

# Biorefining Twin Transition: Digitalisation for Bio-based Chemicals/Materials – Discovery, Design and Optimisation

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**Abstract:** The article discusses the production of platform chemicals from various biological sources, including glycerol, lignin, cellulose, bio-oils, and sea products. It presents the results of catalytic and downstream processes involved in the conversion of these biomass-derived feedstocks. The experimental approaches are complemented by numerical descriptions, ranging from density functional theory (DFT) calculations to kinetic modelling of the experimental data. This multi-scale modelling approach helps to understand the underlying mechanisms and optimize the production of platform chemicals from renewable resources.

**Keywords:** Bioeconomy · Biorefinery · Catalytic conversion · Fractionation and downstream



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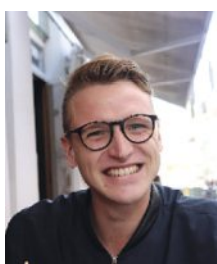
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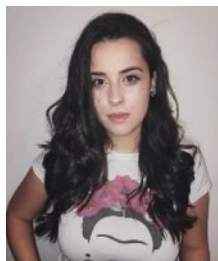
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**Brett Pomeroy** is a PhD student in the Department of Catalysis and Chemical Reaction Engineering specializing in HMF valorization *via* hydrogenation. His work is focused on heterogeneous catalysis synthesis, chemical reaction engineering, and kinetic modelling towards mainly biomass conversion processes.



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## 1. Introduction

Lipids, marine, and lignocellulosic biomasses are ubiquitous and sustainable sources of energy and materials. Their thermochemical and biochemical valorization has a tremendous potential to reduce the carbon emissions and to replace the exploitation of depleting fossil resources with renewable, sustainable and globally available alternative(s). It is essential to explore all available sources, including biomass, which has been demonstrated to be a viable alternative for the production of platform chemicals.<sup>[1]</sup>

Lipids, especially non-edible fats and oils, are already utilized for biodiesel production, where glycerol is the main byproduct, representing roughly 10% of the mass of the biodiesel produced. This led to a decrease of the crude glycerol commercial price due to its high abundance on the world market. Its catalytic valorization technologies to highly valuable and demanded allyl alcohol and glycidol have been demonstrated and patented by the authors. Furthermore, hydrodeoxygenation allows converting lipids or fatty acids into n-paraffins in conventional hydrotreatment units to be directly used as a diesel or jet fuel.

Lignocellulose (LC) is one of the world's most abundant sustainable carbon sources with an estimated annual output of around 170 billion tons/y.<sup>[2]</sup> This biomass includes wood, grass, agricultural wastes, and paper production (by)products. In the past, this material found its main applications as a source of energy due to its calorific value and to produce pulp and paper from the cellulose fibres obtained after the dissolution of hemicellulose and lignin.<sup>[3]</sup>

Whole lignocellulose could eventually be pyrolyzed or solvolyzed to yield liquid oils which can be further hydrotreated to yield liquid fuels,<sup>[4]</sup> while cascade valorization by thermochemical or biochemical fractionation to main three biopolymers (cellulose, hemicellulose and lignin) and their further (catalytic) conversion into value-added products is more economically viable. The production of aromatics, for example, completely relies on an unsustainable crude oil source. Therefore, in recent years, the emphasis of study has been switched to the sustainable production of aromatics. In this context, lignin is currently considered a waste that will become a valuable feedstock for future bio-refineries to produce synthetic fibres, pharmaceuticals, insecticides, detergents, polymers and dyes, among other products. Similarly, (hemi)cellulose can be depolymerized to sugars and further converted to C5 and C6 building blocks and chemicals, including dicarboxylic acids, diols, triols widely used in polymer industry. On the other hand, pulp and cellulose fibres are also increasing in demand globally. The modification of the latter by (de)functionalization allows tuning the surface properties and mechanical properties and even allows replacing the synthetic fibres with functionalized natural ones.

Marine biomass and the corresponding food waste are also available in large quantities and mostly underutilized. This offers a great opportunity for biorefineries to become not only technically but also economically feasible, especially when targeting high added-value products like pigments.

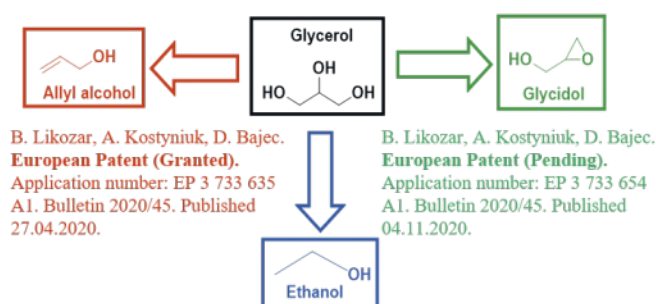
In this work the state-of-the art technologies for converting various biomasses into a wide spectrum of value-added products at various technology readiness levels (TRLs) are presented, as well as the *in-silico* tools for understanding the underlying chemical mechanisms.

## 2. Sustainable Production of Allyl Alcohol, Ethanol and Glycidol: Gas-phase Conversion of Glycerol over New Patented Catalysts in a Packed-bed Continuous Flow Reactor

Glycerol valorization can be carried out in the gas phase over heterogeneous catalysts, where acrolein, acrylic acid, dihydroxyacetone, hydroxyacetone, epichlorohydrin, lactic acid, 1,2-propanediol, 1,3-propanediol, and recently allyl alcohol, ethanol and glycidol are the most valuable products of this process. These products are important for industrial commercialization due to many applications and their high profitability on the world market.

Current industrial processes for the production of allyl alcohol are fossil fuel-based routes from hydrogenation of propylene-derived acrolein or propylene oxide isomerization. Ethanol can be obtained by commercial routes through the hydration of ethylene over a solid acid catalyst or by the fermentation of sugar, grain crops, and waste biomass. Glycidol can be produced commercially *via* two methods: the first method is epoxidation of allyl alcohol (derived from propylene or propylene oxide) with hydrogen peroxide over tungsten oxide or salts of tungstic acid and recently over titanium silicate (TS-1) catalyst. All these methods have substantial obstacles: more than one preparation stage is needed, toxic and non-environment friendly route/compounds, high production cost, unsustainable production, large amount of waste, expensive purification steps, equipment corrosion, hazardous feedstock. Our group has recently implemented the 'green' and one-step allyl alcohol,<sup>[5]</sup> ethanol,<sup>[6]</sup> and glycidol<sup>[7]</sup> production from glycerol without H<sub>2</sub> in a gas-phase packed-bed continuous flow reactor under atmospheric pressure (Fig. 1).

