

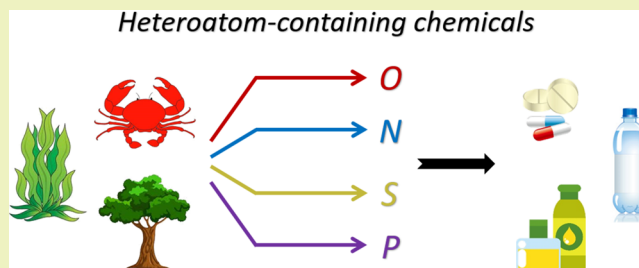
# Sustainable Routes for the Synthesis of Renewable Heteroatom-Containing Chemicals

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**ABSTRACT:** One of the biggest discrepancies between the structure of many utilized chemicals and petrochemicals is the ubiquity of heteroatoms in the former and the lack thereof in the latter. Many commodity chemicals and almost all specialty chemicals and pharmaceuticals contain one or more heteroatoms, but introducing functionalities containing oxygen, nitrogen, sulfur or phosphorus into crude oil-derived chemicals is often a very energy- and resource-intensive endeavor. This and the inevitable depletion of fossil resources in the not too distant future are the main reasons for the development of sustainable ways to produce compounds bearing heteroatoms. Synthesis of oxygen-containing compounds from renewable resources such as starch, cellulose and hemicellulose is already well-known, and the production of phenolic compounds from lignin is garnering significant attention recently. In the meantime, there is a surge in the valorization of chitin from waste crustacean and insect shells for the production of various nitrogen-containing compounds. Much less explored is the valorization of sulfur- and phosphorus-containing biomass components, although they find some high market value applications. Catalysis plays a central role to enable the conversion of biomass into value-added products with high activity and selectivity. Further developments made by chemical engineers and process technologists will be required to make those processes economically feasible and competitive with current synthetic schemes from fossil resources. This perspective highlights the most recent advances and the upcoming challenges in the development of renewable and sustainable routes toward heteroatom-containing chemicals.

**KEYWORDS:** Biomass, Renewable chemicals, Heteroatom-containing compound, Catalysis, Green processes, Chitin, Lignin



## INTRODUCTION

C–H bond activation remains one of the biggest challenges in the current chemical industry because of the stable and unpolarized nature of the C–H bond.<sup>1</sup> Although the high energy density renders hydrocarbons ideal transportation fuels, almost all chemicals in everyday life contain one or more elements other than carbon and hydrogen. For instance, all top 10 pharmaceuticals<sup>2</sup> contain nitrogen elements whereas nine of them contain oxygen as well. Analysis into top 10 pesticides<sup>3</sup> reveals a similar situation (Figure 1). Introducing heteroatom elements into hydrocarbons remains chemically challenging, and current technologies put a strain on our environment due to the formation of chemical waste and high energy consumption correlated with the emission of greenhouse gases. Fuels produced from biomass ideally would have a zero carbon footprint, but for various reasons including the necessity for the removal of high amounts of heteroatoms within biomass shift this approach far from carbon neutral.<sup>4</sup> Direct ways of transforming renewable resources into heteroatom-containing chemicals may circumvent those problems and represent an attractive alternative to conventional processes.<sup>5,6</sup> One example is lignin, one major component of lignocellulosic biomass, which is composed of an extended phenolic network. Its current predominant use is as a heat

source in the pulp and paper industry, while the potential for generating valuable, oxygenated aromatic building blocks is yet to be fully exploited.<sup>7</sup> Another underutilized material is chitin, the second most abundant biopolymer on earth after cellulose, a major component of crustacean waste, the exoskeleton of insects and the cell walls of fungi.<sup>8,9</sup> Despite it probably being the only copious renewable source of N-containing chemicals and materials, the overwhelming majority is currently dumped into landfills and in the ocean.<sup>10</sup> Although S- and P-containing biomass sources are much less abundant, some examples exist and their full potential should be considered and assessed. In parallel, alternative strategies including the conversion of renewable O-containing chemicals into their sulfur- and phosphorus-analogues can offer viable pathways for a more sustainable chemical industry (Figure 2).

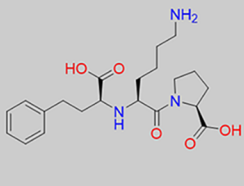
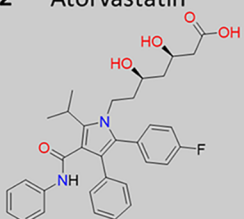
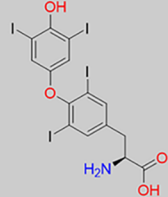
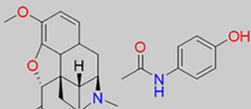
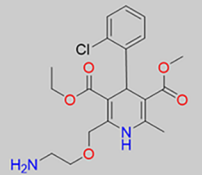
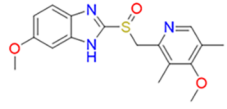
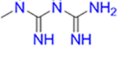
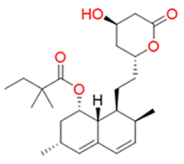
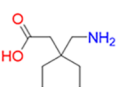
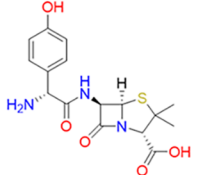
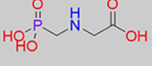
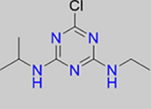
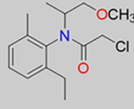

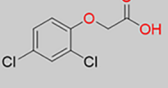
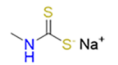
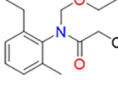


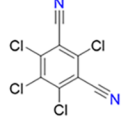
## O-CONTAINING CHEMICALS

Oxygen is the most common heteroatom in all organic matter on this planet. Plant biomass predominantly consisting of cellulose, hemicellulose and lignin makes up a major part of it.

