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The United Nations Sustainable Development Goals for 2030 include targets around reducing hunger for people worldwide (1). There are a number of challenges which industry is working hard to address. In farming, the challenges include crop growth and nutrition and making the most of available land for food production. Once the food is harvested, there are further challenges for the food and beverage industry in ensuring that enough of the produce reaches the people who need it in a fit state for human consumption.

Crop Nutrition and Protection

One of the key crop nutrients is nitrogen. Although the earth’s atmosphere is around 78% nitrogen, most of this is locked in a form that plants cannot use. To make it accessible, it must be ‘fixed’ or reduced into a more active chemical form. Some natural processes can fix nitrogen, including microorganisms living in the roots of certain vegetables as well as events such as lightning strikes. However much of the nitrogen that is used today to produce food for humans comes from the industrial fixation of nitrogen into ammonia, which has grown today into a huge area of industry carried out in many countries worldwide. There are challenges in this industry – not least of which is ensuring the cost effectiveness and energy efficiency of the process. By far the most widely used process is the Haber-Bosch process which produces up to half the nitrogen entering the human food chain. Alternatives are being looked at that are not yet ready for commercial scale roll out but they are gaining interest in the academic community (2).

Another area important to ensuring secure food supply is the protection of crop plants from pests and diseases. The pesticides industry was worth around US$58 billion in 2016 (3) and ways are being sought to ensure both effectiveness and, increasingly, to reduce the social and environmental impacts of chemicals in agriculture (4, 5). There is no doubt that this will be an important area of research for some time to come.

Land Use

It is now recognised that food security can be impacted by other pressures on land use (6). When biofuels were introduced the first generation were based on food crops such as sugars or oils. Now second- and third-generation biofuels, made from ‘waste’ or other forms of non-food competing biomass, are becoming available (7, 8). The challenges in processing matter such as cellulose and lignin are many: catalytic and pyrolytic approaches have been investigated to create efficient ways to prepare fuels that can meet future energy needs as part of an energy mix without detrimental impact on the food supply.

Preventing Food Waste

The story of food does not stop at harvest. There are other areas where industry plays a role in getting food onto people’s plates. Studies suggest that up to one third of food produced worldwide is lost or wasted (9). There is a need for low-cost, sustainable solutions to the problem of food spoilage and waste in increasingly global food supply chains. The platinum group metals (pgms) have proved unlikely allies in the fight against food waste as a number of past articles in this journal have shown (10, 11, 12). There are commercial solutions on the market which involve both pgm and non-pgm materials. For example, the use of nickel catalysts to improve oxidative stability of edible
oils, extending the shelf life, as well as adsorbents, packaging materials and other technological solutions to control the environment around fresh food and prevent spoilage. This is a vibrant area and more research will no doubt reveal new approaches.

In this journal look out for articles detailing the history of ammonia production, the development of new processes for biofuels that do not compete with food and work on new packaging technologies that can help ensure food reaches people, reducing waste in the worldwide food chain.

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Editor, Johnson Matthey Technology Review

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The Role of Noble Metal Catalysts in Conversion of Biomass and Bio-derived Intermediates to Fuels and Chemicals

A review of promising approaches on plant based biomass as a renewable alternative feedstock

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In the face of growing oil demand the use of renewable feedstocks for the potential to supply transportation fuels, electricity, chemicals and materials is increasingly attractive. This review covers novel technologies and pathways to produce liquid fuels and chemical intermediates in an efficient and cost-effective way. Several commercial and pilot scale projects by companies including Anellotech, USA; Johnson Matthey, UK; GFBiochemicals, Italy; Quaker Oats, USA; Changchun Dacheng Group, China; Avantium, The Netherlands; BASF, Germany and Rennovia, USA are highlighted. The review focuses on the use of non-food competing biomass, namely cellulose and hemicellulose biomass, and the use of precious metals to effect the key reaction steps: hydrolysis, dehydration, hydrodeoxygenation, hydrogenation and oxidation. The value added products achieved include fine chemicals and functional materials. Among these are dimethylfuran, methylfuran, 5-(ethoxymethyl)furfural, \( \gamma \)-valerolactone, ethyl levulate and valeric biofuels suitable as fuels and fuel additives as well as renewable alkanes in the C\(_5\)–C\(_{15}\) range for gasoline and diesel fuel applications.

1. Introduction

Over the past century, the world has grown extremely reliant on finite fossil derived sources of carbon. Fossil derived sources such as crude oil, natural gas and coal supply more than three quarters of the world’s energy (Figure 1) and 90% of chemicals and materials (1, 2). The consumption of energy and chemicals is increasing at \(~7\%\) per annum and this has been mostly driven by the growth experienced by the emerging economies. More specifically, global oil demand is expected to grow until 2040, and this is largely as a result of lack of alternatives to

Fig. 1. Total primary world energy supply in 2014.

*a Other includes geothermal, wind, solar, heat and tidal. (Based on IEA data from the Key World Energy Statistics © OECD/IEA 2016, www.iea.org/statistics. Licence: www.iea.org/t&c)
crude oil for the production of transportation fuels and chemicals (1–3).

This growth in demand, combined with diminishing fossil derived fuel reserves, environmental degradation (arising from emission of harmful greenhouse gases associated with processing of fossil derived feedstocks), unreliable supply and price fluctuations have been the main motivations for the exploration of renewable alternatives to fossil derived sources of carbon for the production of energy and chemicals.

The global energy consumption renewables share (including biofuels and waste, geothermal, hydro, solar, wind and tidal) was 15.5% in 2014 and is expected to experience the fastest growth (led by solar and wind) between now and 2040 (3). It is important to point out that among the renewable energy sources, biomass has the potential to supply renewable transportation fuels, electricity, organic chemicals and materials demand. For renewable liquid fuels and chemicals to make a meaningful contribution to this projected rapid growth, substantial investment is needed into the development of technologies and novel pathways to produce renewable liquid fuels and platform chemicals in an efficient and cost-effective way.

Plant biomass is available on a recurring basis and has great potential as a renewable alternative feedstock for the production of fuels and chemicals to effectively reduce reliance on fossil derived resources. Plant biomass is inexpensive and is widely available throughout many geographical locations of the world, making it more accessible than fossil deposits (4–6). One primary source of chemicals is lignocellulose which is abundant in plants.

2. Structure of Lignocellulose

The primary constituents of plant biomass are lignin, carbohydrate polymers ((hemi)cellulose), oils, proteins and other chemicals such as dyes and vitamins. Lignocellulose is highly functionalised and is the main fraction (~90%) of plant biomass. It is composed of the non-edible biopolymers: cellulose, hemicellulose and lignin (Figure 2) (5, 6). In the

Fig. 2. The main components of lignocellulose
present article, we review the use of carbohydrates (sugars and starchy biomass) and carbohydrate polymers (cellulose and hemicellulose biomass) in biorefinery. Recent reviews on the valorisation of lignin are available (7–9).

The main sources of cellulosic feedstock include agricultural, forestry, industrial and municipal wastes and residues (10). Unlike carbohydrates (sugar and starchy biomass) feedstock, cellulosic feedstock is non-edible and does not compete for arable land and therefore avoids conflict with food supply (11).

3. Conversion of Biomass and Biomass-derived Intermediates

3.1 Biomass Conversion versus Crude Oil Conversion: Diverging Approaches

Crude oil feedstock has low functionality which makes it directly suitable for use as a fuel after prior processing (for example cracking and isomerisation). Functional groups, such as C=O and OH, are added to crude oil derived feedstock to produce bulk and specialty chemicals. Here, special care is taken to ensure selective addition of the functional group without over functionalisation of the substrates (Figure 3). Contrastingly, biomass derived feedstocks, such as cellulose and hemicellulose, contain far too much functionality to use directly as fuels or bulk chemicals, and therefore require selective defunctionalisation strategies (5, 12, 13).

3.2 Biomass Conversion Technologies

The three common conversion technologies for carbohydrates and cellulose are shown in Figure 4 (2, 14–16). Although production of first generation biofuels (bio-ethanol and bio-butanol) is well established, this process relies on starch and sugar feeds which compete with the food chain (16). Hydrolysis of cellulosic feedstock to fermentable sugars has been achieved and a number of commercial scale cellulosic ethanol plants have been and are being developed in several countries (for example the USA, Italy, Brazil and Canada) as alternative routes to bio-alcohols as fuels in order to avoid food sources as feedstock (17–20). Slow reaction rate, high cost and sensitivity of enzymes and energy intensive subsequent distillation and drying steps remain challenges to achieving cost-effectiveness in these processes. A cost-effective process that transforms biomass (such as wood, sugarcane bagasse or corn stover) to aromatic compounds has been developed by Anellotech, USA. This process uses zeolite-based catalysts, co-developed with Johnson Matthey, to produce gases...
which are then converted to benzene, xylene and toluene (bio-BTX) (21). Thermochemical processes such as gasification, pyrolysis, torrefaction and liquefaction require intense heating at elevated temperatures, therefore raising energy efficiency concerns. In addition, the selectivity in bio-oils produced from pyrolysis is extremely poor, therefore inevitably requiring expensive additional upgrading and separation steps (22–23). This has led to a number of investigations into novel pathways to reduce costs (24, 25).

4. Recent Advances in Catalytic Approaches for Cellulose Conversion

In this review, we discuss recent advances in catalytic conversion of cellulosic biomass and cellulose derived intermediates to fuels, fuel additives and chemicals. We focus specifically on highlighting the roles and contributions of noble metal catalyst systems in the key reaction steps: hydrolysis, dehydration, hydrodeoxygenation (HDO), hydrogenation and oxidation leading to value added products from cellulosic biomass. The active catalysts’ performance and function, mechanistic pathways of reactions, opportunities for designing better catalytic systems, current industrial processes and barriers to upscaling to demonstration or commercial scale processing are also discussed. We write this review cognisant of the fact that many reviews have been published on the conversion of cellulosic and cellulose derived intermediates using solid and soluble mineral, organic and Lewis acids in aqueous, aqueous-organic biphasic media and ionic liquids (IL) (26, 27). There has also been a large body of work published on noble metal catalysts or noble metal co-catalyst systems promoting key biorefinery reaction steps and processes, thus demonstrating that these metal catalysts are crucial to the advancement of renewable liquid fuels, chemicals and materials. Yet few reports exist that critically assess and summarise the contribution of noble metal catalytic systems. Noble metals included in
this review are: platinum, palladium, ruthenium, rhodium, iridium, osmium, silver and gold. We have also taken the latitude to include copper and rhenium in a few examples. These metals are known to be resistant to oxidation and corrosion and have long been utilised, in catalytic amounts, in chemical transformations.

5. Hydrolysis of Cellulose and Hemicellulose

Hydrolysis of cellulosic biomass (cellulose and/or hemicellulose) involves cleavage of β-1,4-glycosidic bonds of the biopolymer and is the first step in unlocking the potential of cellulosic feedstock (Figure 4). As mentioned previously, hydrolysis by enzymes is established (28). Several kinds of mineral acids, such as hydrochloric acid (HCl), sulfuric acid (H₂SO₄), hydrofluoric acid (HF), nitric acid (HNO₃), phosphoric acid (H₃PO₄), boric acid (H₃BO₃) and organic acids (for example formic acid, oxalic acid, boronic acid, fumaric and acetic acid) have been employed in hydrolysis of cellulose to sugars (4, 14, 29). The first report on cellulose hydrolysis was with H₂SO₄ (0.5 wt%) in 1923. This catalyst promoted the hydrolysis of cellulose in wood waste and gave 50% yield of sugars (glucose and oligosaccharides) at 170°C in aqueous media (30–32). H₂SO₄ has been found to show better catalytic activity than most mineral acids due to its higher acidity (pKₐ<1) (33). The insolubility of cellulose in aqueous media has been a challenge and this has led to the exploration of alternative solvents such as biphasic and ILs (34–38), which turn out to dissolve cellulosic biomass better and enhance the yields of sugars. The use of microwave irradiation has accelerated reaction rates and lowered reaction temperatures (70–100°C) all the while also affording better yields of sugars (39–41). However, problems associated with the use of mineral acids, which include reactor corrosion, separation of product-catalyst solution, recyclability and the use of large amounts of acid that result in waste effluent, have rendered mineral acid catalytic systems unappealing for industrial scale reactions.

Various other acid catalysts have been developed for hydrolysis of cellulosic biomass (cellulose and hemicellulose). These include solid acid catalysts, which have advantages over homogenous acid catalysts, such as ease of separation of the product-catalyst mixture, less waste and thus lower impact on the environment. Solid acid catalysts, generally in the form of metal oxides, carbon-supported SO₃H groups, sulfonated resins, heteropoly acids (HPAs) and zeolites have been investigated. The use of Lewis acids and acidic IL are also known (41–45). While SO₃H group bearing carbonaceous catalysts give good performance, leaching of the SO₃H groups from the support is a problem. Several metal chlorides (for example chromium(II) chloride (CrCl₂), copper(II) chloride (CuCl₂), dysprosium(III) chloride (DyCl₃), ytterbium(III) chloride (YbCl₃), indium(III) chloride (InCl₃), gallium trichloride (GaCl₃), lanthanum(III) chloride (LaCl₃), aluminum chloride (AlCl₃), hafnium(IV) chloride (HfCl₄), tin(IV) chloride (SnCl₄), germanium(IV) chloride (GeCl₄), chromium(III) chloride (CrCl₃), zirconium(IV) chloride (ZrCl₄), titanium(IV) chloride (TiCl₄) and niobium(V) chloride (NbCl₅) have been employed as soluble Lewis acids for cellulosic biomass hydrolysis. In most cases the Lewis acid catalyst plays a dual role of hydrolysis followed by dehydration to 5-hydroxymethylfurfural (HMF) (46).

The use of acidic IL is a unique strategy which can tackle both cellulose solubility issues and bring about efficient hydrolysis. In this catalyst system, the IL acts as the solvent and acid catalyst. In the presence of minimal amounts of water to aid hydrolysis, several IL have been reported to efficiently dissolve and depolymerise cellulose (47–49). While reports on the hydrolysis of cellulose to glucose by Lewis acid catalysts abound in the literature, reports on the use of noble metal catalyst systems solely for hydrolysis are rare.

An example of a noble metal catalyst for the hydrolysis of cellulose is supported Ru catalysts. The effect of the support has been investigated by screening Ru supported on activated carbon, C₆₀, mesoporous carbon and carbon black, with mesoporous carbon giving the best results. The Ru catalyst on mesoporous carbon support gave a combined glucose and oligosaccharide yield of 41%. Interestingly, the mesoporous carbon alone catalysed the conversion of cellulose to oligosaccharides, while the Ru on the mesoporous carbon converted oligosaccharides to glucose. The active species in the conversion of oligosaccharides to glucose was identified as RuO₂·H₂O (49, 50). This indicates the effect of the support on the hydrolysis of cellulose.

Recently, methyltrioxorhenium (MTO) was used as a catalyst for cellulose hydrolysis, at 150°C under microwave irradiation in 1-allyl-3-methylimidazolium chloride, to give a glucose yield of ~25%. The authors proposed that the mechanism of the hydrolysis involves...
nucleophilic attack at the oxygen on the β-1,4-glycosidic bonds by the electron deficient rhenium centre, eventually leading to cleavage of the β-1,4-glycosidic bond (Scheme I) (51).

The reaction was carried out in the IL 1-allyl-3-methylimidazolium chloride, [AMIM]Cl (52). A tetramethylammonium perrhenate [(CH₃)₄N]ReO₄⁻ in [AMIM]Cl system has also been reported for cellulose hydrolysis. This catalyst system produced a mixture of glucose, oligosaccharides and polysaccharides. Notably, the alkyl chain length of the quaternary ammonium perrhenate impacted negatively on the glucose yield; thus as the chain length increased the glucose yield decreased. It was suggested that the mechanism of this reaction involves the perrhenate (ReO₄⁻) forming hydrogen bonding with the hydroxyl groups in cellulose; thus weakening the β-1,4-glycosidic bonds, which in turn enables water molecules to access the β-1,4-glycosidic bond more easily, leading to hydrolysis (52).

Su et al. have investigated CuCl₂ coupled with either chromium(III) chloride (CrCl₃), CrCl₂, palladium(II) chloride (PdCl₂) or iron(III) chloride (FeCl₃) in the hydrolysis of cellulose. They found that paired metal chlorides were particularly active and showed better reaction rates for β-1,4-glycosidic bond cleavage in comparison to mineral acid catalysed hydrolysis. Paired catalytic systems exhibited improved activity compared to monometallic systems. More specifically, the CuCl₂/PdCl₂ pair gave the best yield (73%) of monosaccharides, oligosaccharides and polysaccharides in a reaction where the yield of glucose was 42%. Other products from the reaction were levulinic acid (LA), formic acid, sorbitol and HMF. It must be noted that neither CuCl₂ nor PdCl₂ on their own were active in hydrolysing cellulose, thus pointing to a vital synergistic effect between the CuCl₂/PdCl₂ system (53). In all the reports of noble metal-catalysed hydrolysis of cellulose discussed, no isolation and subsequent characterisation of the products was reported.

Once sugars are formed they can be further transformed into other chemicals which are feedstocks for fuels and chemicals. Scheme II shows how sugars formed from hydrolysis of cellulose can be transformed to these products.

### 6. Conversion of Polysaccharides and Monosaccharides to 5-Hydroxymethylfurfural and Furfural

#### 6.1 Polysaccharides and Monosaccharides to 5-Hydroxymethylfurfural

The dehydration of hexoses affords HMF, some furfural, LA, formic acid and humins. On the other
hand, dehydration of pentoses produces furfural (Scheme II) (2, 4).

HMF and furfural are important platform chemicals that can be upgraded to valuable commodity chemicals, fuels and fuel additives. HMF is formed as an intermediate during dry heating and roasting of foods containing high levels of carbohydrates (54). It has been found in foods and beverages such as dried fruits, baked foods, coffee, honey, citrus juice, grape juice, prune juice, wine and brandy amongst others. Daily HMF intake is estimated at 30 to 150 mg per person and is toxic to humans if ingested at high concentrations (55–57). HMF can be accessed by three dehydration steps of hexose sugars. The mechanistic pathway for acid catalysed dehydration of hexoses by expulsion of three water molecules is said to proceed via acyclic intermediates or cyclic intermediates (58–62). The cyclic mechanism (Scheme III) begins from the cyclic ketofuranose which undergoes dehydration at C₂ to form a carbenium cation, followed by consecutive β-dehydrations in the ring to afford HMF (61).

The acyclic pathway (Scheme IV) proceeds via formation of 1,2-enediol, which is the rate determining step. This is followed by two β-dehydrations and finally ring closure to yield HMF (61).

In both pathways, the selective conversion of hexoses to HMF is influenced by the isomerisation of glucose to fructose. Glucose isomerisation is catalysed by Lewis acids and Brønsted acids (63). Brønsted acids tend to degenerate monosaccharides to various byproducts (64–72) and afford low (<10%) yields of fructose. The use of organic bases such as piperazine, triethylamine, pyrrolidine, ethylenediamine, piperidine and morpholine has been reported. Fructose yields of up to 32% and 63% selectivity were achieved (66). These are the first organic base catalysed glucose

Scheme III. Cyclic pathway for the dehydration of fructose to HMF (Reprinted from (61). Copyright (1990), with permission from Elsevier)
to fructose isomerisation systems that gave yields and selectivities for fructose that are comparable to widely used Lewis acids (68–72).

The conversion of hexoses and cellulosic biomass to HMF has been dominated by Lewis acid and mineral acid catalysts and has recently been reviewed (70). Some noble metal-containing catalytic systems have demonstrated good activity for this transformation (Table I) (71–79).

In 2007, Zhang and coworkers reported that fructose dehydration proceeded in the presence of catalytic amounts of MCl$_2$ and M$'$Cl$_3$ (where M = Cr, Fe, Cu, Pd, Pt and M$'$ = Rh, Rh, Ru, Mo). The catalytic systems were selective to HMF and negligible amounts (0.08%) of LA were produced. Notably, only CrCl$_2$ gave high yields (70%) of HMF from glucose, whereas other Lewis acid catalysts afforded yields less than 10% (71). The role of Cr$^{2+}$ is to convert the α-glucose to β-glucose and isomerise the β-glucose to fructose, which improves the yield of HMF. A mixture of CrCl$_2$ and CuCl$_2$ in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) was used to transform cellulose into HMF (in 59% yield) in a single step. This catalytic system achieved this by prior hydrolysis of cellulose, followed by dehydration of glucose units into HMF. The authors suggest that CrCl$_2$ activates CuCl$_2$ to hydrolyse cellulose into glucose. Separate experiments with a CuCl$_2$ catalyst only and with a paired CuCl$_2$/CrCl$_2$ catalyst (where the relative proportion of CuCl$_2$ in the pair was higher than CrCl$_2$), show that the paired metal chlorides yield more than three times the amount of product (i.e. glucose from cellulose) than the CuCl$_2$ catalyst on its own. On the other hand, the CuCl$_2$/CrCl$_2$ pair with a relatively higher proportion of CrCl$_2$ resulted in a high HMF yield, consistent with CrCl$_2$ being a highly selective catalyst for the conversion of glucose to HMF. The catalytic system could be reused up to three times with consistent activity and selectivity (71).

In another report a solid Ag-containing HPA (Ag$_3$PW$_{12}$O$_{40}$ HPA) was used as a solid catalyst to dehydrate fructose and glucose to HMF. HMF yields of 78% and 76% were obtained from fructose.
and glucose respectively. The Ag₃PW₁₂O₄₀ cluster exhibited higher catalytic activity and selectivity as compared to when Brønsted acids (HCl and phosphotungstic acid (H₃PW₁₂O₄₀)) and Lewis acid (silver nitrate (AgNO₃)) were used separately in glucose dehydration to HMF. Therefore, the higher catalytic activity of Ag₃PW₁₂O₄₀ can be attributed to the synergistic effect of Lewis acid and Brønsted acid sites in the Ag₃PW₁₂O₄₀ cluster. Infrared (IR) experiments revealed that the substrate accumulated on the Ag₃PW₁₂O₄₀ catalysts and could be the reason for the high activity displayed by this catalyst. Fourier transform (FT)-IR spectra of Ag₃PW₁₂O₄₀ and its adsorbed fructose and glucose confirmed the absorption of substrate on part of the catalyst. Notably, the Ag₃PW₁₂O₄₀ cluster as a catalyst could be recycled and reused up to six times (73).

In a further report, CrCl₂ and RuCl₃ in a 4:1 molar ratio catalysed the conversion of cellulose to HMF in [EMIM]Cl IL in a 60% yield. Gram scale production of HMF was achieved with this CrCl₂/RuCl₃ system. Furthermore, lignocellulosic biomass from reed was also converted to HMF (41% yield) and furfural (26%) using the same catalytic system and conditions (74). CuCl₂ in 1-ethyl-3-methylimidazolium acetate ([EMIM][Ac]) has been used to produce HMF in ≈70% yield (75).

Good catalytic performance has been recorded for the dehydration of fructose to HMF with iridium(III) chloride (IrCl₃) and AuCl₃•HCl catalysts in HCl and 1-butyl-3-methylimidazolium chloride ([BMIM]Cl). A HMF yield of 89% was obtained with IrCl₃ catalyst in 30 min at 120°C while AuCl₃•HCl gave 44% HMF yield under the same conditions (77).

### Table I: Selected Noble Metal Catalysed Conversion of Monosaccharide, Polysaccharide and Lignocellulosic Biomass to HMF

<table>
<thead>
<tr>
<th>Carbohydrate</th>
<th>Catalyst (catalyst loading)</th>
<th>Temp., °C</th>
<th>Time, h</th>
<th>HMF Yield, %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fructose</td>
<td>MCl₂ or M’Cl₃ (6 mol%)</td>
<td>80</td>
<td>3</td>
<td>63–83</td>
<td>(71)</td>
</tr>
<tr>
<td></td>
<td>M = Cr, Fe, Cu, Pd, Pt</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>M’ = Rh, Ru, Mo</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fructose</td>
<td>Ag₃PW₁₂O₄₀ (3.3 wt%)</td>
<td>120</td>
<td>1</td>
<td>78</td>
<td>(73)</td>
</tr>
<tr>
<td>Glucose</td>
<td>Ag₃PW₁₂O₄₀ (3.3 wt%)</td>
<td>130</td>
<td>4</td>
<td>76</td>
<td>(73)</td>
</tr>
<tr>
<td>Cellulose</td>
<td>CrCl₂/CuCl₂ (6 mol%)</td>
<td>120</td>
<td>8</td>
<td>59</td>
<td>(72)</td>
</tr>
<tr>
<td>Cellulose</td>
<td>CuCl₂ (20 mol%)</td>
<td>160</td>
<td>3.5</td>
<td>70</td>
<td>(75)</td>
</tr>
<tr>
<td>Cellulose</td>
<td>CrCl₂/RhCl₃ (10 mol%)</td>
<td>120</td>
<td>2</td>
<td>60</td>
<td>(74)</td>
</tr>
<tr>
<td>reed³</td>
<td>CrCl₂/RhCl₃ (10 mol%)</td>
<td>120</td>
<td>2</td>
<td>41</td>
<td>(74)</td>
</tr>
<tr>
<td>Fructose</td>
<td>CuCl₂ (18 mol%)</td>
<td>80</td>
<td>0.10</td>
<td>80</td>
<td>(76)</td>
</tr>
<tr>
<td>Fructose</td>
<td>IrCl₃ (7 mol%)</td>
<td>120</td>
<td>0.5</td>
<td>89</td>
<td>(77)</td>
</tr>
<tr>
<td>Fructose</td>
<td>AuCl₃.HCl (7 mol%)</td>
<td>120</td>
<td>3</td>
<td>44</td>
<td>(77)</td>
</tr>
</tbody>
</table>

*These yields are HPLC yields and were not isolated yields

³26% furfural was also obtained

6.2 Polysaccharides and Monosaccharides to Furfural

The synthesis of furfural has been achieved by using Brønsted and Lewis acid catalysts (80–82). In a report by Zhang et al. CrCl₃, CrCl₃/lithium chloride (LiCl), FeCl₂•6H₂O, CuCl₂•H₂O, copper(II) chloride (CuCl₂), LiCl and AlCl₃ were screened for catalytic activity and selectivity in xylose and xylan conversion to furfural, under microwave irradiation. AlCl₃ gave the best performance for the production of furfural from xylose (82.2%) and xylan (84.8%) (80).