The synthesis of metal-modified ZSM-5 catalysts were achieved by the simple wet impregnation method. The influence of metal(s) species incorporation into ZSM-5 zeolite framework on the acidity–basicity and its catalytic performance was elucidated. The modified zeolite catalysts were thoroughly studied using different analytic techniques to study their structural, morpholo-



- One-step synthesis
- Cost-effective reaction
- Good eco-efficiency
- Cheap heterogeneous catalyst
- Atmospheric pressure
- No need H donor
- Gas-phase reaction
- Packed-bed continuous flow reactor

Fig. 1. Catalytic conversion of glycerol into allyl alcohol, ethanol and glycidol.

gy, acidic, and basic properties. Exhibiting notable performance, the 20%Cs/ZSM-5 catalyst with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1500$  yielded a remarkable 99.6% maximum ethanol yield, and under different reaction conditions, achieved a 40.4% glycidol yield, while the 5%Cs2.5%Fe2.5%Mo/ZSM-5 catalyst stood out for its allyl alcohol selectivity, reaching 46.1% at 98.1% glycerol conversion. All these catalysts exhibited superior catalytic activity in comparison to the literature data at the same time-on-stream. It was found that the best catalytic performance was related to the ample number of surface acid/basic sites (suitable number of basic sites), the strong synergistic interaction between metal(s) species and HZSM-5 zeolite, and to its smaller crystallite size.<sup>[5,7]</sup>

### 3. Lignocellulosic Biomass Fractionation

Lignocellulose (LC) is mainly composed of cellulose, a linear polysaccharide composed of glucose molecules, hemicelluloses, a branched polysaccharide consisting of different monosaccharides (*i.e.*, xylose, arabinose, mannose, and galactose), and lignin, an amorphous highly branched aromatic polymer. Cellulose and hemicellulose can be used as a source of nanocellulose, emulsifiers and platform chemicals such as hydroxymethylfurfural (HMF) and furfural. In addition, lignin can be used to prepare biomaterials such as resins and phenolic compounds.<sup>[2]</sup> The fractionation of lignocellulosic biomass involves the separation and isolation of extractives, hemicellulose, cellulose and lignin from the LC, and represents a crucial step for their cascade valorisation towards the production of targeted value-added chemicals and materials. The current technology used in the pulp & paper industry (*i.e.*, Kraft process) can be considered as an example of biomass fractionation since cellulose is obtained as fibers and lignin and hemicelluloses are extracted from the effluents.<sup>[8]</sup> However, these processes have as their main goal the preparation of cellulosic fibres that still contain other chemicals, such as lignin.<sup>[9]</sup> In the meantime, the preservation of the biopolymers present in the effluents is not considered to result in low-quality biopolymers. For example, Kraft lignin is of low purity and significantly differs from natural lignin because it contains sulphur and has a high content of conjugated groups.<sup>[3]</sup>

To overcome these drawbacks and ensure the economic viability of the LC fractionation, great efforts have been made to develop a process aimed at preserving the molecular structure and properties of all three biopolymers (cellulose, hemicellulose and lignin) and allowing their conversion into more valuable products (Fig. 2). The quality of the lignin and hemicellulose streams could be improved by applying lignin-first, hemicellulose-first fractionations. The fractionation process itself strongly affects the lignin structure and properties and could be tailored accordingly. Therefore, our group's research focuses on understanding organosolv biomass fractionation, especially how the operating conditions affect the lignin structure. The studies were devoted to the analysis of the acid-catalyzed ether bond cleavage mechanisms in (aqueous) organic solvents such as methanol, ethanol, and  $\gamma$ -valerolactone and primarily focused on establishing the correlation between the model compound and the real lignin sample. Moreover,

it represents a first step towards the kinetics and structure–activity relationship of biorefining industrial resources.<sup>[10]</sup>

### 4. Lignin Valorization Processes: Catalytic Hydrotreatment and Depolymerisation for Production of Bio-monoaromatics

Globally, 50 million tons of lignin are annually produced by biorefineries, pulp and paper industries, where lignin is considered to be a low-value by-product. It is burned to cover energy requirements of the process. Instead, lignin could be converted into valued chemicals like benzene, xylene, toluene (BTX) or aromatic building blocks (partially depolymerised lignin) for bio-based materials (*e.g.* polyurethane resins) by catalytic conversion processes. This approach is sustainable for the generation of aromatics due to the fact that lignin is the naturally occurring and only biopolymer with six-membered aromatic rings. Therefore, high-value bio-based materials can be produced by cleaving major dominant linkages in the lignin matrix like  $\beta$ -O-4,  $\beta$ - $\beta'$ ,  $\beta$ -5,  $\beta$ -1', and 4-O-5'. Pyrolysis, cracking, and hydrogenolysis/hydrotreatment are some of the commonly utilized methods for lignin depolymerization.<sup>[11]</sup>

Catalytic lignin valorization is the outcome of several consecutive and simultaneous reactions: cleavage of the end- and/or inter-unit bonds, defunctionalisation and repolymerisation (crosslinking reactions). Lignin depolymerisation products, yields and specific reaction mechanisms depend on the process conditions and methodology applied, for instance acid- or base-catalysed, oxidative, reductive or thermal degradation process.<sup>[12]</sup>

Besides, the hydrotreatment of lignin under solvent free condition has emerged as an attractive strategy to produce aromatics.<sup>[13]</sup> This technique is comparable to cracking of vacuum gas oil (VGO), followed by hydrodesulfurization (HDS) in petroleum re-

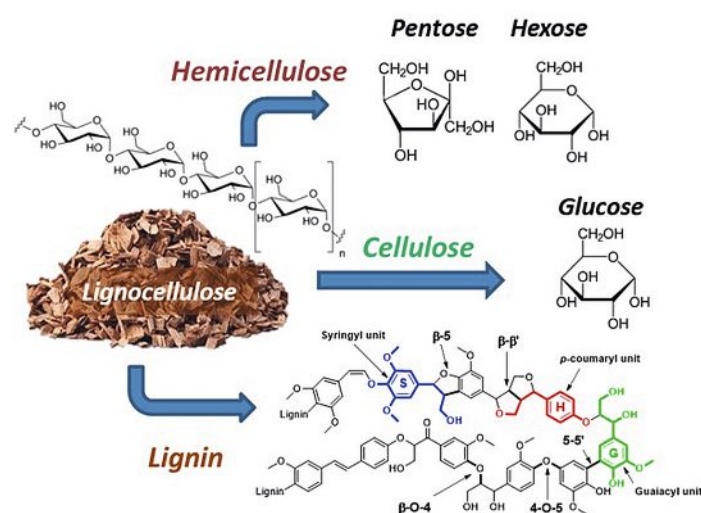


Fig. 2. Components of lignocellulosic biomass being separated during the fractionation.

