes an important target feedstock for the chemicals production and the identification of selective catalysts for its transformation towards value-added products is of major industrial importance. However, the production of biochemicals or biofuels from cellulose is not an easy task due to its robust crystalline structure which makes it an insoluble compound in most organic solvents. This property complicates the use of solid catalysts, and thereby, the discovery and investigation of novel and efficient pathways as well as catalysts for the conversion of cellulose into chemicals are big challenges which heterogeneous catalysis is facing. However, although the research in this field is very intense and novel transformation routes/catalytic materials have been discovered at a high rate, the specific properties of cellulose still impose new requirements.

#### *Catalysts composition*

Solid catalysts are nowadays selected to be highly temperature-stable, because conversions proceed often in the gas phase at high temperature, and to be resistant against relatively non-polar compounds, since the basis of the chemical industry are hydrocarbons. These characteristics immediately lead to the choice of inorganic oxide materials, which meet

both of these requirements [9]. A schematic representation of the shares of each type of catalysts in modern industry is shown in Figure 8.

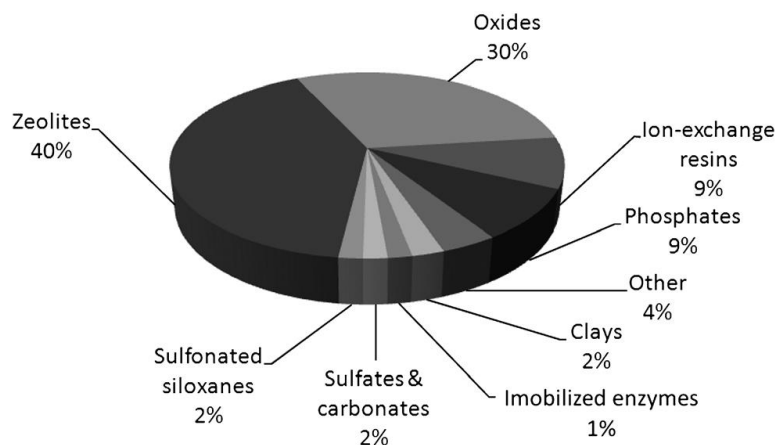


Figure 8. Share of solid catalysts used at the industrial level [9]

Polymeric catalysts are much less suitable for the oil-based chemical industry, because the temperature range for their use is limited and there are substantial swelling and stability problems in organic solvents.

Most biomass conversion processes, with the exception of the important route via pyrolysis/gasification of biomass, typically take place at moderate temperatures, and in the liquid phase, mostly in polar solvents (Figure 9) [10].

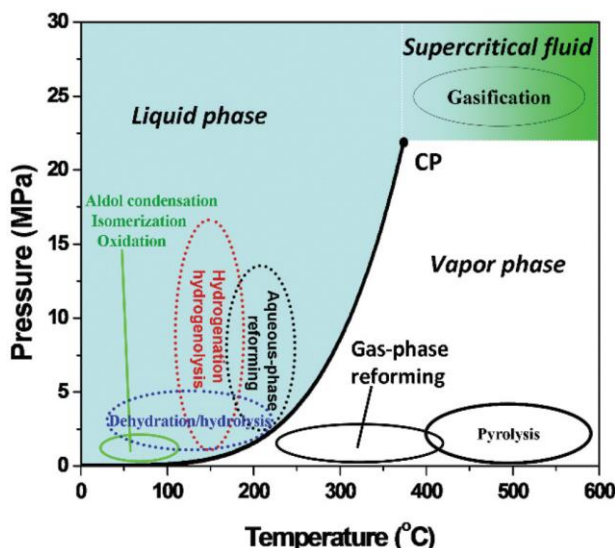


Figure 9. Reaction types based on Temperature and Pressure dependence [10]

This places new requirements on the properties of solid catalysts. They need to be stable against dissolution and leaching in aqueous or highly polar media under different pH

conditions. In addition, many of the biomass components possess strongly chelating groups, which can facilitate leaching and poisoning of the catalytically active phases. Very careful choice of catalyst components is therefore mandatory, and the diversity of biomass will make this problem even more severe. Furthermore, the resistance of the solid catalysts against polar solvents is another significant issue, since the chemical processing of biomass should mainly be carried out in liquid phase because of the polymeric nature of most biomass components.

Having these points in mind, one may expect a shift of the solid materials used in biomass conversion towards polymeric organic solids, although inorganic solids will definitely continue to have major importance. Nevertheless, organic polymers or organic/inorganic composites could have quite interesting properties in biomass conversion processes, since they allow wide variation in surface functionality and can be tuned between hydrophobic and hydrophilic behavior (vide infra). However, the use of such materials as solid catalysts is much less developed than that of the more classical catalytic materials, such as main group oxides and transition metal oxides. For instance, although porous polymers can be produced, this field is in a less mature state than the field of inorganic porous solids, and fine tuning of porosity for a wide variety of different polymers is still a difficult task. Nevertheless, this field appears to be an interesting direction for further research, which is expected to increase substantially in importance in the years to come. For instance, macroreticulated acid resins revealed to be interesting materials for the catalytic depolymerization of cellulose in ionic liquids.

### *Active sites*

The productivity of the oil industry and the quality of liquid fuels could only be improved during the 20th century due to the massive R&D in the field of solid acids.

The typical acid-catalyzed reactions in chemical industry are shown in Figure 10 (in some of these conversions, catalysts are bifunctional, and more than the acid functionality is needed) [9].

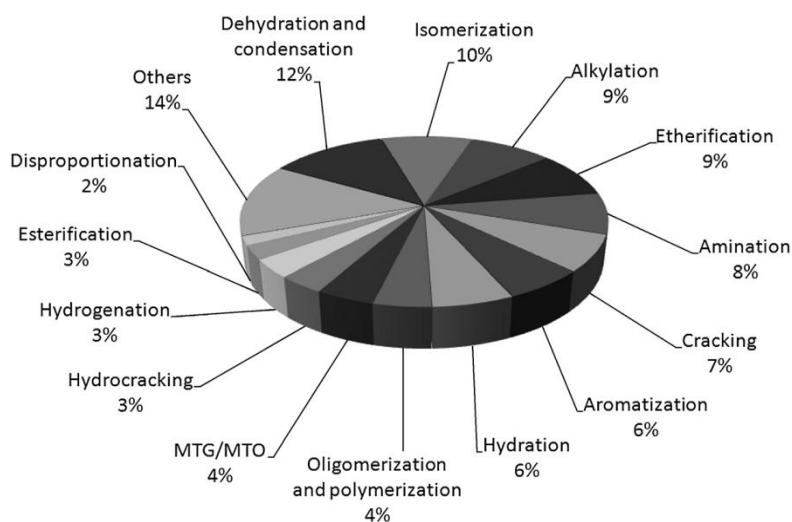


Figure 10. Comparative view of typical acid-catalyzed reactions in chemical industry [9]

Solid bases, however, received much less attention, mainly because hydrocarbon conversions in the petrochemical industry, such as cracking, isomerization or alkylation, are governed by carbocation chemistry, which requires acid catalytic sites. Reactions catalyzed by zeolites and oxides represent, respectively, ca. 40 and 28% of all acid–base catalyzed processes. Despite the importance of zeolites as acid catalysts for the current chemical processes, the catalytic processing of biomass faces the transformation of much larger and bulkier substrates that cannot access the zeolite micropores. This suggests that this class of materials might not have the same central importance for the conversion of biomass as they had and still have in the petroleum industry. However, as soon as the polymeric biomass is broken down to a sufficient extent, the catalytic transformation of platform chemicals obtained from biomass, e.g. ethanol, furfural, glycerol and levulinic acid, can take advantage of the unique properties of zeolites as catalysts for organic reactions.