Furfuryl alcohol (FA) has also been obtained directly from xylose using a combination of Pt/SiO₂ and ZrO₂–SO₄ catalysts. The SiO₂ was reported to promote xylose to xylulose isomerisation (with xylose conversion of 65%), while the ZrO₂–SO₄ catalysed the dehydration of xylulose to furfural. Finally, furfural was selectively transformed to FA by Pt/SiO₂ (81).
6.3 5-Hydroxymethylfurfural and Furfural as Sources of Biofuels

Sections 6.1 and 6.2 provide avenues to HMF and furfural, versatile renewable platform chemicals that can provide access to a variety of biofuels and chemicals (Schemes V and VI). Since the 1920s, the Quaker Oats Process has been producing furfural and FA from agricultural residues (83). AVA Biochem, Switzerland, produces 300 tonnes of 90% purity aqueous HMF and 20 tonnes of highly pure crystalline HMF per annum, (84) and there are examples of patented pilot scale processes that have produced HMF using organic catalysts, mineral acid catalysts and without a catalyst (85–88). Although Lewis and Brønsted acid catalysts have dominated efforts to produce these platform chemicals, noble metal containing catalytic systems (including monometallic and bimetallic species) have shown remarkable efficacy in converting HMF and furfural to the chemicals illustrated in Schemes V (89) and VI (90). In Section 7 we will discuss some of the noble metal promoted catalytic transformations illustrated in Schemes V and VI.

7. Conversion of Furfural and 5-Hydroxymethylfurfural to Value Added Chemicals and Fuels

As shown in Schemes V and VI, HMF and furfural are precursors for the synthesis of a variety of valuable chemicals and fuel additives (89–90). These can be accessed via specific reaction pathways including hydrogenation, rehydration, etherification, esterification, aldol condensation, hydrolysis and HDO (89–92). This review highlights recent literature reports of dimethylfuran (DMF), 2-methylfuran (2-MF), 5-(ethoxymethyl) furfural (EMF), 2,5-dimethyl-tetrahydrofuran (DMTHF), 2-methyl tetrahydrofuran (MTHF), FA, cyclopentanone (CPO) and pentanediols produced by noble metal containing catalytic systems (88–124).

7.1 Polysaccharides and Monosaccharides to 2,5-Dimethylfuran, 2-Methylfuran, 2,5-Dimethyltetrahydrofuran, 2-Methyltetrahydrofuran and 5-Ethoxymethylfurfural

In comparison to the leading biofuel, bioethanol, DMF has a higher energy density (30 MJ l⁻¹), a higher octane number of 119 and a lower volatility (boiling point = 92–94°C) than bioethanol (Table II). Furthermore, it is immiscible with water therefore, in this regard, is similar to gasoline. These properties make DMF a better biomass derived liquid fuel. Policy limitations and/or cost-effective production of DMF at an industrial scale are likely reasons why DMF has not yet been taken

Scheme V. Various derivatives of 5-HMF (Reprinted with permission from (89). Copyright (2014) American Chemical Society)
up as a fuel additive of choice, given its many technical advantages over bioethanol. DMF can be obtained from the HDO of HMF in the presence of a catalyst. Metal catalysts have been widely used to promote this reaction (88). For example, Dumesic et al. used a CuRu/C catalyst system that produced 71% DMF in 10 h when 1-butanol was used as the solvent of the reaction at 220°C and 6.8 bar H₂ (91). This catalyst system could also be utilised to promote the conversion of HMF to DMF, where the HMF was initially prepared by mineral acid catalysed dehydration of corn stover (93).

An even better catalyst system was reported by Wang et al. with a selective bimetallic catalyst (PtCo nanoparticles supported on hollow carbon nanospheres, PtCo@HCS) for the conversion of HMF to DMF at 180°C with a 98% yield in 1-butanol. The PtCo@HCS could be recycled and

<table>
<thead>
<tr>
<th>Property</th>
<th>DMF</th>
<th>MF</th>
<th>Ethanol</th>
<th>Gasoline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₆H₈O</td>
<td>C₅H₆O</td>
<td>C₂H₆O</td>
<td>C₆–C₉</td>
</tr>
<tr>
<td>Molecular weight, g mol⁻¹</td>
<td>96.13</td>
<td>82.04</td>
<td>46.07</td>
<td>100–0105</td>
</tr>
<tr>
<td>Boiling point, °C</td>
<td>92–94</td>
<td>63–66</td>
<td>78</td>
<td>95–99</td>
</tr>
<tr>
<td>Energy density, MJ l⁻¹</td>
<td>30</td>
<td>28.5</td>
<td>21</td>
<td>31</td>
</tr>
<tr>
<td>Water solubility</td>
<td>immiscible</td>
<td>immiscible</td>
<td>miscible</td>
<td>immiscible</td>
</tr>
<tr>
<td>Research octane number (RON)</td>
<td>119</td>
<td>103</td>
<td>110</td>
<td>97</td>
</tr>
<tr>
<td>Density @ 20°C, kg m⁻³</td>
<td>890</td>
<td>913</td>
<td>791</td>
<td>745</td>
</tr>
<tr>
<td>Flash point, °C</td>
<td>−1</td>
<td>−11</td>
<td>14</td>
<td>0.71–0.77</td>
</tr>
</tbody>
</table>

*aAdapted with permission from (92). (Copyright (2015) American Chemical Society)*

Scheme VI. Various derivatives of furfural (Reprinted (adapted) with permission from (90). Copyright (2016) American Chemical Society)
reused up to three times, although by the third cycle, a drop in DMF yield (from 98 to 72%) occurred (94). The role of the catalyst support in this reaction appears to be critical. For example, when Pt nanoparticles supported on activated carbon (Pt/AC) and graphitic carbon (Pt/GC) were employed in this reaction, only 9% and 56% DMF yields respectively were achieved. However, PtCo nanoparticles on activated carbon (PtCo/AC) and graphitic carbon (PtCo/GC) gave conversions of 100% HMF and 98% DMF, effectively proving that the two metals work cooperatively to transform HMF into DMF. Selective HDO of HMF over Ru/CoO$_2$ and PdAu/C has also been reported. These reactions were conducted in tetrahydrofuran (THF) using H$_2$ at 130°C for 24 h and at 60°C for 6 h respectively; giving excellent DMF yields of 100% and 93.4% respectively (95, 96). It is interesting to note that Ru and Pd alone without either Co or Au are less effective in catalysing HMF to DMF. X-Ray photoelectron spectroscopy (XPS) spectra of PdAu/C catalyst reveal that Pd atoms in the PdAu/C may have electronic poor states (after charge transfer from Pd to Au atoms occurs) which strongly contributed to the enhancement of HDO activity thus improving DMF yield.

Notably, Ru/C and Pd/C with and without ZnCl$_2$ in converting HMF to DMF were reported by Zu et al. (96); Ru/C/ZnCl$_2$ produced 41% DMF and 52% 2,5-dihydroxymethyl furan (DMHF) and Ru/C alone gave a minimal amount of DMF from HMF. The higher activity displayed by the bimetallic catalyst (Ru/C/ZnCl$_2$) as compared to Ru/C suggests enhanced HDO in the presence of Zn$^{2+}$, provided by the synergy between the two metals. It also explains why Pd/C/ZnCl$_2$ gave better yield than Ru/C/ZnCl$_2$ in this study (97, 98). In the presence of a Brønsted acid Amberlyst®-15, instead of ZnCl$_2$, a mixture of products was obtained from HMF, namely DMTHF (13%), DMF (6%), tetrahydrofurfuryl alcohol (THFA) (3%), 2,5-bis(hydroxymethyl)tetrahydrofuran (DTHF) (23%), 2-methyltetrahydrofuran-5-aldehyde (4.5%) and methylytetrahydrofurfuryl alcohol (6%) and 2-hexanone (1.6%) (Schemes V and VI). This suggests that the acidity of ZnCl$_2$ is not the only reason for the enhanced activity of the catalyst, resulting in high DMF yield. Since the authors detected leached zinc in the solution, it is likely that the role of Zn$^{2+}$ which leaches into solution during the reaction is as described by Abu-Omar and co-workers, where Zn$^{2+}$ ions bind to the substrate and activates its cleavage upon encountering Ru–H or Pd–H sites on the catalyst surface (98).

Similarly, in the presence of a RhCl$_3$/HX catalytic system (X = I and Cl), a mixture of furan ring saturated and ring-opening products were also obtained from xylose, glucose, fructose, sucrose, inulin, cellulose and corn stover. The reaction is conducted in aqueous media and the main products obtained were DMTHF (up to 85% from fructose and 80% from cellulose) and MTHF (up to 80% from xylose and 56% from corn stover) (99, 100). These are gas chromatography (GC) yields and have not been isolated. DMTHF has been hydrogenated to 1,6-hexadiol, which was converted into caprolactone and caprolactam (101).

Generally, molecular hydrogen has been the source of hydrogen in HDO reactions; but the use of hydrogen transfer reagents is safer than using molecular hydrogen in HDO reactions. Here, formic acid as a hydrogen source in the conversion of HMF, fructose and lignocellulose (with Ru/C catalyst) to chemicals provide useful examples of non-molecular hydrogen in HDO reactions. For example, when HMF was used as a substrate, 37% DMF, 43% 5-formyloxymethyl furfural (FMF) and 3% LA were obtained. Other examples include the initial direct conversion of lignocellulose and carbohydrate substrates in a Brønsted acid IL to catalyse the conversion of these substrates to HMF, and then subsequent use of formic acid as hydrogen source and Ru/C as catalyst to convert HMF to FMF, which was further converted to DMF. Interestingly, the feedstock in this reaction appears to be crucial in determining the yield of DMF. The yields of DMF from cellulose is 16% whilst the yield is 10% from sugars compared to when pure HMF was used as the substrate (37%) (102). Isopropyl alcohol can also be used as a hydrogen source in place of formic acid in the Ru/C catalysed conversion of HMF to DMF. The yield of DMF obtained was 81% and the reaction was said to proceed by the formation of 2,5-bis(hydroxymethyl)furfural as an intermediate (103).

MF has a high density (913 kg cm$^{-3}$), low flash point (~11°C) and low solubility in water, unlike ethanol. The energy density of MF is higher than that of ethanol and similar to DMF (Table II) (91). MF is a water soluble liquid, it is flammable and has a chocolate odour. It is also used as feedstock, as a solvent and has been widely used in pesticides and the perfume industry (104, 105). MF production proceeds by dehydration of xylose followed by HDO of furfural. The best catalyst for this reaction is a polymer supported Pd(II) complex which exhibited 100% yield conversion of furfural into MF with H$_2$ pressure <1 bar at 180°C (106).
EMF is another compound that can be accessed by etherification of HMF (Scheme V). It is a potential biofuel and has an energy density of 30.3 MJ l⁻¹, which is higher than that of ethanol and comparable to gasoline. It has, thus, been proposed as an additive and/or substitute for diesel as a fuel (89–91). Lin and coworkers have used Ag₃H₃PW catalysts, prepared through a H⁺ exchange for Ag⁺, for esterification of HMF to EMF. In using this series of catalysts, Ag₃H₃PW displayed higher catalytic performance than Ag₃HPW and Ag₃PW in the etherification of HMF; producing a 69.5% yield of EMF when fructose was the starting material. The catalyst could be recycled and showed no marked decrease in activity (107).

In addition to EMF, 2,5-bisalkoxymethylfurans have also been identified as potential renewable liquid fuels. Bell and coworkers have reported a one-pot process involving the sequential dehydration and reductive etherification of fructose to 2,5-bisalkoxymethylfurans. The dehydration and etherification of fructose was performed using Amberlyst®-15 and Pt/Sn/alumina at 110°C to form 5-(alkoxymethyl)furfurals and 2-(2,2-alkoxyethyl)-5-(alkoxymethyl)furan. At 60°C and under H₂ pressure, 5-bisalkoxymethylfurans and 2,5-bisalkoxymethyl furans could still be obtained in good yields (108).

7.2 Polysaccharides and Monosaccharides to Furfuryl Alcohol and Pentanediols

FA is prepared industrially by the catalytic hydrogenation of furfural using Ni and Cu/CrO catalysts. If the catalyst used is not selective, hydrogenation of furfural yields not only the desired products but also a variety of byproducts including furan, THF, THFA and ring-opening products, such as pentanol and pentanediols (Scheme VI) (109–114). Pd/SiO₂ as catalyst for the hydrogenation of furfural using 1 bar of H₂ at 230°C has been reported by Sithithsa et al. to produce FA in a yield of 65% (109). Similarly, furfural transformation to FA has been performed in the vapour phase using silica supported Pt nanoparticles. With small Pt nanoparticles on SiO₂, decarboxylation of furfural to furan was observed while larger sized Pt nanoparticles produced furan and FA (Scheme V) (110).

HDO of furfural can also produce 1,2-pentanediol (1,2-PDO), 1,4-pentanediol (1,4-PDO) and 1,5-pentanediol (1,5-PDO) which can be used as monomers for the synthesis of polyesters (Scheme VI) (111). In an investigation of the effect of adding noble metals (including Ru, Rh, Pt, Pd) to Ir-ReOₓ/SiO₂ in the one-pot conversion of furfural to 1,5-PDO, Pd 0.66 wt%-Ir-ReOₓ/SiO₂ was found to be superior. The Pd 0.66 wt%-Ir-ReOₓ/SiO₂ gave 71.4% 1,5-PDO while 28.6% of the products consisted of 1,4-PDO, 1,2-PDO, 1-pentanol, 2-pentanol, THFA and 2-MTHF (112).

Catalyst characterisation revealed that Pd–Ir–ReOₓ/SiO₂ catalyst consisted of Pd metal particles with ReOₓ species (Pd–ReOₓ) and Ir metal particles with ReOₓ species (Ir–ReOₓ) (Figure 5). The Pd–ReOₓ species catalyse hydrogenation of furfural into THFA and the Ir–ReOₓ species catalyse the HDO of THFA to 1,5-PDO. The ReOₓ species modified Pd sites (i.e. decreased Pd metal average particle size) and increased the dispersion of Pd metal. This effect of ReOₓ is said to be linked to the high performance of Pd–Ir-ReOₓ/SiO₂ in the hydrogenation of furfural into THFA. Supported Ir was found to be in the metallic state and the Re species form low valent oxide clusters (ReOₓ) that partially cover the Ir metal surface, therefore the Ir–ReOₓ species can catalyse the hydrogenolysis of THFA to 1,5-PDO (112).

More recently, Huber et al. reported a new process for the production of 1,5-PDO (84% yield) from furfural. This route to 1,5-PDO proceeds via hydrogenation → dehydration/hydration → ring-opening tautomerisation and → hydrogenation.
reactions, using Ni, γ-Al₂O₃ and Ru catalysts respectively. While this process has more reaction steps than conventional hydrogenation of furfural to THFA followed by HDO of THFA to 1,5-PDO, techno-economic assessments demonstrate that the process is economically viable (113).

Hronec and co-workers described a novel, highly selective transformation of furfural to CPO (Scheme V). Selective rearrangement of furfural to CPO by 5%Pt/C is achieved in water, at reaction temperatures of 140°C to 190°C and hydrogen pressures of 30 to 80 bar. Notably, when 5% Ru/C and 5% Pd/C were used under the same conditions, a mixture of typical furfural hydrogenation products (FA, THFA, MF and MTHF) were obtained (114).

Homogeneous catalysts such as [Pd(OAc)₂] / D²BPF (D²BPF = 1,1′-bis(di-tertbutylphosphino) ferrocene), [Rh(CO)₂(acac)] / H₂WO₄, [CP*Ru(OTf)₂(μ-H)]⁺ / HOTf (CP* = CpMe₂ and OTf = CF₃SO₂⁻) and cis-[Ru(6,6′-Cl₂bpy)₂(OH)₂] (OTf)₂ (6,6′-Cl₂bpy = 6,6′-dichloro-2,2′-bipyridine) catalyse HDO of C–O bonds (115–118). For example, [CP*Ru(OTf)₂(μ-H)]⁺ / HOTf is an efficient catalyst for the dehydration of 1,2-PDO followed by hydrogenation to form n-propanol under acidic conditions. This catalyst produced 54% n-propanol after 30 h at 92% 1,2-PDO conversion (119, 120). These homogeneously catalysed reactions are typically carried out at temperatures ranging from 80°C to 120°C, meaning the active species is likely a molecular catalyst or a ‘cocktail’ of catalysts, comprising molecular catalyst and nanoparticles (121).

Direct conversion of furfural to γ-valerolactone (GVL) by Brönsted and Lewis acid zeolite catalysts has been reported. Up to 80% GVL yield was achieved through Meerwein-Ponndorf-Verley (MPV) reduction of furfural to FA, followed by hydrolysis of FA to LA and then selective MPV hydrogenation of LA to GVL (122, 123).

7.3 Polysaccharides and Monosaccharides to Levulinic Acid, Ethyl Levulinate and γ-Valerolactone

Acid catalysed dehydration of hexoses leads to the formation of HMF, which can undergo rehydration in acidic medium to give LA and formic acid (Scheme V). LA is a particularly attractive platform molecule, because it can be converted into valuable chemicals and advanced biofuels (124). For example, valeric biofuels which are compatible with current transportation fuels are accessible from LA (125, 126). If dehydration of hexoses is carried out in ethanol, then esterification of LA with ethanol leads to ethyl levulinate (EL) (Scheme V).

EL is an acceptable diluent for biodiesel fuels with high saturated fatty acid content (127).

GFBiochemicals’ Caserta plant in Milan, Italy, currently produces LA and its coproduct FA from non-edible biomass feedstock (wood, grass, wheat straw and cellulose) via an acid catalysed process (ATLAS Technology™). This company also has plans to expand its production portfolio to LA derivatives, such as LA-esters and LA-ketals, GVL, MTHF and methylbutanediol (MeBDO) (128).

Hydrogenation of LA in the presence of a metal catalyst with an external H₂ source or formic acid as the source of hydrogen gives GVL. GVL is a promising bio-derived molecule and it is attractive for its physical and chemical properties. It has low toxicity, an acceptable and definitive smell which makes detection of leaks and spills easy, it is safe to store and move globally in large quantities, has high flash (96°C) and boiling (207°C) points as well as a low melting point (−31°C). It is also used as an additive in the food industry and as a green solvent (129–133). Bond et al. have proposed a pathway to renewable butene, using GVL, which can be oligomerised to long chain alkenes for liquid fuels and commodity chemicals production. Using formic acid as the source of hydrogen in the hydrogenation of LA is more economical because dehydration of hexoses produces formic acid in equimolar amounts to LA. In the presence of a catalyst, formic acid decomposes to carbon dioxide and H₂ and hence can be used as an internal source of hydrogen (Scheme VII) (131).

Quaker Oats, USA, produces GVL on a commercial scale from LA using chromium(III) oxide (Cr₂O₃) and copper(II) oxide (CuO) at 200°C (134). Metal catalysts, such as Pd, Ir, Ni, Cu, Pt, Re, Rh, Au and Ru have been used in the presence of H₂ to produce GVL from LA (135–138). Manzer studied this reaction using Ir, Rh, Ru, Pd, Rh, Pt and Re supported on carbon, and found that 5% Ir, Pd and Ru were active in the conversion of LA to GVL but their selectivity to GVL was rather low. Ni had the lowest activity and selectivity under the same conditions and Ru had the best activity and selectivity (Figure 6) (135).

While heterogeneous catalysts have dominated LA to GVL reactions, (135–141) homogenous catalysts have also been studied. Particularly, water soluble homogeneous catalysts have been attractive because GVL does not form an azeotropic mixture with water, therefore the catalyst can be recovered by distillation and reused (129–131, 142). Hydrogenation of LA
to produce GVL has been examined in aqueous solution using various water soluble phosphine ligands in combination with the metal precursors Ru(acac)$_3$ and RuCl$_3$•xH$_2$O (Table III) (143–147). GVL was obtained in 97% yield within 5 h, using a Ru(acac)$_3$/TPPTS (TPPTS = p(C$_6$H$_4$-m-SO$_3$Na)$_3$) catalytic system (144, 147).

Formic acid was used as a hydrogen source in [(η$^6$-C$_6$Me$_6$)Ru(bpy)(H$_2$O)]SO$_4$ catalysed transformation of LA, in water, to give in GVL and 1,4-PDO. In this same study, [Ru(acac)$_3$/PBu$_3$/NH$_4$PF$_6$ afforded 100% GVL from LA (142).

Mika et al. demonstrated that LA could be reduced effectively to GVL in the presence of an in situ catalyst generated from Ru(acac)$_3$ and different sulfonated phosphines with the general formula R$_n$P(C$_6$H$_4$-m-SO$_3$Na)$_{3–n}$ ($n$ = 1, 2; R = Me, iPr, nBu, Cp) without the need for a base. The $^{i}$BuP(C$_6$H$_4$-m-SO$_3$Na)$_2$ showed the highest activity at 99% GVL. The catalyst was successfully recycled for six consecutive runs without loss of activity (146).

Ir trihydride catalysts bearing a PNP pincer ligand showed extremely high activity in LA to GVL conversion giving up to 98% GVL yield. Recovery of the catalyst was demonstrated. This was done by removal of the product by vacuum and the remaining catalyst was redissolved in LA and exhibited similar activity to before distillation (149). Conversion of LA to GVL was studied using p-cymene Ru(II) N-heterocyclic carbene (NHC) complexes as (pre)catalyst in water. The complex (Table III) was reduced in situ to form highly catalytically active Ru nanoparticles which deactivated in subsequent catalytic runs due to aggregation (150).

Horváth and coworkers showed that LA and a small excess of formic acid can be converted to GVL in the presence of Shvo’s catalysts. At 100°C, the catalyst rearranged to form a Ru hydrido catalytically active species (Table III) and yields higher than 99% after 8 h were recorded. The formation of 1,4-PDO and MTHF, the typical side products of the reduction of GVL with molecular hydrogen, was not observed (131).