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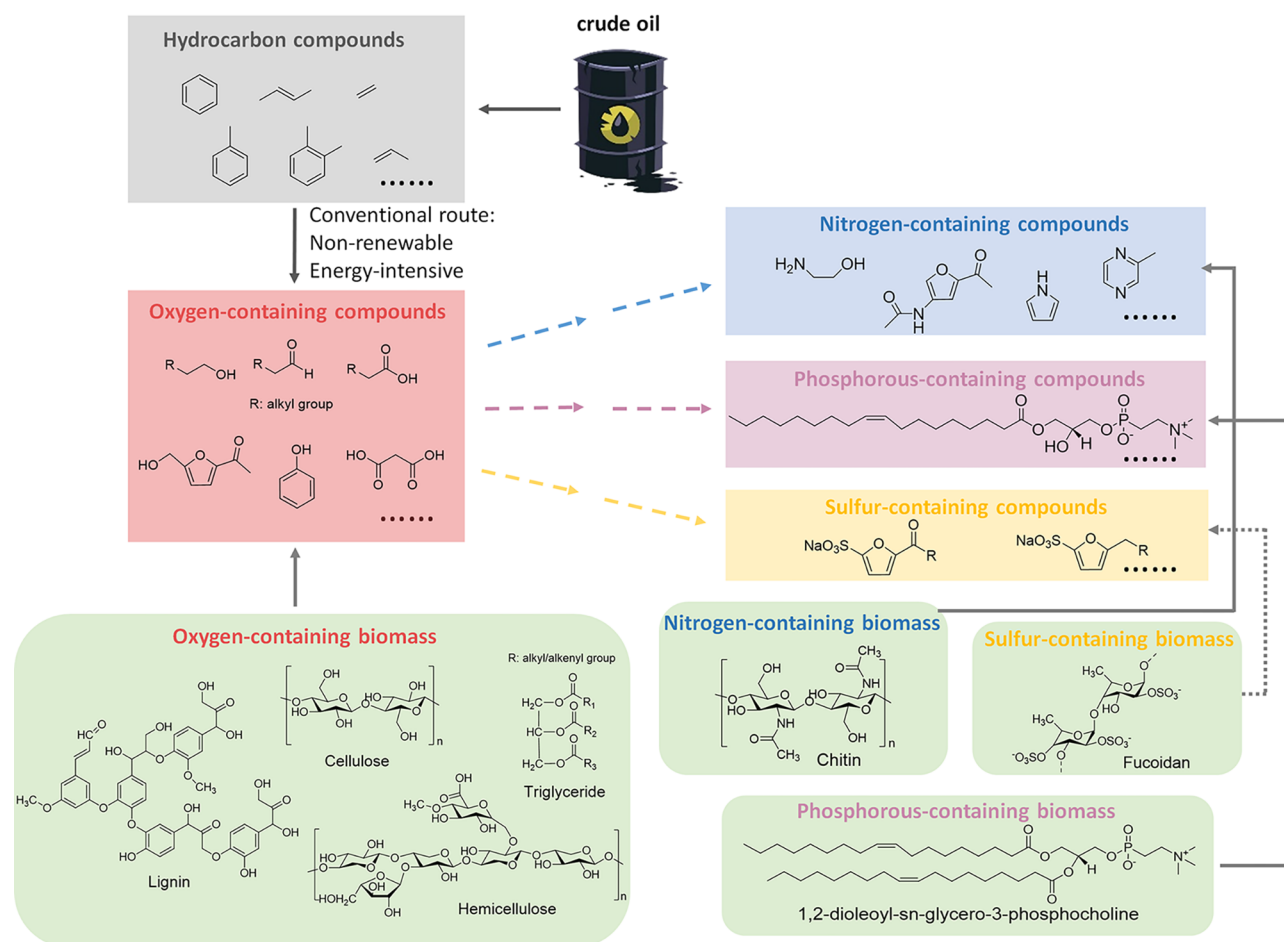
Top 10 Pharmaceutical Products by Prescriptions in 2016				
1 Lisinopril 	2 Atorvastatin 	3 Levothyroxine 	4 Hydrocodone-Acetaminophen 	5 Amlodipine 
6 Omeprazole 	7 Metformin 	8 Simvastatin 	9 Gabapentin 	10 Amoxicillin 
Top 10 Conventional Agricultural Pesticide Active Ingredients in 2012				
1 Glyphosate 	2 Atrazine 	3 Metolachlor 	4 Dichloropropene 	5 2,4-Dichlorophenoxyacetic acid 
6 Metam sodium 	7 Acetochlor 	8 Metam Potassium 	9 Chloropicrin 	10 Chlorothalonil 

**Figure 1.** Chemical structures of the top 10 pharmaceutical products by prescription in 2016 and top 10 conventional agricultural pesticide active ingredients in 2012 with heteroatoms (except halogens and alkali metals) marked in color.

The valorization of plant biomass components for the production of biofuels,<sup>4,5,11–22</sup> various oxygen-containing platform<sup>23–28</sup> or even higher value chemicals<sup>11,13,16,17,29–34</sup> have been either achieved or are currently under investigation. Homogeneous and heterogeneous catalysts are among the most common tools to convert lignocellulosic biomass into more useful chemical products. Until relatively recently, the potential of lignin, the only abundant aromatic oxygenated biopolymer has been underestimated and thus far, large-scale industrial processes solely focus on the conversion of polysaccharides. The reason might be the heterogeneity and recalcitrance of lignin due to its extended C–C and C–O linking network or the change of the native lignin structure during the processing of lignocellulosic biomass under harsh conditions. Along this line, lignin was either actively stabilized before further treatment of the sugar components<sup>35–37</sup> or lignin was extracted from the biomass resource first.<sup>38,39</sup> Gaining a more fundamental understanding on the processes involved in biomass fractionation,<sup>40–43</sup> lignin depolymerization<sup>40,41,44</sup> and

its partial or complete defunctionalization<sup>45–50</sup> may facilitate the development of more efficient catalyst, reactor and process designs. A certain emphasis has been put on the production of biorenewable polymers<sup>51–53</sup> because they are desirable products and are made from simple repeating units.<sup>54</sup> In this Perspective, we will limit the discussion on alternative pathways toward three dicarboxylic acids as polymer precursors, to highlight how some of the most important synthetic polymers or substitutes thereof are achieved from renewable sources.

Adipic acid, arguably the most important dicarboxylic acid in industry, is a major component of nylon-66 alongside its diamine pendant. The majority of this precursor is currently produced from crude oil by the nitric acid oxidation of KA oil (a mixture of cyclohexanol and cyclohexanone) made from benzene. Another process starts from cyclohexene utilizing hydrogen peroxide as milder and slightly more environmentally benign oxidant but the significantly higher substrate price prevents large-scale industrial applications.