The decrease in the oxygen content of biomass raw materials is possible by three types of reactions—dehydration, hydrogenolysis and hydrogenation. From these transformations, only hydrogenation is not an acid-catalyzed reaction, underlining the importance of acid catalysis also in biomass-based processes. The primary step, the hydrolysis of lignocellulosic materials, which is also acid catalyzed, does not change significantly the O/C and H/C ratios. However, this initial reaction is the prerequisite of the subsequent de-functionalization reactions, since the depolymerization provides the small molecules that are the entry point for subsequent transformations, which decrease the O/C ratio.

Metal oxides can suffer textural, morphological and structural changes in liquid phase. In aqueous reaction media several dissolution–precipitation equilibria can be established,

which might reduce the lifetime of solid catalysts. Aluminum oxides are important supports for metals and oxide catalysts in chemical industry. However, water can affect the tailored properties of these materials. For instance, sol-gel derived mesoporous alumina can suffer deterioration of their properties by simple exposure of these materials to humidity. In a number of cases, the loss of metal from catalysts happens primarily due to support leaching by dissolution in the reaction medium. It is important to keep in mind that several acidic and chelating compounds are formed during the processing of biomass, which can make the reaction medium very aggressive to various solid catalysts.

Metal and supported metal catalysts are also important materials employed in a number of reactions such as hydrogenation, oxidation and C–H bond activation. The challenge in this field is to find catalysts resistant against the aggressive reaction media and harsh conditions usually found in biomass processing. Leaching is the major issue not only because it can decrease the catalyst lifetime, but also because the leached metal ions have to be removed from the products. Moreover, the leached metal ions, even at ppm levels, can also have a detrimental effect on the oxidative stability of biofuels.

### *Porosity of catalysts*

Porosity is one of the most important properties of solid materials, crucial for many practical applications, such as sorption and catalysis. These pore systems are often necessary to create sufficiently high surface areas needed for high activity.

The most abundant components of biomass have high molecular weight ( $10^3$  to  $10^7$  g mol<sup>-1</sup>) and are not soluble in conventional solvents. Both characteristics make the transport of biomass molecules into pores very cumbersome. The molecular dimensions of individual sugar molecules are rather small; for instance,  $\beta$ -glucose has a length of 0.58 nm along the axis C-1 and C-4 (Figure 11).

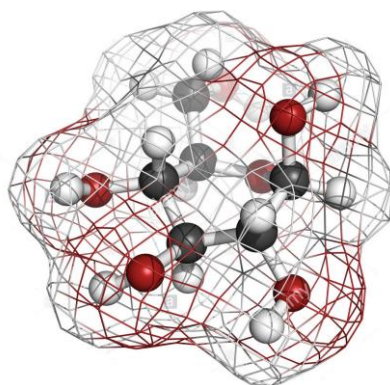


Figure 11. Structure of glucose [11]

However, expanding this dimension to a single chain of cellulose containing 1000 anhydroglucose units, a length of 580 nm is found. Of course, in solution, such macromolecules are never fully extended, and diffusion of chain-like molecules in pore systems is possible by a reptation process. Nevertheless, for the processing of polymeric biomass severe mass transfer limitations have to be expected, requiring careful selection of the materials and tailoring of the pore sizes. Moreover, if the lignocellulosic materials are insoluble in the reaction medium, such as water, a dispersion of two solids (substrate and catalyst) is observed. In these cases, even if the individual cellulose chains would be able to enter the pore system of the catalyst, almost no interactions between substrate and catalyst are expected, since the solid particles of the substrate, consisting of polymeric chains, would not be able to enter the pore system.

In fact, cellulose slurries in water can suffer catalytic cracking to a certain extent, resulting in the formation of smaller molecules. It seems that two-step mechanisms are responsible in such systems. The mechanism is schematized in Figure 12.

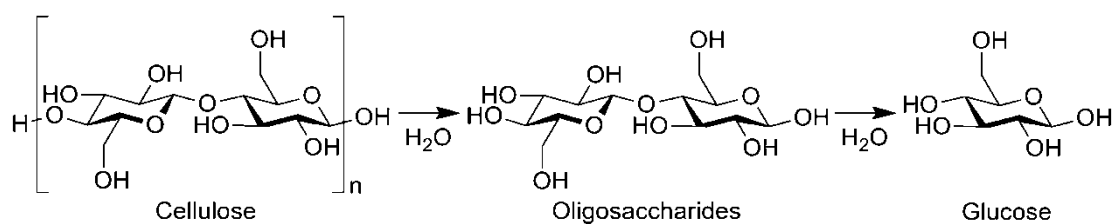


Figure 12. Hydrolysis of Cellulose to Glucose [9]

Firstly, a partial hydrolysis of biomass proceeds, involving Brønsted acidic species either released by the solid material or formed in the reaction medium. Subsequently, the reactions involving the solid catalyst take place when the oligomers are small enough to access the pore system. Thus, the porosity of the solid catalyst can play a fundamental role in the catalytic activity and selectivity, because it determines to what extent the initial hydrolysis needs to proceed in homogeneous phase before starting the heterogeneously catalyzed reactions. There is also the possibility that the reaction starts on the external active sites of the catalysts. However, due to the fact that a dispersion system with two solid phases exists, such contributions are probably small.

Taking into account the above mentioned considerations, the development of solid catalysts with high efficiency in biomass valorization became an important area of research both to academic and industrial level. Most of the recently developed catalysts (e.g., metal-



organic frameworks, carbon based catalysts, solid phase ionic liquids, magnetic iron oxides) were recently reviewed by Sels and co-workers [1].

Metal–organic frameworks (MOFs) are of particular research interest for biomass upgrading and considered as a promising alternative to typical porous zeolites and silica catalysts while the carbon based catalysts present a number of advantages such as the large specific area, strong hydrothermal stability, great possibilities of surface functionalization, a very high number of active sites suitable for biomass transformation and strong hydrophobic nature.