Solvent free conversion of LA to GVL has been achieved with pyrazolyl-phosphite and pyrazolyl-phosphinite Ru(II) complexes as (pre)catalysts, using both molecular hydrogen and formic acid as hydrogen sources. With H$_2$ (15 bar) 100% GVL yield obtained at 110°C, while with formic acid at 100°C, 100% GVL was obtained. In order to understand whether formic acid acts as a hydrogen transfer reagent or a source of H$_2$ through prior decomposition, in situ NMR studies, where the reaction was monitored in a J Young nuclear magnetic resonance (NMR) tube containing the (pre)catalyst, KOH and formic acid at 120°C, were carried out. Within 30 min of the reaction, hydrogen gas was observed by proton (1$^H$)-NMR spectroscopy with a H$_2$ signal at 4.56 ppm. The active species was found to be a cocktail of...
Table III  Selected Homogeneous Noble Metal Homogenous Catalysts That Have Been Used in the Hydrogenation of LA to GVL (131, 142–151)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T, °C</th>
<th>Reductant</th>
<th>Time, h</th>
<th>GVL, %</th>
<th>TOF, h⁻¹, mol⁻¹GVLmol⁻¹Ruh⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(acac)₃]/PBu₃/NH₄PF₆</td>
<td>160</td>
<td>H₂ 100 bar</td>
<td>18</td>
<td>100</td>
<td>(143, 144)</td>
<td></td>
</tr>
<tr>
<td>[Ru(acac)₃]/P(n-Oct)₃</td>
<td>160</td>
<td>H₂ 100 bar</td>
<td>18</td>
<td>99</td>
<td>(143)</td>
<td></td>
</tr>
<tr>
<td>[Cp*Ir(4,4-di-OH-bpy)(H₂O)]SO₄</td>
<td>120</td>
<td>H₂ 10 bar</td>
<td>1</td>
<td>98</td>
<td>12,200</td>
<td>(142)</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>H₂ 10 bar</td>
<td>4</td>
<td>87</td>
<td>4326</td>
<td>(148)</td>
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<tr>
<td>[η⁶-(C₆Me₆)Ru(bpy)(H₂O)]SO₄</td>
<td>70</td>
<td>HCO₂Na</td>
<td>18</td>
<td></td>
<td></td>
<td>(143)</td>
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<tr>
<td>[Ru(acac)₃]/TPPTS</td>
<td>140</td>
<td>H₂ 70 bar</td>
<td>12</td>
<td>95</td>
<td>(146)</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>H₂ 50 bar</td>
<td>5</td>
<td>97</td>
<td>(147)</td>
<td></td>
</tr>
<tr>
<td>[Ru(acac)₃]/R₂P(C₆H₄-m-SO₃Na)₂</td>
<td>140</td>
<td>H₂ 100 bar</td>
<td>1.8</td>
<td>92</td>
<td>6370 (TON)</td>
<td>(145)</td>
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<tr>
<td>RuCl₃.xH₂O/PPh₃</td>
<td>200</td>
<td>HCO₂H/pyridine</td>
<td>6</td>
<td>93</td>
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<td></td>
<td></td>
<td>HCO₂H/NET₃</td>
<td>6</td>
<td>95</td>
<td>(147)</td>
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<tr>
<td>[Ru(acac)₃]/Triphos</td>
<td>160</td>
<td>H₂ 100 bar</td>
<td>18</td>
<td>95</td>
<td>(144)</td>
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<tr>
<td>Triphos = PPh₂PPh₂PPh₂</td>
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<tr>
<td>[Ru(acac)₃]/Triphos</td>
<td>160</td>
<td>H₂ 100 bar</td>
<td>18</td>
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<tr>
<td>[Ru(acac)₃]/Triphos</td>
<td>110</td>
<td>H₂ 20 bar</td>
<td>12</td>
<td>100</td>
<td>202</td>
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<tr>
<td>[Ru(acac)₃]/Triphos</td>
<td>120</td>
<td>HCO₂H/KOH</td>
<td>16</td>
<td>100</td>
<td>200</td>
<td>(151)</td>
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</table>

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a No base added  
b 1,4-PDO and MTHF were also produced  
c Cp* = η⁶-C₅Me₅  
d TPPTS = p(C₆H₄-m-SO₃Na)₂  
e R = Me, Pr, cyclopentyl, iBu, iPr  
f Potassium hydroxide (KOH) 1.2 equiv.  
g 95%, 1,4-PDO was produced  
h KOH 0.05 equiv.  
i KOH 1 equiv.
nanoparticles and molecular catalysts as evidenced by mercury poisoning tests. The catalyst could be recycled and reused up to three times (151).

8. Conversion of Polysaccharides, Oligosaccharides and Monosaccharides to Sugar Alcohols and Hydrocarbons

8.1 Polysaccharides and Monosaccharides to Sugar Alcohols and Diols

Hydrogenation of cellulose, oligosaccharides, disaccharides and monosaccharides results in the formation of sugar alcohols or polyols such as xylitol, sorbitol and mannitol which are important chemicals widely used as monomers in the plastics industry. Sugar alcohols also have applications in the food industry in the substitution of sugars such as glucose, sucrose and fructose. Xylitol is most frequently used in place of sugar, as it has similar sweetness and lower energy content than sucrose. From sugar alcohols it is also possible to produce renewable hydrogen and hydrocarbons which will be discussed in Section 8.2 of this review (152–161).

The catalytic conversion of cellulose to sugar alcohols is a two-step process, which includes hydrolysis of cellulose to monosaccharides, followed by the hydrogenation of the sugars to sugar alcohols. Sels and coworkers used water soluble HPAs and a Ru/C catalyst to transform cellulose to sugar alcohols. At 190°C and (95 bar H2), the conversion of cellulose was 100% with 85% yield (152). Palkovits et al. have also demonstrated that the transformation of cellulose to sugar alcohols was possible using a combination of HPAs and Ru/C. Sugar alcohols were obtained in a yield of 81% (153). Liu et al. have also demonstrated cellulose to sugar alcohols conversion with Ru/C at 245°C and 60 bar H2. They obtained 40% sugar alcohols of which 30% was sorbitol and 10% mannitol (154). It is striking to see that in the presence of HPAs, which are acidic, catalytic conversion of cellulose to sugar alcohols on Ru/C proceeds to give higher yields at comparably lower temperatures than when no HPAs are added.

Hydrolytic hydrogenation of cellulose was shown by Fukuoka et al. The reaction gave 58% sorbitol yield at 190°C in water over a Ru/AC catalyst (155). Tsubaki et al. have presented a catalytic system that consists of Pt/RGO (RGO = reduced graphene oxide) for the hydrogenation of cellulose and cellulbiose to sorbitol. Sorbitol yield was 91.5% from cellulbiose and 58.9% from cellulose (156). Ru and Os complexes have been used, as homogeneous catalysts, in conversion of fructose (to glycerol, propylene glycol (PG), ethylene glycol (EG) and sugar alcohols) (157, 158), mannose and inulin (to sugar alcohols) (159) and glucose (to sorbitol) (160). Recently, Wang and coworkers reported the first example of a highly selective homogenous Ru(II)/H2SO4 catalytic system which promoted the conversion of cellulbiose and cellulose (at 100°C and 50 bar H2 over 16 h) to sorbitol, 1,4-sorbitan, glucose and a negligible amount of HMF (0.1%). Starting from cellulbiose, 91.4% sorbitol, 3.1% 1,4-sorbitan and 5.3% glucose were afforded at 100% conversion, whilst from cellulose 21.9% sorbitol, 7.6% 1,4-sorbitan and 8.4% glucose were produced at 40% conversion. Sorbitol can be further converted to sorbitan and isosorbide; thus suggesting that the sorbitan in the above study may have been produced from further reaction of the sorbitol. The authors further proposed a mechanism for the reaction (Scheme VIII) which involved in situ generation of the catalytically active Rh–H species 1 which inserted into the C=O bond of glucose (to form 2) of the initially hydrolysed cellulose. This is then followed by a metal–ligand assisted proton transfer to the glucose O1 and C1 3 coupled with sorbitol expulsion to regenerate the (pre)catalyst (161).

EG, 1,2-PG, 1,3-PG and glycerol are the simplest sugar alcohols and are used as emulsifiers, dehumidifying agents, anti-freeze agents, lubricants, solvents, polymer monomers and as pharmaceutical intermediates. Diols are currently produced from fossil derived feedstock (petroleum) by hydration of propylene and ethylene oxide (162). In 2008, Chen and coworkers reported the direct conversion of cellulose to EG in a yield of 61% using a nickel-tungsten carbide catalyst (163). Since then, studies aimed at understanding the reaction mechanism of cellulose to EG and 1,2-PG have been conducted (164–167). The major mechanistic pathway involves hydrolysis of cellulose (to glucose and oligosaccharides) → retro-aldol condensation (of glucose to form glycol aldehyde and erythrrose) → hydrogenation of glycol aldehyde to EG. If glucose isomerises to fructose, then 1,2-PG is formed (Scheme IX) (165, 166).

Catalysts such as Ru/AC/H2WO4 have been employed in cellulose conversion to EG (168). Liu and coworkers reported efficient conversion of cellulose into EG, 1,2-PG and sorbitol, as dominant products on Ru/C in the presence of tungsten...
tri oxide (WO$_3$). It was found that WO$_3$ crystallites catalysed hydrolysis of cellulose as well as selective C–C bond cleavage, while Ru/C was responsible for hydrogenation (169).

EG and 1,2-PG production from sugar alcohols has also been reported. The most studied are sorbitol and xylitol while Ni- and Ru-based catalysts are most used. For example, Ru nanofibres, Ru/C, Ni-Re and Ni/Al$_2$O$_3$ in the presence of bases such as calcium hydroxide (Ca(OH)$_2$), calcium oxide (CaO), KOH and sodium methoxide (NaOMe) catalyse sugar alcohols to EG and 1,2-PG (170–173).

The Changchun Dacheng Group, China, has developed a process that produces 10,000 tonnes of 2,3-butandiol (2,3-BD) annually. This process integrates bio and catalytic conversion by firstly enzymatically (by glucoamylase) hydrolysing starch to glucose. Then a catalyst is employed in conversion of the glucose to sorbitol, which is then catalytically cracked into a mixture of C$_2$ to C$_4$ diols and polyols. After purification steps, 97% purity 1,2-PG, EG and 2,3-BD are obtained, in which the yield of 2,3-BD is 5% (167).

8.2 Renewable Hydrogen and Hydrocarbons from Polysaccharides, Disaccharides and Monosaccharides

Cellulose, oligosaccharide, disaccharide or monosaccharide and sugar alcohols have been transformed to hydrogen and hydrocarbons (alkanes). This work was pioneered by Dumesic (26, 174–177). Aqueous phase dehydration/hydrogenation (APD/H) produces alkanes and aqueous phase reforming (APR) leads to hydrogen and gaseous alkanes (primarily methane) (26, 174–177). Cortright and coworkers have demonstrated that hydrogen can be produced from sugars and sugar alcohols in an aqueous phase reforming process using a Pt-based catalyst. Glucose was converted to hydrogen and gaseous alkanes, with a hydrogen yield of 50% (174). Later, they used Pt/SiO$_2$–Al$_2$O$_3$, Pd/SiO$_2$–Al$_2$O$_3$ and Pt/Al$_2$O$_3$ to
convert sorbitol to hexane. Sorbitol is transformed on these bifunctional catalysts by a pathway that involves the formation of hydrogen and CO\textsubscript{2} on the appropriate metal catalyst (Pt or Pd) and the dehydration of sorbitol on a solid acid catalyst (SiO\textsubscript{2} or Al\textsubscript{2}O\textsubscript{3}). This is followed by hydrogenation of the dehydrated intermediates (for example isosorbide or enolic species) by hydrogen produced in the water gas shift reaction on Pt or Pd, which leads to the overall conversion of sorbitol to alkanes plus CO\textsubscript{2} and water (175).

Beller has recently described a procedure for hydrogen generation from biomass (such as glucose, fructose, cellobiose, cellulose and lignocellulose) using Ir and Ru pincer-complexes as (pre)catalysts. Hydrogen was produced using ppm amounts of (pre)catalyst at a turnover frequency (TOF) of up to 10,269 h\textsuperscript{-1} (from cellobiose in 1 h) and a turnover number (TON) of up to 6125 (from cellulose in 1 h) (176).

Dumesic proposed that C\textsubscript{7} to C\textsubscript{15} alkanes (which have a molecular weight appropriate for transportation fuel components) can be produced from carbohydrates by acid catalysed dehydration, followed by aldol condensation (over solid base catalysts) to form large organic compounds. These molecules may be converted into alkanes by HDO over bifunctional catalysts (Mg-Al oxide and Pd/Al\textsubscript{2}O\textsubscript{3}) (177). The total HDO of cellulosic biomass including biomass derived substrates such as
glucose, xylose, sugar alcohols, LA, HMF and furfural to produce C\textsubscript{5} to C\textsubscript{15} alkanes has recently been reviewed (178).

9. Conversion of Cellulose, Disaccharides and Monosaccharides to Organic acids

9.1 Polysaccharides, Disaccharides and Monosaccharides to Levulinic Acid, Formic Acid, Acetic Acid and Glycolic Acid

Cellulose and glucose derived carbohydrates can be transformed into a range of organic acids (Scheme X) (89–91, 179).

The formation of LA from cellulose in the presence of mineral acids or Lewis acids has been extensively studied. This multistep process involves hydrolysis of cellulose to glucose $\leftrightarrow$ fructose $\rightarrow$ dehydration of fructose to HMF $\rightarrow$ and rehydration of HMF to LA and formic acid (Section 7.3) (180–182). Acetic acid can be obtained by hydrothermal oxidation of glucose or cellulose in the presence of a base, such as NaOH and Ca(OH)$_2$ (183, 184).

Efficient, VO$^{2+}$, Pb$^{2+}$ and Ni$^{2+}$ catalysed conversion of glucose, cellulose and lignocellulose into lactic acid, which is a high value chemical used for the production of fine chemicals and biodegradable plastics, has been achieved. Lactic acid yields ranging from 25% to 60% were obtained at high temperatures (185–187). This topic has been reviewed (188).

Another approach reported by Jin et al. is the conversion of glucose or cellulose to HMF and lactic acid, then oxidation of the lactic acid and HMF to give acetic acid (189). Glycolic acid production from cellulose has been less studied, nonetheless Keggin-type Mo polyoxometalates (POMs) have been successfully employed in the conversion of cellulose to glycolic acid (190).

Apart from being a coproduct of HMF hydration, formic acid can be produced from cellulose via oxidation. Formic acid is a starting material for the production of formate esters, which can be utilised in the production of a large variety of useful organic derivatives such as aldehydes, ketones, carboxylic acids and amides. It has been used in the rubber, agricultural and pharmaceutical industries. It has applications as a mordant, auxiliary agent in the dyeing industry, a disinfectant and its formate salt is a useful de-icing agent (191). Notably, formic acid has energy content at least five times higher than that of commercially available lithium ion batteries and therefore represents a convenient hydrogen carrier in fuel cells making it a highly exploitable chemical on the hydrogen energy storage front (192).

Currently formic acid is produced from fossil derived feedstock. The production of formic acid from renewable resources such as cellulose is desirable for the advancement of green chemistry.

Scheme X. Reaction pathways for the conversion of biomass derived glucose into organic acids (89–91, 179)
Formic acid has been produced from glucose and cellulose using alkali metal bases (193), vanadium substituted Keggin-type POM \((\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40})\) (194) and ferric sulfate \((\text{Fe}_3(\text{SO}_4)_3)\) (194).

9.2 Polysaccharides, Disaccharides and Monosaccharides to 2,5-Furandicarboxylic Acid, Gluconic Acid and Glucaric Acid

The oxidation of HMF can generate 2,5-furandicarboxylic acid (FDCA) (Scheme XI), which is an important platform molecule, which has been identified as a potential alternative to petroleum-based terephthalic acid for the production of resins and polymers (195, 196). FDCA is produced by a two-step process from cellulose or sugars (197). HMF is first prepared from C\(_6\) sugars or cellulose (59–62), followed by HMF oxidation to FDCA with oxidants (198), metal catalysts (199–204) or enzymes (205).

Recently, Avantium in The Netherlands and BASF, Germany, have announced that they are jointly preparing for the construction of the world’s first commercial plant for FDCA production from sugars. The Avantium process transforms fructose to HMF methyl ether, which is then oxidised (by \([\text{Co(OAc)}]\) or \([\text{Mn(OAc)}]\) and NaBr) to FDCA. The FDCA (replacement for petroleum-based terephthalic acid) will be combined with EG to produce polyethylene furanoate (PEF), a next generation polyester. PEF is 100% bio-based and has a high market potential as a future packaging and film material (206).

Gluconic and glucaric acid are important intermediates and are used in the pharmaceutical, detergent and food industries (207). Currently, gluconic and glucaric acid are mainly produced by the enzymatic oxidation of glucose. Research efforts have been devoted to developing catalytic oxidation of glucose to gluconic acid (208–211). For instance Au/TiO\(_2\) is an effective glucose oxidation catalyst and in the aqueous phase (using O\(_2\) oxidant) at 40–60\(^\circ\)C, 100% conversion of glucose and 100% selectivity of gluconic acid was recorded in 4 h (212).

Comotti \textit{et al.} used mono and bimetallic catalysts (Rh, Pd, Pt and Au) supported on carbon to effect the transformation of glucose to glucic acid in water. The combination of Au-Pd resulted in 100% selectivity (213). The direct conversion of cellobiose to gluconic acid is more necessary, however few reports of the route are known. The conversion of cellobiose and cellulose to gluconic acid over POM-supported Au nanoparticles \((\text{Au/Cs}_{2.2}\text{H}_{0.8}\text{PW}_{12}\text{O}_{40})\) was reported. \(\text{Cs}_{2.2}\text{H}_{0.8}\text{PW}_{12}\text{O}_{40}\) without Au exhibited a low activity for the conversion (25%) of cellobiose and the main product was glucose. Upon loading of Au particles, the conversion of cellobiose increased to 96% and gluconic acid was the major product. This meant that the acidic sites \((\text{Cs}_{2.2}\text{H}_{0.8}\text{PW}_{12}\text{O}_{40})\) catalysed the hydrolysis of cellobiose and cellulose, and Au nanoparticles are responsible for the oxidation of glucose to gluconic acid (214). Cellobiose conversion to gluconic acid has also been demonstrated using sulfonated carbon supported Pt \((\text{Pt/C–SO}_3\text{H})\) where 47% yield was obtained (215).

There are some studies on the oxidation of glucose to glucaric acid. A Pt/SiO\(_2\) (4 wt\%) catalyst afforded 66% yield of glucaric acid at 90\(^\circ\)C under 5 bar of O\(_2\), while at 119\(^\circ\)C under 280 bar of O\(_2\) over a Pt–Au/TiO\(_2\) \((4\text{Pt}–4\text{Au wt%})\) catalyst a 71% yield of glucaric acid was recorded (216, 217). Rennovia, USA, has developed a two-step catalytic process for producing adipic acid from glucose. The process starts by a selective catalytic oxidation of glucose to glucaric acid, followed by a selective catalytic HDO of glucaric acid to adipic acid (Scheme XI) (216–218). The Rennovia renewable adipic acid process offers potential for significant commercial and environmental advantages compared to the current petrochemical process for the production of adipic acid (218).

![Scheme XI. Rennovia's two-step process for production of bio-adipic acid from glucose (216–218) (Reprinted with permission from (218))](image-url)
10. Conclusion and Outlook

Efficient and environmentally friendly conversion of cellulosic biomass and cellulose derived intermediates to renewable fuels, fuel additives and chemicals is of great interest to meet future liquid fuels and chemicals demand.

(a) Much effort has been focused on hydrolysis of cellulose and hemicellulose to sugars by mineral acids and Lewis acids in biphasic liquids and IL. While reactions carried out in IL or IL bearing acids give better yields, the use of IL is limited by their cost.

(b) Examples of noble metal catalysts, sometimes coupled with Lewis acids, (dominated by Cr-based which is also highly efficient) are used in cellulose hydrolysis and direct conversion of cellulose to HMF show that the presence of noble metals enhances the activity through a synergy between the two metals. Also the Cr species used is not suitable for large scale production due to toxicity. Hydrolysis of cellulose to fermentable sugars has been achieved and furfural has been produced (from agricultural waste) on a commercial scale since the 1920s, and also lignocellulosic HMF has reached industrial scale through the AVA Biochemicals process.

(c) HMF and furfural can be transformed by hydrogenation, rehydration, etherification, esterification, aldol condensation and hydrogenolysis or HDO to a variety of products which are biofuel candidates and intermediates for the synthesis of fine chemicals and functional materials. Among these DMF, MF, EMF, GVL, EL and valeric biofuels, known to be promising fuels and fuel additives, have superior properties compared to bioethanol. Conversion of HMF and furfural to these compounds via HDO is largely dominated by heterogeneous and homogeneous noble metal-based catalytic systems. Homogeneous catalysts dominate the downstream transformation and do not feature much in upstream processing. This has hampered the opportunity to gain a comprehensive insight into the role of individual components during catalytic transformations (at the molecular level) which can aid rational catalyst design. The effect of bimetallic systems versus monometallic systems shows that there is merit to having two metals forming a catalytic system, particularly where one metal serves as the acidic site (for dehydration or hydrolysis) and the other provides the HDO or oxidation site. Accessing these compounds by HDO and hydrogenation requires hydrogen and hence, where will the hydrogen come from? Renewable hydrogen can be obtained from biomass by APR or sourced from water by its electrolysis with electricity derived from wind or solar energy.

(d) The conversion of cellulose and sugars to organic acids and sugar alcohols has been studied extensively, and further HDO of sugar alcohols can lead to renewable alkanes in the C\textsubscript{5}–C\textsubscript{15} range for gasoline and diesel fuel applications. Like most petroleum refining processes, biorefinery processes, particularly the downstream processes in (c) and (d), are all efficiently promoted by noble metal catalysts with Ru leading the group in the following trend: Ru>>Pt ≈ Pd = Au>Rh>Ir>>Os. This highlights the need to design processes with metal recovery in mind, in order to reclaim expensive metals from waste streams for sustainability, environmental clean-up and possibly as a new source of metals for industry (219, 220).

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Ammonia and the Fertiliser Industry: The Development of Ammonia at Billingham

A history of technological innovation from the early 20th century to the present day

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It is over 100 years since the Haber-Bosch process began in 1913 with the world’s first ammonia synthesis plant. It led to the first synthetic fixed nitrogen, of which today over 85% is used to make fertiliser responsible for feeding around 50% of the world’s human population. With a growing population and rising living standards worldwide, the need to obtain reliable, economic supplies of this vital plant nutrient for crop growth is as important as ever. This article details the historic background to the discovery and development of a process “of greater fundamental importance to the modern world than the airplane, nuclear energy, spaceflight or television” (1, 2). It covers the role of the Billingham, UK, site in developing the process up to the present day. The technology was pioneered in Germany and developed commercially by BASF. In 1998 ICI’s catalyst business, now Johnson Matthey, acquired BASF’s catalytic expertise in this application and now Johnson Matthey is a world-leading supplier of catalyst and technology for ammonia production globally.

1. Introduction

Ammonia is the second most produced industrial chemical worldwide. Of the four chemicals, ammonia, methanol, hydrogen and carbon monoxide that rely on similar syngas processes for their production, ammonia is the most complex requiring the highest number of catalytic steps. Ammonia is one of the most important chemicals produced globally with approximately 85% being used as fertiliser for food production (3). The other 15% of ammonia production is used in diverse industrial applications including explosives and polymers production, as a refrigeration fluid and a reducing agent in nitrogen oxides (NOx) emissions control. Ammonia synthesis from atmospheric nitrogen was made possible in the first part of the 20th century by the development of the Haber-Bosch process. It remains the only chemical breakthrough recognised by two Nobel prizes for chemistry, awarded to Fritz Haber in 1918 (4) and to Carl Bosch in 1931 (5). The development of ammonia synthesis directly addressed “The Wheat Problem” as foretold by Sir William Crookes in 1898 (6) whereby a shortage of available reserves (of wheat) would only allow the world’s population to continue to expand to about two billion which would be reached around 1930. Thus, in the early 20th century, the need to increase food production led to the development of the fertiliser industry.

Today, the global value of ammonia production is estimated to be over US$100 billion, with the largest individual plants being capable of producing 3300 metric tonnes per day (mtpd) or 3640 short tonnes per day (stpd) (7). To achieve this scale many improvements have been made over the last 100 years in both process and catalyst technology.

After describing historical aspects of the original ammonia technology development by Haber, Bosch et al. in Germany, and the background to
the requirement for efficiency improvements, this paper uses perspectives from Billingham, UK, to describe some of the technological contributions that came from there in the development of ammonia production.

2. The Growing Need for Nitrogen

In just over 100 years the ammonia production industry has grown massively and continues to do so to feed the ever expanding world population. The development of the remarkable iron catalyst by Alwin Mittasch (8) and the technology for the synthesis of ammonia from nitrogen and hydrogen by Fritz Haber and Carl Bosch led to BASF starting to operate the world’s first ammonia synthesis plant in 1913. Researchers estimate that about half of today’s food supply is dependent on the nitrogen originating from ammonia-based fertilisers (9). Between now and 2050, while the world population will grow by 30%, the demand for agricultural goods will rise by 70% and demand for meat by 200% (10). This is linked with fundamental shifts in the demand curve for food, especially caused by population growth, rising affluence leading to changes in diet in many countries and in some regions increasing use of food crops to produce fuel. The environmental, human health and climatic aspects of ammonia and fertilisers in the growth scenarios have been reviewed elsewhere (11, 12). Ammonia production technology has and continues to advance under the competitive challenges in the industry that demands an ever more energy efficient process, with lower emissions that can operate with high reliability for extended periods between shutdowns. There have been dramatic increases in environmental performance and energy efficiency over the last 100 years, but with modern steam reforming processes energy utilisation is nearing the theoretical minimum (13) (Figure 1) and looking forward, specific energy consumption can only be reduced marginally, if at all, for the most efficient modern plants.

Worldwide ammonia production is largely based on modifications of the Haber-Bosch process in which \( \text{NH}_3 \) is synthesised from a 3:1 volume mixture of \( \text{H}_2 : \text{N}_2 \) at elevated temperature and pressure in the presence of an iron catalyst. All the nitrogen used is obtained from the air and the hydrogen may be obtained by one of the following processes:

- Steam reforming of natural gas or other light hydrocarbons (natural gas liquids, liquefied petroleum gas or naphtha)
- Partial oxidation of heavy fuel oil or coal.

In ammonia production technology the type of feedstock plays a significant role in the amount of energy that is consumed and carbon dioxide (CO\(_2\)) produced. About 70% of global ammonia production is based on steam reforming concepts using natural gas, with the use of steam reforming of natural gas considered the best available technology from the point of view of energy use and CO\(_2\) emissions, Table I (14). The use of coal and fuel oil are predominately restricted to China, which exhibits a strong divergence in the ammonia feedstock versus the rest of the world.