fining industries. Zeolites are typically utilized to crack, while Ni/Co promoted Mo/W based sulfide catalysts are applied for HDS. In the case of lignin hydrotreatment, a catalyst with dual properties (breaking the C–C/C–O bonds followed by hydrodeoxygenation (HDO)) is necessary for production of aromatics. Since, Ni/Co promoted Mo/W-based catalysts are known for excellent HDS and HDO activity<sup>[4,14]</sup> and external-solvent-free hydrotreatment of lignin reaction generally performed at high pressure and temperatures (>350 °C and > 50 bar H<sub>2</sub>). Several catalysts, metal sulfides, phosphides, carbides including noble metals, are reported in literature for the lignin hydrotreatment. However, when considering technical lignin like Kraft or lignosulfonates, the noble metal catalysts are not suitable as they are deactivated by the sulfur present in lignin. During catalytic hydrotreatment of lignin, a number of parallel and consecutive reactions may occur in gas (gasification of products), liquid and solid (repolymerization) phase, as shown in Fig. 3.<sup>[15]</sup> Minimizing reactions that occur in the gas and solid phases, for which the acidity of the catalyst is responsible, is crucial when looking for compounds like BTX. The acidity of the catalysts also plays a vital role in lignin depolymerization and repolymerization of oligomers formed.<sup>[16,17]</sup> Consequently, the catalyst design must incorporate features like moderate acidity and high HDO capability to produce high yields of aromatics. Also, it is evident that ball milling of lignin followed by catalytic hydrotreatment has a great influence in lignin depolymerization.<sup>[18]</sup>

## 5. Conversion of Biomass towards Aldaric/Adipic Acids in an Environmentally Benign and Sustainable Way

Production of glucaric acid from glucose, and subsequent conversion of glucaric to adipic acid is of great interest. Glucaric acid is used as an ingredient in detergents, a substitute for phosphates, and in the food and pharmaceutical industries. It has been recognized as one of the top value-added compounds derived from biomass, by the US Department of energy in 2004.<sup>[19]</sup> Furthermore, the market cap for adipic acid, the main raw material for the production of nylon 66, surpasses 7 billion USD *per year*.

Glucaric acid is industrially obtained by glucose oxidation with nitric acid and/or bleaching agents, which is technologically demanding and ecologically taxing.<sup>[20]</sup> It offers a reasonable selectivity but is burdensome due to NO<sub>x</sub> emissions and nitric acid discharge. Current research focus is the production of glucaric acid by direct oxidation of glucose with molecular oxygen. Research is focused on heterogeneous catalysis using metallic or bimetallic catalysts in an aqueous solution of glucose. Heterogeneous catalysts often contain gold, platinum, or both. The goal of the process is the selective oxidation of terminal C-atoms of glucose. Although patents describing these processes have already been filed, commercialization is still out of reach.

In work being done by our department, we synthesized and characterized different gold monometallic and bimetallic catalysts containing either platinum or copper (unpublished data). We found out that both bimetallic catalysts outperformed their monometallic counterpart in regards to yield. Additionally, the gold–platinum catalyst showed higher selectivity than the gold–copper catalyst. Our current research focus is to improve the yield of glucaric acid with different reactor engineering and catalyst design approaches. Additionally, we aim to identify the rate limiting steps in the whole three-phase reaction system. Fig. 4 describes the possible reaction routes for the production of adipic acid from renewable biomass, compared to petro-chemical production route.

The current industrial process is heavily dependent on oil, since cyclohexane and cyclohexanol are acquired from fossil resources. Another problem is that for every ton of adipic acid produced, over 16 tons of CO<sub>2</sub> are emitted.<sup>[21]</sup> Like in the production of glucaric acid, nitric acid and hazardous NO<sub>x</sub> emissions are problematic, but also the conversion is maintained at low values

due to exothermicity of the reaction, which is an additional safety hazard for large scale production.

A study performed by our department revealed a possible production route for adipic acid with a rhenium on carbon catalyst. The results indicate, that when methanol is used as the solvent, there is no need for additional hydrogen gas. In a single-step reaction the precursor is first esterified with methanol. The protected precursor is then hydrodeoxygenated, where the -OH groups are removed. This is followed by subsequent hydrogenation of the double bonds. The final yield of monohexenoates was 93% under optimized conditions.

The overall goal is to combine oxidation of glucose to glucaric acid and then hydrodeoxygenation of the latter to adipic acid in a cascade reactor system. This would drastically lower the costs and enhance the competitiveness of the process among the already established production processes.

## 6. 5-(Hydroxymethyl)furfural (HMF) and Furfural (F) Production Processes

The conversion of cellulose, a glucose polymer, and hemicellulose, a pentose-rich fraction of biomass residues into different furanics (furfural and hydroxymethylfurfural) is a promising alternative to produce a wide range of bio-based chemicals and polymers.<sup>[22]</sup> However, the conversion of pentoses and hexoses from real biomass streams appears to be difficult due to their complex chemical composition and the unstable nature of sugars and furanics.

Both homogeneous catalysis and heterogeneous acid catalysts are commonly applied for hexose and pentose dehydration.<sup>[23]</sup> However, the use of mineral acids and salts can often cause corrosion and poses a safety risk.<sup>[24]</sup> Therefore, solid acid catalysts such as various resins, zeolites, *etc.* have been preferred recently. In addition, the formation of insoluble resinous compounds as a result of reactions between furanics and saccharides, as well as furanics alone, can negatively affect product selectivity and reaction yield.<sup>[25]</sup>

Another important aspect is the choice of solvent, since the commonly used solvents stabilize the products/reactants and prevent their degradation to complex polymeric species, the humic substances.<sup>[26]</sup> To further improve the yield and selectivity of furans, organic solvents can be used as reaction media. They can either be miscible or form two phases with water, thus preventing the problematic humin formation.

A recent study by our group has also shown that no additional catalyst is required to achieve sufficient yield of furans in subcritical water, which could be due to the thermal degradation of saccharides or the formation of H<sup>+</sup> at high temperatures in liquid water.<sup>[27]</sup> Moreover, we demonstrated that the reactivity among saccharides can differ significantly. Aldohexoses such as glucose usually require an additional step of isomerization to ketohexoses such as fructose, which are later very easily converted to 5-HMF. Pentoses, on the other hand, are usually more prone to be converted to furfural, even without an isomerization step and demonstrate higher yields and selectivities.