On the other hand solid phase ionic liquids (SILs), such as supported ILs and polymerized ILs have drawn great attention due to the particular interactions between the anionic and cationic parts of ILs. This can show a conceivable constructive effect in stabilizing acid–base and active metal centers, which could be beneficial for cascade biomass upgrading. Not the last, magnetic catalysts can be efficiently separated from the reaction mixture using an external magnetic field, without affecting their catalytic properties, conferring them a great advantage upon most of the developed solid catalysts.

Nevertheless there are many advantages in favor of carbon based catalysts, even though there are still a few drawbacks that limit their potential. The major ones are regarding high production costs and the lack of large scale methods for their synthesis, both being strongly connected one to another. Still, there is a lot of work to be done in order to explore the whole potential of these materials.

## **Chapter 2. Humins – from waste to value added products**

### **2.1 Biomass valorization**

In today's world, one of the greatest problems is the ecology of our Planet. We have a lot of problems with the Planet's ecosystems and climate because of our industry that produces millions of tons of wastes during a year. Things dramatically develop as we move towards a point in which the natural resources will not be able to withstand such an amount of by-products that harm the living beings and the environment. In fact, one of the key problems for industry is our dependence on the fossil fuels, as these are the raw material for tons of industrial procedures on which our civilization relies. Taking this into consideration, in the last years, humans have begun to search for new sources of primal matter to supply our needs. Of course, this represents a massive challenge to all of the researchers and their teams implied

in this work, not just because of the complexity of the task itself, but also because of the amount of carbon dioxide we produce, schematically illustrated in Figure 13 [12], this being one of the most abundant pollutants.

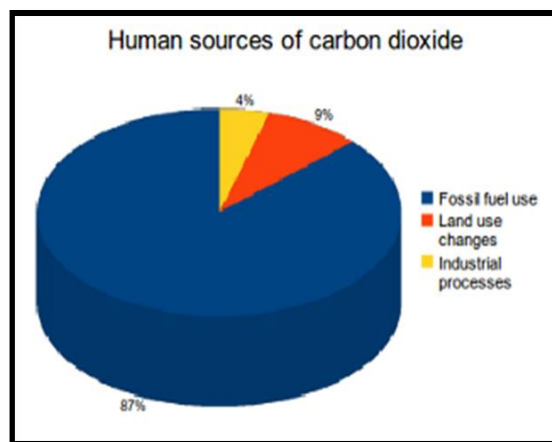


Figure 13. Human sources of carbon dioxide [12]

For producing electricity there were found some solutions in the face of solar panels and wind mills. For the car industry, electrification seems a good option; also there are projects that try to develop hydrogen based engines. Even though for some of the processes there were found solutions, either temporary or not, with the time passing, people realized that it is no easy job in finding renewable sources of carbon for the chemical and pharmaceutical industries. On one hand, the chemical industry does not produce that much of carbon dioxide, but on the other hand, these industries produce a lot of other wastes, and in order to get rid of them, we have to use many different procedures that sometimes can be even more expensive than the production process itself.

This fact, has led to an interest in other ways of getting rid of the wastes created by mankind, and one of the most promising ones is the waste valorization. This procedure implies transforming by-products of industrial processes into compounds that can serve as raw materials or starting points for other transformations based on the molecules that we obtain.

In chemical and pharmaceutical industry, molecules to serve as a source of carbon atoms are needed, in order to be able to shape the compounds already existent, into the ones are needed. Driven by this, multiple paths in order to provide the industry with the necessary materials and molecules were taken, but the one more interested is the biomass valorization.

Biomass is chosen because, first of all, it is very abundant, can be found everywhere on earth and it will be always regenerated. Secondly, in biomass a huge amount of molecules

can be funded because of its diversity. Another reason is the fact that biomass can be also obtained in different industrial procedures as a by-product. So, the industry have some great starting points in order to find ways to put into value the biomass and by this to also diminish the amounts of waste that are produced.

## **2.2 HMF general knowledge, applications**

The commercial production of wood sugars for ethanol production was first considered at the beginning of the 20th century. Lignocellulose, a very abundant material, comprises important bio-polymers (cellulose, hemicellulose and lignin). Among these cellulose and hemicellulose are of high importance, since they are formed from monomers of glucose (or other types of sugar in the case of hemicellulose), and can be used as a carbon source in fermentation processes for the production of ethanol [13].

There are already a noticeable amount of chemical building blocks that are derived from renewable sources. One of them is the 5-hydroxy-methylfurfural (HMF) and it plays an important role because of the procedures used in it's obtaining – firstly it was obtained from fructose, then it was discovered it can be also prepared from glucose, and then even from cellulose [13]

Cellulose is formed by anhydro-D-glucopyranose units linked by  $\beta$ -1 $\rightarrow$ 4-glycosidic bonds, and thus hydrolytic degradation is necessary to obtain sugar monomers. Hydrolytic degradation should be controlled to avoid formation of oligo-saccharides and to prevent monosaccharides from reacting at the high temperatures used. [14]

In contrast to cellulose, hemicellulose is a polymer formed by different sugar units such as glucose, galactose, mannose, xylose and arabinose, and it does not form crystalline regions, making it more amenable to hydrolysis. Additionally, the rate of hydration depends on the sugar type, and decreases following the order xylose > mannose > glucose. Consequently, hemicellulose is hydrolysed faster than cellulose. [13]

Whereas dehydration of hexoses produces HMF, pentoses can lead to production of furfural. The compounds that can be obtained starting from HMF are shown in Figure 14. As figure shows HMF is very useful not only as intermediate for the production of the biofuel dimethylfuran (DMF) and other molecules, but also for important molecules such as levulinic acid, 2,5-furandicarboxylic acid (FDA), 2,5-diformylfuran (DFF), dihydroxymethylfuran and 5-hydroxy-4-keto-2-pentenoic acid. [13]

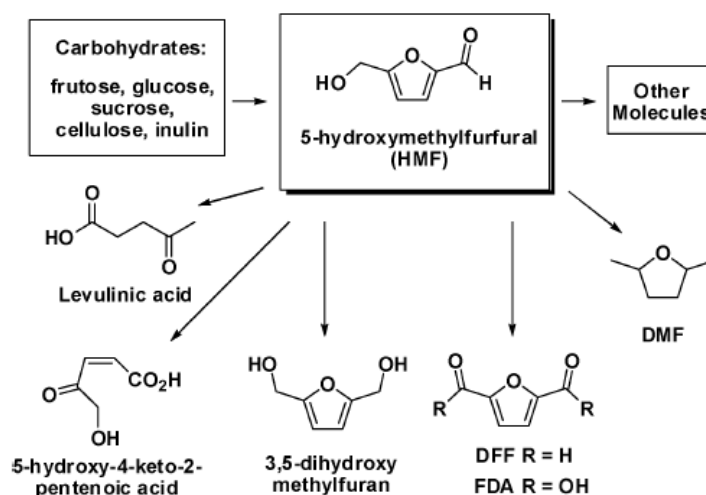


Figure 14. HMF and its possible applications. [13]

### 2.3. Humins: generation and structure

The synthesis of 5-hydroxymethylfurfural (HMF), 5-alkoxymethylfurfural and levulinic acid (LA) by acid catalyzed fructose dehydration, is complemented with the formation of substantial quantities of a black tarry by-product, a complex polyfuranic polymer, called humins [15].