![Figure 1. Historical efficiencies of ammonia process technologies](image)

Table I  Comparative Energy and CO\(_2\) Emissions of Different Ammonia Processes and Feedstocks

<table>
<thead>
<tr>
<th>Energy source</th>
<th>Process</th>
<th>Energy, GJ t(^{-1})_\text{NH}_3</th>
<th>CO(_2) emissions, tonnes t(^{-1})_\text{NH}_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas</td>
<td>Steam reforming</td>
<td>28</td>
<td>1.6</td>
</tr>
<tr>
<td>Naphtha</td>
<td>Steam reforming</td>
<td>35</td>
<td>2.5</td>
</tr>
<tr>
<td>Heavy fuel oil</td>
<td>Partial oxidation</td>
<td>38</td>
<td>3.0</td>
</tr>
<tr>
<td>Coal</td>
<td>Partial oxidation</td>
<td>42</td>
<td>3.8</td>
</tr>
</tbody>
</table>
accounts for 95% of global coal-based ammonia capacity with around 80% of the plants in China being coal-based.

The production of ammonia is a very energy demanding process, the energy use of the steam reforming process is about 28–35 GJ per tonne ammonia (GJ t\textsuperscript{–1}\textsubscript{NH\textsubscript{3}}). Figure 2 shows the theoretical, practical and operating level energy efficiencies for ammonia plants based on steam reforming. Energy efficiencies vary widely for ammonia plants currently in operation due to age, feedstock, energy costs and utility constraints. Most plants operate well above the practical minimum energy consumption with the best performers (top quartile) ranged between 28 and 33 GJ t\textsuperscript{–1}\textsubscript{NH\textsubscript{3}} and an average efficiency of 37 GJ t\textsuperscript{–1}\textsubscript{NH\textsubscript{3}}. It has been estimated that if all plants worldwide were to achieve the efficiency of the best plants, energy consumption could fall by 20–25% (15). A feature of the industry is that most plants are being continually reviewed for improvements and revamp ideas can be subsequently implemented that improve efficiency.

3. Technology Development at Billingham, UK

Following pioneering work by Fritz Haber on the process (4), Alwin Mittasch on the catalyst (8), and Carl Bosch on the technology (5) the ammonia synthesis process came to Billingham, UK, in the early 20th century. An ammonia factory being located at Billingham, UK, grew out of the needs of World War I when the British government needed to develop technology to produce synthetic ammonia for producing explosives. Billingham was chosen partly for its proximity to a then-new North Tees electricity generating station nearby; although later developments to the process required less electric power than had been assumed. It is worth noting that even before the plant was begun the possibility for post-war use for fertiliser production was recognised. This was recorded in a report by the Chemical Society in 1916:

“With some foresight a plant erected primarily for a military purpose might be easily adapted in peace time to agricultural objects” (16).

However by the time the plant (known as the Government Nitrate Factory) was completed, World War I was over. The site was put up for sale in 1919 (Figure 3), and was purchased by Brunner Mond & Co Ltd (16) who converted it to make ammonia-based fertilisers. The company was set up as a subsidiary called Synthetic Ammonia and Nitrates Ltd. This became part of ICI in December 1926,
when ICI was formed from the merger of Brunner Mond, Nobel Explosives, the United Alkali Company and the British Dyestuffs Corporation.

3.1 The Coke Oven Process of Syngas Production

The ammonia plants built at Billingham in the 1920s and 1930s employed the classic Haber-Bosch process based on coke, the same as the production technology used in Oppau, Germany. The first Billingham plant was a 24 mtjd (26 stpd) unit that made its first ammonia in December 1924. The original process is shown in Figure 4.

The first stages of gas production were at atmospheric pressure. Alternate streams of steam and then air were fed into gas generators containing hot coke to make ‘water-gas’ (hydrogen-rich) and producer gas (nitrogen-rich). These streams were purified using iron oxides to remove hydrogen sulfide and a shift converter to convert most of the carbon monoxide to CO₂ and H₂. The ‘catalysed gas’ was compressed in reciprocating compressors. CO₂ was removed by counter-current scrubbing with circulating water and the scrubbed gas was further compressed, washed with copper liquor to remove residual CO and CO₂ and then fed as make-up gas to the synthesis loop which contained a large number of parallel converter vessels (Figure 5).

Using this technology the rise in output from the site is shown in Figure 6. As well as scale improvement there were improvements in effectiveness. In 1929, A. H. Cowap, Chief Engineer, noted: “a striking feature is an ever increasing rapidity of work. The first large unit No. 3 Unit cost £5¼ million pounds and was completed in 27 months (of which 7 months was a labour stoppage for a coal strike). No. 4 and No. 5 units cost £11 million pounds and
have been completed in 2 months” (16). Despite improvements, by the late 1950s increasing costs of coal and the intrinsic inefficiency of syngas generation from coke had made this process uncompetitive.

3.2 Partial Oxidation and Plant Safety

The first step to improve process efficiency from coke-oven syngas production was utilisation of higher pressure oil gasification units, a Texaco gasification unit at Billingham for heavy fuel oil was later converted for naphtha feed. Syngas was produced at 30 bar (440 psi) pressure by reaction of the hydrocarbon with steam and a limited supply of oxygen at 1500°C (2732°F). The partial oxidation process reduced both the capital and operating costs of low pressure gas generation, eliminated the need for low pressure compression and offered greater feedstock flexibility. The principle disadvantage of the process was its requirement for an air separation plant to supply oxygen. In these early days the challenges for safe operations and engineering of these air separation units (ASU) were significant.

In 1959 at Billingham’s partial oxidation plant a serious explosion occurred during the commissioning of the ASU which led to three fatalities (17). This incident resulted in a long delay in the partial oxidation plant achieving beneficial operation by which time steam reforming technology development had advanced sufficiently to make it a more competitive route for syngas production.

Within the industry frequent explosions in oxygen plants encouraged engineers to meet and share information. The very first symposium to discuss safety in air and ammonia plants, called Safe Design and Operation of Low Temperature Air Separation Plants, was held in 1955. This meeting became an important event organised annually to improve the safety performance of the ammonia industry. It continues accomplishing these objectives by sharing information on incidents, safety practices, plant performance and technology improvements, with the 62nd meeting of AIChE Safety in Ammonia Plants and Related Facilities Symposium being held in 2017 (18).

3.3 Steam Reforming of Light Naphthas

Steam reforming of hydrocarbons provides the most economic source of hydrogen gas for ammonia synthesis. The general steam reforming reaction is shown in Equation (i):

\[ \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O} \rightarrow n\text{CO} + (2n+1)\text{H}_2 \]  

(i)

The reaction was known to proceed at 700–800°C (1292–1470°F) over a promoted and supported nickel catalyst. ICI was amongst pioneers in methane steam reforming and commercial units had been built at Billingham in 1936 to reform propane/butane byproducts of hydrogenation of coal as part of synthetic hydrocarbons production (Oil Works). This reforming process was operating at atmospheric pressure.

In the 1950s natural gas was not available in the UK (discovery and exploitation of North Sea gas was still some 15–20 years distant), however increasing quantities of light distillate hydrocarbons (naphtha) were available at falling prices. Sulfur free naphthas had been successfully reformed by the catalyst research group at Billingham in 1938 at atmospheric pressure. What was needed was the development of the process to operate at higher pressures to avoid compression costs. The world’s first pressurised steam naphtha reforming process...
was designed at Billingham and was brought into commercial operation at Heysham, UK, in 1962 (19). The main problems were adequate desulfurisation of the feed, and suppression of carbon deposition on the reforming catalyst without the use of excessive steam ratios. Desulfurisation of the feed was addressed by development of feed purification technology involving hydrogenation catalysts (nickel-molybdenum, cobalt-molybdenum) along with zinc oxide absorbents capable of reducing sulfur to very low levels. The problem of carbon formation was solved by the development of new types of alkaliised catalysts (20).

Due to equilibrium considerations, to achieve a low methane slip a temperature of around 1000°C (1830°F) is required, however the metallurgical limit for a ten-year life of the available tube materials was a design exit temperature of 800°C (1470°F). To overcome this constraint, the new steam reforming process adopted two reforming stages as shown in Figure 7 (21). Now familiar to us as primary and secondary reformers, these unit operations are still present in nearly all ammonia plants.

3.4 Steam Reforming Modernisation

Having developed a viable steam reforming process, the syngas units at Billingham were modernised with four pressured naphtha steam reforming units built in 1962–1963 (Figure 8). Each unit included a primary (tubular) reformer with 4” (100 mm) internal diameter tubes and a reaction length of 20 ft (6 m). Operating at 14 bar (200 psi), the reformed gas, containing 10–12% CH₄, was collected in headers near the ground and passed to the air injection burner in the secondary reformer. After secondary reforming were waste heat recovery, two stage CO shift, further heat recovery, cooling and CO₂ removal. The process was rapidly adopted and by the mid-1960s over 100 steam reforming process licences had been sold from Billingham to the following reputed engineering contractor licensors: Power Gas Corporation (later Davy Power Gas, now Johnson Matthey), Foster Wheeler (now AMEC), Selas, M. W. Kellog (now KBR), Friedrich Uhde GmbH (now thyssenkrupp Industrial Solutions GmbH) and Humphreys & Glasgow (now Jacobs).
The new steam reforming front end occupied an area of 14,160 m² (3.5 acres) – a little less than 10% of the area occupied by the coke based processes that it replaced. Using space freed up by the reformers, improvements to the gas purification and compression were introduced. The existing CO₂ removal process employed water washing at 55 bar (798 psi) and consumed significant energy leading to high capital and operating costs. Chemical absorbents with higher capacity for CO₂ removal had become available, such as the Benfield process (potassium carbonate) and Vetrocoke (arsenious oxide), and these were adopted on different Billingham plants in the early 1960s. These processes achieved CO₂ slips of <0.1% dry.

3.5 Development of Single Stream Plants

As can be seen with the four reformers above, in contrast to a modern single stream plant, in the early 1960s many units of process equipment (such as compressors and synthesis reactors) still had to be used in parallel. A ‘single stream’ concept emerged for new ammonia plants and Billingham engineers designed and engineered a 360 mtpd (397 stpd) ‘single stream’ plant. Commissioned at Severnside, UK, in 1963, it was, at that time, the largest single stream ammonia plant in the world. The plant used the steam naphtha reforming process, a hot potassium carbonate based CO₂ removal system, a copper liquor CO removal system and had two high temperature shift (HTS) beds, however parallel reciprocating compressors driven by electric motors were used for synthesis gas compression.

Although more active copper-based catalysts were known to be able to accomplish the shift reaction at ~250°C (482°F), they were very sensitive to poisoning by sulfur and could not be used with syngas made from coke. The virtually sulfur free syngas obtained from steam reforming allowed these copper-based shift catalysts to be used, achieving an equilibrium CO conversion of ~0.2% dry. ICI developed its own robust and reactive Cu catalyst for this application (22). The combined low level of residual carbon oxides from CO₂ removal and CO shift was now low enough that they could be made inert by methanation before the synthesis loop. As a result of all of the improvements considered so far – steam reforming, shift, CO₂ removal and methanation – by the mid-1960s it was possible to carry out all operations in single stream reactors.

Early design memos for the Billingham plants in the 1920s had discussed the relative economics of reciprocating and centrifugal compression. They showed that the relative efficiency of rotary compressors for the later compression stages would be low except at high throughputs (Figure 9). This low efficiency was one of the reasons for excluding centrifugal compressors for all but the low pressure stages and this reasoning still prevailed at the beginning of the 1960s; however it was now challenged. A second plant for ICI Severnside, with a capacity of 545 mtpd (600 stpd), led to what was described as “possibly the most important event in the history of the development” of the single stream ammonia plant (23). Figure 10 (24) showing the increase in output of ammonia converters from 1930 to the mid-1960s illustrates the revolution in scale taking place. By then the normal ammonia unit size was already 600 mtpd (662 stpd) capacity and plants with lower capacity than this were being regarded as small.

In late 1962, a meeting was held in which Ron Smith, Vice President of Operations at M. W. Kellogg, opined that the capacity of ammonia plants was bound to increase and queried why the synthesis loop pressure could not be reduced from 325 bar (4700 psi) to 150 bar (2200 psi), thus removing the need for reciprocating compressors. Although not successful for that plant bid soon afterwards discussions began on how a large plant could be built – and the plant design was established which quickly became a new technology era that came...
to dominate the industry with a capacity of ‘1000 stpd’ (900 mtpd).

In January 1964, M. W. Kellogg was awarded a contract for two ‘1000 stpd’ (900 mtpd) plants to be built at Billingham. The design incorporated a number of important features:

- The steam naphtha reforming process at 31 bar (450 psi) pressure
- A loop pressure of 131 bar (1900 psi) allowing the use of centrifugal compressors
- Improved plant efficiency by recovering heat to generate 103.5 bar (1500 psi) high pressure steam superheated to 450°C (850°F) for use on steam turbine drives.

The steam was generated at a higher pressure than that required by the process, so energy was recovered by expanding the steam through turbines to the pressure level required by the process. This greatly enhanced process efficiency. Within a few weeks a third plant was announced, they were the largest plants built at that time.

### 3.6 M. W. Kellogg Ammonia Units

As the M. W. Kellogg plants incorporated the steam naphtha reforming process, Billingham engineers worked closely with their counterparts from M. W. Kellogg in the design of the reformers, shown in Figure 11. As by the mid-1960s exploration was ongoing for North Sea gas this was considered and a feature of the reforming process was that the plants could be readily converted to lighter hydrocarbons.

### 3.7 Use of Natural Gas Feedstock

In the 1970s Billingham’s ammonia plants changed from naphtha feeds to run on the newly commercialised natural gas from the North Sea, however the favourable gas contract was on an interruptible supply basis, meaning that with short notice the feedstock could be cut when demand...
for natural gas was high. If natural gas supply was interrupted the plants were configured to switch feedstock on-line to liquefied petroleum gas (LPG) propane feedstock (which was stored locally in underground salt caverns), bringing a demand for catalysts that could cope with feedstock flexibility. This brought new requirements for a catalyst with lower potash and higher activity in order to optimise the reformer for this feedstock.

By the end of the decade there were two light potash catalysts: 25-3 (1.6% K$_2$O) for natural gas feeds and 46-9 (2.2% K$_2$O) for LPG feeds. By the end of the 1970s, ICI Katalco had a product range very similar to the present: 57-series non potash, 25-series light potash, and 46-series naphtha catalyst. By this point the catalyst beds were operating at temperatures up to 1000°C (1832°F) and 35.6 bar (516 psi), primarily due to improvements in metallurgy.

In the 1970s, it was recognised that appropriately formulated low-temperature shift (LTS) catalysts could be self-guarding not only in regard to sulfur, but also towards chloride. It was also recognised that the benefits in terms of shift activity and bed life accruing from the use of fresh LTS catalyst outweighed the cost savings realised by reusing discharged LTS catalyst. All LTS catalysts subsequently developed by ICI and Johnson Matthey were therefore optimised to maximise their self-guarding capability.

These catalyst systems were utilised in the three M. W. Kellogg ammonia plants and also in the ICI designed Ammonia IV plant (Figure 13). Designed for 1000 mtpd (1100 stpd), this was commissioned in 1978 and was able to achieve a throughput of about 1125 mtpd, (1240 stpd) without significant modification.

### 3.8 The Ammonia V Process

Ammonia technology continued to develop and Billingham-based engineers were tasked with the design of a fifth ammonia plant for Billingham (Ammonia V or ‘AMV’). Economic considerations meant that capital cost had to be reduced whilst improving plant efficiency. Although market conditions in the early 1980s meant that the plant was never built at Billingham, the designs for Ammonia V evolved into the AMV process. The first AMV design was commissioned at Courtright, Canada, in August 1985 (Figure 14), producing 1120 mptd (1234 stpd) at a total energy requirement of 29 GJ per metric tonne (lower heating value, LHV). Ammonia production was achieved 43 hours after feed gas introduction, believed to be a record at that time (25). The AMV process also featured a low pressure synthesis loop operating at about 85 bar (1230 psi) featuring a new cobalt-promoted high-activity ammonia synthesis catalyst (KATALCO™ 74-1) which had been developed specifically for the project.

As a highly efficient process operating with a low steam ratio, the plant was one of the first to suffer from byproduct formation and pressure drop increase due to HTS over reduction. Copper was added to the HTS catalyst formulation to create an
over reduction resistant formulation which was first installed in 1987.

### 3.9 The Leading Concept Ammonia Process

By the mid-1980s, the two ammonia plants at Severnside were becoming uncompetitive and a decision had to be made: improve their efficiency, replace them or close the site. Improving the efficiency was thought unfeasible and it was decided to develop a new process to replace them. This led to the leading concept ammonia (LCA) process technology being developed at Billingham (Figure 15).

The LCA process used a combination of new equipment, new catalysts and improved construction and procurement techniques. The range of developments included:

- **KATALCO 61-2** (the first low-temperature hydro-desulfurisation (HDS) catalyst)
- **PURASPEC™ 2020** (the first low-temperature sulfur removal absorbent)
- **KATALCO 83-1** (the first application of a process gas heated reformer (GHR), isothermal shift catalyst specifically developed to resist the high operating temperature)
- **KATALCO 11-4** (a low-temperature methanation catalyst)
- **KATALCO 74-1** (a catalyst which could be used in an ammonia synthesis loop at 80 bar (1160 psi) pressure, even lower than in the AMV process).

The unique process together with extensive automation start-up sequences meant the plants were amongst the most automated ever. The second plant at Severnside made ammonia only 19 hours after natural gas was first introduced.

### 3.10 Catalyst Developments

Catalyst developments continued into the 1990s. Figure 16 illustrates the dramatic improvement in the activity of one particular catalyst which resulted from a combination of on-going development and the incorporation of learning from the development of the technology for LTS catalysts.

A step change occurred in 1997 due to the acquisition of the BASF syngas catalyst business by ICI’s catalyst business (since acquired by Johnson Matthey). The acquisition of the BASF activities allowed the knowledge of two historic companies to be combined and in this case the best of both companies created a new improved LTS catalyst. Methanol is an unwanted byproduct that may be formed in LTS reactors and is the main volatile organic compound (VOC) emitted from ammonia production plants. It is formed as a byproduct in both high-temperature and low-temperature shift. Through the 1990s byproduct methanol was an increasing concern for plants as environmental emissions came under closer attention. More selective catalysts became available that made less methanol. BASF previously had low methanol LTS catalysts, K3-110 and K3-111, which suffered from issues relating to physical strength and poisons resistance. ICI had LTS products with good strength characteristics, but could not mimic the BASF low methanol recipe due to patent protection. The combination of the two businesses meant that a low methanol, high-strength product could be developed. The results were KATALCO 83-3K, launched in 1997, and KATALCO 83-3X,

![Fig. 15. LCA plant in Severnside, UK](image-url)

![Fig. 16. Relative LTS activity of successive generations of the KATALCO catalysts. The numbers within the bars refer to the catalyst series](image-url)
which was launched in 1998 with 90% reduction in methanol byproduct formation compared to previous generations of catalyst (Figure 17).

3.11 Developments in Catalyst Shape

The effect of shape on reforming catalysts has been recognised for a long time (21). For steam reforming catalysts, the reaction occurs in a very thin layer at the surface of the pellet. Therefore developments focused on techniques to develop the shape, maximising the external surface area of the catalyst pellets whilst at the same time considering the resistance to flow caused by the way the catalyst packs in the tube. The shape of the steam reforming catalysts evolved from the original cubes (circa 1930s) to Raschig rings (circa 1940s) to ICI Katalco 4-hole (circa 1980s) and finally the current KATALCO QUADRALOBE™ shape. At each iteration, for similar sized pellets the activity increased and the pressure drop decreased (20). Increasing the catalyst activity also allowed the reforming reaction to progress at a lower temperature, which meant the tubes were also at a lower temperature as shown by the measured tube wall temperature (TWT). The lower the peak maximum TWT, the longer the tube metallurgy lasts before failure, with a difference of as little as 20°C (68°F) doubling the tube life.

Since the 1990s design tools such as finite element analysis have been used to assist with the design and optimisation of catalyst shape. The latest development for the steam reforming process is the CATACEL™ technology, which Johnson Matthey purchased in 2014. CATACEL SSR™ is a stackable structural catalytic reactor for the production of hydrogen from natural gas. It is made from a high-temperature stainless steel foil coated with a reforming catalyst. This structure allows higher heat transfer and can provide significant capacity increase to reformers or lower pressure drop compared to standard pelleted catalysts.

Further developments have been made by shaping the pellets in some of the other reactors which follow the steam reformer in the production of syngas at the front-end of the plant, notably the HTS and methanator. For example, KATALCO 71-5F (Figure 18) is a shaped 5-lobe pellet HTS catalyst which exhibits lower pressure drop, increased strength and increased voidage. Similarly, for the methanation reactor, KATALCO 11-6MC (Figure 19) uses a 4-hole clover leaf shape to provide lower pressure drop with increased bed voidage. The benefit of pressure drop reduction in the front end varies from plant to plant depending on the individual process constraints. Generally

Fig. 17. Relative LTS selectivity of the KATALCO catalysts, measured by methanol production rate. The numbers above the bars refer to the catalyst series

Fig. 18. Shaped HTS catalyst KATALCO 71-5F

Fig. 19. Shaped methanation catalyst KATALCO 11-6MC
pressure drop is welcome and a small increase in energy efficiency can be gained if it is reduced.

3.12 The Dual-Pressure Process

In 1998, ICI and Uhde (now thyssenkrupp Industrial Solutions (tkIS)) formed an alliance in the field of ammonia technology resulting in a variety of new developments, the most public of which was the dual-pressure ammonia process (28). The resulting 3300 mtpd (3640 stpd) plant was a step change in the scale of plant design available and offered a reduction of specific production costs through economies of scale. These are still being built today as the world's largest ammonia plants.

The key innovation in the Uhde dual-pressure ammonia process was an additional medium-pressure once-through ammonia synthesis step operating at around 110 bar (1595 psi), connected in series with the conventional high-pressure ammonia synthesis loop at around 200 bar (2900 psi), Figure 20. The first plant based on this process was the SAFCO IV ammonia plant in Al Jubail, Saudi Arabia, started up in 2006. With a capacity of 3300 mtpd (3640 stpd) it was by far the largest ammonia plant worldwide, Figure 21.

Since then tkIS's Uhde dual-pressure process has been implemented in other similar scale plants recently commissioned in regions of the world with an abundance of low cost natural gas feedstock (Table II).

4. Ammonia Production Today

Figure 22 shows the current plant capacity and year of construction for all operating ammonia plants. There is a clear progression of increasing plant scale with time. Market needs for individual plants will differ, leading to a range in plant capacities. There are however preferred plant sizes which have become ‘standard’ in the industry for which references and documented plant designs exist. These can be clearly seen in Figure 22 at capacities of 600 mtpd, 1000 mtpd, 1360 mtpd, 1500 mtpd, 2000–2200 mtpd and most recently 3300 mtpd (3640 stpd). It is notable that, as well as being the largest production units in the world, the emission limits for the new US fertiliser projects (ammonia and downstream plants) are amongst the lowest in the world, with the design levels for emissions of NOx, N2O, CO and volatile organic compounds (VOC) being significantly

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Fig. 20. Schematic of the Uhde process dual-pressure ammonia synthesis section
below current recognised best available techniques (BAT) values (26).
In just over 100 years, the nitrogen fertiliser industry based on ammonia production has grown massively (Figure 23). Drivers behind this growth have been, and remain, increasing global population (Figure 24) (9) coupled with increased plant size to achieve better economies of scale. Although the picture is more complex than this (for example, one could ask which came first: fertiliser or population growth?), together this has created demand for increased capacity and increased reliability from that capacity.

5. Conclusion

Over the last century, scientists and engineers have made a significant contribution to the nitrogen industry. Some of these have been based at Billingham, UK, whose heritage now resides with Johnson Matthey and the challenge is to continue

Table II 3300 mtpd tkIS Uhde Ammonia Plants with Johnson Matthey Catalyst

<table>
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<tr>
<th>Plant</th>
<th>Location</th>
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<th>Start-up year</th>
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</table>

Fig. 22. Trends of plant capacity vs. year of construction

Fig. 21. SAFCO IV Uhde dual-pressure process (Image courtesy of tkIS)
Fig. 23. Global Haber-Bosch ammonia production from mid-20th century to the present. Over 99% of fixed nitrogen production today is by the Haber-Bosch process (2) (Copyright The Fertilizer Institute, used with permission)

Fig. 24. Demographic drivers for Haber-Bosch nitrogen and its use in fertiliser: “...the lives of around half of humanity are made possible by Haber-Bosch nitrogen” (2, 9) (Copyright The Fertilizer Institute, used with permission)
this legacy and make an equally significant contribution to the future of this vital industry. The fundamental ammonia synthesis process and catalysts developed by Haber-Bosch and Mittasch can still be clearly recognised in even the most modern ammonia plants. However, the process efficiencies and environmental performances have been dramatically improved over the last 100 years, most particularly in the preparation of the synthesis gas, benefiting both ammonia production and other syngas-based processes. Because energy utilisation within modern processes is near the theoretical minimum, specific energy consumption can be reduced only marginally, if at all. There are many future challenges for ammonia and the fertiliser industry, which fall outside the scope of this historical overview.