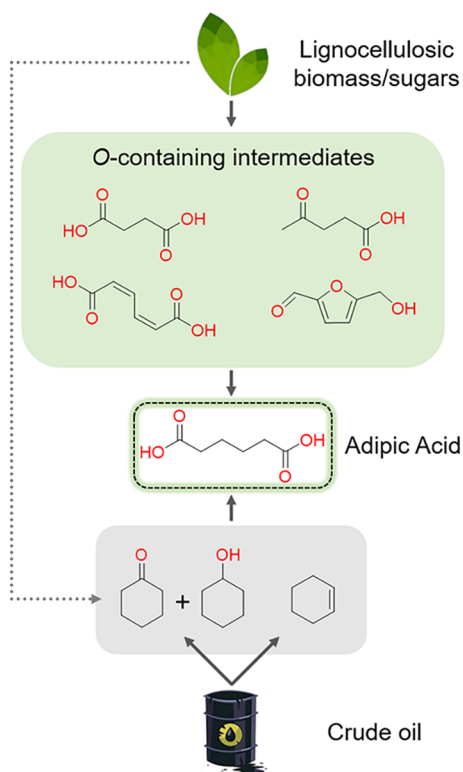


**Figure 2.** Overview of the suggested pathways for the production of heteroatom-containing chemicals from renewable resources, contrasted to their current production from crude oil.

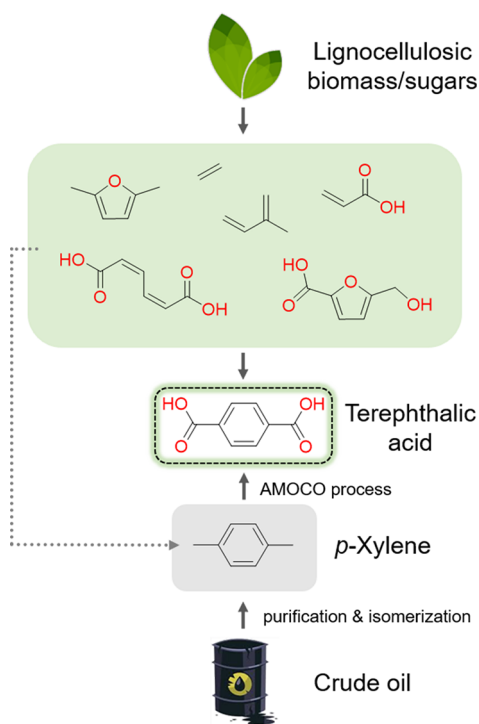
In the past two decades, various processes have been developed to employ lignocellulosic biomass or sugar resources for the sustainable production of adipic acid, avoiding the use of carcinogenic benzene (Figure 3).<sup>55</sup> Drivers of this technology are biotechnology/biocatalysis, chemical catalysis advances and often a combination of both.<sup>56,57</sup> Glucose has been converted into glucaric acid on a heterogeneous catalyst using molecular oxygen followed by a hydrogenation reaction to the dicarboxylic acid.<sup>58</sup> Alternatively, mucic acid derived from galactose was converted into an adipic acid ester in a homogeneous rhenium-catalyzed deoxydehydration reaction and a subsequent platinum-catalyzed transfer hydrogenation.<sup>59</sup> Two of the most prevalent sugar-derived platform chemicals, levulinic acid and 5-hydroxymethylfurfural (5-HMF), have been shown to be convertible into adipic acid. Levulinic acid needs to be transformed into  $\gamma$ -valerolactone<sup>60</sup> and subsequently into a mixture of several pentenoic acid derivatives by reactive distillation in the presence of a solid acid catalyst. A homogeneous palladium-catalyzed carbonylation reaction then produces adipic acid in good yields.<sup>61</sup> Multiple pathways exist for the production of adipic acid from 5-HMF. For instance, 5-HMF can be converted into hexanediol by reduction and ring-opening over heterogeneous catalysts, followed by oxidation to adipic acid using a biocatalyst.<sup>62,63</sup> Another pathway that relies solely on chemical catalysts includes the conversion of 5-HMF into 2,5-furandicarboxylic acid (FDCA),<sup>64</sup> which can be subsequently converted into adipic acid via a metal-free

process.<sup>65</sup> Via dearomatization, deoxygenation and dealkylation, several lignin-derived monomers could possibly be funneled into a KA oil which can then be further oxidized into adipic acid relying on the conventional process.<sup>66,67</sup> Despite its reliance on a renewable feedstock, the harsh oxidative conditions are environmentally harmful. In another approach, depolymerized lignin was converted to muconate using an engineered strain of *Pseudomonas putida* KT2440, the product subsequently purified and hydrogenated to adipic acid using a conventional platinum catalyst supported on activated carbon.<sup>68–71</sup> The electrocatalytic reduction of muconic acid at room temperature under atmospheric pressure has been considered as an alternative and possibly more sustainable pathway toward several products such as adipic acid.<sup>72</sup>

Another very common monomer is terephthalic acid, the precursor of polyethylene terephthalate (PET), especially useful for the production of synthetic fibers and drinking bottles. The conventional synthesis starts from oil reformates. Various purification steps including crystallization, distillation and freezing are necessary to obtain purified *p*-xylene, which then needs to be oxidized to the respective dicarboxylic acid in the Amoco process employing molecular oxygen as oxidant and acetic acid as solvent.<sup>73</sup> Particularly relevant for the synthesis of terephthalic acid from biorenewable resources is the Diels–Alder reaction of various alkenes and dienes (Figure 4).<sup>74</sup> *p*-Xylene is accessible from biomass via several pathways. In one recent example, 5-HMF was converted into dimethylfuran and



**Figure 3.** Conventional crude oil-based and new biomass-based pathways for the production of adipic acid.



**Figure 4.** Conventional crude oil-based and new biomass-based pathways for the production of terephthalic acid.

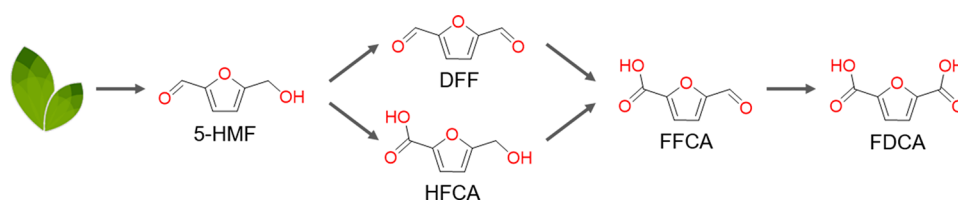
then reacted with ethylene to yield the cycloadduct which can then be transformed into *p*-xylene by dehydration. Surprisingly, a phosphorus-containing zeolite leads to yields close to 100% due to the superior selectivity toward the desired product.<sup>75</sup> Alternatively, acrolein and isoprene, two common products