Humins are heterogeneous amorphous biomacromolecules, considered to have the idealized morphology of spherical core-shell architecture [16]. The chemical structure of humins consists of furfural and hydroxymethylfurfural moieties also with carbohydrate, levulinate and alkoxy methylfurfural chains linked together into macromolecules by ether, acetal bonds or aliphatic linkages. The nature of terminal groups could be of carboxylic, ketone, aldehyde and/or hydroxyl nature. Also the presence of certain solvents such as acids or alcohols during the carbohydrate dehydration reactions could lead to the appearance of other functional groups such as alkoxy and ester groups. [17]

Despite the fact that humins were discovered almost a century ago, and as product resulting from prolonged sugar degradation reactions in the caramelisation process, its main application is still limited to energy and heat applications such as burning and gasification. Its valorization into higher added-value applications will be the key for making biomass conversion processes economically feasible. [15]

The mechanism of the humins formation is supposed to be an acid catalyzed condensation between its formed intermediates but it is also possibly to be formed directly from the starting carbohydrate during their transformation to HMF/MMF/LA, leading to a

network of furan rings. A model structure by furan rings connected via alkylene moieties is proposed by van Zandvoort [18] and schematized in Figure 15.

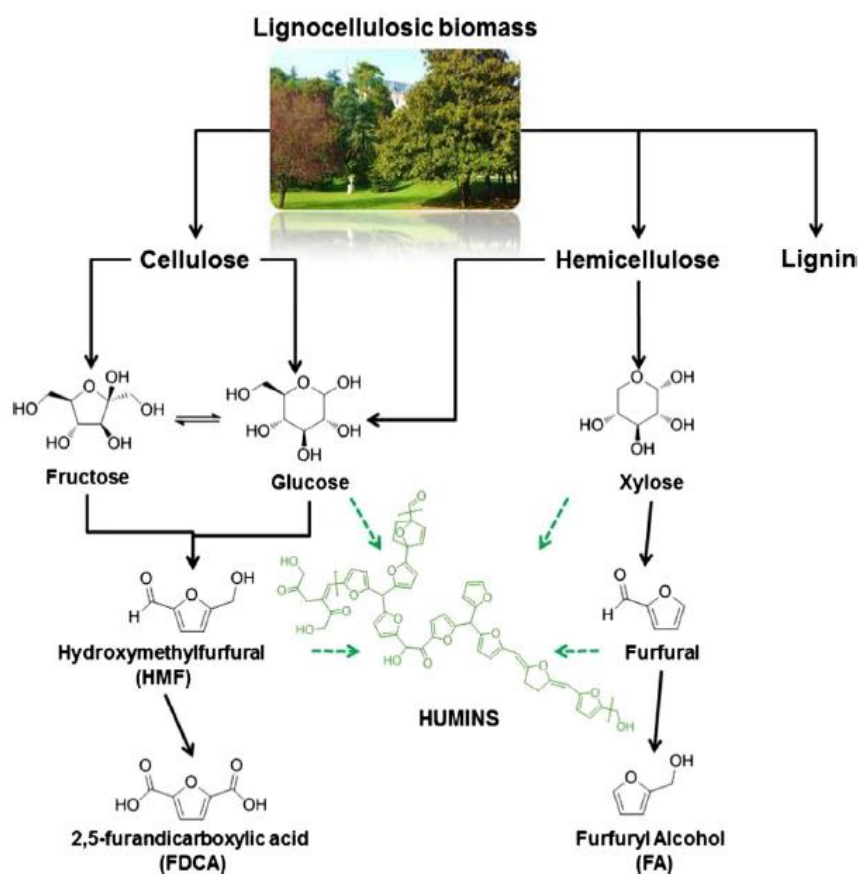


Figure 15. Mechanism of formation of humins [15]

The formation of humins is reported in most papers during the synthesis of HMF, LA (levulinic acid), or FF (furfural) from polysaccharides. The yield of humin is influenced by process parameters such as the type of substrate, time, temperature, and type of acid catalyst. For example, in an aqueous rich medium, humin yields vary from 5.3–27.5 wt% during the formation of FF from xylose using HCl or the solid acid  $\text{Yb}(\text{OTf})_3$  as catalyst [19]. In the case of cellulose conversion to LA, humin yields range from 25–45 wt%. In the case of HMF production, 10–50 wt% of sugar substrates are converted into humin. Humin is thus a major waste fraction during sugar conversion [19].

Efforts have been made to suppress the formation of humin, for example, by co-feeding alcohol to stabilize HMF by esterification and thus prevent its further conversion to humin. However, the yield of humin is still 14–22 wt%. Despite intensive investigation on the various conversion routes of polysaccharides, understanding of the pathway of humin

formation is poor. Furthermore, a clear description of the nature of humin itself is lacking. Generally, humin consists of carbon-rich agglomerate particles. It is composed of approximately 50–66 wt% C, 25–46% wt% O, and the remainder is H. [19]

From the studies that have been performed in the past several years, it can be supposed that humins, either soluble or insoluble, are macroscopic particles whose formation is thermodynamically favoured in the reactions used for synthesis of HMF (5-hydroxymethylfurfural) and LA (levulinic acid) from lignocellulosic biomass. Typically the dimensions of the insoluble particles are superior to the ones that are soluble and the only difference between them is their dimension – their structure is supposed to be the same as the Raman spectroscopy analysis shows very similar spectrums.

## **2.4. Humins applications**

At the very beginning of the humins research and studying, it was considered as a useless byproduct. Since the problem of ecology started to grow, researchers had to develop methods of valorization of biomass that are sustainable, with a good yield, with few byproducts and with using as little energy as possible in order to be competitive with the fossil fuel industry. This was a massive challenge for everyone that entered the green chemistry path for obtaining valuable compounds from renewable sources.

As the things are evolving quickly, humins were found to form in many industrially suitable processes as HMF or LA obtaining, and due to this fact, there were significant losses in the raw material used for these synthesis. Therefore, scientists had to develop processes that could potentially give the wastes a new life, thus recovering losses caused by their formation.

In the first place, the humins were simply burned in order to provide the necessary heat for the industrial processes that were taking place at the very same factories that produced humins. Still, their value as a combustion material is very low, since their properties do not make them perfect for this purpose.

Since humins contain approximately 60% carbon [19], researchers considered it can be used as feedstock for production of synthesis gas or hydrogen via gasification. Hydrogen is largely used in biorefinery, and H<sub>2</sub> from external sources is quite costly. Some of the reactions that are related to biomass conversion are transformation of LA to GVL ( $\gamma$ -valerolactone) and hydrogenation of glucose to sorbitol. However, minimizing the use of external H<sub>2</sub> for making biofuels/green chemicals is mandatory in order to raise the processes value and to minimize

the losses in production. Still, the idea was not transformed into a full size industrial process but there were performed some studies on this topic.