For now, the ammonia industry will be with us more or less in its present form for decades to come (27). The present production capacity for synthetic ammonia of over 175 million metric tonnes per year will continue to grow at 1–2% every year to satisfy the increasing demands for food and ammonia-based intermediates from an increasing number of people enjoying increasing welfare.

**Trademarks**

KATALCO, PURASPEC, QUADRALOBE, CATACEL and SSR are trademarks of Johnson Matthey.

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Further Reading


The Author

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A Re-assessment of the Thermodynamic Properties of Palladium

Improved values for the enthalpy of fusion

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Droitwich, Worcestershire, UK

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The thermodynamic properties were reviewed by the author in 1995. A new assessment of the enthalpy of fusion has led to a revision of the thermodynamic properties of the liquid phase and although the enthalpy of sublimation at 298.15 K is retained as 377 ± 4 kJ mol⁻¹ the normal boiling point is revised to 3272 K at one atmosphere pressure.

Introduction

The thermodynamic properties of palladium were reviewed by the author in 1995 (1). At that time the value for the enthalpy of fusion was considered to be tentative since it differed significantly from the only known experimental value. Newly considered enthalpy of fusion values now indicate that the original selected value was almost certainly incorrect and a more likely value has been suggested which leads to a major alteration to the selected values for the liquid phase. Additional measurements of the vapour pressure do not alter the selected enthalpy of sublimation value of 377 kJ mol⁻¹ but the accuracy can now be refined to give a 95% confidence value of ±4 kJ mol⁻¹.

Solid

Selected values in the low-temperature region as given in the previous review (1) were based mainly on the specific heat values of Boerstoel et al. (2), Clusius and Schachinger (3) and Mitacek and Aston (4) and continue to be considered satisfactory. However only limited information was given in the original review which above 50 K consisted of specific heat values at 10 K intervals from 50 to 100 K and at 20 K intervals from 100 to 280 K and with the value at 298.15 K also included. This is now considered to be far too little information and instead a comprehensive review of the low-temperature thermodynamic properties is given in Table I.

In the high-temperature solid region closely agreeing specific heat values derived from the enthalpy measurements of Cordfunke and Konings (5) (528 to 848 K) and the direct specific heat measurements of Miiller and Cezairliyan (6) (1400 to 1800 K) were selected since they were in excellent agreement with an extrapolation of the selected low-temperature values and allowed a single smooth specific heat curve to represent both the low- and high-temperature regions. More recent high-temperature specific heat values by Milošević and Babić (7) (248 to 1773 K) differ significantly from the selected values showing a trend from 1.3% lower at 323 K to 3.9% lower at 723 K to 5.9% lower at 1223 K to 5.9% lower at 1773 K. However, at the low-temperature change over point at 270 K the measurements of Milošević and Babić show a sharp change in the slope of the specific heat curve compared to the selected low-temperature values, indicating that these high-temperature measurements are incompatible with those obtained at low temperatures. On these grounds the original high-temperature values were retained and can be represented by Equation (i) to cover the range from 298.15 K to the accepted melting point at 1828.0 K:
### Table I Low Temperature Thermodynamic Data

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**Notes to Table I**

- $C^o_p$ is specific heat
- $H^o_T - H^o_0$ is enthalpy
- $S^o_T$ is entropy
- $-G^o_T - H^o_0$ and $-(G^o_T - H^o_0 K)/T$ are free energy functions
(300 to 1825 K) trend from 2.6% lower at 300 K to 5.3% lower at 800 K to an average of 1.5% higher above 1600 K (Figure 1). Enthalpy measurements of Holzmann (9) (575 to 1177 K) trend from 0.4% higher to 1.7% higher whilst those of Jaeger and Veenstra (10) (573 to 1772 K) scatter from 0.7% lower to 1.4% lower with an average of 1.1% lower (Figure 2). More recent enthalpy measurements of Cagran and Pottlacher (11) (1550 to 1828 K)

Equivalent enthalpy and entropy equations are given in Table II and derived thermodynamic values are given in Table III.

In comparison with the selected equations the specific heat values of Vollmer and Kohlhaas (8) (300 to 1825 K) trend from 2.6% lower at 300 K to 5.3% lower at 800 K to an average of 1.5% higher above 1600 K (Figure 1). Enthalpy measurements of Holzmann (9) (575 to 1177 K) trend from 0.4% higher to 1.7% higher whilst those of Jaeger and Veenstra (10) (573 to 1772 K) scatter from 0.7% lower to 1.4% lower with an average of 1.1% lower (Figure 2). More recent enthalpy measurements of Cagran and Pottlacher (11) (1550 to 1828 K)

Table II Thermodynamic Equations Above 298.15 K

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<td>( C^\circ_p ) (J mol(^{-1}) K(^{-1})) = 24.0658 + 9.55408 \times 10^{-3} T - 5.31329 \times 10^{-6} T^2 + 2.02516 \times 10^{-9} T^3 - 57,835.6/T^2</td>
</tr>
<tr>
<td>( H^\circ_T - H^\circ_{298.15} ) (J mol(^{-1})) = 24.0658 T + 4.77704 \times 10^{-3} T^2 - 1.77109667 \times 10^{-6} T^3 + 5.06290 \times 10^{-10} T^4 + 57,835.6/T - 7750.91</td>
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<tr>
<td>( S^\circ_T ) (J mol(^{-1}) K(^{-1})) = 24.0658 \ln (T) + 9.55408 \times 10^{-3} T - 2.656645 \times 10^{-6} T^2 + 6.7505333 \times 10^{-10} T^3 + 28,917.8/T^2 - 102.4348</td>
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<table>
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<th>Liquid: 1828.0 to 3300 K</th>
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<tr>
<td>( H^\circ_T - H^\circ_{298.15} ) (J mol(^{-1})) = 41.2000 - 10,903.0</td>
</tr>
<tr>
<td>( S^\circ_T ) (J mol(^{-1}) K(^{-1})) = 41.2000 \ln (T) - 208.9240</td>
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Notes to Table II

- \( C^\circ_p \) is specific heat
- \( H^\circ_T - H^\circ_{298.15} \) is enthalpy
- \( S^\circ_T \) is entropy

Table III High Temperature Thermodynamic Data

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<th>( H^\circ_T - H^\circ_{298.15}, ) J mol(^{-1})</th>
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<th>$S^o_T$, J mol$^{-1}$ K$^{-1}$</th>
<th>$-(G^o_T - H^o_{298.15})/T$, J mol$^{-1}$ K$^{-1}$</th>
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Notes to Table III

$C^o_p$ is specific heat

$H^o_T - H^o_{298.15}$ is enthalpy

$S^o_T$ is entropy

$-(G^o_T - H^o_{298.15})/T$ is the free energy function

Fig. 1. Percentage deviations of specific heat in the high-temperature region
determined using the rapid pulse heating technique trend from 1.4% to 3.7% lower in the solid range (Figure 3).

**Liquid**

Drop calorimetry enthalpy measurements by Treverton and Margrave (12) were initially determined over the range 1846 to 2334 K on the International Practical Temperature Scale of 1948 (IPTS-48) but a short note added in the proof indicated further corrections for radiation losses and a conversion to the temperature scale IPTS-68. However only the amended liquid specific heat value and the liquid enthalpy at the melting point (given as 1827 K) were given. After correction for atomic weight, to the melting point of 1828.0 K and to the International Temperature Scale of 1990 (ITS-90), the liquid enthalpy at the melting point is $H^0_T - H^0_{298.15} \text{ K} = 63,151 \text{ J mol}^{-1}$ which in combination with the enthalpy of the solid at the melting point leads to an enthalpy of fusion of $16.08 \pm 0.74 \text{ kJ mol}^{-1}$. This is notably lower than actual experimental values of $17.64 \text{ kJ mol}^{-1}$ determined by Nedumov (13) using differential thermal analysis and rapid pulse heating values of $17.4 \pm 2.0 \text{ kJ mol}^{-1}$ determined by Seydel et al. (14, 15) and $16.98 \text{ kJ mol}^{-1}$ determined by Cagran and Pottlacher (11). The reason why the indirect determination of the enthalpy of fusion was low is not known but may be due to either an overestimation of the enthalpy values for the solid or, more likely,
to the fact that even the revised values of Treverton and Margrave had still not accounted for all of the systematic errors that may have been present in their measurements. Not including the measurement of Seydel et al., because of the large uncertainty, the two other enthalpy values were equivalent to entropy of fusion values of 9.65 J mol\(^{-1}\) K\(^{-1}\) and 9.29 J mol\(^{-1}\) K\(^{-1}\) respectively. Kats and Chekhovskoi (16) noted that for a particular structure type the entropies of fusion (\(\Delta S_M\)) could be linearly related to the melting points (\(T_m\)) by means of the equation

\[
\Delta S_M = aT_m + b
\]

where \(a\) and \(b\) are constants. For the face-centred cubic platinum group metals rhodium, iridium and platinum selected entropy of fusion values of 12.21 ± 0.38 J mol\(^{-1}\) K\(^{-1}\) at a melting point of 2236 K for rhodium (17), 15.20 ± 0.41 J mol\(^{-1}\) K\(^{-1}\) at a melting point of 2719 K for iridium (18) and 10.83 ± 0.46 J mol\(^{-1}\) K\(^{-1}\) at a melting point of 2041.3 K for platinum (19) when fitted to the above equation extrapolated to 9.52 J mol\(^{-1}\) K\(^{-1}\) for palladium, in excellent agreement with the above experimental entropy values. The two experimental entropy values for palladium were therefore combined with the values for rhodium, iridium and platinum and were fitted to the equation:

\[
\Delta S_M = 6.4574 \times 10^{-3} T_m - 2.3211
\]

with the derived value for palladium as 9.483 ± 0.40 J mol\(^{-1}\) K\(^{-1}\) where the error is assigned to match those obtained for the other elements. The derived enthalpy of fusion value is rounded to 9.52 J mol\(^{-1}\) K\(^{-1}\) of fusion values of 12.21 ± 0.38 J mol\(^{-1}\) K\(^{-1}\) at 1828 K to 5.8% lower at 2900 K. This confirms the suggestion that other liquid enthalpy measurements obtained by Treverton and Margrave also appear to be systematically low with, for example, the values obtained for vanadium (20) being on average 2.4% lower than the preferred values of Berezin et al. (21) and Lin and Frohberg (22).

The liquid specific heat determined by Treverton and Margrave (12) on IPTS-68 corrected to the value 41.20 ± 1.38 J mol\(^{-1}\) K\(^{-1}\) on ITS-90 which is notably higher than the value for the liquid of 37.3 J mol\(^{-1}\) K\(^{-1}\) determined by Cagran and Pottlacher (11) (1828 to 2900 K) using rapid pulse heating. However, it is noted that Cagran and Pottlacher obtained a specific heat value for the solid which is some 10% to 16% lower than the selected values. Therefore, the value of Treverton and Margrave was selected on the assumption that the apparently lower enthalpy values obtained are due to a constant systematic error. Over the range 1828 to 3300 K the actual enthalpy can be expressed as (Equation (ii)):

\[
H^\circ_T - H^\circ_{298.15\ K}\ (J\ mol^{-1}) = 41.2000 T - 10,903.0
\]

Equivalent specific heat and entropy equations are also given in Table II whilst derived thermodynamic properties are given in Table III. The more recent liquid enthalpy measurements of Cagran and Pottlacher (11) trend from 3.3% lower at 1828 K to 5.8% lower at 2900 K.

**Gas**

Selected values are based on the 143 energy levels selected by Engleman et al. (23). The thermodynamic properties were calculated using the method of Kolsky et al. (24) and the 2014 Fundamental Constants selected by Mohr et al. (25, 26). Derived thermodynamic values based on a one bar standard state pressure are given in Table IV.

**Enthalpy of Sublimation at 298.15 K**

Because of a general lack of detail as to what temperature scales were used and problems associated with the exact measurement of temperature, no attempt was made to correct vapour pressure measurements to ITS-90 from what would have been contemporary scales. For results given in the form of the Clausius-Clapeyron equation, \(\log(p) = A + B/T\) (where \(p\) is pressure and \(T\) is temperature), the enthalpy of sublimation was calculated at the two temperature extremes and averaged. For the measurements of Walker et al. (27), Lindscheid and Lange (28) and Chegodaev et al. (29) no temperature ranges were given and therefore these measurements were not included. From Table V, in view of possible systematic errors in the earlier measurements, only the twelve determinations from Taberko et al. (42, 43) to Ferguson et al. (51) were considered. The unweighted average value of 377 kJ mol\(^{-1}\) is assigned an accuracy of ±4 kJ mol\(^{-1}\) which is equivalent to a 95% confidence level (two standard deviations).

**Vapour Pressure Equations**

The vapour pressure equations as given in Table VI were evaluated for the solid from free energy.
Table IV Thermodynamic Properties of the Gaseous Phase

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<th>$T$, K</th>
<th>$C_{p}$, J mol$^{-1}$ K$^{-1}$</th>
<th>$H^{0}<em>{T} - H^{0}</em>{298.15}$ K J mol$^{-1}$</th>
<th>$S^{0}_{T}$, J mol$^{-1}$ K$^{-1}$</th>
<th>$-(G^{0}<em>{T} - H^{0}</em>{298.15}$ K)/$T$, J mol$^{-1}$ K$^{-1}$</th>
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<td>42.172</td>
<td>96,558</td>
<td>231.489</td>
<td>202.229</td>
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Notes to Table IV
- $C_{p}$ is specific heat
- $H^{0}_{T} - H^{0}_{298.15}$ K is enthalpy
- $S^{0}_{T}$ is entropy
- $-(G^{0}_{T} - H^{0}_{298.15}$ K)/$T$ is the free energy function
- $H^{0}_{298.15}$ K $- H^{0}_{0}$ K $= 6197.4$ J mol$^{-1}$
### Table V Enthalpies of Sublimation at 298.15 K

<table>
<thead>
<tr>
<th>Authors</th>
<th>Ref.</th>
<th>Method</th>
<th>Temperature range, K</th>
<th>$\Delta H^{\circ}_{298.15 \text{ K}}$ (II), kJ mol$^{-1}$</th>
<th>$\Delta H^{\circ}_{298.15 \text{ K}}$ (III), kJ mol$^{-1}$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Babeliowsky</td>
<td>(30)</td>
<td>MS</td>
<td>1250–1730</td>
<td>385 ± 4</td>
<td>–</td>
<td>(a)</td>
</tr>
<tr>
<td>Trulson and Schissel</td>
<td>(31)</td>
<td>MS</td>
<td>1370–1785</td>
<td>382 ± 5</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Haefling and Daane</td>
<td>(32)</td>
<td>KE</td>
<td>1388–1675</td>
<td>332 ± 7</td>
<td>352.9 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>Alcock and Hooper</td>
<td>(33)</td>
<td>Trans</td>
<td>1673–1773</td>
<td>459</td>
<td>376.1 ± 2.4</td>
<td></td>
</tr>
<tr>
<td>Zanitsanov</td>
<td>(34)</td>
<td>KE</td>
<td>1537–1841</td>
<td>368 ± 22</td>
<td>375.9 ± 1.2</td>
<td>(b)</td>
</tr>
<tr>
<td>Dreger and Margrave</td>
<td>(35)</td>
<td>L</td>
<td>1220–1640</td>
<td>362 ± 11</td>
<td>380.6 ± 1.0</td>
<td></td>
</tr>
<tr>
<td>Hampson and Walker</td>
<td>(36)</td>
<td>L</td>
<td>1294–1488</td>
<td>365 ± 4</td>
<td>373.4 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Norman et al.</td>
<td>(37)</td>
<td>KEMS</td>
<td>1485–1710</td>
<td>381</td>
<td>380.5 ± 0.1</td>
<td>(c)</td>
</tr>
<tr>
<td>Strassmair and Stark</td>
<td>(38)</td>
<td>L</td>
<td>1361–1603</td>
<td>372 ± 14</td>
<td>373.3 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>Myles</td>
<td>(39)</td>
<td>TE</td>
<td>1515–1605</td>
<td>372</td>
<td>372.0 ± 0.1</td>
<td>(c)</td>
</tr>
<tr>
<td>Darby and Myles</td>
<td>(40)</td>
<td>TE</td>
<td>1517–1608</td>
<td>372</td>
<td>371.8 ± 0.1</td>
<td>(c)</td>
</tr>
<tr>
<td>Novosolov et al.</td>
<td>(41)</td>
<td>TE</td>
<td>1730–1938</td>
<td>363</td>
<td>370.0 ± 0.4</td>
<td>(c)</td>
</tr>
<tr>
<td>Taberko et al.</td>
<td>(42, 43)</td>
<td>Evap</td>
<td>1828–2023</td>
<td>381 ±10</td>
<td>376.9 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>Zaitsev et al.</td>
<td>(44)</td>
<td>KE</td>
<td>1267–1598</td>
<td>377 ± 1</td>
<td>377.3 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>Bodrov et al.</td>
<td>(45)</td>
<td>AA</td>
<td>1511–1678 (s) 1842–2046 (l)</td>
<td>389 ± 4</td>
<td>394 ±12</td>
<td>376.6 ± 0.2</td>
</tr>
<tr>
<td>Naito et al.</td>
<td>(46)</td>
<td>KEMS</td>
<td>1567–1758</td>
<td>386</td>
<td>375.5 ± 0.5</td>
<td>(c)</td>
</tr>
<tr>
<td>Chandrasekhariala et al.</td>
<td>(47)</td>
<td>KEMS</td>
<td>1439–1724</td>
<td>373 ± 5</td>
<td>377.9 ± 0.2</td>
<td>(d)</td>
</tr>
<tr>
<td>Stølen et al.</td>
<td>(48)</td>
<td>KEMS</td>
<td>1523–1743</td>
<td>389</td>
<td>375.5 ± 0.5</td>
<td>(c)</td>
</tr>
<tr>
<td>Bharadwaj et al.</td>
<td>(49)</td>
<td>KEMS</td>
<td>1627–1818 (s) 1833–2041 (l)</td>
<td>378 ± 7</td>
<td>380 ±8</td>
<td>377.7 ± 0.2</td>
</tr>
<tr>
<td>Kulkarni et al.</td>
<td>(50)</td>
<td>KEMS</td>
<td>1237–1826</td>
<td>375 ± 2</td>
<td>381.7 ± 0.3</td>
<td>(e)</td>
</tr>
<tr>
<td>Ferguson et al.</td>
<td>(51)</td>
<td>KE</td>
<td>1473–1825 (s) 1840–1973 (l)</td>
<td>373 ± 7</td>
<td>385 ±7</td>
<td>377.8 ± 0.4</td>
</tr>
</tbody>
</table>

**Notes to Table V**

- $\Delta H^{\circ}_{298.15 \text{ K}}$ (II) and $\Delta H^{\circ}_{298.15 \text{ K}}$ (III) are the Second Law and Third Law enthalpies of sublimation at 298.15 K
- (a) Value given only at 298.15 K
- (b) Two runs combined since individual Second Law values were 433 kJ mol$^{-1}$ and 312 kJ mol$^{-1}$ respectively
- (c) Values given only in terms of the Clausius-Clapeyron equation
- (d) Average of two runs
- (e) Average of five runs

**Methods**

- AA: atomic absorption
- Evap: evaporation
- KE: Knudsen effusion
- KEMS: Knudsen effusion mass spectrometry
- L: Langmuir free evaporation
- MS: mass spectrometry
- TE: torsion effusion
- Trans: transpiration
### Table VI Vapour Pressure Equations

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature range, K</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid</td>
<td>900–1828</td>
<td>14.71536</td>
<td>0.220029</td>
<td>-45,349.16</td>
<td>-1.26392 × 10⁻³</td>
<td>2.03201 × 10⁻⁷</td>
</tr>
<tr>
<td>Liquid</td>
<td>1828–3300</td>
<td>92.57304</td>
<td>-10.78530</td>
<td>-51,305.62</td>
<td>3.94374 × 10⁻³</td>
<td>-2.33142 × 10⁻⁷</td>
</tr>
</tbody>
</table>

### Table VII Free Energy Equations Above 298.15 K

**Solid: 298.15 to 1828.0 K**

\[
G^o_T - H^o_{298.15 K} (J mol^{-1}) = 126.5006 T - 4.77704 \times 10^{-3} T^2 + 8.85548333 \times 10^{-7} T^3
- 1.68763333 \times 10^{-10} T^4 + 28.917.8/ T - 24.0658 T \ln (T) - 7750.91
\]

**Liquid: 1828.0 to 3300 K**

\[
G^o_T - H^o_{298.15 K} (J mol^{-1}) = 250.1240 T - 41.2000 T \ln (T) - 10,903.0
\]

Note to Table VII

\(G^o_T - H^o_{298.15 K}\) is the free energy function

### Table VIII Transition Values Involved with the Free Energy Equations

<table>
<thead>
<tr>
<th>Transition</th>
<th>Temperature, K</th>
<th>ΔHₕₗ, J mol⁻¹</th>
<th>ΔSₕₗ, J mol⁻¹ K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fusion</td>
<td>1828.0</td>
<td>17,340.00</td>
<td>9.4858</td>
</tr>
</tbody>
</table>

### Table IX Vapour Pressure

<table>
<thead>
<tr>
<th>T, K</th>
<th>p, bar</th>
<th>ΔGᵣ, J mol⁻¹</th>
<th>ΔHᵣ, J mol⁻¹</th>
<th>p, bar</th>
<th>T, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>5.16 × 10⁻⁶</td>
<td>338,411</td>
<td>377,000</td>
<td>10⁻¹⁵</td>
<td>911</td>
</tr>
<tr>
<td>300</td>
<td>1.32 × 10⁻⁵</td>
<td>338,172</td>
<td>376,991</td>
<td>10⁻¹⁴</td>
<td>956</td>
</tr>
<tr>
<td>400</td>
<td>3.31 × 10⁻⁴</td>
<td>325,314</td>
<td>376,433</td>
<td>10⁻¹³</td>
<td>1005</td>
</tr>
<tr>
<td>500</td>
<td>2.20 × 10⁻³</td>
<td>312,606</td>
<td>375,794</td>
<td>10⁻¹²</td>
<td>1060</td>
</tr>
<tr>
<td>600</td>
<td>7.59 × 10⁻²⁷</td>
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<td>375,087</td>
<td>10⁻¹¹</td>
<td>1122</td>
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<tr>
<td>700</td>
<td>3.47 × 10⁻²</td>
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<td>374,321</td>
<td>10⁻¹⁰</td>
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<tr>
<td>800</td>
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<td>275,250</td>
<td>373,504</td>
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<td>1269</td>
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<tr>
<td>900</td>
<td>5.43 × 10⁻¹⁶</td>
<td>263,019</td>
<td>372,644</td>
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<td>1000</td>
<td>7.86 × 10⁻¹⁴</td>
<td>250,886</td>
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<td>1100</td>
<td>4.56 × 10⁻¹²</td>
<td>238,843</td>
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<tr>
<td>1200</td>
<td>1.33 × 10⁻¹⁰</td>
<td>226,882</td>
<td>369,956</td>
<td>10⁻⁵</td>
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<td>1300</td>
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<td>369,093</td>
<td>10⁻⁴</td>
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<td>1400</td>
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<td>10⁻³</td>
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<td>1500</td>
<td>2.16 × 10⁻⁷</td>
<td>191,403</td>
<td>367,558</td>
<td>10⁻²</td>
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</tr>
<tr>
<td>1600</td>
<td>1.36 × 10⁻⁶</td>
<td>179,680</td>
<td>366,926</td>
<td>10⁻¹</td>
<td>2770</td>
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</table>

(Continued)
<table>
<thead>
<tr>
<th>( T, , K )</th>
<th>( p, , \text{bar} )</th>
<th>( \Delta G^\circ_T, , \text{J mol}^{-1} )</th>
<th>( \Delta H^\circ_T, , \text{J mol}^{-1} )</th>
<th>( p, , \text{bar} )</th>
<th>( T, , K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1700</td>
<td>( 6.89 \times 10^{-6} )</td>
<td>167,994</td>
<td>366,399</td>
<td>1</td>
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<tr>
<td>1800</td>
<td>( 2.91 \times 10^{-5} )</td>
<td>156,336</td>
<td>365,979</td>
<td>NBP</td>
<td>3271.88</td>
</tr>
<tr>
<td>1828 (s)</td>
<td>( 4.23 \times 10^{-5} )</td>
<td>153,076</td>
<td>365,880</td>
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<tr>
<td>1828 (l)</td>
<td>( 4.23 \times 10^{-5} )</td>
<td>153,076</td>
<td>348,540</td>
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<tr>
<td>1900</td>
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<td>145,388</td>
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<tr>
<td>2000</td>
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<td>134,742</td>
<td>347,378</td>
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<td>346,961</td>
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<td>( 2.02 \times 10^{-3} )</td>
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<td>1.130</td>
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</table>

Notes to Table IX

\( \Delta G^\circ_T \) is the free energy of formation at one bar standard state pressure and temperature \( T \) and \( \Delta H^\circ_T \) is the enthalpy of sublimation at temperature \( T \).