from renewable resources, were converted into an aldehyde intermediate which underwent a dehydroaromatization-hydrodeoxygenation cascade reaction on a supported tungsten carbide catalyst to yield *p*-xylene without the necessity to add redoxactive components.<sup>76</sup> Besides that, the direct conversion of Diels–Alder reactants to terephthalic acid or its esters has been shown.<sup>77</sup> Upon selective oxidation of 5-HMF to its monocarboxylic acid derivative, a reaction with ethylene in the presence of a Lewis acid catalyst was successful, a reaction otherwise impossible with FDCA.<sup>78</sup> Similar to the production of adipic acid, muconic acid can serve as a starting materials for diethyl terephthalate. Only upon esterification the cycloadduct formed over a silicotungstic acid catalyst and then further dehydrogenated in the presence of a palladium catalyst reaching yields of above 80% based on muconic acid.<sup>79</sup> A different pathway to obtain muconates from renewable resources is the cross metathesis of sorbates and acrylates employing common ruthenium-based catalysts.<sup>80</sup> Due to its aromaticity and high oxygen content, lignin seems to be an ideal starting point for the production of terephthalic acid. Indeed, a synthesis starting from lignin-derived phenolic acids had been proposed previously. Vanillic and syringic acid were selectively demethoxylated and carboxylated using a two-step process in a fixed-bed reactor.<sup>81</sup> We envisage that lignin can be directly converted into terephthalic acid by appropriate funneling of the various obtained aromatic monomers.

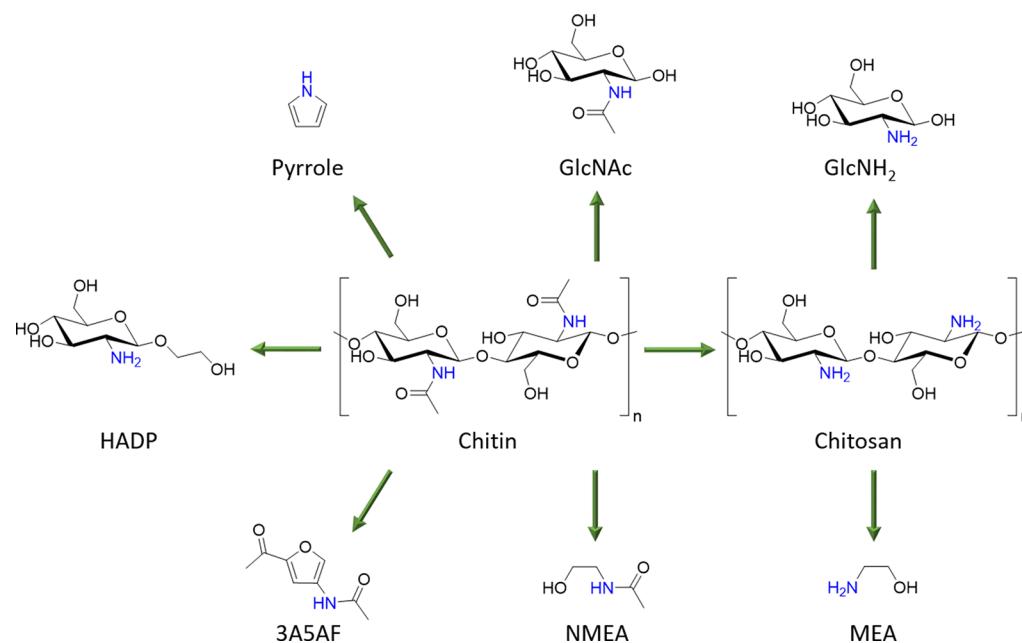
FDCA is a component of polyethylene furanoate (PEF) that is considered a potential substitute for PET for certain applications where a higher gas barrier and glass transition temperature or a lower melting point are required. Due to its heteroaromatic structure, FDCA is not easily achieved from crude oil but is synthesized from biomass resources. The most common process for the production of FDCA relies on the selective oxidation of 5-HMF through a range of well-known intermediates (Figure 5). The reaction has been achieved by using homo- or heterogeneous catalytic processes as platinum,<sup>82–84</sup> gold,<sup>87,89,91,92</sup> and ruthenium<sup>93,94</sup> or non-noble metals including iron,<sup>94,95</sup> nickel,<sup>88</sup> cobalt,<sup>93,96</sup> manganese,<sup>93,96</sup> zirconium<sup>95</sup> or zinc.<sup>94</sup> Some examples for the oxidation of 5-HMF to FDCA avoiding the use of metals exist<sup>97–101</sup> but are limited by the requirement of stoichiometric oxidants other than air or low catalyst recyclability.

Besides those conventional catalytic methods, photo- and electrocatalytic routes have been investigated. Cobalt-thiopyrphrazine-moieties bound to graphitic carbon nitride afforded FDCA in up to 96% yield from 5-HMF using a simulated sunlight-mediated room temperature and ambient pressure aerobic oxidation. The interaction between the cobalt complex and C<sub>3</sub>N<sub>4</sub> promotes the formation of singlet oxygen and disables the generation of less selective hydroxyl radicals as evidenced by active spin trapping and EPR.<sup>102</sup> In 2016, a system was reported to couple water splitting with the electrochemical oxidation of 5-HMF to FDCA. The hydrogen evolution reaction occurred at around 200 mV lower potential at the same current density if the biomass-derived alcohol was oxidized instead of the formation of molecular oxygen. Ni<sub>2</sub>P nanoparticles supported on metallic nickel, hierarchically porous nickel- or nanocrystalline copper foam all achieved faradaic efficiencies close to unity and were robust for more than 10 h.<sup>103–105</sup>





**Figure 5.** Possible pathways for the synthesis of 2,5-furandicarboxylic acid (FDCA) from plant biomass. Intermediates are hydroxymethylfurfural (5-HMF), 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HFCA) and 5-formyl-2-furancarboxylic acid (FFCA).



**Figure 6.** Chemical structures of chitin, chitosan and several derived N-containing compounds.

In most reports, the oxidation of the aldehyde group in the 5-HMF substrate is faster than the alcohol oxidation. With this knowledge, the research community should focus more on the development of efficient catalysts for the relatively mild oxidation of alcohols to aldehydes using green reaction conditions such as water as solvent, oxygen as oxidant and a recyclable catalyst possibly based on non-noble metals. Photo- and electrocatalytic processes can possibly provide more sustainable pathways but much more effort needs to be devoted to improve catalyst, reactor and finally process optimization.