In order to obtain gases from a solid, there has to be performed a gasification procedure, and for solids rich in carbon, this requires two steps. First, the volatiles should be removed from the solid in order to be processed in a separate reaction. This step is performed prior to gasification at temperatures lower than the gasification temperature, usually between 400 and 600 °C. After the volatile molecules have escaped from the solid, the remaining mass has to react with oxidative agents such as oxygen or steam which represents the second step.

However, in the case of humins, their structure remains almost the same as it undergoes very small changes and Hoang et al [19] have proved this by taking some HR-SEM images of the humins before and after the first gasification step (Figure 16).

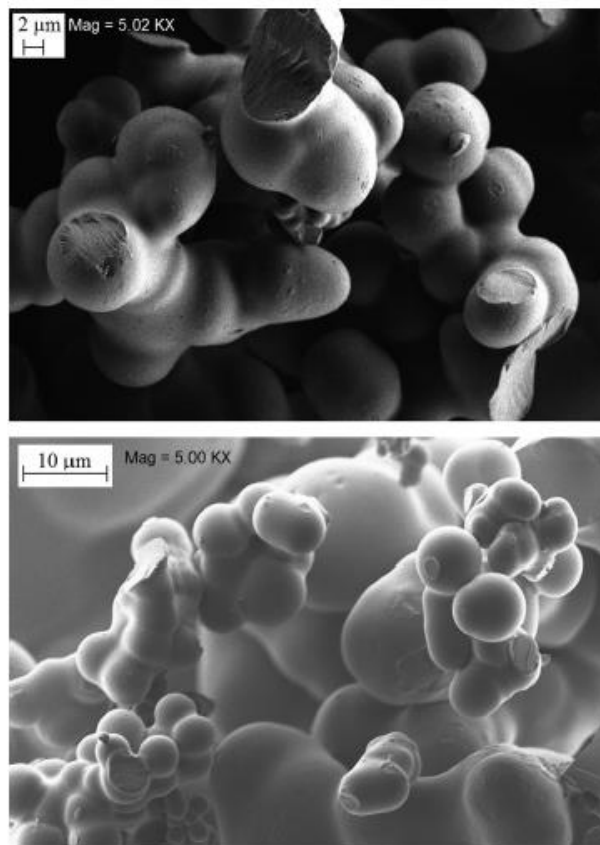


Figure 16. Fresh humins (top) compared to humins after heating at 750 °C (bottom) [19]

The second step is the actual gasification procedure. In order to perform this step in the classical manner, the probe has to be thermally treated at more than 1000 °C. In the case of humins, the yield of the process will be very low because of their complex structure and

great resistance. As to make the yield closer to 100% there should be used catalytic gasification.

This procedure is advantageous over the thermal process because of the improvement of reactivity, and thus the decrease of the reaction temperature. Moreover, tar, which is often formed during the conversion of highly carbonaceous materials, can be gasified completely in the presence of a catalyst. The catalytic gasification of biomass and biomass-derived syngas has been reviewed by several groups of researchers and the catalysts used in biomass gasification can be divided into two distinct groups. The primary catalysts are generally added directly to the biomass prior to gasification. They enhance the gasification rate of the remaining char. The second group of catalysts helps in tar destruction, hence increasing the gas yields. [19]

Despite extensive studies on the development of efficient catalysts for the reforming of oxygenate biomass-based compounds and tar, catalysts in the first group are based on conventional, off-the-shelf materials. Usually inexpensive, disposable materials such as dolomite, alkali metals, or alkaline earth metals are used as primary catalysts. It is well-known that alkali metals enhance the reactivity of biomass, char, and coal in dry or steam reforming. The gasification rate is improved dramatically. In addition, alkali metals are moderately active towards tar reforming. Almost complete conversion of humin can be achieved in the presence of  $\text{Na}_2\text{CO}_3$  catalyst at  $750\text{ }^\circ\text{C}$ . The addition of  $\text{CO}_2$  provides stability to the catalyst for continuous operation. [19]

Researchers have rapidly understood that gasification and combustion are some methods for valorization of humins, but they are not worth enough the effort needed to actually transform them, so a new method had to be found. One of the first came from J.M. Pin et al. [20] as to use humins in order to obtain bio-based composites.

The starting point for the research was the PFA (polyfurfuryl alcohol). The PFA-bio-based thermosetting resin is largely used in different applications such as foundry resins and composites, wood adhesives and most importantly in impregnation, because of its strong resistance for biological degradation. The major drawback of the PFA network is its high fragility, so the thermomechanical properties need to be modified. Combination with bio-based compounds modifies advantageously the PFA thermomechanical behavior such as introduction of triglyceride flexible moieties. Moreover, it has been proven that the PFA can interact with heterogeneous macromolecular compounds such as tannin or lignin which are also well-known biorefinery byproducts. [20]



According to the above-mentioned features, polyfurfuryl alcohol (PFA) was logically chosen for being combined with humins for three main reasons: (I) The PFA is a biobased polyfuranic, so combination with humins leads to fully biobased furanic resins. (II) The PFA network develops under acid-induced polycondensation, which is also one of the postulated routes for the humins growth. (III) Regarding composite applications, introduction of humins into the dense cross-linked PFA network could modify the thermomechanical properties. The first aim of this work was to prepare stable and homogeneous PFA/humins thermoset resins. [20]

Four different samples were prepared in order to be able to make a clear comparison between the PFA and the PFA/humins resins. The first two were undoped FA (furfuryl alcohol) and humins alone, then two different resins made from FA/humins/MA(maleic anhydride) with weight ratios of FA/humins/MA of 95/0/5% and 40/55/5, respectively. The FT-IR spectra of the samples clearly indicate a more complex network of furanic cycles due to the connections between the FA oligomers with humins. Taking it into this consideration, there was proposed a structure for the FA/humins thermoset resin represented in Figure 17.

The mechanical behaviour of the obtained resins was quite different from the one of neat FA or pure humins. There was observed a decrease in brittleness of the furanic matrix and an increase in the interfacial bonding with the cellulose fibers which were impregnated with these resins. Also, the tensile strength was two times higher than that for neat FA or FA/lignin composites.