Enthalpy of sublimation at 0 K: \( \Delta H^\circ_0 = 376.247 \pm 4.000 \, \text{kJ mol}^{-1} \)

NBP is the normal boiling point at one atmosphere pressure (1.01325 bar)

functions for the solid and the gas at 50 K intervals from 900 K to 1800 K and the melting point and for the liquid at the melting point and at 50 K intervals from 1850 to 3300 K and were fitted to the following equation (Equation (iii)):

\[
\ln (p, \, \text{bar}) = A + B \ln (T) + \frac{C}{T} + D T + E T^2
\]  

(iii)

Acknowledgement

The author is indebted to Venkatarama Venugopal, Bhabha Atomic Research Centre, India, for supplying the vapour pressure data corresponding to the measurements of Kulkarni et al. (50).

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The Author

John W. Arblaster is interested in the history of science and the evaluation of the thermodynamic and crystallographic properties of the elements. Now retired, he previously worked as a metallurgical chemist in a number of commercial laboratories and was involved in the analysis of a wide range of ferrous and non-ferrous alloys.
A Facile Green Tea Assisted Synthesis of Palladium Nanoparticles Using Recovered Palladium from Spent Palladium Impregnated Carbon

Biosynthesising palladium nanoparticles using green tea as a reducing agent

Ansari Palliyarayil, Kizhakkoottu Kunjunny Jayakumar, Sanchita Sil* and Nallaperumal Shunmuga Kumar
Defence Bioengineering and Electromedical Laboratory (DEBEL), Defence Research and Development Organization (DRDO), C. V. Raman Nagar, Bangalore-560 093, India

*Email: sanchitasil@debel.drdo.in

Palladium impregnated activated carbon (Pd/C) filters play a major role in air quality management by the removal of toxic carbon monoxide from confined environments. However, Pd is an expensive metal and therefore, recovery and reuse of Pd from spent filter cartridges is highly desirable. The objective of the present study was to biosynthesise Pd nanoparticles (NPs) using green tea as a reducing agent. The source of Pd for the NP synthesis was spent Pd/C. Three different acid based Pd extraction protocols constituting of hydrochloric acid-hydrogen peroxide (HCl-H₂O₂), 2 M HCl and aqua regia were systematically explored. The Pd impregnated carbon was characterised using scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS), ultraviolet-visible (UV-vis) spectroscopy, X-ray powder diffraction (XRD) and atomic absorption spectrometry (AAS) before and after Pd extraction. It was found that the aqua regia based extraction protocol was the most efficient among the three chosen acid or acid mixtures with an average absolute yield of 96%. Finally, an attempt was made towards one pot biosynthesis of Pd NPs from the recovered extract by using green tea as a reducing agent. The synthesised NPs were characterised using UV-vis spectroscopy, SEM and XRD.

Introduction

Activated carbon is a versatile adsorbent possessing high surface area, microporous structure and a high degree of surface reactivity. As an adsorbent, activated carbon has found application in economic sectors as diverse as the food, pharmaceutical, chemical, petroleum, nuclear, automobile and vacuum industries as well as for the treatment of drinking water, industrial and urban wastewater and industrial flue gases. According to the European Council of Chemical Manufacturers’ Federation (European Chemical Industry Council or Cefic), it is defined as non-hazardous, processed, carbonaceous material having a porous structure and a large internal surface area (1). It is known as a ‘universal adsorbent’ due to its efficiency and has been employed for the adsorptive removal of impurities from exhaust gas and wastewater systems (2–7).

One of the ways to improve the efficiency of activated carbon is by impregnation of metals (8). Impregnated activated carbon has been extensively used for gas purification, catalysis,
civil and military gas protection (9–15). It has also been successfully used in air cleaning filters in confined environments for the removal of toxic pollutants. These filters act as the ‘lungs’ of a closed system that ensure air purification, thereby maintaining a level of toxic pollutants under the permissible limits. Pd is one of the metals which is impregnated on carbon in air cleaning filters. It acts as a catalyst by oxidative removal of CO as carbon dioxide, as shown in Equation (i):

\[
\text{CO} + \frac{1}{2}\text{O}_2 \xrightarrow{\text{Pd}} \text{CO}_2
\]

Pd as a catalyst is present in the range 4–8% by weight of total carbon (16, 17). Once the filter becomes saturated, it must be replaced. However, this is a cost intensive process and recovery of Pd is highly desirable so that it can be recycled and used for subsequent impregnation. Additionally, metal-containing wastes such as spent filters cannot be disposed of directly due to environmental concerns (18). According to a review by Butler, in the year 2011 alone, about 22% of the Pd market consisted of recovery from autocatalysts and jewellery scrap (19).

Many processes have been reported in the literature for extraction of Pd by using different solvents such as ortho-8-hydroxyquinoline, HCl, a HCl-H\textsubscript{2}O\textsubscript{2} mixture and aqua regia (20–23). The objective of this study was to identify a simple, cost effective and scalable technique for Pd recovery that allows reuse of the recovered metal for various applications and can be easily adopted by industry. In the present work, a systematic study for the recovery of Pd from Pd impregnated (6.5%) activated carbon was conducted using three different extraction routes. The first method comprised of digestion with 2 M HCl, the second consisted of digestion with a HCl-H\textsubscript{2}O\textsubscript{2} mixture while the third used aqua regia for digestion. The details of the processes are provided schematically in the Supplementary Information (SI) accompanying this article online.

Additionally, it is important to reuse the extracted metal for various applications. As an extension of this study, biosynthesis of Pd NPs using a ‘green’ route was also conducted. It is known that metal NPs show unique properties different from their bulk counterparts and have therefore found applications in the areas of optoelectronics, catalysis, photothermal therapy, surface enhanced Raman spectroscopy (SERS) detection and biological labelling (24). Recently, the syntheses of metal NPs by following green chemistry principles have attracted a great deal of attention (25–29). In the present work, green tea extract was used as a reducing agent for the biosynthesis of Pd NPs. Green tea, an infusion of *Camellia sinensis* leaves, is rich in polyphenols which are important biologically active components having antioxidative, antimitogenic and anticarcinogenic effects (30–32). Chemically, green tea is a complex mixture of polyphenols including flavonoids, caffeine, amino acids, organic acids, proteins, volatiles (low molecular weight aldehydes and alcohols), minerals like sodium, potassium and calcium and trace elements (aluminium, manganese, selenium and iron) (30–46). Flavanols and flavonols are the two major classes of polyphenols present in green tea (approximately 16–30% of the dry weight of the fresh leaf) (30, 33). The phenolic acid-type biomolecules which are present in the green tea infusion play a major role in the conversion of metal ions into metal NPs by reduction. During the NP formation, these biomolecules form complexes with metal ions present in the solution and reduce them into corresponding metals through an electron transfer mechanism. The catechins (flavan-3-ols), which are colourless, astringent and water soluble compounds, are characterised by the meta-5,7-dihydroxy substitution of the A-ring and di- or trihydroxy substitution of the B-ring as shown in Figure 1(a) and are the predominant species which are easily oxidisable. These are responsible for the biological activity of green tea. Green tea catechins are composed of eight catechin monomers (30, 34, 45–49), the structures of which are given in Figure 1. The polyphenol profile of green tea along with their percentage composition is tabulated in the Supplementary Information (SI1).

The Pd NPs biosynthesised from the recovered extract using green tea as the reducing agent were characterised using UV-vis spectroscopy, SEM and XRD.

**Materials and Methods**

**Chemicals**

Spent Pd impregnated activated carbon (Pd/C) was received from Active Char Pvt Ltd, India. Analytical grade HCl, sodium hydroxide (NaOH), H\textsubscript{2}O\textsubscript{2}, sodium borohydride (NaBH\textsubscript{4}) and nitric acid (HNO\textsubscript{3}) were purchased from Merck Specialities Pvt Ltd, India. Ethanol was purchased from Changshu Yangyuan Chemical Co Ltd, China. All these chemicals were used as received without further purification. All aqueous solutions were prepared in distilled water.
Instrumental Details

The pH of the spent Pd/C was measured using a CyberScan pH 510, Eutech Instruments Pte Ltd, Singapore. SEM studies for carbon samples were carried out with a Quanta 200 ESEM, Icon Analytical Equipment Pvt Ltd, India, and EDS with a Genesis XM4, Icon Analytical. Field emission scanning electron microscope (FESEM) studies of the Pd NPs were performed using an Ultra-55, Carl Zeiss AG, Germany. The scanning was carried out using an in-lens secondary electron detector, the voltage was maintained at 2.0 kV and 5.0 kV, and the working distance was kept at ~10 mm and 5 mm respectively. The XRD analysis was carried out with an X’Pert PRO diffractometer, PANalytical, Spectris Plc, The Netherlands, using CuKα radiation of wavelength $\lambda = 1.54$ Å with 40 kV generator voltage and 30 mA tube current. The 2θ value for the analysis was selected between 5° and 90°. A BELSORP-mini II surface area analyser, MicrotracBEL Corp, Japan, was used to measure the surface area by a nitrogen adsorption method at −196°C. A Lambda™ 25 UV-vis spectrophotometer, PerkinElmer Inc, USA, was used to carry out the study of pH variation during palladium(II) chloride (PdCl₂) precipitation. Scanning between the wavelengths 200–900 nm was performed to measure the absorbance values using the Lambda 25 software. Quantitative analysis was carried out with the help of an iCE™ 3500 AAS, Thermo Fisher Scientific, USA, in air-acetylene mode using the SOLAAR™ software.

Characterisation of Palladium Impregnated Activated Carbon

All the physical and chemical properties of the spent catalyst (Pd/C) were studied as per the Indian standards IS 877:1989 and IS 2752:1995 (reaffirmed in 2016). For each analysis, moisture free samples were used.

Palladium Recovery

All the extraction studies were carried out with moisture free Pd/C. The spent Pd/C was oven dried at 110°C for 4 h. To check the repeatability of the results, the extraction studies were carried out in duplicate.

In the first method, recovery of Pd from Pd/C was achieved using a HCl-H₂O₂ (10% HCl and 5% H₂O₂)
mixture. The details of the process are provided in the Supplementary Information (SI2). The reaction occurs as shown in Equations (ii) and (iii) (23):

\[
Pd/C + 4HCl + H_2O_2 \rightarrow H_2PdCl_4 + C + 2H_2O \quad (ii)
\]

\[
4H_2PdCl_4 + NaBH_4 + 2H_2O \rightarrow 4Pd + NaBO_2 + 16HCl \quad (iii)
\]

The obtained filtrate was made up to a definite volume and analysed for Pd content using AAS. Reduction of the Pd extract was performed by slow addition of 1% NaBH\(_4\) to the filtrate under magnetic stirring and the reaction temperature was maintained at 95–100°C (Equation (iii)) (23). The completion of the reduction process was monitored with the help of UV-vis spectroscopy. The precipitated Pd was filtered out, oven dried at 110°C and was analysed quantitatively by AAS.

In the second approach the extraction of Pd from Pd/C was achieved using 2 M HCl. The details of the process are provided in the Supplementary Information (SI2). The filtrate was analysed for Pd content using AAS after making up to a definite volume. The pH of the extract was raised by using NaOH solution to precipitate Pd as PdCl\(_2\). The precipitation of PdCl\(_2\) usually occurs at pH 9.5 (20). Initially the pH of the extract was raised to pH 6 to check for precipitation of any impurities such as chlorides of iron or other metals. No precipitation was observed in this range. The pH of the extract was then further raised up to pH 11 to ensure the completion of the precipitation of Pd as PdCl\(_2\). The precipitated PdCl\(_2\) was filtered by using a previously weighed G-3 crucible. The precipitate was then oven dried at 110°C and quantitatively analysed by AAS. Equations (iv), (v) and (vi) describe the chemical reactions:

\[
2Pd/C \xrightarrow{\text{Calcination, O}_2} 2PdO + C \quad (iv)
\]

\[
PdO + 4HCl \rightarrow H_2PdCl_4 + H_2O \quad (v)
\]

\[
H_2PdCl_4 + 2NaOH \rightarrow PdCl_2 + 2NaCl + 2H_2O \quad (vi)
\]

In the final approach, Pd was extracted from Pd/C using \textit{aqua regia}. The details of the process are provided in the Supplementary Information (SI2). The reaction proceeds according to Equations (vii) and (viii) respectively. The filtrate was made up to a definite volume and analysed for Pd using AAS. Part of the filtrate was used to remove nitrate ions and the residue was dissolved in acid (20% HCl) for precipitation of Pd as PdCl\(_2\) as described in Equation (vi).

\[
Pd/C + 3HCl + HNO_3 \rightarrow PdCl_2 + C + NOCl + 2H_2O \quad (vii)
\]

\[
PdCl_2 + 2HCl \rightarrow H_2PdCl_4 \quad (viii)
\]

The precipitated Pd was then quantitatively analysed by AAS.

### Synthesis of Palladium Nanoparticles

Green tea extract used for the synthesis of Pd NPs was prepared by heating 0.25 g of tea leaves (Tetley green tea from TATA global beverages) with 50 ml of distilled water at 80–85°C for 2 min followed by filtration. Since the amount of Pd recovered using the HCl-H\(_2\)O\(_2\) method was less compared to the other two methods (see Table I), only extracts from the 2 M HCl and \textit{aqua regia} methods were used for the synthesis of NPs. In this case, 40 ml of the Pd extract (pH adjusted to pH 5.5–6) was

### Table I Recovery of Palladium Estimated by Atomic Absorption Spectrometry Measurement using Different Extraction Media

<table>
<thead>
<tr>
<th>Method</th>
<th>Sample 1, %</th>
<th>Sample 2, %</th>
<th>Average recovery, %</th>
<th>Standard deviation with respect to absolute recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HCl-H(_2)O(_2)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extract</td>
<td>58.68</td>
<td>59.09</td>
<td>58.89</td>
<td>0.5939</td>
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<tr>
<td>Absolute recovery</td>
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<td>56.80</td>
<td>56.38</td>
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<tr>
<td><strong>2 M HCl</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extract</td>
<td>75.01</td>
<td>73.56</td>
<td>74.29</td>
<td>0.6576</td>
</tr>
<tr>
<td>Absolute recovery</td>
<td>73.65</td>
<td>72.72</td>
<td>73.19</td>
<td></td>
</tr>
<tr>
<td><strong>\textit{Aqua regia}</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extract</td>
<td>93.95</td>
<td>98.73</td>
<td>96.34</td>
<td>3.4577</td>
</tr>
<tr>
<td>Absolute recovery</td>
<td>93.84</td>
<td>98.73</td>
<td>96.29</td>
<td></td>
</tr>
</tbody>
</table>
heated with 2 ml of green tea extract at 90–95°C for 15–45 min with continuous stirring at 400 rpm. In the case of *aqua regia* extract, the extract was evaporated to dryness for the removal of nitrate ion. The obtained residue was dissolved in a minimum quantity of 20% HCl followed by addition of 40 ml distilled water and this solution was used for NP synthesis. The reaction was carried out in the dark to prevent the effect of light. The colour change of the solution from light to dark brown indicated the formation of Pd NPs. The formation of Pd NPs was further monitored by using UV-vis spectroscopy. The synthesised Pd NPs were then washed with deionised water by centrifugation at 10,000 rpm for 10 minutes. The process was repeated three times followed by dispersion in ethanol and the resulting dispersion was used for characterisation studies. The morphology of the biosynthesised Pd NPs was obtained by using FESEM. The Pd NPs were also studied using XRD.

**Results and Discussion**

**Palladium on Carbon**

The results of the characterisation of Pd/C are compiled in Table II.

The Pd/C was observed to have 11.53% moisture content. Although moisture content does not have any detrimental effect on the adsorption efficiency of carbon, it essentially dilutes the carbon content which necessitates additional weight compensation during the filtering process (50). One of the quality indicators for activated carbon is the ash content which is defined as the residue that remains when the carbonaceous portion is burnt off. Ash essentially consists of minerals such as silica, aluminium, iron, magnesium and calcium. This is generally not desirable and lower values are indicative of a good quality carbon. Sometimes ash may also interfere with the carbon adsorption by competitive adsorption and catalysis (51). The obtained ash content for the material used in the present study was 8.62% as it also contains Pd. Since the pH values of most commercial carbons are produced by their inorganic components, the ash content may affect the pH of the carbon. The acidic or basic nature of an activated carbon depends on its preparation and inorganic matter content along with the chemically active oxygen groups on its surface. In addition, the kind of chemical treatment to which the activated carbon is subjected would also determine the pH. The pH of the Pd/C used in this study was slightly alkaline suggesting that the carbon surface was essentially negatively charged (1).

The iodine number provides an idea of the micropore content of the activated carbon by adsorbing iodine from solution. Additionally, it also provides qualitative information about the surface area (52, 53). From the obtained iodine number in the present study (1463.4 mg g⁻¹), it can be concluded that the surface area of the Pd/C carbon is ≥1100 m² g⁻¹ which is also confirmed by the BET surface area measurement value (1550.5 m² g⁻¹). Adsorption capacity, an important property of an adsorbent material, was calculated with respect to decolourising power. The high value of decolourising power (365.47 mg) indicates that the Pd/C is a good adsorbent. Since methylene blue comes under the category of a cationic dye, a higher value for methylene blue adsorption indicates the presence of more negative charges on the Pd/C. This can be further corroborated from the pH value which is slightly in the alkaline range (54, 55).

SEM and EDS studies were carried out for the Pd/C before and after extraction via the described routes. Figure 2 depicts the micrographs of Pd/C and Figure 2(a) depicts the SEM microstructure of Pd/C before Pd removal. The Pd/C possesses pores of diameter in the micrometre range. On treatment with acids, HCl-H₂O₂, 2 M HCl and *aqua regia* as shown in Figures 2(b), 2(c) and 2(d) respectively, a visible change in the morphology of Pd/C treated with *aqua regia* was observed compared to the morphology of Pd/C treated with HCl-H₂O₂ and 2 M HCl. In the case of HCl-H₂O₂ and 2 M HCl treated Pd/C (Figures 2(b) and 2(c) respectively), there is no visible difference in surface morphology compared to the pure Pd/C. The HCl-H₂O₂ treated Pd/C appears to be flakier which may be due to grinding of Pd/C before the extraction. The *aqua regia* treated Pd/C (Figure 2(d)) shows a more porous structure with

<table>
<thead>
<tr>
<th>Test</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>11.53%</td>
</tr>
<tr>
<td>Ash content</td>
<td>8.62%</td>
</tr>
<tr>
<td>pH</td>
<td>9.30</td>
</tr>
<tr>
<td>Decolourising power</td>
<td>365.47 mg</td>
</tr>
<tr>
<td>Iodine number</td>
<td>1463.4 mg g⁻¹</td>
</tr>
</tbody>
</table>
an increase in the pore densities. The EDS study of Pd/C reveals the presence of Pd on its surface. The disappearance of the Pd peak in the EDS spectrum of *aqua regia* treated Pd/C reveals that *aqua regia* treatment removes Pd effectively (*Figure 2(d)*) and is the most effective method for the extraction of Pd from Pd/C. This was also confirmed from AAS and XRD studies.

UV-vis spectrophotometric studies were carried out during the course of Pd recovery for all three acid digestion routes. The UV-vis spectra are provided in *Figure 3*. The trend of the decrease in absorption peaks during the progress of the reaction towards Pd recovery was monitored and is shown as an inset in the figure. In the case of Pd removal using HCl-H$_2$O$_2$ digestion as shown in *Figure 3(a)*, absorption peaks centred at 231 nm and 277 nm respectively were obtained from the Pd containing solution, which are characteristics of Pd(II). The UV-vis spectra were acquired at different stages of reduction: during and after completion of the reaction. There was a steady decrease in the absorption band which finally disappeared at the end of the reduction. Similarly, in the case of recovery of Pd using 2 M HCl and *aqua regia* respectively, the UV-vis spectra at different pH were obtained which showed a steady decrease in the absorption band as the solution became depleted of Pd. At pH 11, the Pd(II) absorption peak disappeared which marked the completion of the Pd(II) precipitation.

The energy level ordering of the transition metal d-orbitals is greatly influenced by the ligand which is manifested in the spectroscopic transition. Additionally, the orbital interaction with ligands influences the magnitude of orbital splitting. In the case of complexes with π-donor ligands such as (PdCl$_4$)$_2$–, the energetic ordering is perturbed by π-donating ligands such as chloride (56). Based on the different acid treatments, the absorbance spectra show little shifts in the values. The absorbance values for the (PdCl$_4$)$_2$– complexes

---

**Fig. 2.** SEM and EDS graphs of: (a) Pd impregnated carbon (Pd/C); (b) Pd/C treated with HCl-H$_2$O$_2$; (c) Pd/C treated with 2M HCl; (d) Pd/C treated with *aqua regia*. The SEM images were taken at magnifications 500× and 5000× respectively.
formed using various acids show bands around 231 nm and 277 nm in the case of HCl-H$_2$O$_2$ based extraction whereas there is an appearance of an additional band around 211 nm and 218 nm in the case of 2 M HCl and aqua regia based extraction routes respectively. All the observed absorbances can be attributed to a ligand-to-metal (Cl$^-$ to Pd(II)) charge transfer transition for (PdCl$_4$)$_2^-$ (57, 58).

AAS was employed to quantitatively analyse the amount of Pd recovered using the three extraction routes. The initial estimation was carried out using the Pd(II) solution immediately after acid digestion. The AAS analysis results are provided in Table I.

It is observed that aqua regia based digestion was most effective in recovering Pd, followed by the 2 M HCl and HCl-H$_2$O$_2$ routes with an average yield 96%, 74% and 59% respectively for the three acids. Pd was then precipitated from the three extracts by using NaBH$_4$ in the case of the extract from HCl-H$_2$O$_2$, and by increasing the pH of the solution in the case of the 2 M HCl and aqua regia extracts. Finally, AAS studies were performed on the final recovered Pd. The aqua regia extract gave the highest recovery of Pd at 96%, followed by the 2 M HCl (~73%) and HCl-H$_2$O$_2$ (~56%) extracts. All the extractions were carried out in duplicate and the results were reproducible within <5% variation as mentioned in Table I. The detailed calculations are included in the Supplementary Information.

An ash test was carried out on the Pd/C after aqua regia extraction. The amount of ash obtained from the Pd/C treated with aqua regia was 0.71%. The ash content value also reflects that the aqua regia treatment effectively removes Pd from the spent Pd/C.

XRD studies were carried out on Pd/C before and after treatment and the spectra are shown in Figure 4. The XRD pattern of Pd/C (Figure 4(a)) exhibited two broad peaks at 20 corresponding to 25.56° and 43.89° respectively. The peaks are
attributed to the (002) and (100) plane, respectively, characteristic of the hexagonal diffraction pattern of the graphitic structure. In addition to these two broad peaks, five major diffraction peaks centred at 2θ 40.51°, 47.00°, 68.47°, 82.38° and 86.87° were also present in the XRD pattern for Pd/C (Figure 4(a)). The appearance of these five peaks indicates the presence of Pd on the surface of Pd/C possessing (111), (200), (220), (311) and (222) planes (Bragg reflection) of the face centred cubic (fcc) crystalline structure. Two broad peaks characteristic of the hexagonal diffraction pattern of the graphitic structure were also observed in the XRD pattern for acid treated Pd/C (Figures 4(b), 4(c) and 4(d)). In the case of Pd/C treated with aqua regia, all five Pd peaks disappeared, indicating the complete leaching out of Pd from the Pd/C. The XRD pattern for 2 M HCl treated Pd/C shows peaks corresponding to Pd indicating the presence of Pd on the surface of Pd/C, implying that the extraction with 2 M HCl was not effective and the Pd/C contained some Pd even after treatment. The observation was in agreement with the EDS, XRD and AAS results. For the Pd/C treated with HCl-H$_2$O$_2$, all five peaks were absent and the pattern was similar to the spectrum obtained for Pd/C treated with aqua regia. However, the recovery percentage was lower for the HCl-H$_2$O$_2$ method compared to the aqua regia and 2 M HCl based extraction methods.

**Nanoparticles**

As mentioned in the earlier section, it is important to develop processes for the reuse of the recovered metal. In this direction, biosynthesis of Pd NPs was carried out with the obtained extracts using green tea as the reducing agent. The flavonoid
(+)-catechin, an antioxidant present in green tea, is responsible for the formation of NPs. The reaction follows an electron transfer mechanism involving the release of both electrons and protons from the molecule (59). (+)-Catechin has two different pharmacophores, the catechol group in ring B and the resorcinol group in ring A (Figure 1(a)). Additionally, at position 3, it has a hydroxyl group in ring C (Figure 1(a)). Electrochemical studies on flavonoids show the trends of their electron donating ability. It has been shown that compared to resorcinol ring A, catechol ring B is more easily oxidisable, the ring with lower redox potential. The stability of various catechin radicals will follow the sequence: 4'-OH, 3'-OH, 7-OH, 5-OH (59, 60).