In our laboratory, we used a commercial H-beta zeolite catalyst to study different reaction parameters for the production of furfural from pentose sugars in batch reactors. In addition, the effect of external and internal resistance on mass transfer was evaluated and experimentally verified. The primary pentose sugar studied was xylose, but the effects of several other pentoses such as arabinose and ribose from natural sources were also investigated. In an effort to develop a sustainable process, water was primarily used as a solvent, but the effects of various short-chain alcohols and dimethyl sulfoxide (DMSO) were also studied. The use of DMSO as a solvent in this reaction proved to be suitable as it prevents the formation of humic substances with a yield of up to 70 mol%.<sup>[70]</sup>

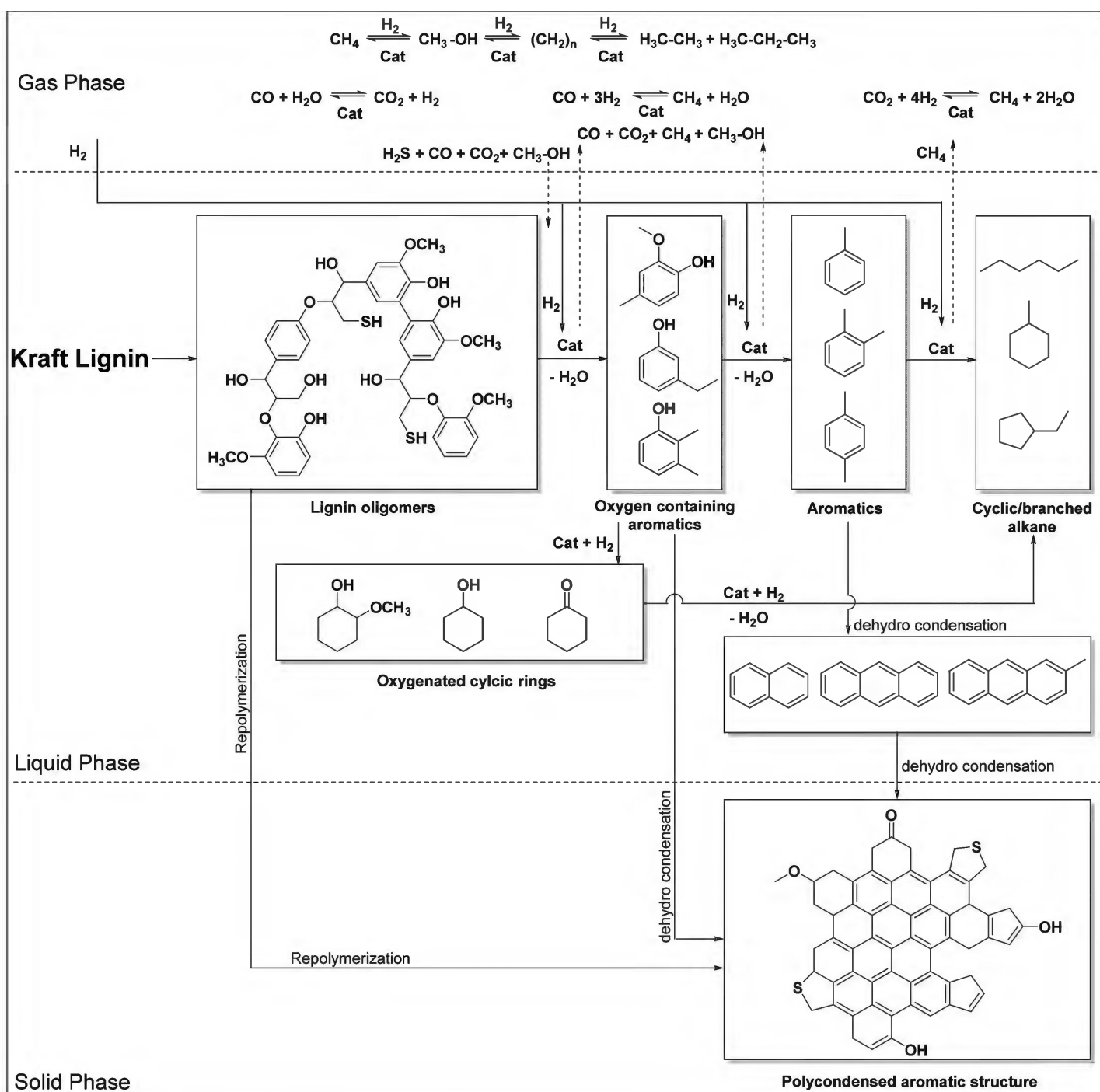


Fig. 3. Hydrotreatment process showing various reactions in solid, liquid and gas phases. Reproduced with permission from Chowdari *et al.*<sup>[15]</sup> *ACS Sustain. Chem. Eng.*, published by ACS, 2019.

## 7. HMF Conversion to Diols and Triols

HMF is a crucial platform chemical that has enormous potential. As a result of its diverse functionality including an aldehyde alcohol, and furan ring, it can be converted into a large assortment of value-added bio-based chemicals that are of interest in the polymer industry. Hydrogenation has been identified as one of the most promising conversion methods to achieve these chemicals. Generally, hydrogenation occurs under high hydrogen pressures (50–100 bar), moderate temperatures up to 250 °C in presence of a heterogeneous solid catalyst. In terms of active catalysts, transition metals such as nickel have been recognized to be effective and are economically favourable over more expensive noble metals, however, they typically require promoters to enhance activity and tune product selectivity.

An initial study reported by our department demonstrated the critical role of nickel species amongst carbon-supported nickel-based catalysts to facilitate dehydration of HMF towards dimethylfurfural (DMF), a potential biofuel with a higher energy density than bioethanol.<sup>[28]</sup> Only when applying an acidic support such as alumina was it possible to achieve ring saturation and ring opening reactions yielding 2,5-bishydroxymethyltetrahydrofuran (BHMTHF) and 1,2,6-hexanetriol (1,2,6-HT), respectively.<sup>[29]</sup> BHMTHF is of interest as it has been recognized as a potential bio-based alternative in polyester manufacturing. On the other hand, 1,2,6-HT is the most desirable chemical that can be obtained from HMF, which is an intermediate for 1,6-hexanediol used in adhesives, coatings, and paint applications with a global market value of \$600 million USD. Though, until now, it has been entirely made from benzene with subpar yields and harsh reagents.