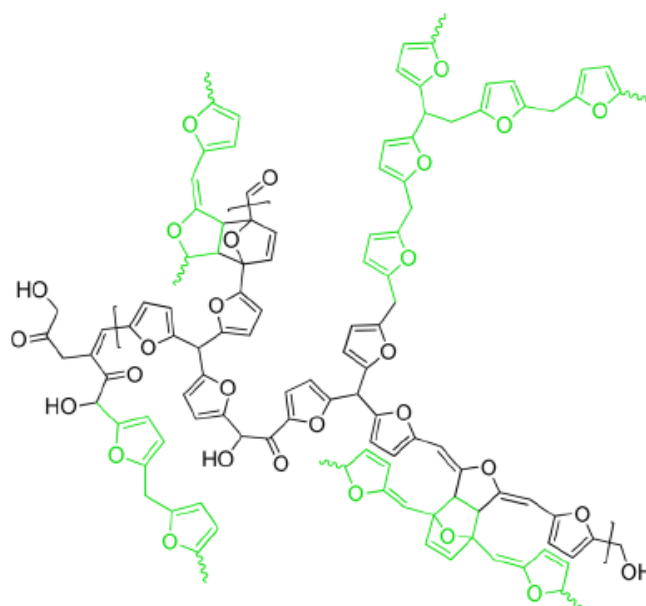


Figure 17. Proposed structure for PFA(green)/humins(black) thermoset resins [20]

This study demonstrates that humins can be valorized as an active component into PFA and in the meantime decreases its brittleness, which is one major drawback of the pure polyfurfuryl alcohol bio-based thermoset. As proof-of-concept, this precursory work opens gates to further develop reactive humins-based resins both for wood adhesion (plywood, fiberboards) and for wood durability. [20].

Further works are being conducted thanks to the efforts made by the J.M. Pin and his team [20] in order to demonstrate the capability of humins to be used as dopants for obtaining these thermoset resins and many other studies were performed as to find new applications for humins in order to increase the viability of the biomass valorization procedures.

## **Chapter 3. Carbon quantum dots – CQDs**

### **3.1 General knowledge**

Quantum dots are particles of size smaller than Bohr exciton radius ( $\leq 10$  nm), usually made from semi-conductors. However, more recently nanoparticles have also been obtained from different chemical elements, such as Au (gold). The name of the researcher which discovered quantum dots is Alexey Ekimov and by discovering them, he opened a new era for chemistry in the early 1981. He found in glass matrix particles as small as 2 nm and it was a shocking discovery.

Carbon-based quantum dots consisting of graphene quantum dots (QGDs) and carbon quantum dots (CQDs, C-dots or CDs) are a new class of carbon nanomaterials with sizes below 10 nm. They were first obtained during the purification of single-walled carbon nanotubes through preparative electrophoresis in 2004 [21] and then via laser ablation of graphite powder and cement in 2006 [22]. Carbon-based quantum dots with fascinating properties have gradually become a rising star as a new nanocarbon member due to their benign, abundant and inexpensive nature [23]. While carbon is a black material, with a low solubility in water and weak fluorescence, carbon-based quantum dots possess a good solubility and strong luminescence, for which they are referred to as carbon nanolights [24].

Moreover, compared to traditional semiconductor quantum dots and organic dyes, photo luminescent carbon-based quantum dots are superior in terms of high (aqueous) solubility, robust chemical inertness, facile modification and high resistance to photo bleaching. On one hand the superior biological properties of carbon based quantum dots, such as low toxicity and good biocompatibility, entrust them with potential applications in

bioimaging, biosensor and drug delivery. On the other hand, the outstanding electronic properties of carbon-based quantum dots as electron donors and acceptors, causing chemiluminescence and electrochemical luminescence, endow them with wide potentials in optronics, catalysis and sensors. [23]

### 3.2 Methods of synthesis

Since their discovery, Carbon Quantum Dots (Carbon QDs or CQDs) were heavily studied in order to find the optimal method for their synthesis and viable methods for their functionalization. Roughly, the methods of synthesis can be divided in two main groups – the first one being the so called “bottom-up” and the other one being “top-down”. Using both of the methods, the nano-particles that are obtained can be modified either during the synthesis itself or after the synthesis is done.

Nevertheless, there are also some issues that need to be considered prior the synthesis: (I) carbonaceous aggregation during carbonization, which can be avoided by using electrochemical synthesis, confined pyrolysis or solution chemistry methods, (II) size control and uniformity, which is important for uniform properties and mechanistic study, and can be optimized via post-treatment, such as gel electrophoresis, centrifugation, and dialysis and (III) surface properties that are critical for solubility and selected applications, which can be tuned during preparation or post-treatment. [23] In the Table 2 there are summarized the advantages and disadvantages of several methods for obtaining Carbon QDs.

Table 2. Methods of synthesis for Carbon QDs with their advantages and disadvantages. [25]

	Methods	Merits	Demerits
Top-down	Laser ablation	Controllable morphology and size	Complicated operation, high cost
	Electrochemical oxidation	High purity, high yield, controllable size, good reproducibility	Complicated operation
	Chemical oxidation	Easy operation, large scale production, no elaborate equipment	Non-uniform size distribution
	Ultrasonic treatment	Easy operation	Instrumental wastage, high energy cost
Bottom-up	Microwave synthesis	Short reaction time, uniform size distribution, easy size control	High energy cost
	Thermal decomposition	Easy operation, solvent-free, low cost, large scale production	Non-uniform size distribution
	Hydrothermal treatment	High quantum efficiency, low cost, non-toxicity	Low yield

The first one to be described is **chemical ablation**. This method implies 2-3 steps depending on the purpose of the synthesis. In the first step strong oxidizing acids carbonize small organic molecules to carbonaceous materials. The obtained materials can be further cut into small sheets by controlled oxidation. This method may suffer from harsh conditions and drastic processes. Peng and Travas-Sejdic [26] reported a simple route to prepare luminescent CQDs in an aqueous solution by dehydrating carbohydrates with concentrated  $H_2SO_4$ , followed by breaking the carbonaceous materials into individual CQDs with  $HNO_3$ . Finally passivating, which represents the third step, with amine-terminated compounds as for example 4,7,10-trioxa-1,13-tridecanediamine. The surface passivation was essential for the photoluminescence (PL) of these CQDs. The emission wavelength of these CQDs can be tuned by differing the starting material and the duration of the nitric acid treatment. [23]

**Electrochemical soaking** is a powerful method to prepare CQDs using various bulk carbon materials as precursors. However, there are only a few reports about electrochemically carbonizing small molecules to CQDs. A preparation method via the electro chemical carbonization of low-molecular-weight alcohols is proposed by Zhang et al. [27] Two Pt sheets were used as the working and auxiliary electrode, and a calomel electrode mounted on a freely adjustable Luggin capillary was used as the reference electrode. The alcohols were transformed into CQDs after electrochemical carbonization under basic conditions. The sizes and graphitization degrees of these particles increase with the increasing of the applied potential. The resultant CQDs with amorphous core exhibited excellent excitation and size dependent PL properties without complicated purification and passivating procedures. It is notable that the quantum yields (QYs) of these CQDs can reach 15.9%. Carbon QDs can be prepared from different small molecular alcohols showing low toxicity to human cancer cells. [23]