During the formation of the NPs, catechin forms a chelation complex with the Pd$^{2+}$ ion, followed by an electron transfer that reduces Pd$^{2+}$ to Pd$^{0}$ and oxidises catechin to quinone (59, 61). The reduction mechanism for the conversion of Pd$^{2+}$ to Pd$^{0}$ by green tea is schematically expressed by using a representative catechin monomer in Figure 5. This can be stoichiometrically expressed as Equation (ix):

$$n\text{Pd}^{II} + 2R-(OH)_n \rightarrow n\text{Pd}^{0} + 2nR=O + 2nH^+ \quad \text{(ix)}$$

where $R$ and $n$ represent the heterocyclic or alkyl groups and the number of the hydroxyl groups oxidised by Pd$^{II}$ species, respectively. Therefore, it is apparent that the formation of Pd NPs follows a 1:1 reaction and the amount of Pd NPs formed will be proportional to the amount of Pd$^{II}$ present in the solution.

The formation of NPs from the extracts (2 M HCl and aqua regia methods) was identified with the help of a UV-vis spectrophotometer. The UV-vis spectra are provided in Figures 6(a) and 6(b). The UV-vis spectrum of green tea shows an absorption peak centred at 273 nm. The absorption peaks centred around 211 nm, 234 nm and 277 nm corresponding to Pd$^{II}$ extracted from 2 M HCl and aqua regia start disappearing as the reaction proceeds, indicating the formation of Pd NPs. The complete reduction of Pd$^{II}$ to Pd$^{0}$ was confirmed by the appearance of a broad continuous absorption band (62). NP formation was further confirmed by FESEM images as shown in Figures 7(a) and 7(b). It is evident from the micrographs that fine NPs are formed which are well separated from each other. The approximate size of the synthesised NPs was calculated from the FESEM images. Although agglomerated particles are also visible in the image, the majority (~94%) of the formed NPs fall within the size range of 1–25 nm (Figures 8(a) and 8(b)).

The crystalline nature of the biosynthesised Pd NPs was confirmed by XRD analysis. The spectra are shown in Figure 9. The XRD pattern for Pd NPs prepared from the aqua regia extract shows five major diffraction peaks centred at 2θ 39.95°, 46.4°, 67.92°, 81.70° and 86.19°. The observation...
Fig. 6. UV-vis spectra for the Pd NPs synthesised from: (a) 2 M HCl extract; (b) \textit{aqua regia} extract.

Fig. 7. FESEM images for Pd NPs synthesised from: (a) 2 M HCl extract; (b) \textit{aqua regia} extract.

Fig. 8. Particle size distribution of Pd NPs synthesised from (a) 2 M HCl extract; (b) \textit{aqua regia} extract. The inset shows the reaction mixture before and after the formation of Pd NPs.
is similar for the Pd NPs prepared from the 2 M HCl extract with peaks centred at 2θ 40.07°, 46.65°, 68.03°, 82.02° and 86.00°. As mentioned in the previous section, the appearance of the five peaks represents the fcc structure of Pd. The results observed here are in agreement with previously published reports, thereby confirming a nanocrystalline form of Pd (63–66). The crystallite size of the Pd NPs was calculated using the Scherrer equation (67). On the basis of the (111) peak, the average crystallite size of the Pd NPs prepared from aqua regia and 2 M HCl extract was calculated to be ~13 nm and ~23 nm respectively. The synthesised Pd NPs can be effectively used as a potential impregnant for the preparation of fresh Pd/C. Further studies on CO removal are being carried out with the Pd NPs impregnated Pd/C and shall be published later.

**Economic Comparison**

A tentative economic comparison was made for the three methods employed in this study towards the extraction of Pd from 1 kg of spent Pd/C. Three criteria to estimate economic viability were considered: materials, process and Pd recovery. The comparison method is summarised in the Supplementary Information (SI2c). Considering the cost of the chemicals involved in the extraction, the cost was slightly higher for the HCl-H2O2 and aqua regia methods compared to the 2 M HCl extraction route. However, the 2 M HCl extraction takes ~4 h and ~5 h for the HCl-H2O2 and aqua regia methods respectively. It can thus be concluded from the material and process points of view that the three extraction routes are more or less similar, even though the HCl-H2O2 and aqua regia routes are slightly costly in terms of materials. However, the major cost incurred for Pd/C catalysts is the amount of Pd used for impregnation. As mentioned earlier, the percentage recovery of Pd was highest for the aqua regia based extraction method at ~96%, followed by the 2 M HCl (~73%) and HCl-H2O2 (56%) extraction methods. This suggests that the cost for the development of a fresh Pd/C with 6.5% Pd derived from extracted Pd could be greatly reduced by using the aqua regia route, with a ratio of ~1:7:11 corresponding to aqua regia, 2 M HCl and HCl-H2O2 extraction routes respectively. From a commercial perspective, the aqua regia based extraction procedure is an attractive method for the recovery of Pd as the method is economical, simple and highly effective.

**Conclusion**

Studies on Pd recovery from a spent activated carbon filter impregnated with Pd (Pd/C) were carried out. Recovery studies were performed using three acid or acid mixtures: 2 M HCl, HCl-H2O2 and aqua regia respectively. The absolute yield of the Pd obtained by different extraction methods showed a decreasing trend with aqua regia (~96%) > 2 M HCl (~73%) > HCl-H2O2 (~56%). Biosynthesis of Pd NPs from the recovered Pd was successfully carried out using green tea as the reducing agent.
The synthesised Pd NPs had a crystallite size of ~13 nm (aqua regia extract) and ~23 nm (2 M HCl extract) and the particles were well separated. It is also clear from the XRD results that the synthesised Pd NPs had a fcc crystalline structure. The present study indicates that the recovered Pd could be reused successfully for the ‘green’ synthesis of Pd NPs which in turn can be effectively used for the development of fresh Pd/C for the removal of pollutants.

Further studies on impregnation and CO removal efficiency of the biosynthesised Pd NPs are being carried out in our laboratory. The authors are hopeful that with further optimisation of the experimental parameters, the synthesised NPs will have the potential to be reused for different applications.

Acknowledgement

The authors are grateful to Dr U. K. Singh, Director, DEBEL, for constant encouragement and support to carry out the work. The authors would also like to thank Dr Kadirvelu, Scientist, Centre for Life Sciences, Bharathiar University, India and D. R. Nayak, IISc, Bangalore for conducting the SEM-EDS.

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“Food Packaging”


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Introduction

“Food Packaging” is the seventh volume of Nanotechnology in the Agri-Food Industry, a series aimed at bringing together the most recent and innovative applications of nanotechnology in the agriculture and food industries and to present future perspectives in the design of new or alternative foods. The volume “Food Packaging” presents the development of novel nano-bio-materials and the enhancement of barrier performance of nondegradable and biodegradable plastics in industrial packaging. Like the rest of the series, the book is edited by Dr Alexandru Mihai Grumezescu at the Department of Science and Engineering of Oxide Materials and Nanomaterials, Politehnica University of Bucharest, Romania, who is an experienced and widely published researcher and editor in the field of nano- and biostructures.

The book comprises 20 independent chapters authored by academics from 17 countries. Each chapter reviews recent developments in a chosen area of food packaging. Altogether, the book gives a full account of the efforts made by scientists across the world starting from the 1990s but mostly in the first 15 years of the 21st century in developing advanced polymer packaging materials for food, by adopting the approaches of nanotechnology and biomaterials, and progress made, particularly in the following areas:

- Barrier properties
- Ecofriendly and/or cost effective packaging
- Active packaging
- Intelligent packaging.

Although the book itself is not structured into different sections, this review covers all 20 chapters by categorising them into the above listed themes.

Nanotechnology and Improvement of Barrier Properties

Good barrier properties are key requirements for food packaging materials. Compared to glass, metal and ceramics, the barrier properties of polymer materials to gases and liquids are inferior and enhancement is often needed. Nanotechnology has emerged as a successful approach. Improvement of barrier performance is the central topic of many of the chapters in this book and nanotechnology is extensively discussed.

Chapter 1 by Iman Soltani et al. (North Carolina State University, USA) concentrates on the fundamental aspects of nanotechnological strategies for high barrier polymer food packaging materials. Two strategies are presented: applying inorganic coatings to the surface of plastics and developing nanocomposites. Starting with classifying coatings according to the number of
layers, a clear overview of the inorganic coating approach is provided. The history and technology of applying a single layer (10–100 nm) of metal and oxide/nitride coating to the surface of polymers with physical (for example thermal or sputtering) vapour deposition (PVD), chemical vapour deposition (CVD) and atomic layer deposition (ALD) methods are described. For multilayer coatings, the authors focus on relatively recently developed layer-by-layer assembly (LBL) coating. The evolution of LBL technology, including the interaction and layer building mechanism employed, the range of materials used for fabrication, from the original multilayer of oppositely charged polymer to charged particles (for example globular protein) and charged platelets (exemplified by exfoliated natural clays such as montmorillonite, MMT), and the fabrication methods from simple dipping to spraying and spin coating, is accounted.

The ability to improve barrier properties is presented and the shortcomings of coating methods, which are defects and adhesion issues, are explained. The authors introduce the polymer nanocomposites (PNC) strategy to overcome these drawbacks and focus on polymer clay nanocomposites (PCNs). Methods to prepare and characterise PCNs are summarised. The well-recognised four typical morphologies of layered silicates polymer micro/nanocomposites: phase separated, exfoliated, intercalated and intercalated plus flocculated are cited and depicted (Figure 1). These correlate directly to the barrier enhancement effect. Following a theoretical discussion of molecular transport in polymers and nanocomposites, case studies are included to provide a clear comparison of the barrier enhancement abilities of the routes discussed. Typically, improvement of up to 3, 3, 4 and 1 order of magnitude (against O₂) can be achieved relative to the base polymer materials for PVD/CVD, ALD, LBL coating and PCNs, respectively. The authors highlight the commercial importance of PCNs for their facile processability, mechanical robustness and lengthy stability, despite their relatively modest barrier efficacy.

Nanocomposites are no doubt the most appreciated nanotechnology in this book and are discussed by many authors separately in the

![Fig. 1](https://doi.org/10.1595/205651318X696350)
other 16 chapters, as a key solution to improve not only the barrier performance but other properties as well.

Studies of a special type of polymer nanocomposites, polymer/graphene nanocomposites are specifically reviewed in Chapter 20 by Ahmad Allahbakhsh (Tarbiat Modares University and Islamic Azad University, Iran). In outlining the concept of substituting nanoclay with graphene in polymer nanocomposites for barrier and reinforcement, the author underlines the use of functionalised or oxidised graphene (graphene oxide (GO)) instead of pure graphene in polymer nanocomposites for achieving dispersibility and compatibility of the nanoparticles. The preparation (through chemical exfoliation and micromechanical exfoliation of graphite) and the properties of GO and its covalent and non-covalent interaction with polymers are discussed, which pave the way to review studies of nanocomposites of GO with a number of polymers: polypropylene, polyethylene, polystyrene terephthalates, polyvinylalcohol, polylactic acid, and pullulan. The preparation of nanocomposites by melt compounding, in situ polymerisation and solution blending routes plus LBL techniques, and the effective reduction of permeation to gases are described.

Chapter 18 by Karolth Espinosa et al. (UNCONICET, Argentina) deals specifically with polypropylene/talc nanocomposites. Through a detailed description and a review of their processing, including film blown technology, and the morphology, mechanical properties and barrier performance of the final films, the authors present the feasibility of using polypropylene/talc nanocomposites as low cost improved barrier materials as well as the scalability challenge.

The enhancement of barrier properties is further studied by other authors in depth in Chapters 2, 5, 12, 13 and 20. In Chapter 5, Xueyan Yun et al. (Inner Mongolia Agricultural University, China) discuss the fabrication of high barrier plastics and their application for food packaging. In addition to nanocomposites, coating and LBL assembly technologies, the authors provide an overview of more traditional technologies such as polymer orientation/stretching and blending. The authors also discuss using organic coatings to enhance barrier properties, for example polyvinylidene chloride on polyethylene terephthalate. Improved preservation of various foods by enhanced polymer films, including meat products, chilled meat, cheese, salad sauce, seafood and agricultural products, is demonstrated by case studies. As the basis of the discussion, fundamentals of food packaging, such as the impact on the shelf life of factors such as light, oxygen, carbon oxides and moisture through the mechanisms of oxidation and photooxidation, degradation of protein and vitamins, colouration, growth of microorganisms and other physical or chemical reactions are provided.

**Bio-nanocomposites and Ecofriendly Packaging**

Judging by the market size and the huge volume of materials consumed, the packaging industry may be seen as a materials intensive industry. There has been extensive research on ecofriendly packaging to minimise the impact on the environment. A solution is using bioplastics – biodegradable polymers or polymers made from renewable resources. This book follows the trend with 14 chapters discussing natural, bio-polymer or biodegradable polymer packaging.

Renewability is a big advantage in bioplastics. This is exemplified in Chapter 7 by Ana Sofia Lemos Machado Abreu et al. (University of Minho, Guimarães, Portugal). The authors discuss bioplastics from agro-wastes for food packaging applications. An overview of a number of petroleum based biodegradable polymers and polymers from renewable resources is provided. It is interesting that the authors enlist polyethylene as a biodegradable polymer for its
hydro/oxodegradation ability and the possibility to blend it with well-known biodegradable polymers. Cellulose is highlighted as a polymer which is available from plants, bacterial processes and in particular from agro-wastes. In presenting renewable cellulose and its derivatives as potential food packaging materials, studies on extracting cellulose from agro-wastes, physical blending of cellulose with other biodegradable polymers, chemical modification of cellulose in ionic liquids and graft polymerisation of cellulose are reviewed.

Nanocomposites play a significant role in bio-polymer packaging. Chapter 10 by Ana Sofia Lemos Machado Abreu et al. (University of Minho, Guimarães, Portugal) discusses biodegradable polymer nanocomposites for packaging applications. The chemistry of various natural polymers including soy, corn-Zein, starch, cellulose, chitosan and other polysaccharides and synthetic or bacterial-based polyesters including polycaprolactone, polylactic acid and polyhydroxyalkanoates are summarised. Studies on nanocomposites of these polymers are reviewed. A short discussion of the biodegradation process and its limitations is provided. A few examples of commercial biodegradable polymer food packages are given by the authors. In Chapter 3, Sushama Talegaonkar et al. (Jamia Hamdard, India; Mendel University, Czech Republic, and University of Natural Resources and Life Sciences, Austria) thoroughly review the research on the commonly used nanoparticle fillers including nanoclay, nano-cellulose, silicon dioxide, carbon nanotubes, silver dioxide, zinc oxide, titanium dioxide and the nanocomposites of common natural polymer cellulose, starch and chitosan. The authors attempt to look at bio-nanocomposites from the angle of active and intelligent packaging.

Chapter 19 by Aleksandra R. Nesic and Sanja I. Seslija (University of Belgrade, Serbia) focuses on the influence of nanofillers on the properties of polysaccharide based nanocomposites. Following an overview of food packaging materials (materials type, criteria and trends), the authors review polymer nanocomposites research by type of nanofillers. The characteristics of the nanofillers and the properties and functions of the respective nanocomposites are summarised. Next the authors provide comprehensive knowledge about the sources of extraction, physical structure and physical-chemical properties of nine commonly seen polysaccharides and their application including food packaging materials via a nanocomposites route. A further hurdle to overcome for commercialising polysaccharide nanocomposite packaging materials is identified by the authors at the end of the chapter.

ZnO nanocomposites with polyhydroxyalkanoates are further discussed in Chapter 6 by Ana M. Díez-Pascual (Alcalá University, Spain). The synthesis, structure, properties and applications of polyhydroxyalkanoate polymers and ZnO nanoparticles are detailed. Studies on nanocomposites of ZnO with two specific polyhydroxyalkanoates: polyhydroxybutyrate and polyhydroxybutyrate-co-valerate are reported. The barrier properties of bio-nanocomposites of biodegradable polymers with nanofillers are thoroughly discussed in a number of chapters, particularly in Chapters 2, 12 and 13. Chapter 2 by Giulio Malucelli (Politecnico di Torino, Alessandria, Italy) provides a literature survey of biocomposites containing nanofillers of different morphology (three-dimensional (3D) spherical and polyhedral particles, two-dimensional (2D) nanofibers and one-dimensional (1D) platelets) and of different chemistry (for example colloidal silica, polyhedral oligomeric silsesquioxanes, carbon black, nanoclays and starch nanocrystals). An improvement of barrier properties by tens of percent can be seen. The authors also dedicate one section to the LBL method, highlighting its advantages such as effective barrier property improvement, imparting of other additional functions, process simplicity and eco-friendliness.

Chapter 12 by Marina Patricia Arrieta et al. (Institute of Polymer Science and Technology, Madrid and Polytechnical University of Valencia, Alcoy, Spain) aims at elucidating the role of nanoparticles in improving the barrier properties of bioplastics and assessing the impact of the shape of nanoparticles to barrier properties. The research of bio-nanocomposites of biodegradable polymers (polylactide, polycaprolactone, polyhydroxybutyrate, polyhydroxybutyrate-co-valerate, plasticised starch and polyvinyl alcohol) with MMT, cellulose nanocrystals and ZnO nanoparticles as representative 1D, 2D and 3D geometry nanofillers is described in detail. The additional influence of factors such as surface properties of nanoparticles and their interaction with components of the bioplastics, adhesion and crystallisation on barrier properties is discussed. The extra antimicrobial benefits of nanocomposites containing ZnO is also specified.

Chapter 13 by Kateryna Fatyeyeva et al. (Normandie University and University of Rouen, France) focuses on high barrier biopolymer/clay nanocomposites. The authors clearly outline the
background on nanocomposites, government regulation, biopolymers, clays and biopolymer/clay nanocomposites. Mechanistic understanding and the barrier properties of nanocomposites formed by nanoclay with polysaccharides, proteins, aliphatic polyesters and mixtures of polymers are reviewed in detail. As well as enhancing the concept of improving barrier properties by clay nanocomposites, a full picture of the influence of the biopolymer and nanoclays themselves as a component to the final nanocomposites is provided. The future development of biopolymer/clay nanocomposites is discussed. The barrier properties of bioplastics are also a focus of Chapter 14.

Despite the potentials of bioplastics and some examples of commercial products, more research and development is needed to make bioplastics more comparable to traditional petroleum based polymers in properties and performance to achieve full commercialisation success in food packaging. This is highlighted by many authors in the above chapters. The authors also look at future directions for development.

**Active Packaging**

A significant step in food packaging is active packaging, which can proactively extend the shelf life, maintain or even improve the condition of packaged food. Functional nanocomposites, nanocomposites of physically, chemically or biologically active nanoparticles play vital roles and have become an important route for active packaging. This book records the progress in active packaging, in particular nanocomposites for active packaging.

Active packaging including antimicrobial packaging and modified atmosphere control is highlighted as a trend in Chapter 19. In Chapter 8, readers can learn how metals and metal oxides, carbon nanotubes and biopolymer nanoparticles are incorporated into polymers to impart antimicrobial, UV-blocking and anti-oxidant functionalities. In Chapter 3, several commercial product examples of atmosphere control packaging (for moisture, oxygen and carbon dioxide) are briefly described.

Antimicrobial and antibacterial packaging is well addressed in this book. Both Chapter 15 by Iva Rezić et al. (University of Zagreb, Croatia) and Chapter 16 by Majid Montazer et al. (Amirkabir University of Technology, Iran) are dedicated to antimicrobial nanocomposites. Together the two chapters present essential information about the antimicrobial properties of a list of nanoparticles including metals (silver, copper, iron), metal oxides (titania, ZnO, copper oxide, ferrous oxide, magnesium oxide), carbon nanotubes, nanoclays, biopolymers (chitosan, nisin, alginate) and their composites with polymers. Chapter 16 concentrates on bio-nanocomposites. It is worth mentioning that toxicological properties of nanoparticles and the health, ethical and regulatory issues related to antimicrobial packaging are well discussed in the two chapters. The antimicrobial properties for ZnO-based bio-nanocomposites are also discussed in Chapters 6 and 12.

**Nanodiamond** is a special class of bioactive nanoparticles. Chapter 9 by Katarzyna Mitura et al. (Koszalin University of Technology, PLASTMOROZ Sp. z o.o. Sp. and Koszalin University of Technology, Poland) presents a complete report of bioactive packaging with nanodiamond particles. A full account of nanodiamonds, including their sources of origin, preparation, modification, morphology, properties, antimicrobial, antioxidant and biomedical activity, cyto-toxicology and their increasing application in coatings and nanocomposites is provided. Readers are shown the ways in which nanodiamonds differ from metals and metal oxides deriving from their electronic structure and zeta potential.

An interesting type of active packaging is provided by flavour and aroma. Chapter 17 discusses nanoencapsulation of flavour and aroma for food packaging. The science of flavour and aroma is summarised in the chapter. Natural aromatic substances are often synthesised by living organisms as a defense mechanism or as secondary metabolites and have antioxidant, antibacterial and antifungal properties. By incorporating these into food packaging they can reduce the most common spoilage pathogens and prevent deterioration of food quality. A proven effective process is for flavours and aromas to be micro- or nano-encapsulated into capsules and incorporated as particles into packaging materials. Encapsulation technology and the materials used for encapsulation, and studies of largely successful incorporation of nanocapsulated flavours into polymer films for food packaging, are reviewed.

In Chapter 11, Mythili Prakasam et al. (University of Bordeaux, France) discuss flexible packaging for nonthermal decontamination by high hydrostatic pressure, which may be classed as a special type of active packaging. High hydrostatic pressure processing technology is described, including the materials requirements, the working mechanism and its impacts on physical, chemical, mechanical,
barrier and active migration properties of packaging materials particularly multilayer packaging.

**Intelligent Packaging**

Intelligent packaging communicates information on the state of the package and packed goods to owners and customers. It has been a target of research and development and several types of intelligent packaging are emerging. Chapter 4 by Viviane Dalmo et al. (Federal University of Rio Grande do Sul and Polymer Technology Center at Trinuo, Brazil) describes some developments in the area of encapsulation of sensors for intelligent food packaging. Commercial interest in intelligent packaging is assessed by the authors at the beginning of the chapter and readers are shown that the market is growing in size. A few products currently on the market or in development such as freshness, integrity and time-temperature indicators, radio frequency identification tags and embedded sensors are then described. An overview of the chemistry and processing technology of current and emerging packaging materials is made in the context of encapsulating sensors. The authors highlight the sol-gel method as a versatile way to encapsulate and develop packaged sensors. Sol-gel chemistry, in particular silane chemistry, is discussed and the development of sol-gel encapsulated sensors, for example dyes or indicators, and their application in packaging to detect amine, formaldehyde and pH changes for food quality monitoring are reviewed. A summary of the current regulation status of intelligent and active packaging in Europe and the USA is included.

Intelligent packaging is also discussed in some other chapters of the book. Chapter 8 mentions the development of nanocomposites containing nanoparticles as intelligent indicators, for example TiO$_2$ as a UV-activated oxygen indicator, chiral nematic nanocrystalline cellulose as a humidity indicator, Ag/Cu nanoparticles and carbon nanotubes as freshness indicators and quantum dots as microorganism growth indicators. In Chapter 3, a commercial product indicating oxygen levels is briefly described.

**Conclusions**

As with similar books, the volume is primarily a collection of reviews published in scientific journals and little patent literature is included, although in some chapters brief summaries of the commercial technology are provided. Many readers, especially those researchers from industry, may be interested to learn more about the commercial status of the technologies discussed in this book. As the book is written by many groups of independent authors, inevitably readers may find that there is some overlap in content between some of the chapters. There appear to be some plain language errors easily spotted in parts of the current edition.

Nevertheless, the book has succeeded in presenting readers with the frontiers of food packaging materials science. The state-of-the-art in developing high barrier and multifunctional food packaging materials using nanotechnology and biodegradable or renewable polymers is well documented, as well as fundamental knowledge, scientific background and insights into the future development of packaging materials. The book provides a comprehensive reference for the design of food packaging materials, development of technology and the manufacturing of food packaging products, and thus will certainly appeal to professionals working on food packaging from both industry and academia. The book will also interest general readers including graduate and undergraduate students in materials science and engineering.

**References**

The Reviewer

Chun-tian Zhao is a Senior Polymer Scientist and Research Group Leader at Tracerco, a Johnson Matthey company. He has interests in a broad range of polymer based technologies including microencapsulation and controlled release, membrane materials, sensors and medical devices, biodegradable polymers and food packaging, water treatment and oil field chemicals.
“Air Pollution Control Technology Handbook”, Second Edition

By Karl B. Schnelle Jr., Russell F. Dunn (Vanderbilt University, Nashville, Tennessee, USA) and Mary Ellen Ternes (Crowe and Dunlevy, Oklahoma, USA), CRC Press, Boca Raton, USA, 2016, 429 + xxvi pages, ISBN 9781138747661, £60.00, US$79.95

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Introduction

When the first edition of this book by Karl B. Schnelle and Charles A. Brown was published (1) some 16 years ago, there were a number of texts available that covered various aspects of pollution emissions and their control, including “Practical Handbook of Environmental Control” by Conrad P. Straub (2) that gave in tabular form a huge amount of easily accessed relevant data, and the monumental text by B. J. Finlayson-Pitts and J. N. Pitts (3). Schnelle and Brown’s book was a guide focusing on the sources of air pollutants, their measurement and the control of pollutants from industrial plants.