**N-Containing Chemicals.** As mentioned earlier, chitin might be the most promising biomass source for the production of renewable N-containing chemicals due to its sheer abundance and high nitrogen content of around 7% by weight. It has been estimated that 6–8 million tons of crustacean shell waste are produced annually, whereas bioproduction of insect shells are several orders of magnitude higher. Consequently, the concept of shell biorefinery, targeting the fractionation and utilization of various components in shells, was proposed and developed.<sup>10</sup>

Chitin is responsible for the high rigidity of insects' exoskeletons and crustaceans' shells and is structurally similar to cellulose despite the fact that the former has *N*-acetyl side chains on the C-2 position instead of a hydroxyl group. Normally, chitin occurs together with calcium carbonate and proteins and thus, fractionation is the inevitable first step for the generation of chitin-derived products.<sup>106,107</sup> Tremendous efforts have been devoted to the utilization of chitin- and

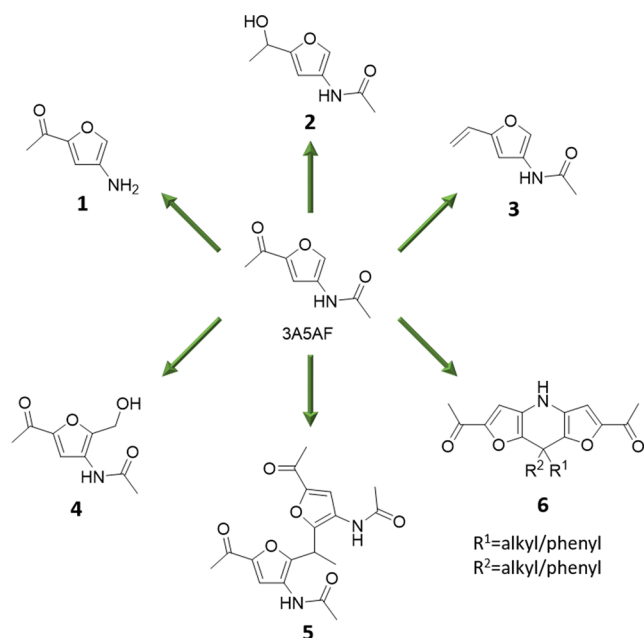
chitosan-derived materials for a range of applications such as bioplastics,<sup>108</sup> biomedical applications<sup>109–111</sup> and adsorbent materials for wastewater treatment<sup>112,113</sup> but besides that, chitin is an ideal starting material for a range of heteroatom-containing chemicals. In the following, we will focus on N-containing chemicals from chitin, some of which are depicted in Figure 6, although many compounds that do not contain nitrogen are also available, such as acetic acid, several polyols, 5-HMF and other deaminated furan derivatives.<sup>114–120</sup>

The most apparent product from chitin is *N*-acetylglucosamine via hydrolysis, but the harsh reaction conditions lead to a significant deacetylation.<sup>121</sup> An enhanced process was developed to depolymerize chitin under retention of the acetyl group by a mechanochemical process with the addition of catalytic amounts of sulfuric acid. The ball-milled chitin–sulfuric acid mixture can then be hydrolyzed or methanolysed to yield two different products.<sup>122</sup> Alternatively, the conversion of chitin into glucosamine can be selectively enhanced by using a mixture of aprotic polar solvents with water and acid amounts that are lower than previously reported. Cosolvents increased the glucosamine yield from less than 1% in pure water to up to 80% in a mixture of water and diethylene glycol diethyl ether.<sup>123</sup> A simple three-step procedure including a mechano-catalytic hydrolysis in the presence of sulfuric acid followed by a short high-temperature hydrolytic treatment and a hydrogenation with a heterogeneous ruthenium catalyst at pH 3.0 without any intermediate purification yielded the monomer in up to 52% yield.<sup>124</sup> Other sugar derivatives such as hydroxyethyl-2-amino-2-deoxyhexopyranoside (HADP) and 2-

acetamido-2-deoxysorbitol were also obtained after chitin conversion.<sup>120,125,126</sup>

Among the obtained N-containing compounds, high yields of N-acetylmonoethanolamine (NMEA), a possibly useful agent for CO<sub>2</sub> absorption among other applications, were achieved by reductive treatment over a noble metal catalyst. Although the conversion could not be enhanced by adding base such as sodium hydroxide, the selectivity toward certain products could be influenced significantly.<sup>120</sup> Besides aliphatic N-containing compounds, several aromatic heterocycles are available from chitin. One example is pyrrole, which was the main product (alongside pyrazine and pyridine) obtained after a short treatment of chitin at 325 °C using a basic aqueous solution. The addition of ammonia solution led to yields of up to 12 mol % from chitin within 1 min.<sup>118</sup>

Special emphasis should be placed on a very unique furan-derivative: 3-acetamido-5-acetylfuran (3A5AF) available both from chitin and its monomeric sugar.<sup>127–131</sup> The uncommon substitution pattern on the furan ring cannot be easily achieved by conventional synthetic methods from petrochemicals but is an essential structural motif in compounds such as proximicin antibiotics,<sup>132</sup> pyrrolisine<sup>133</sup> and hyrtioseragine A and B,<sup>134</sup> all of which are molecules with biological activity. Since the development of one-step production of 3A5AF from chitin and its monomer, many pathways for the synthesis of derived compounds have been proposed and some of them were realized recently, creating a chemical space with a range of N-containing chemicals<sup>135</sup> (Figure 7). Upon cleavage of the