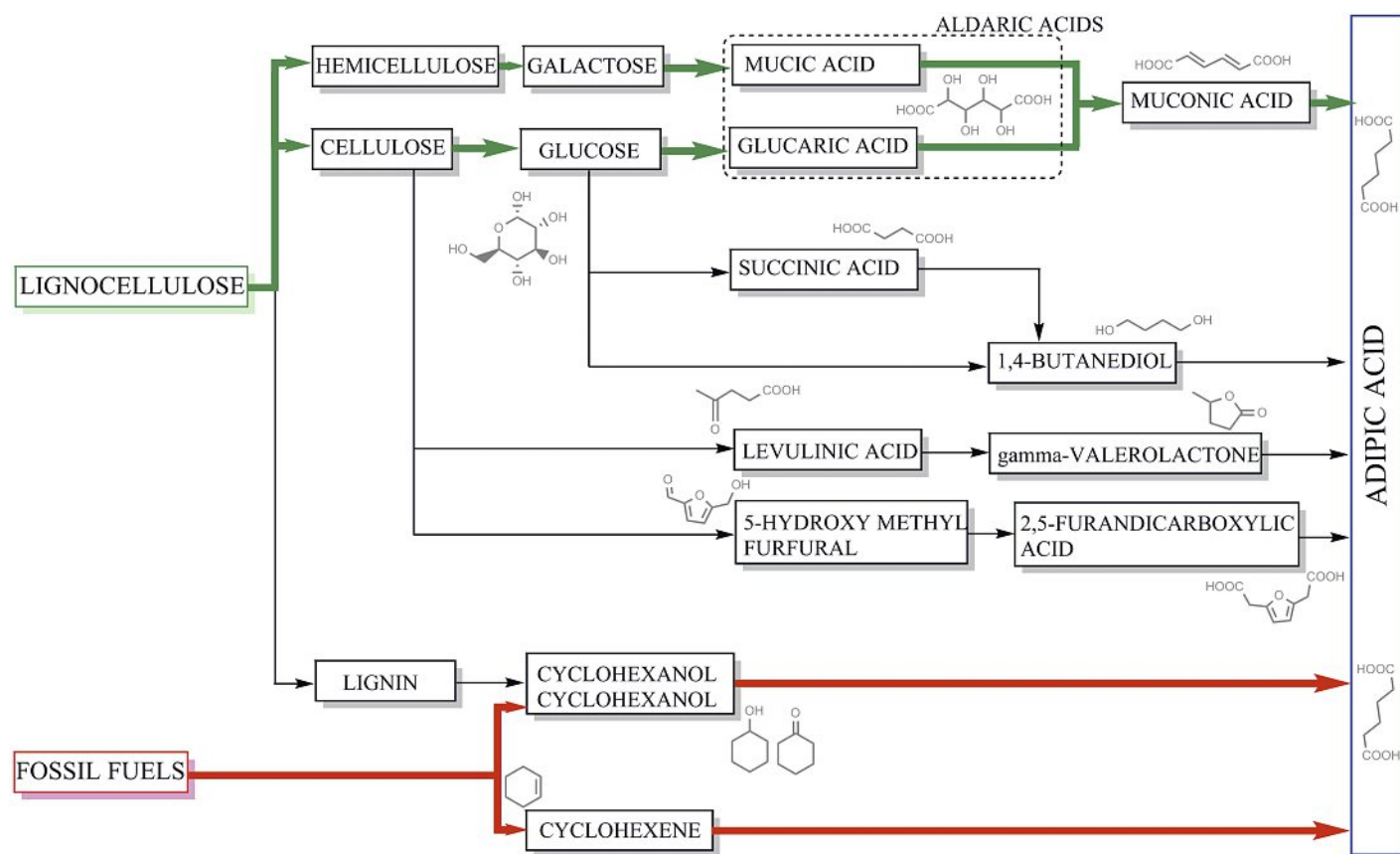


Fig. 4. Comparison of conventional petrochemical adipic acid production and a sustainable production from lignocellulosic biomass.

Furthermore, it was discovered that when incorporating water into the solvent system along with THF, all dehydration reactions were essentially eliminated, leaving BHMTHF and 1,2,6-HT as the sole products. Finally, our department also presented a study demonstrating that by modifying the acidic-basic properties of the catalyst surface with ceria pretreated under different conditions, it was possible to enhance 1,2,6-hexanetriol yield.<sup>[30]</sup>

## 8. Enzymatic Conversion of Lignin and Biomass-derived Chemicals

Biomass is an abundant and renewable source of various new and greener chemicals. In order for its full utilization, new processes and technologies need to be developed. These processes must not only be efficient but also more environmentally friendly in order to also tackle the ever-growing problem of pollution of natural environments.

As aforementioned, lignin is a renewable source of value-added chemicals like aromatic compounds, however, due to its heterogeneous structure it is highly resistant to degradation and subsequently underutilized. It can be depolymerized by chemical methods like pyrolysis, oxidation, gasification, and hydrolysis under supercritical conditions,<sup>[31]</sup> but these require a high amount of energy, use or produce compounds that pollute the environment and are usually very unspecific. In nature, microorganisms like white-rot fungi have been shown to have high lignin-degrading capacity.<sup>[32]</sup> Thus, as an alternative to conventional chemical processes, isolated microbial enzymes can be used. Enzymes like laccases, peroxidases and  $\beta$ -etherases have already been shown to be active on the lignin polymer or its model compounds in *in vitro* reactions.<sup>[33]</sup> However, the mechanism of action for each enzyme type is different and can result in either depolymerization ( $\beta$ -etherase system) or polymerization (laccases, peroxidases) of lignin or lignin model compounds. Enzymatic activity is also influenced by a wide variety of factors which need to be optimized

in order to obtain the best selectivity and product yields. Thus, although enzymatic lignin conversion shows great potential, more research is needed in order to make it viable for large-scale industrial use.

Enzymatic biocatalysis can also be used in the production of biomass-derived platform chemicals. One example is 2,5-furandicarboxylic acid (FDCA). FDCA's most promising use is as a replacement of terephthalate in oil-based plastics like polyethylene terephthalates.<sup>[34]</sup> FDCA is mostly produced from C6 sugars *via* HMF which can be oxidized to FDCA through three intermediates: 2,5-diformylfuran (DFF) or 5-hydroxymethyl-2-furoic acid (HMFA) and 5-formyl-2-furoic acid (FFA) (Fig. 5). Most chemical methods for the production of FDCA from HMF require harsh conditions resulting in high energy expenditure as well as environmental pollution. Thus, as a greener alternative, enzymatic catalysts can be used. However, only a few enzymes have been shown to be active against HMF and other reaction intermediates, and, in order to obtain a complete conversion of HMF to FDCA, multi-enzyme reactions were needed<sup>[35,36]</sup> (Fig. 5). In a study done by our department, we used different commercially available enzymes in oxidation reactions with HMF and its intermediates.<sup>[37]</sup> The study aimed at understanding the conversion mechanism of HMF to FDCA by selected enzymes, since by understanding the reaction pathway, as well as substrate specificity and the effect of substrate concentration, we would be able to better optimize this process and obtain the best product yields in the future. Six different enzymes, *i.e.* horseradish peroxidase and lignin peroxidase, alcohol and galactose oxidase, catalase and laccase, were used in single and multi-enzyme reactions. We determined that none of the selected enzymes or enzyme combinations were capable of complete conversion of HMF to FDCA. However, we showed that combining enzymes with complementary activities can markedly increase the reaction efficiency and subsequent product yields.