**Thermal decomposition** has been used to synthesize different semiconductor and magnetic nanomaterials. Recent studies have shown that external heat can contribute to the dehydration and carbonization of organics and turn them into CQDs. This method offers advantages of easy operation, solvent-free approach, wide precursor tolerance, short reaction time, low cost and scalable production [25]. An interesting approach was described by Ma et al. [28] This group synthesized N-doped CQDs with graphene-like structures by the direct carbonization of ethylene diamine tetraacetic acid (EDTA) heated in a sand bath at 260–228 °C. The species produced during EDTA decarboxylation might gradually fuse together to give graphite like structures under the solid-state reaction conditions, which is supported by the fact that the N-containing compounds can be converted into various graphitic carbon nitrides

at much higher pyrolysis temperatures. Martindale et al. prepared CQDs with a high yield of 45% by the straightforward pyrolysis of citric acid at 180 °C for 40 h. The resultant CQDs have an average size of  $6.8 \pm 2.3$  nm with a relatively broad size distribution. [29]

**Hydrothermal treatment** is a low cost, environmentally friendly and nontoxic route to produce novel carbon-based materials from saccharides, organic acids, juice or waste peels. Generally, a solution of organic precursor is sealed and reacted in a hydrothermal reactor at high temperature and high pressure. Bourlinos et al. [31] produced surface functionalized CQDs with visible fluorescence stimulated by a wide range of excitation wavelengths via hydrothermal treatment of ammonium citrate or 4-aminoantipyrine at 280 °C for 2 h. The as-prepared CQDs are monodispersed with sizes less than 10 nm and they are effectively dispersible in various solvents depending on the nature of the passivation agent. Zhang et al. [30] established a green one-step hydrothermal route to prepare CQDs by using L-ascorbic acid as a carbon source at 180 °C for 4 h. The water-soluble CQD solutions are very stable for at least six months at room temperature with stable fluorescence, which do not change over a wide pH range and even in solvents with strong ionic strengths. [25]

### 3.3. Applications

As in the cases of many other new materials to the world, Carbon Quantum Dots are heavily studied in order to figure out all the suitable applications for them. This part of their research is very important due to the fact that without important application, CQDs will remain just a demonstration of skill in the synthesis of advanced materials. An illustration of the applications of the CQDs that are known at present can be seen in Figure 18.

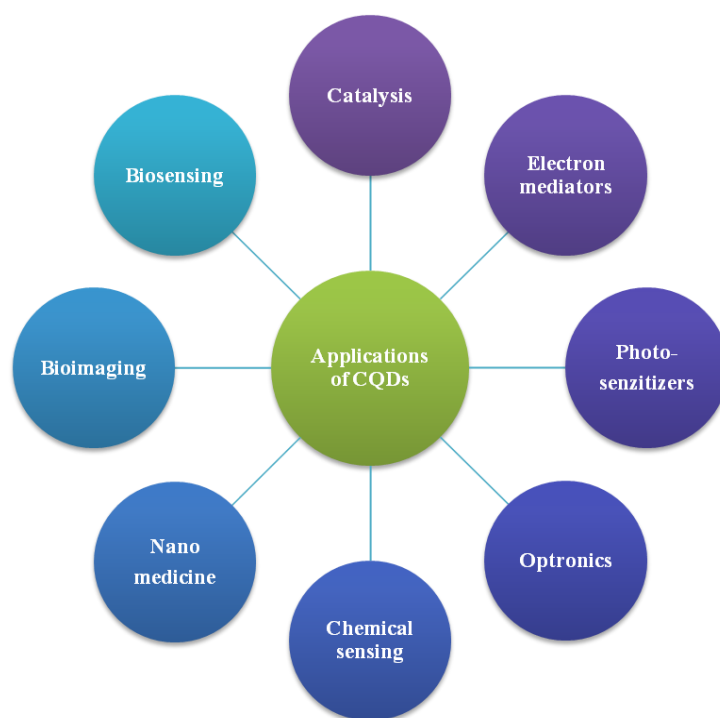


Figure 18. Applications of Carbon Quantum Dots

**Bioimaging.** As previously mentioned, CQDs have multiple advantages over semiconductor quantum dots, including comparable optical properties and good chemical and photochemical stability. Most importantly, carbon is largely non-toxic and environmentally friendly. These traits make CQDs very desirable as alternatives to semiconductor quantum dots to visualize biological systems both *in vitro* and *in vivo*. In general, the carbon cores of CQDs themselves are not toxic and any cytotoxicity of CQDs is primarily due to surface passivating agents on their surface. It has been demonstrated that surface passivating agents of low cytotoxicity can be used safely at high concentrations for *in vivo* imaging. For example, PEGylated CQDs showed no noticeable toxic effects *in vivo* up to 23 days when intravenously injected 8–40 mg/kg (CQD/bodyweight) into mice for toxicity evaluation. Physiological indicators were all at similar levels for mice exposed to different dosages of CQDs and the NaCl control, thereby suggesting the non-toxicity of CQDs at exposure levels and times beyond those typically used in *in vivo* imaging studies. No abnormalities were observed in harvested organs although the amounts of CQDs found in liver and spleen were higher than those found in other 16 organs. Moreover, cell viability was measured after cells had been treated with different amounts of CQDs. It was found that the average cell viability is greater than 95% at CQD concentrations up to 1.8 mg/ml. [31] These results clearly demonstrated that CQDs are much more biocompatible than semiconductor quantum dots.

Even though agents with high cytotoxicity profiles are used to coat them, CQDs modified in this way can still be used for in vivo applications if these agents are maintained at low concentrations and/or the incubation time is kept relatively short. [32]

**Chemical sensors** can be created from CQDs and they function by monitoring the changes in their fluorescence intensity under external physical or chemical stimuli, Carbon QDs were used to detect substances in small quantities such as DNA,  $\text{PO}_4^{3-}$ , thrombin, glucose, nitrite, biethiol,  $\text{Fe}^{3+}$ , pH,  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ . [23]

An interesting application of CQDs is in the field of chemical  $\text{Hg}^{2+}$  sensing. The detection of heavy metals such as is of utmost importance because of their dangerous effect on the environment and human health. CQDs were used for chemical sensing due to their low toxicity, water solubility, high photo stability and superior chemical stability.