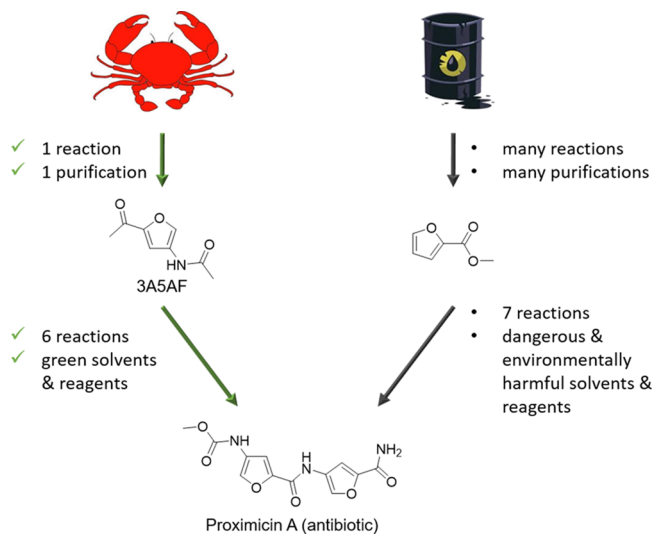


**Figure 7.** Nitrogen-bearing chemical space derived from 3A5AF.

amide, a renewable amine (1) can be obtained whereas the selective reduction of the acetyl-group over the amide group can be achieved by reduction with sodium borohydride or catalyzed transfer hydrogenation affording product 2. Under certain conditions, the spontaneous formation of alkene 3 was observed probably due to the elimination of the formed alcohol. Upon the use of a stronger reductant such as lithium aluminum hydride, both carbonyls were reduced and the cyclic structure of the furan ring was opened.<sup>136</sup> The reaction of 3A5AF with several ketones such as acetone, butanone or

benzophenone surprisingly yielded a novel dihydrofuro-pyridine scaffold 6, and produced 4 with formaldehyde via hydroxymethylation of the furan ring. Reaction with acetaldehyde under the same conditions led to the formation of the cross-linked furan derivative 5.<sup>137</sup>

Another step toward shell biorefinery has been achieved recently by showing the complete synthesis of proximicin A, an antibiotic and cytostatic agent, from chitin as starting material. The currently existing synthetic procedure from crude oil contains a plethora of chemical reactions and multiple separation processes to even obtain the substituted furan derivative. Subsequently, another seven steps are required, which involves the use of dangerous, environmentally harmful reagents and solvents, and generates significant amounts of chemical waste due to the employment of protecting groups.<sup>132,138</sup> In stark contrast, 3A5AF was obtained from chitin in one step with a single purification. In the following, six reactions are sufficient to synthesize proximicin A in a sustainable way utilizing green solvents and reagents that can be obtained from renewable resources (Figure 8).<sup>139</sup> Despite those growing efforts, more studies should be devoted to explore the full potential of this unique platform chemical.



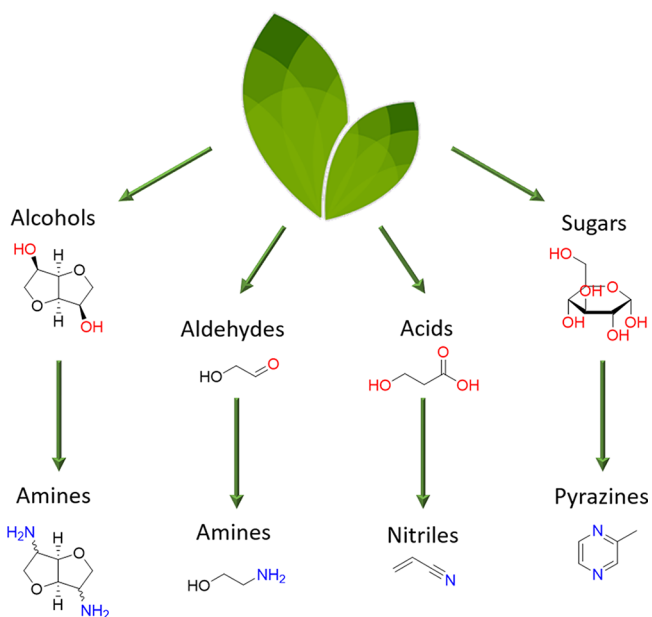
**Figure 8.** Comparison of the synthesis of proximicin A from crude oil and chitin.

A polymer that is closely related to chitin is chitosan, obtained after deacetylation of 50% of the sugar units.<sup>140</sup> Due to the free amine functionality, the properties are very different from chitin regarding the basicity, solubility in water and chemical reactivity. Processes for the synthesis of N-containing chemicals from chitosan are so far limited to the depolymerization and formation of ethanolamine<sup>120</sup> and glucosamine<sup>141</sup> (Figure 6) using a catalytic reductive or a microwave-assisted method, respectively.

The fractionation and pretreatment of plant biomass for cellulose, hemicellulose and lignin have already been well-developed.<sup>32</sup> In contrast, much less has been achieved for the fractionation of shells. Current practice heavily relies on a two-step process, a first demineralization step using strong mineral acids followed by a deproteinization step employing strong bases, resulting in huge amounts of chemical waste and high cost of the product.<sup>142–144</sup> The efficient use of chitin as starting material for the synthesis of N-containing chemicals is therefore

limited by the detrimental environmental impact of the fractionation process. There is an urgent need for the development of more environmentally benign and cost-efficient processes. One example has been reported recently, where a simple pretreatment of prawn shells in hot glycerol improved the removal of both the protein and the mineral fraction by citric acid.<sup>145</sup> Although this method might already prove more favorable than the conventional industrial method, a procedure employing nonstoichiometric amounts of organic or even mineral acids is highly desirable in the future.

**Amines from Renewable Oxygenates.** Almost all kinds of O-containing functional groups have been shown to be convertible into their N-containing counterparts using ammonia as sole nitrogen source and possibly oxygen as abundant and atom-economic oxidant.<sup>146</sup> Previous developments in the synthesis of biobased amines have been reviewed in detail<sup>147</sup> and thus only selected most recent developments will be discussed here (Figure 9).



**Figure 9.** Recent developments in the synthesis of organic nitrogen-containing compounds from oxygenates using ammonia; oxygen atoms that are removed or replaced during the process are depicted in red.