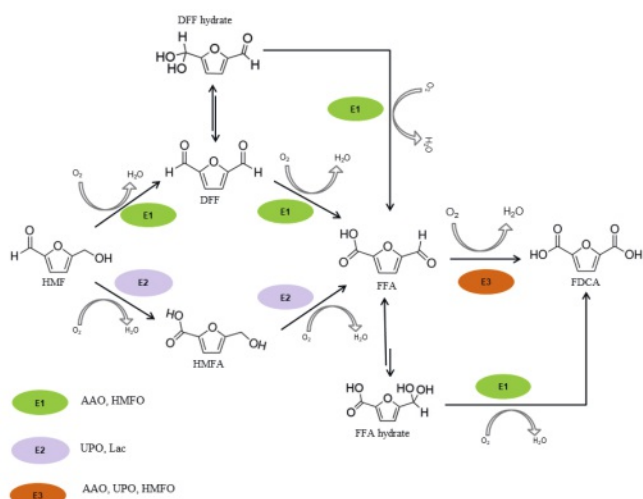


Fig. 5. Schematic representation of oxidation routes of HMF to FDCA by different enzymes (E). AAO – aryl-alcohol oxidase; HMFO – HMF oxidase; UPO – unspecific fungal peroxidase; Lac – laccase. Reproduced with permission from Cajnko *et al.*,<sup>[37]</sup> *Biotechnol.*, published by Springer Nature, 2020.

## 9. Catalytic Conversion of Lipids to n-Paraffins: Hydrogenolysis and Transformation Pathways for Biofuel Systems

Lipids in the form of bio-oils and waste oils are currently utilized for the production of renewable diesel, sustainable aviation fuels and can be utilized for a number of platform chemicals such as fatty alcohols, esters and aldehydes (Fig. 6). The lipid sources are numerous, however the goal is to move away from the sources that compete with food towards more advanced and also demanding sources such as microalgae and waste oil streams.<sup>[38]</sup> For the preparation of fuels, common defunctionalisation catalysts such as supported NiMoS<sub>x</sub> and CoMoS<sub>x</sub> catalysts are used since they include all of the desired functions and can ensure a stable process in very demanding environments – at high temperatures, with streams that include number of impurities in the form of P, Fe, Ca, S and more. The triglycerides thus undergo hydrogenolysis to fatty acids and are then reduced to alkanes through a net of reduction, dehydration, C–C scission and hydrogenation reactions.<sup>[17]</sup> In our research, we are focused on the in-depth understanding of catalyst functions such as hydrogenolysis, C–C scission, dehydration, esterification and hydrogenation. We studied the connection between the catalyst structure, such as hydrogen activation, acidity, basicity, and the kinetic expression of the catalyst function. Herein, our end goal was the isolation of the desired catalyst functions towards high selectivity and activity for the production of the platform chemicals such as fatty alcohols, fatty aldehydes or esters from bio-sources. For this purpose, we have recently published the most accurate kinetic analysis done up to date of palmitic acid hydrodeoxygenation including 8 reactive species and 11 transformations showing the impact of hydrogen on the deoxygenation of intermediates and calculating the kinetic parameters such as reaction rate constants, activation energies. Beyond that we show that the implementation of adsorption selectivity is required to fully describe the hydrodeoxygenation process. We have calculated the impact of external and internal mass transfer.<sup>[39]</sup>

## 10. Crustacean Waste Valorization – A Step towards a Shell Biorefinery

World population growth allied with the challenges scaling-up the production of land-derived food crops have contributed to an intensive fish and aquaculture production. Current predictions

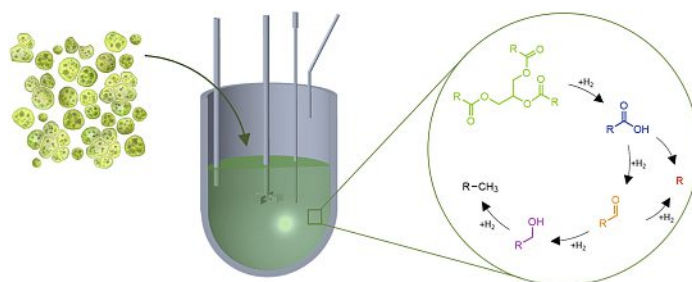


Fig. 6. The abstract representation of the hydrodeoxygenation process for the algae oil. Reproduced with permission from Marinič *et al.*,<sup>[38]</sup> *Renew. Energy.*, published by Elsevier, 2023.

report a 21–44 million tons increase in food from the sea by 2050, which represents a 36–74% increase compared to current yields.<sup>[40]</sup> Of the seafood traded annually, crustaceans are of particular interest, however only 40% of them are edible meat. Consequently, 16.6 million metric tons of crab, shrimp and lobster shells waste are produced globally.<sup>[41]</sup> Crustacean shells are composed of 20–30% proteins, 30–40% calcium carbonate, 20–30% chitin and small amounts of astaxanthin.<sup>[42]</sup> The proteins could be used as fertilizers and for animal feed. Calcium carbonate has multiple uses in pharmaceutical, agricultural, construction and paper industries. Chitin and its water-soluble derivative chitosan display a wide range of applications in medicine, food and beverages, cosmetics, agriculture, and healthcare industries.<sup>[43]</sup> Yet, from these compounds, only chitin is being industrially isolated, presenting a market value of 42.3 billion USD in 2020 that is projected to reach 69.3 billion USD by 2028.<sup>[44]</sup>

Up to date, our department has presented three different technologies for chitin extraction from shrimp shells wastes<sup>[45–47]</sup> as well as four processes to convert chitin into chitosan.<sup>[42,48]</sup> Chitin extraction routes from shrimp shells waste are: *i*) a deep eutectic solvents (DES)-based extraction,<sup>[45]</sup> *ii*) a hybrid organic acid and dielectric barrier discharge (DBD) plasma extraction<sup>[46]</sup> and *iii*) a conventional eco-solvents extraction.<sup>[47]</sup> Chitin deacetylation routes use an adaptation of the conventional process with *i*) 40 wt% and *ii*) 50 wt% of NaOH,<sup>[48]</sup> *iii*) a hybrid novel approach based on DES and NaOH under milder conditions,<sup>[42]</sup> and *iv*) pure DES or in aqueous solution.<sup>[48]</sup> Depending on the process, it is possible to isolate pure chitin with 80% extraction yield and convert it to chitosan with a degree of deacetylation (DDA) higher than 80%. The presence of DES allows the reduction of NaOH used for the deacetylation, however it is still not possible to only use DES as greener solvents for this task. With the optimized conditions, choline chloride:malic acid allowed a DDA ≈ 40%, which falls slightly behind the threshold value (50%) for chitin to be considered chitosan. Among chitin isolation studies, the most promising one proposed a full biorefinery approach (Fig. 7) as a sustainable cost-effective business model.<sup>[47]</sup> Herein, it was possible to recover most of the compounds present in the shrimp shells, namely chitin, proteins and astaxanthin, using simple and scalable techniques that are already being applied by the industry, and with more environmental friendly solvents. Lastly, the business model shows the feasibility of using this technology to develop a shell biorefinery, especially considering the profits for astaxanthin.