Qu et al. [33] reported a preparative route toward distinctive fluorescent CQDs from dopamine (DA). Such CQDs exhibit excellent PL properties, and they can be used for multicolor bioimaging. More importantly, these CQDs were used as a new  $\text{Fe}^{3+}$  type of sensor for label-free detection of  $\text{Fe}^{3+}$  and dopamine (DA) with high sensitivity and selectivity

The method relies on the fact that  $\text{Fe}^{3+}$  can oxidize the hydroquinone groups on the surfaces of CQDs to the quinone species, which can quench the fluorescence of the CQDs and DA, can effectively shelter the fluorescence quenching due to their competition with CQDs to react with  $\text{Fe}^{3+}$ . It offers a convenient “mix-and-detect” protocol for rapid detection of and DA and can be easily accomplished with a rapid one-step (within 10 min) operation. Moreover, this sensing platform exhibits high sensitivity and selectivity towards  $\text{Fe}^{3+}$  and DA versus other metal ions and the other DA analogues. Furthermore, no further chemical modification of the CQDs was required, which offers the advantages of simplicity and cost efficiency. More importantly, the new strategy eliminates the need of QDs, organic dyes, and/or organic solvents, showing much more environmentally friendliness. [23]

In recent years, **photocatalytic processes** have gained tremendous momentum as greener alternatives in organic synthesis. Interest in photo catalysis has been motivated in part by the realization that sunlight is effectively an inexhaustible energy source. However, the high energy of UV and short wavelength visible light may adversely damage organic compounds. The demonstrated capability of harnessing long wavelength light and energy exchange with solution species of CQDs offers an excellent opportunity for their use as photocatalysts in organic synthesis. Indeed, a recent study has indicated that smaller CQDs (1–4 nm) are effective NIR light-driven photocatalysts for selective oxidation of benzyl alcohol to benzaldehydes with good conversion efficiency (92%) and selectivity (100%), due

to their excellent catalytic activity for  $\text{H}_2\text{O}_2$  decomposition and NIR light driven electron transfer property. [34]. The mechanism of this reaction is presented in the following Figure 19. The  $\text{H}_2\text{O}_2$  molecules are adsorbed on CQDs prior the reaction. These molecules are decomposed into active oxygen species ( $\text{HO}\cdot$ ), which have strong oxidation ability and are able to oxidize benzyl alcohol to benzaldehyde or benzoic acid. Additionally, a  $\pi$ - $\pi$  interaction exists between CQDs and benzyl alcohol or benzaldehyde, facilitating the adsorption of benzyl alcohol and benzaldehyde on the surface of CQDs. With NIR light irradiation, the photo induced electron transfer ability of CQDs can protect benzaldehyde produced in the first step.

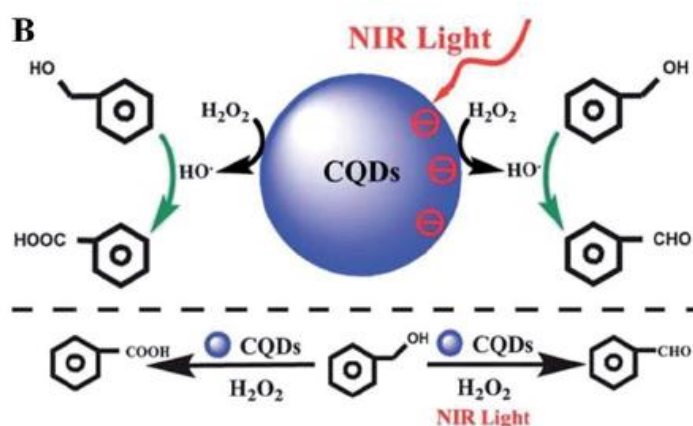


Figure 19. The mechanism of selective oxidation of benzyl alcohol [34].

Further studies suggested that the photo catalytic activity of CQDs can be effectively modulated by doping and by tailoring the surface groups. On the other hand, larger CQDs (5–10 nm) synthesized by electro-chemical ablation of graphite showed light-induced proton properties in solution, which can be used as acid catalysts to catalyze a series of organic transformations in aqueous media under visible light. [32]

### Titanium oxide-based catalysts

As one of the most popular photocatalysts,  $\text{TiO}_2$  has been used in the removal of organic pollutants and in the generation of  $\text{H}_2$  through water splitting. However, a major drawback in its photocatalytic efficiency resides in its ineffective utilization of visible light as the irradiation source. Because the bandgap of bulk  $\text{TiO}_2$  lies in the UV region (3.0–3.2 eV), only less than 5% of sunlight is utilized by  $\text{TiO}_2$ . Therefore, bandgap engineering by possible modification of  $\text{TiO}_2$  – based materials is one of the plausible approaches to enhance the performance of  $\text{TiO}_2$  photocatalysts. [32]



In view of their attractive optical properties and up-conversion in particular, a nanocomposite of CQDs and TiO<sub>2</sub> is expected to realize the efficient usage of the full spectrum of sunlight. One of the first to try this combination was Li et al. using methylene blue (MB) as a model compound, showed that TiO<sub>2</sub>-CQD nanocomposites are able to completely degrade MB (50 mg/mL) within 25 min under visible light irradiation, where only <5% of MB is degraded when pure TiO<sub>2</sub> is used as the photocatalyst. [35]

This example drove the studies of combining the TiO<sub>2</sub> with CQDs and of course much more work has been done. There were studied the behavior of the CQDs-TiO<sub>2</sub> nanotubes and CQDs-TiO<sub>2</sub> nanosheet composites which turned out to be similar to the one described before. After discovering these types of compounds, researchers started mixing together CQDs with other metal oxides like Fe<sub>2</sub>O<sub>3</sub> and Cu<sub>2</sub>O. Besides the combination with metal oxides, there was studied the possibility of combining the CQDs with metal phosphates like Ag<sub>3</sub>PO<sub>4</sub>. All of the above mentioned combinations were created in order to harness the full spectrum of sunlight and find the one with the best photocatalytic activity. [32]

Even though the combination of CQDs with metal oxides can give a significant increase in the photocatalytic activity comparing to the metal-oxides alone, there is still a lot of work to be done in order to increase the lifespan of the as prepared catalysts and maintain their catalytic activity throughout the time.

## Perspectives

During acid-catalyzed dehydration of carbohydrates large amounts of so-called humins are typically formed, leading to great losses of feed and, therefore, to great efficiency losses in biorefinery operations. In order to improve the process efficiency, humins formation should be avoided but this alternative is quite difficult since the humin formation is thermodynamically favored. An alternative with an extremely important economically value is the valorization of humins to functional materials production.

In this context, the main scope of the dissertation thesis is to develop a versatile and easy method for the synthesis of bifunctional TiO<sub>2</sub>-CQDs nanocomposites with acid and photooxidation properties, able to utilize in an effective way the visible light as irradiation source. To reach this scope worthless humins by-product, generated in the glucose acid-dehydration, will be used for the production of carbon quantum dots (CQDs) with small (1-4 nm) and large (5-10 nm) sizes. The obtained CQDs will be later used in developing TiO<sub>2</sub>-CQDs nanocomposites. For comparison SiO<sub>2</sub>-CQDs nanocomposite will be also synthesized.

Once demonstrated their photocatalytic efficiency in classically degradation tests of model compounds such as methylene blue (MB), and their light-driven acid ability in the glucose dehydration, the novel nanocomposites will be tested in the production of dicarboxylic acids (ie, succinic acid and 2,5-furandicarboxylic acid (FDCA)) directly from glucose. Such an approach not only increases the economically value of the carbohydrates valorization but also makes the transition from a linear economy (in which the resulted worthless by-products are separated and disposed) to a circular economy (in which the resulted worthless by-products either are recirculated into the system or are transformed into valuable products) - the key element for sustainable development.

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