Due to the versatility and abundance of renewable alcohols and the attractiveness of primary mono- and diamines as organic building blocks or for polymer applications, efficient interconversions need to be developed. It is commonly postulated that the amination of alcohols occurs via a “hydrogen borrowing” mechanism where a carbonyl compound is formed as an intermediate which is then converted into the imine and subsequently reduced to the amine.<sup>148,149</sup> Therefore, it seems to be attractive to start with a carbonyl compound and employ a reducing agent to produce alcohols.<sup>150,151</sup> One example is the production of ethanolamine from cellulose in a two-step process with a yield above 10% using hydrogen gas as reducing agent and a heterogeneous ruthenium catalyst for the reductive amination.<sup>152</sup> Inspired by the naturally occurring aldolase enzyme, the direct reductive aminolysis of glucose toward several short-chained amines with carbon yields up to 87% have been achieved.<sup>153,154</sup> Likewise, the amination of isomannide, a renewable sugar-derivative, in water using a

heterogeneous ruthenium catalyst has been demonstrated. This process can be extended to the conversion of other biogenic alcohols such as ethanol or hexane-1,6-diol.<sup>155</sup>

Most recently, a process has been developed for the production of acrylonitrile, a valuable substrate for the synthesis of a range of resins, polymers and carbon fibers, from renewable resources including lignocellulosic biomass. A fermentation process was used to produce an organic acid from sugars, which was then converted into acrylic acid, esterified and converted into the respective nitrile with ammonia using an inexpensive catalyst. Life cycle assessment showed that on a very large scale, the produced acrylonitrile reached a price below 1\$/lb, avoiding the link with sometimes volatile fossil fuel prices. It also represents a safer process and could thus become a realistic alternative to the prevailing Sohio process. Extending the substrate scope to more expensive nitriles might render the process economically competitive even at smaller scales.<sup>156</sup>

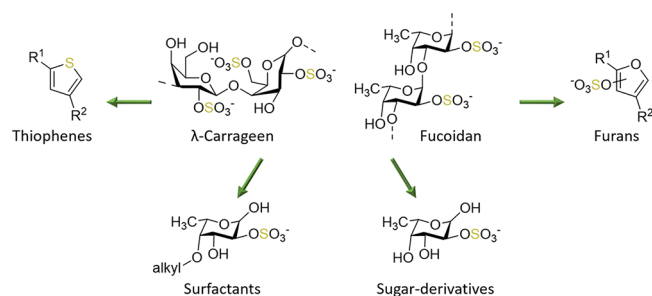
The synthesis of another N-containing aromatic heterocyclic compound, 2-methylpyrazine, has been realized from different renewable sugars and ammonia using catalytic amounts of tungsten clusters. Glucose, fructose and xylose all turned out to be valuable starting materials. Optimization studies showed that close to 30 mol % yield can be achieved, rendering the process attractive compared to conventional routes starting from petrochemicals.<sup>157</sup> A similar product (2-hydroxymethyl-5-methylpyrazine) was synthesized from dihydroxyacetone and diammonium hydrogen phosphate without the use of a catalyst with up to 72% yield.<sup>158</sup>

Vanillic acid has been shown to be convertible into two isomeric pyridine dicarboxylic acids using ammonium chloride as nitrogen source by modifying the protocatechuate pathway of *Rhodococcus jostii* RHA1. Wheat straw biomass can be used directly together with a minimal growth medium for the synthesis of the diacids. The close resemblance of the products to terephthalic acid hint at the potential use for polymer applications although the changed electronic structure in the aromatic ring and the enhanced coordination abilities of the pyridine moiety should lead to different properties.<sup>159</sup>

One crucial aspect for the conversion of O-containing functional groups into N-containing ones is atom efficiency. Ideally, ammonia can be used leading to the formation of water as the only byproduct. Furthermore, robust and general procedures that apply to the widest possible range of oxygenates preferably employing a recyclable and cheap catalyst need to be developed and employed for products that are already in use and manufactured from fossil fuel resources.

## ■ S-CONTAINING CHEMICALS

Sulfur is a ubiquitous element in chemical industry. Natural resources for sulfur-containing chemicals are widely unexplored even though some plant biomass, especially algae, carry high amounts of sulfated polysaccharides. In the current endeavor to produce biofuels from algal biomass, harnessing a part of that biomass for the synthesis of renewable sulfur-containing chemicals could become attractive. Some of those sulfated polysugars are used widely as thickening agent, and as anticoagulants, anticancer or anti-inflammatory agents.<sup>160</sup> Carrageenans and fucoidan belong to the more commonly used polysaccharides but their full chemical potential has yet to be developed and evaluated (Figure 10). Fucoidan, for example, is primarily found in brown algae and brown seaweed making up around 10–20 wt % of the dry algae weight.<sup>161</sup> Despite its perceived health benefits, any large scale applications are



**Figure 10.** Proposed sulfur-bearing chemical space derived from sulfated polysaccharides.

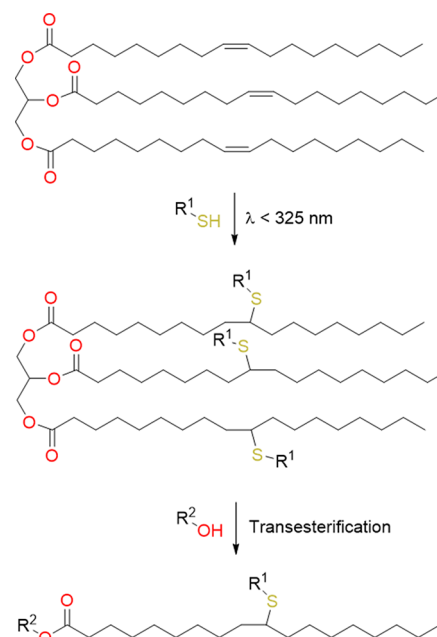
currently limited by the horrendous price. Based on the structural similarity to previously mentioned polysaccharides, the synthesis of similar products including oligomeric or monomeric sugars and sugar-derivatives and different heterocyclic chemicals such as thiophenes and sulfated furans are envisioned from both carrageenans and fucoidan. Some of those compounds can be expected to find applications in the synthesis of organic electronics,<sup>162</sup> as surfactants<sup>163</sup> or for biomedical applications.<sup>164</sup> Any work along this line will motivate the development of more efficient processes for the isolation and purification of sulfur-containing polysaccharides which are essential first steps to increase the economic viability.

Other strategies to convert renewable feedstock into S-containing chemicals either employ organic compounds containing sulfur, gaseous  $\text{SO}_3$  or elemental sulfur. Most studies on renewable S-containing products emphasize the production of polymers<sup>165–167</sup> or sorbent materials,<sup>168,169</sup> which lie beyond the scope of this perspective. It has been shown that lubricating oils can be synthesized from different vegetable oils in a two-step process using a photochemical approach. Thiyl radicals bind to unsaturated bonds in the fatty acids and a transesterification step yields the sulfur-containing esters (Figure 11).<sup>170,171</sup> In principle, renewable alcohols can be used for the transesterification step and the development of procedures yielding thiols from biogenic alcohols would be beneficial.