## 11. Cellulose Nanomaterials Biocomposites

Cellulose is the main component of lignocellulosic biomass, representing between 35% and 50% of total mass. This makes it the most abundant biopolymer on Earth.<sup>[49]</sup> Its hierarchical structure allows extraction of cellulose nanoparticles in two forms: cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs). According to standard terms proposed by Technical Association



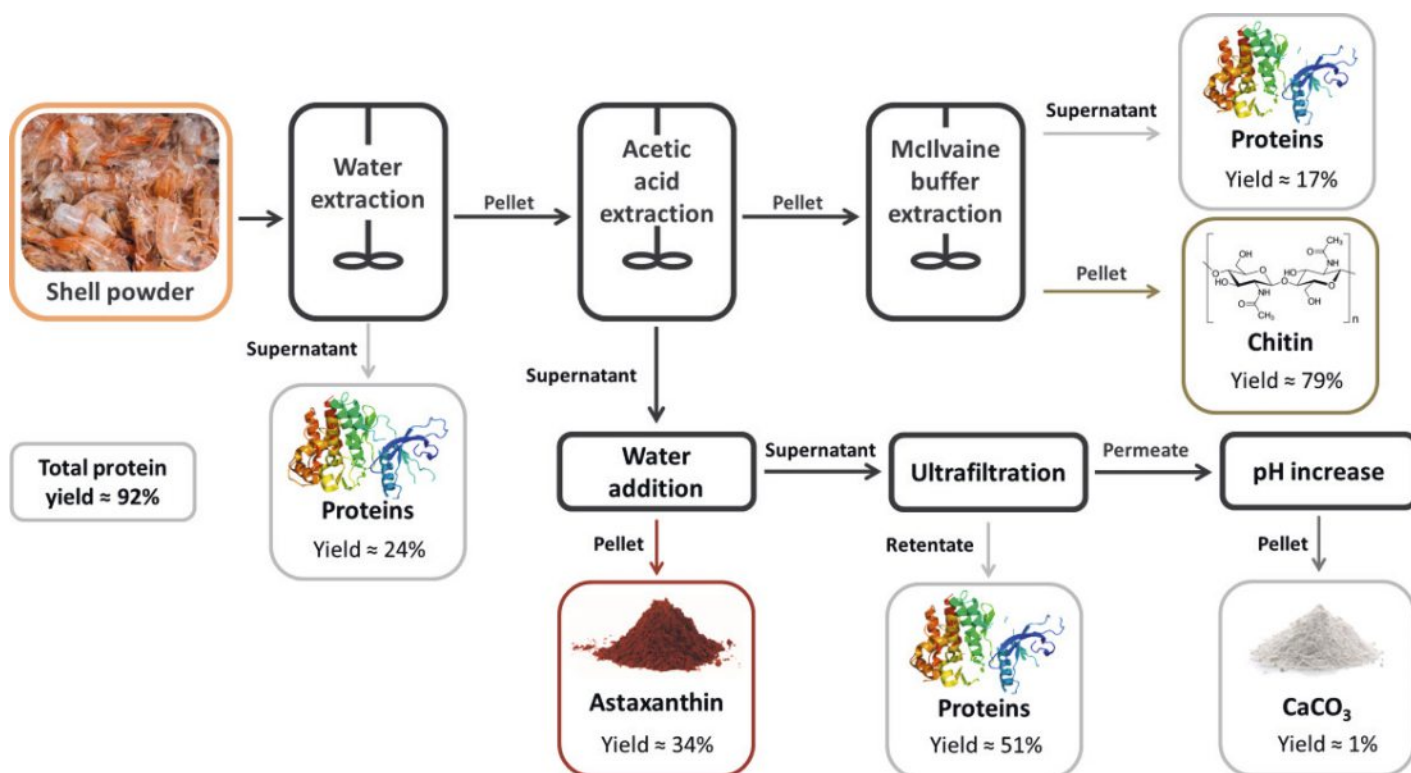


Fig. 7. Schematic representation of our shrimp shell biorefinery.<sup>[47]</sup>

of the Pulp and Paper Industry, CNCs are short, rod-shaped with a width up to 10 nm and aspect ratio greater than 5, while CNFs are long fibrilous networks with diameter of a single fibril measuring up to 30 nm and up to few micrometers in length (TAPPI WI 3021). These materials exhibit high specific surface and mechanical strength and are, due to their origin, biodegradable, biocompatible and non-toxic. As such, they are useful in various applications such as drug delivery, wastewater treatment, biomedical applications, fire resistant materials and packaging.<sup>[50]</sup>

Our research focuses on the latter, exploiting cellulose nanomaterials as sole component or in biocomposites with other biopolymers such as chitosan and alginate. However, the surface of cellulose and its derivatives is rich in hydroxyl groups resulting in a hydrophilic behaviour which presents a limitation in broader applications due to incompatibility with hydrophobic or positively charged matrices such as polylactic acid or chitosan and high sensitivity to water when used as the main material. The solution to this drawback lies in functionalization of the surface hydroxyl groups while maintaining shape, size and crystallinity of cellulose nanomaterials. This can be carried out through various reactions on the surface (esterification, carbamation, silylation, polymer grafting), adsorption of hydrophobic substances or plasma processing.<sup>[51]</sup>

Esterification, especially acetylation, is one of the most commonly used functionalization reactions for minimizing the hydrophilic effect in cellulose nanomaterials. It was shown that acetylated compatibility between CNCs and (bio)polymers is improved, mirroring in higher mechanical strength as well as better thermal resistance.<sup>[52]</sup> To successfully transfer such technology to larger scales, detailed knowledge of mechanisms and kinetics is needed.<sup>[53]</sup>

Plasma treatment was shown to be ultrafast (with the process lasting no longer than 20 s) and highly efficient in conversion of initially hydrophilic surfaces of CNFs films to hydrophobic.<sup>[54]</sup> Furthermore, when applied to chitosan/CNCs biocomposite, mechanical strength and water vapor barrier were improved by such long-lasting surface coatings.<sup>[55]</sup>

## 12. Bio-based Covalent Adaptable Networks (CANs) – The Solution to Greener Thermosets

Thermoplastics are plastic polymers composed of long linear chains held together by intermolecular interactions (*e.g.*, van der Waals forces). Thermosets, on the other hand, contain permanent covalent bonds connecting these linear chains, which are formed during the curing (hardening) process. This extensive crosslinking between polymer chains creates a three-dimensional network of bonds that confer thermosets better mechanical properties, thermal stability and chemical/environmental resistance when compared to thermoplastics.<sup>[56]</sup> Hence, thermosets are fundamental in several industrial applications such as coatings, adhesives, electronics, aircrafts.<sup>[57]</sup> However, this curing process is also responsible for the thermosets' main drawback, *i.e.* their non-reprocessable character, thus their only possible fate is their disposal, which leads to environmental issues.