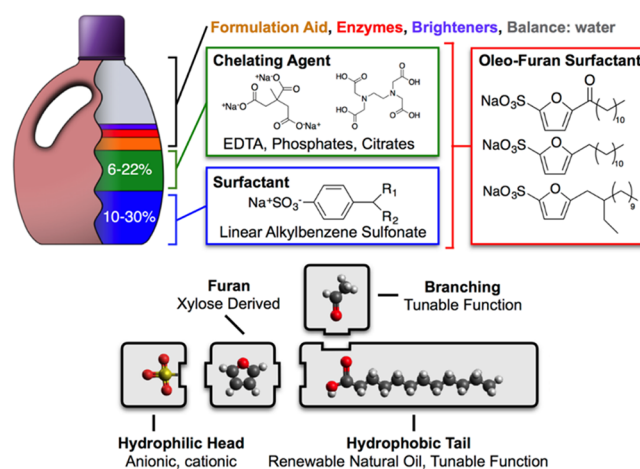
It was shown recently that a sulfonated surfactant based on furan and fatty acids, two completely renewable components, show excellent performance in forming micelles in hard water and at low temperatures (Figure 12). Several common fatty acids ranging from seven to 18 carbon atoms were linked to furan by a heterogeneously catalyzed Friedel–Crafts acylation, which then underwent sulfonation under mild conditions. Common surfactant mixtures contain 6–22% of chelating agents depending on water property, to avoid the inhibition effect of divalent metal cations in micelle formation. This fraction is no longer necessary for the new material, due to the extraordinary micelle formation ability of oleo-furan-based surfactants even in the presence of metal cations. The exceptional quality of the renewable surfactants and the low price of the feedstock could possibly render the process economically competitive and enable the use of ecologically more benign common products.<sup>172</sup>

## ■ P-CONTAINING CHEMICALS

Phosphorus is an essential element in living organisms, but abundant sources of P-containing biopolymers are widely unknown. Nevertheless, biological membranes are known to contain a high fraction of phosphorus as part of their



**Figure 11.** Synthesis of sulfur-containing lubricating oils from mostly renewable resources.



**Figure 12.** Structure and possible utilization of surfactants almost entirely based on renewable feedstock. (Reprinted with permission from ref 172.)

membrane lipids such as phosphatidylcholine (such as shown in Figure 2). Some studies have been devoted to the hydrolysis of those lipids into various phosphorus-containing chemicals.<sup>173–175</sup> Although organophosphorus compounds do not belong to the most common intermediates and products in chemical industries, they are used as pesticides,<sup>176</sup> herbicides<sup>177</sup> or in certain medical applications.<sup>178</sup> To find biorenewable alternatives for those fossil-fuel-derived compounds, novel sources of phosphorus from biomass need to be explored and conversion strategies have to be developed.

## ■ CONCLUSION

In summary, processes for the synthesis of heteroatom-containing chemicals from renewable resources are in steady development with many promising systems been presented. Though renewable oxygen-containing chemicals have been most extensively studied, more efforts are required to be



devoted to other heteroatom-containing chemicals to explore potential new platform chemicals and associated further transformation into fine chemicals. Generally, we need to make use of chemical functionalities within biobased feedstock as much as possible, as any further conversions inevitably require energy, resources and generate waste. If unavoidable, any additional treatments need to be done in accordance with the 12 principles of green chemistry especially considering the use of catalytic reagents, atom economic procedures and energy efficiency. Along this line, novel procedures employing electro- or photochemistry can be beneficial and should be developed further for a broader range of biorenewable compounds.<sup>179,180</sup>

For many heteroatom-containing biopolymers, more efficient and environmentally benign fractionation methods to extract them from the native state, and enhanced strategies for the transformation of separated components into a variety of value-added products are needed. In the case of lignocellulosic biomass, various strategies to stabilize the different components during biomass treatment such as the lignin-first approach emerged. Similarly, mild methods have to be developed for the fractionation of shell biomass into its components. The same challenges await S- and P-containing biopolymers once good sources have been discovered and the range of obtainable molecules has been extended.

As highlighted recently, the biorenewable feedstock has to be utilized entirely in order to make biorefinery competitive with current fossil fuel-based refinery schemes.<sup>181</sup> All those processes should then be assessed based on a thorough technological, economic and environmental evaluation before they are ready for scaling up development.<sup>182</sup> All current technological advances and all available products from a biomass resource need to be considered in an integrated manner estimating their global warming potential, the cumulative energy demand and operating costs. In most cases, a particular feed split ratio for several products probably has the highest feasibility potential from different aspects.<sup>183</sup> The interdependence between several products of a biorefinery has already become very clear in some cases, such as biodiesel production, in which it is only economically viable and environmentally beneficial if processes for glycerol upgrading can be integrated. Beyond that, computational tools should be developed that enable decision-makers acting in the most reasonable way possible given a certain set of conditions that inevitably will deviate massively throughout different countries and regions.

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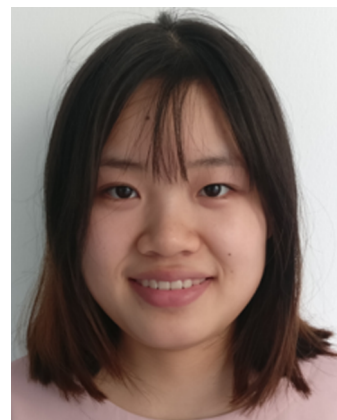
### Notes

The authors declare no competing financial interest.

## Biographies



Max J. Hülsey was born in Berlin, Germany. He received a B.Sc. degree in Biochemistry and M.Sc. degree in Chemistry from Heidelberg University in 2015 and 2017, respectively. During his Master's thesis, he worked with Prof. Yuriy Román at the Massachusetts Institute of Technology on the valorization of lignin. Since 2017, he is conducting his Ph.D. with Prof. Ning Yan at the National University of Singapore, focusing on the synthesis, utilization and spectroscopic investigation of various single-atom catalysts.



Huiying Yang was born in Jiangxi, China. She received her B.S. degree in Biomedical Engineering from Nanjing University. She is currently a Ph.D. student in Prof. Ning Yan's group in the Department of Chemical and Biomolecular Engineering at the National University of Singapore. Her research focus is on developing simple and efficient methods for shell fractionation and valorization.



Ning Yan was born in Sichuan, China. He received his B.S. and Ph.D. degrees in Chemistry from Peking University in 2004 and 2009, respectively. After a stay at École Polytechnique Fédérale de Lausanne

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