Covalent adaptable networks (CANs) have emerged as an attractive solution to overcome the thermosets bottleneck, as shown in Fig. 8. By introducing dynamic covalent bonds (DCB) instead of the permanent cross-links present in classical thermosets, the polymer can be subjected to an external stimulus, enabling the reversible reaction of the crosslinking process. Thus, chemically crosslinked CANs can be reprocessed and thermally recycled, making them more sustainable than traditional thermosets.<sup>[56]</sup> This is especially the case of bio-based CANs, which are derived from renewable sources like vegetable oils,<sup>[58]</sup> lignin<sup>[59]</sup> or lignin-based derivatives,<sup>[56]</sup> natural rubbers<sup>[60]</sup> and sugars.<sup>[61]</sup>

Lignin is of considerable interest to form bio-based CANs owing to its abundance of alcoholic, phenolic and carbonyl groups. Functionalization of these moieties to create ester and/or imine DCB are feasible alternatives to develop reprocessable thermosets.<sup>[56]</sup> Vanillin, the enzymatic hydrolysis product of lignin, and eugenol, a depolymerization product of lignin, have been used as lignin 'models' to prepare bio-based CAN.<sup>[62,63]</sup> The former contains highly reactive phenolic hydroxyl and aldehyde groups, thus presenting one of the most suitable approaches for the preparation of high-performance bio-based thermosets. Considering our

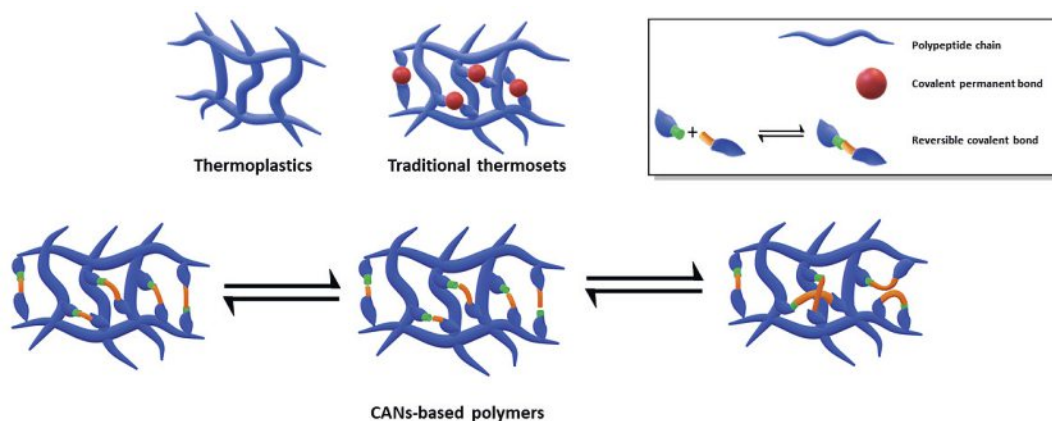


Fig. 8. A schematic representation of thermoplastics, thermosets and modern CANs-based polymers. Reversible dynamic covalent bonds are the key for CANs-based polymers.

extensive experience working with lignin depolymerization and functionalization, we are now also working on the replacement of the hazardous bisphenol A (BPA) with a lignin-chemical platform to form the bio-based epoxy resin.

### 13. Atomistic Simulations

Recently, computational power has reached levels that allow for first-principles simulations of biorenewables on heterogeneous catalysis. Simulations employing up to ~1000 atoms are possible on commonly accessible computing facilities, and even larger systems can be successfully tackled on petascale supercomputers. Most commonly, density functional theory (DFT) is used for electronic-level calculations because it presents a favourable compromise between the cost and accuracy. The depth of theoretical analyses varies from simple determinations of adsorption modes<sup>[64]</sup> to complex mechanistic studies.<sup>[65]</sup>

The Sabatier principle, in essence stating that for optimum performance of a catalyst its interaction with the reactants must not be too strong neither too weak, can be theoretically probed by DFT. For hydro(deoxy)genation of eugenol, it has been shown that Pt binds the reactant too strongly (−3.9 eV), and Ni (−3.0 eV) and Cu (−2.0 eV) too weakly, while Ru performs best.<sup>[66]</sup> Juxtaposing experimental catalyst performance and theoretical calculations of the adsorption strength revealed a typical volcano. Later on, the experimentally pinpointed superior Ru catalyst was used in a mechanistic study where atomistic simulations revealed the most probable reaction pathway and its dependence upon hydrogen coverage.<sup>[65]</sup>

While the full mechanism must contain all transition states, useful trends and correlations can be obtained even when they are foregone. For instance, furfural hydrogenation proceeds differently over MoO<sub>2</sub> and MoO<sub>3</sub>. DFT simulations focusing solely on the stability of the involved intermediates<sup>[67]</sup> have explained why MoO<sub>2</sub>(111) and MoO<sub>3</sub>(111) have better selectivity towards IPL (isopropyl levulinate) than MoO<sub>2</sub>(100) and MoO<sub>3</sub><(100). On the former two, the conversion of IPL to ALAC (alpha-angelica lactone) is endothermic, while on the latter two it is exothermic. DFT can also be used to predict the most stable surface termination and the shape of nanoparticles, as it was also done in this work.

DFT is most powerful when used in complement with experiments and empirical modelling. In hydrodeoxygenation of straight-chain C6 oxygenates over NiMo catalysts, only stable intermediates were followed by off-line analyses of the products in batch reactions. DFT was used to construct a full reaction network, to rule out the improbable reaction pathways and calculate tentative activation barriers and reaction energies, which were then used as initial approximations in empirical microkinetic modelling of the experimental results. It was shown how Ni doping improves the activity of Mo-based catalysts by lowering activation barriers.<sup>[68]</sup> In other applications, the link is reversed as the accuracy of common DFT is insufficient to differentiate between

the energy of different geometric isomers of alkenes. Hence, as an input into the model, we used experimental data on the relative concentrations of different isomers of unsaturated C6 dicarboxylic acids during a heterogeneous production of adipic acid from gluconic acid.<sup>[69]</sup>

The use of atomistic simulations is thus two-fold. They can be used to help explain the observations or, more promising, to build predictive models, which are intended for intelligent optimization of the reaction conditions, substrate and catalyst formulations.

### 14. Conclusions and Outlook

With the increase in high performance computing, machine learning and artificial intelligence, the discovery, optimization and industrialization of novel bio-based pathways can be facilitated. Indeed, biomass is beside CO<sub>2</sub> our only sustainable carbon resource, but has its inherent challenges of mobilization, recalcitrance and complexity, which is limiting the scale of conversion. This is especially valid when applications beyond brute force methodologies, such as pyrolysis, combustion or gasification are concerned, targeting base or specialty bio-based chemicals.

Herein, we outline, present and road-map numerous par excellence examples, dealing with lignocellulose, lipids and various marine sources, where multi-scale modelling simulations support or even resolve some key challenges; nonetheless, the latter being quite unique to date, this exciting field is bound to evolve in the future.

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