The second edition of the “Air Pollution Control Technology Handbook” retains the original senior author, K. B. Schnelle (now Emeritus Professor at Vanderbilt University, Nashville, Tennessee, USA), joined by Professor R. F. Dunn from the same university and Mary Ellen Ternes, a Vanderbilt graduate now an environmental lawyer. Like the first edition, the present book has 24 chapters with related titles and the same general layout with a focus on the situation in the USA.

US Air Quality Legislation

The first short chapter (12 pages) ‘Historical Overview of the Development of Clean Air Regulations’ gives a historical overview of the US clean air regulations and is similar to that in the first edition with a small difference being that the references, instead of being at the end of the chapter, are now collected together in a separate section before the index at the end of the book. The larger second chapter (25 pages) entitled ‘Clean Air Act’ delineates the development of the US legislation. Tabular information has been updated to February 2015 and some more recent references are included. These two chapters provide a particularly readable and useful source for those wanting to gain insight into the way US air quality legislation has developed over several decades, resulting in major air quality improvements in many urban areas.

Air Emission Permits and Atmospheric Pollutant Modelling

The third chapter ‘Air Permits for New Sources’ (12 pages) explains the procedures necessary when an air permit is required before the construction of plant in the USA that adds or modifies a source of
pollution. It goes through the procedural elements and details them for applications that include secondary emissions and the primary emissions rates, although only one additional reference is given compared with the first edition. The next chapter (13 pages) called 'Atmospheric Diffusion Modelling for Prevention of Significant Deterioration Permit Regulations and Regional Haze' highlights the need for appropriately tall stacks which, while not preventing emissions from entering the atmosphere, do reduce ground level pollution to low enough concentrations so as not to be harmful around the source. The approach is qualitative and nonmathematical in outlining atmospheric diffusion models and reference is made to several computer models, particularly those available through the US Environmental Protection Agency (EPA) Air Quality Modelling Group. Strangely the original two references in this chapter were not extended or updated.

Pollutant Monitoring

The fifth chapter (8 pages) deals with 'Source Testing' by which is meant determining the concentration and/or quantity of pollutant at its source, for example a stack. Sampling techniques are covered in some detail and the following chapter (18 pages) 'Ambient Air Quality and Continuous Emissions Monitoring' includes details of the federal reference analytical methods for a wide range of pollutants and the calibration of continuous measurement procedures. No additional references were added to the two of the first edition.

Financial Aspects of Environmental Compliance

The short seventh chapter (7 pages) called 'Cost Estimating' is concerned with financial aspects of air pollution control and, for instance, examines the ways of determining the trade-offs between capital and operating costs. Chapter 8 (11 pages) 'Process Design and the Strategy of Process Design' outlines the decisions involved in the choice, design and implementation of pollution control processes. Illustrative examples are taken from the first edition, one of which is the elimination of brown NOx plume from a stack with the chosen control being a packed counter-flow absorption tower. Although this illustrates various intended points the nature of the chemistries involved are not considered nor are today's difficulties and costs associated with transport and disposal of spent absorption solution. As a result unless there are special reasons for not doing so, catalytic ammonia selective catalytic reduction (SCR) is now usually chosen for such NOx control requirements and this efficient process enables modern very low NOx emissions standards to be achieved. Catalytic ammonia SCR technology is briefly discussed later in the book (pages 280–281).

The ninth chapter (9 pages) returns to financial considerations and is called 'Profitability and Engineering Economics' which in separate short sections deals with profitability analysis, effect of depreciation, capital investment and total product cost.

Pollutant Removal Processes

Chapter 10 (8 pages) gives an introduction to control of gaseous pollutants with a focus on volatile organic compounds (VOCs) and their stripping and absorption. Little is said about VOC catalytic oxidation that is commonly used to meet stringent emissions standards today, although later in the book under 'Catalytic Incineration' (pages 235–237) this topic is discussed. Chapter 11 deals with 'Adsorption for Hazardous Air Pollutants and Volatile Organic Compounds Control' (58 pages). This is a major improvement over the corresponding shorter chapter (42 pages) in the first edition that when it appeared was dated and did not consider more efficient tower packings but concentrated on older types such as saddles, the use of which would result in considerably oversized and costly towers that could be improved by the use of modern packings. The present chapter includes more recent generations of mass transfer packings that allow for much more practical and far less costly tower designs. A wide variety of modern structured metal packing devices are illustrated. The twelfth 35 page chapter considers 'Absorption for Hazardous Air Pollutants and Volatile Organic Compounds Control' using solid absorbents such as activated carbons, activated aluminas, silica gels and molecular sieves (zeolites). Their operational advantages and disadvantages are detailed before examining ways of predicting breakthrough times and the necessary in situ regeneration methods available in different situations if charges are not to be replaced.

Chapter 13 'Thermal Oxidation for Volatile Organic Compounds Control' in 17 pages considers three thermal oxidation processors and each is addressed in turn: thermal oxidation (flares), thermal oxidation and incineration and catalytic
oxidation, with most space given to various types of flaring. Only a couple of pages are given to ‘Catalytic Incineration’ although its use is common today. The important role of heat recuperation in many situations is stressed. While the following rather longer Chapter 14 looks at the ‘Control of Volatile Organic Compounds and Hazardous Air Pollutants by Condensation’ in 20 pages, that might be thought more appropriately placed before the previous chapter because of the relative removal efficiencies of the processes involved. Indeed condensation is often the preliminary process for removing high levels of volatile organic compounds with the advantage of recovering what might be valuable material, followed by one of the processes discussed in the earlier chapter which can eliminate organics to the desired low levels. Like the first edition, this chapter has two appendices: one on the derivation of the area model for a mixture condensing from a gas and the second giving the calculation method or ‘algorithm’.

The short (8 pages) Chapter 15 ‘Control of Organic Compounds and Hazardous Air Pollutants by Biofiltration’ is in some ways a gas analogue of reed bed treatment of effluent waters. Here process gas is passed through a moist porous bed of material containing microorganisms (fungi, bacteria and actinomycetes) fed with oxygen and suitable nutrients maintained at an appropriate temperature and pH. When operated correctly good performance can be obtained that is competitive with alternative technologies. The four page Chapter 16 entitled ‘Membrane Separation’ has been lengthened compared with the first edition but still cites only rather old references. What is covered is useful but could have been beneficially expanded. The advantages, such as recovery of a pollutant in a fairly concentrated stream that is also possible with some processes previously discussed in Chapter 12, could have been highlighted, and indeed the present short chapter could well have been cognated into the earlier one.

**NOx and SOx Pollutant Removal**

Chapter 17 ‘NOx Control’ has 13 pages, and as in the first edition nitrous oxide (N\(_2\)O) is included in the term NOx although it usually refers to molecules containing one nitrogen and one or more oxygen atoms and generally is not meant to include N\(_2\)O (4). Combustion processes account for most of the atmospheric NOx with highway vehicles and other transportation being major contributors. The interesting graph of NOx emissions from various sources starting in 1970 only extends to 1997, as in the first edition, and it is a pity so much relevant more up-to-date information was not included. The lowering of NOx from a variety of burner technologies is covered before flue gas treatment techniques are considered. Selective noncatalytic reduction, selective catalytic reduction, ozone oxidation prior to absorption of the nitric acid so formed (Scheme I), catalytic oxidation and absorption of the resulting NO\(_2\) in alkaline solution, and finally oxidation in a corona induced plasma are all discussed. Given the significance of NOx emissions from highway vehicles and other transportation sources and the efficient catalytic systems available to control them it is curious they were not considered in the context of relevance to treating NOx emissions from other sources.

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2
\]
\[
2\text{NO}_2 + \text{O}_3 \rightarrow \text{N}_2\text{O}_5 + \text{O}_2
\]
\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3
\]

Scheme I

Chapter 18 ‘Control of SOx’ has 20 pages and like the first edition relies much on the 1998 paper by Charles Brown (5). The most significant sulfur emission into the atmosphere is sulfur dioxide that is produced in many combustion processes, often at levels higher than the corresponding NOx, with a major source being coal fired power stations. When oxidised to sulfur trioxide (SO\(_3\)) its reaction with water leads to formation of sulfuric acid often formed as fine nanoparticles. There is an interesting graph showing sulfur dioxide emission trends from various sources that starts from 1970 but only extends to 1997; so missing almost two decades of key data. Several acid gas removal processes are discussed including the calcium-based process that involves partial aerial oxidation of first-formed calcium sulfite to very stable calcium sulfate (Scheme II). This process is widely used in coal-based power stations. More expensive sodium-based processes using sodium carbonate or hydroxide are then considered but in all of these situations disposal of spent solution or solid is required that can be expensive today.
of water to sulfuric mist are discussed, but not the deliberate conversion to sulfuric acid when large amounts of sulfur dioxide are available. Here the clean-up costs are offset by a commercially saleable product.

\[
\text{SO}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaSO}_3 + \text{H}_2\text{O}
\]

\[
2\text{CaSO}_3 + \text{O}_2 \rightarrow 2\text{CaSO}_4
\]

Scheme II

**Particulate Pollutant Removal from Gas Streams**

Particulate matter (PM) emissions down to nanoparticle sizes similar to those of bacteria and virus particles have in recent years attracted growing attention because of their serious health implications. Chapter 19 on ‘Fundamentals of Particulate Control’ has 10 pages and usefully covers some of the basic concepts in this area but does not include the various particle measuring techniques nor emphasise the current importance of nanoparticle control.

‘Hood and Ductwork Design’, covered in the 14 page Chapter 20, as its title suggests, deals with the removal of pollutants from specific environments, and like the first edition provides a useful guide to design a variety of hood types and the importance of smooth bends in ducting to prevent erosion when high velocity particles are present. Cyclones are widely used for removal of relatively large particles from process gas streams, and in recent years related technology has been employed in domestic vacuum cleaners. Chapter 21 entitled ‘Cyclone Design’ provides an overview of their design and applications in 11 pages. After outlining fundamental operating principles typical dimensions are given with details such as pressure-drop, before the theoretical collection efficiency limitations are derived that correspond to internal gas rates of between 50 and 100 feet per second.

Wet scrubbing usually involves spraying a mist of water into a gas stream containing PM so as to increase particle size via one or more mechanisms to facilitate their removal trapped in liquid. Chapter 22 deals with the 'Design and Application of Wet Scrubbers' in 26 pages. With traditional micron-sized particles removal efficiency decreases with particle size and normally wet scrubbing is employed for removing particles above about a micron in size. As well as providing particulate control, wet scrubbing can also selectively remove certain gaseous components so serving a dual function. Mechanisms of particle growth in a mist of liquid are reviewed before outlining different types of wet scrubbers and the key factors needed for their design and implementation. Although there was some rearranging of the material from the first edition, it remains effectively the same in the new edition and there is no significant updating of the text or references.

Filtration of particles from a dry gas stream and especially from an air stream is frequently done using a variety of porous materials including ‘ceramic candles’, paper cartridges and fabric bags. On the large scale fabric bags are convenient to operate, shake and empty with the important attraction of being cost effective and traditionally units having several bags are called ‘baghouses’. Chapter 23 called ‘Filtration and Baghouses’ in its 23 pages discusses some of the fundamentals of filtration and bag fabric properties, before turning to factors such as pressure drop during use and the effect of removing the collected filter cake. The modes of bag failure include fibre weakening during use caused by flexing or chemical attack. Their design should provide high geometric surface and for optimal performance often a fresh bag is first treated with large particles to encourage the development of a filter cake on the surface to prevent entraining small particles within the fabric that leads to high pressure drop. The last section on design theory is an addition over that in the first edition and includes factors such as the number of compartments as well as an example of a baghouse design.

Like elsewhere in the book, the final Chapter 24 called ‘Electrostatic Precipitators’ closely follows that in the first edition without updating the now rather old references or highlighting the relevance of any recent developments. Notwithstanding this the coverage in 15 pages of this important technology for removal of PM is very useful. In an electrostatic precipitator a potential of several tens of kilovolts is applied to thin wires spaced a few inches apart that run through holes in collector plates. The applied potential is sufficient to form a corona around the wires without flash-over or sparking, and ions from the corona collide with larger particles thus charging them so they migrate to the oppositely charged collecting plate surfaces where they are retained until deliberately removed. More important for smaller particles is diffusion charging where a charge is acquired by particles moving in a sufficiently high potential gradient. The nature and particularly the resistivity of the particles concerned
is important for efficient electrostatic precipitation, and for example flue gas from power plants burning low sulfur coal has to be conditioned by introducing into the gas small amounts of sulfuric acid or its precursor sulfur trioxide. A range of additives have been used in different situations.

**References and Index**

As mentioned previously rather than have references listed at the end of each chapter as in the first edition, in the second edition they are collected together in eleven pages before a useful general index which occupies a similar number of pages.

**Conclusions**

The second edition of the “Air Pollution Control Technology Handbook” closely follows the outline and content of the first edition, with some updates in several places. The updated review of the Clean Air Act is well done and a notable feature is in the much enlarged Chapter 11 on the use of packed towers for absorption of volatile organic compounds that now includes modern metal structured tower packing designs. Overall this book provides a useful general reference for chemical engineers and others involved with the control of pollution emissions from industrial plants and as such it should be available in appropriate libraries.

**References**


**The Reviewer**

Martyn Twigg retired as Johnson Matthey’s Chief Scientist in 2010. Since retiring Martyn has maintained research activities with several universities in the UK and overseas, and has honorary positions at some. His consulting business is thriving with work in a variety of areas many of which are providing new and exciting challenges, additionally novel catalytic systems have been developed and put into production.
Johnson Matthey Highlights

**A selection of recent publications by Johnson Matthey R&D staff and collaborators**


A technically feasible biological gas-to-liquid fuel (bio-GTL) process is demonstrated for the first time. The aerobic methanotrophic bacterium, *Methylomicrobium buryatense*, was used to produce a maximum fatty acid content of 10% of dry cell weight from CH$_4$ in batch cultures in a continuous gas sparging fermentation system. Novel lipid extraction methodology with advanced catalyst design was then used to prove the feasibility of upgrading phospholipids to hydrocarbon fuels. Up to 95% of the fatty acids were recovered by two-stage pretreatment and hexane extraction of the aqueous hydrolysate. The extracted lipids were then upgraded by hydrodeoxygenation using a palladium on silica catalyst. The final hydrocarbon mixture is 88% pentadecane.

**Heavy Duty Diesel Engine Emission Control to Meet BS VI Regulations**

S. Chatterjee, M. Naseri and J. Li, SAE Technical Paper 2017-26-0125, 2017

From 2020 the BS VI emission regulations in India will require both advanced NOx control and advanced PM control along with particle number limitations. This will require implementation of full diesel particulate filter (DPF) and simultaneous NOx control using SCR technologies. This presentation gives an overview of various DOC, DPF and SCR catalyst technologies and their applications, with respect to their implementation for BS VI HDD regulations. DPF technologies have already been implemented in systems for the Euro VI and US 10 HDD regulations.

**Quantitative 3D Visualization of the Growth of Individual Gypsum Microcrystals: Effect of Ca$^{2+}$:SO$_4^{2–}$ Ratio on Kinetics and Crystal Morphology**


The present study elucidates the influence of the ratio of Ca$^{2+}$ to SO$_4^{2–}$ ions at constant supersaturation on the rate of growth at the major crystal faces of gypsum. The 3D time-evolution of microcrystals are measured by *in situ* AFM and these measurements are coupled to a diffusion model. The growth rate at the {100} and {001} faces is found to be highly sensitive to solution stoichiometry, with needle-like crystals forming in Ca$^{2+}$-rich solutions and plate-like crystals forming in SO$_4^{2–}$-rich solutions. The highest growth rate was found using a stoichiometric solution of Ca$^{2+}$:SO$_4^{2–}$.

**Unravelling the Mystery of Palladium Acetate**


Pd$_3$(OAc)$_6$, 1, is used to catalyse organic transformations such as C–H activation and cross-coupling and is used for manufacturing pharmaceuticals and agrochemicals. There are two typical impurities found in commercial samples. This study systematically investigates high purity palladium acetate, 1, and the two main impurities: palladium acetate nitrite, 2, and polymeric palladium acetate, 3. 3 was found to be just as active as 1 or 2 under specific conditions, but shows reduced performance at lower temperatures and in the absence of a phosphine ligand. In pre-catalyst manufacture, pure 1 gave the best yield and purity, and hence may be the ideal choice for reliable results.
Full Deflection Profile Calculation and Young’s Modulus Optimisation for Engineered High Performance Materials


The effects of microstructural design and sintering process used in the manufacture of engineered materials for additive manufacturing applications in medicine, engineering and technology are studied. A new methodology is presented which shows that the full deflection profile can be calculated from video recordings of bending tests, Young’s modulus can be characterised by an optimisation algorithm and optical distortions can be quantified. The results are compared with other standard tests. The new procedure allows the Young’s modulus of highly stiff materials to be evaluated with greater accuracy than possible with previous bending tests and extends to this class of materials the possibility to evaluate both the elastic modulus and the tensile strength with a single mechanical test.

Enhanced MEA Performance for PEMFCs under Low Relative Humidity and Low Oxygen Content Conditions via Catalyst Functionalization


A new way to enhance catalyst performance for the next generation of catalytic materials for PEMFCs is demonstrated. Functionalised annealed-Pt/Ketjen black EC300j(a-Pt/KB) and dealloyed-PtNi/Ketjen black EC300j(d-PtNi/KB) catalysts using p-phenyl sulfonic acid improved the performance of MEAs in PEMFCs. The size of Pt and PtNi catalyst particles was increased and there was additional leaching of Ni from the PtNi catalyst. Formation of nanoporous PtNi nanoparticles was promoted. Catalyst layers with narrower pore size distributions were formed. Improved high current density performance was observed under reduced RH conditions especially when using reactant gases with low relative humidity.

Reverse Monte Carlo Studies of CeO$_2$ using Neutron and Synchrotron Radiation Techniques


The structure of a crystalline CeO$_2$ was extracted by a reverse Monte Carlo analysis from neutron total scattering (consisting of both neutron diffraction and pair-distribution functions) and CeL$_3$- and K-edge EXAFS data. A notable difference was observed between using short ranged X-ray absorption spectroscopy data and using medium long range pair-distribution functions and neutron diffraction data regarding the disorder of Ce atoms. This demonstrates the significance of studying multiple length scales and radiation sources.

Understanding and Overcoming the Limitations of Bacillus badius and Caldalkalibacillus thermarum Amine Dehydrogenases for Biocatalytic Reductive Amination


The kinetic and thermostability parameters were investigated for a newly engineered amine dehydrogenase from a phenylalanine dehydrogenase from Caldalkalibacillus thermarum and were compared against an existing amine dehydrogenase from Bacillus badius. The former showed an increased thermostability (melting temperature, T$_m$) of 83.5°C compared to 56.5°C for the latter. This newly engineered enzyme was also
used in the reductive amination of up to 400 mM of phenoxy-2-propanone (c = 96%, ee (R) <99%) in a biphasic reaction system using a lyophilised whole-cell preparation. The lower turnover number of the existing amine dehydrogenase compared to their phenylalanine dehydrogenase counterpart was studied by computational docking simulations.

**Key Considerations for High Current Fuel Cell Catalyst Testing in an Electrochemical Half-Cell**


An economical and novel half-cell method for swiftly and accurately measuring oxygen reduction catalysts in different practical electrode formats, including GDE and bonded GDE/membrane layers is shown. The challenges in developing such a test platform were highlighted with a concise summary of key design considerations and fuel cell current densities of ~1 A cm⁻² were achieved. A simple, reproducible process of measuring catalyst performance was provided by constant current polarisations with IR drop measurement at each stage. At a substantially lower testing cost the ORR activity of commercial products was accurately provided by the half-cell used in this study and showed good agreement with measurements made in fuel cell hardware. Many types of GDE and CCM with different catalyst layers can be characterised by this half-cell method.

**Mild sp²Carbon–Oxygen Bond Activation by an Isolable Ruthenium(II) Bis(dinitrogen) Complex: Experiment and Theory**


At temperatures below 40ºC the isolable ruthenium(II) bis(dinitrogen) complex [Ru(H)(N₂)₂(PCI₃)] reacts with aryl ethers (Ar–OR, R = Me and Ar) comprising a ketone directing group to achieve sp²C–O bond activation. The oxidative addition of the C–O bond to Ru(II) happens in an asynchronous manner with Ru–C bond formation prior to C–O bond breaking in a low energy Ru(II)/Ru(IV) pathway for C–O bond activation, was concluded by DFT studies. sp²C–H bond activation was demonstrated to be more simplistic compared to sp²C–O bond activation by experiments and DFT calculations.

**Combined In Situ XAFS/DRIFTS Studies of the Evolution of Nanoparticle Structures from Molecular Precursors**


The formation of PdO nanoparticles from two different impregnated Pd precursors, Pd(NO₃)₂ and Pd(NH₃)₄(OH)₂ were studied, and was captured by a spectroscopic method for advanced in situ characterisation. The temperature assisted pathway for ligand decomposition was identified by time-resolved diffuse reflectance infrared Fourier transform spectroscopy which demonstrated that NH₃ ligands are oxidised to N₂O and NO⁻ species but NO⁻ ligands help join Pd centres via bidentate bridging coordination. By using this spectroscopic method in conjunction with simultaneous X-ray absorption fine structure spectroscopy, the following nucleation and growth mechanisms of the previous metal oxide nanoparticles were determined. The formation and growth of larger PdO nanoparticles at lower onset temperature (<250ºC) was assisted by the bridging capability of Pd(NO₃)₂. However, impregnation from [Pd(NH₃)₄]²⁺ results in well isolated Pd centres attached to the support which needs a higher temperature (>360ºC) for migration to develop observable Pd–Pd distances of PdO nanoparticles.

**Electrochemical and Spectroscopic Characterization of an Alumina-coated LiMn₂O₄ Cathode with Enhanced Interfacial Stability**


The electrochemical performances and stability of the LiMn₂O₄ cathode at high temperatures were enhanced by pristine LiMn₂O₄ which was synthesised by solid state route and coated by an Al₂O₃ layer through co-precipitation process. A pure phase and crystallised nanomaterial forming clusters were observed by XRD, scanning and transmission electron microscopy. Galvanostatic cycles at several charge/discharge rates were used to study the cycling performances of pristine and modified materials. A combination of galvanostatic cycles at 1C and electrochemical impedance spectroscopy at T = 25ºC and T = 50ºC show that the electrode/electrolyte interface of Al₂O₃-modified LiMn₂O₄ is stabilised by suppressing Mn dissolution which exhibits improved cycleability particularly at high temperatures.
Coordination Compounds of Hexamethylenetetramine with Metal Salts: A Review

Properties and applications of a versatile model ligand

Reviewed by Jia Kaihua* and Ba Shuhong
Military Chemistry and Pyrotechnics, Shenyang Ligong University, Shenyang, 110186, China

*Email: 15998277518@163.com

Hexamethylenetetramine (hmta) was chosen as a model ligand. Each of the four nitrogen atoms has a pair of unshared electrons and behaves like an amine base, undergoing protonation and N-alkylation and being able to form coordination compounds with many inorganic elements. The ligand can be used as an outer coordination sphere modulator of the inner coordination sphere and as a crosslinking agent in dinuclear and multinuclear coordination compounds. It can also be used as a model for bioactive molecules to form a great number of complexes with different inorganic salts containing other molecules. Studies of hmta coordination compounds with different metal salts have therefore attracted much attention. The present review summarises the synthesis, preparation, structure analysis and applications of coordination compounds of hmta with different metal salts.

Introduction

Hexamethylenetetramine as a reagent has been used as a source of −CH=N− and −CH= functions. It has a cage-like structure and is considered to be a crucial basic material for the chemical industry. It has been used in many fields including as a curing agent for phenolic resins (1), as an accelerator in vulcanisation (2), in food preservatives (3) and explosives (4) because of its useful properties including high solubility in water and polar organic solvents (5). In addition, hmta can act as a multifunctional ligand, using its N atom to form coordination complexes with many transition metals (6–10). It has been employed to prepare complexes with metals, and has been increasingly applied in chemical synthesis where it has received increasing attention due to its simple operation, mild conditions and environmental friendliness (11, 12).

1. Coordination with Metal Salts

A large number of complexes of hmta and metal salts have been studied and reports on their synthesis, preparation, structure analysis and applications in medicine and military are summarised below.

1.1 Coordination with Metal Salts of Main Group Elements

The magnesium dichromate hmta complex was first crystallised by Debuquet and Velluz with 5H₂O in 1933 (13), but subsequent analysis showed the presence of six water molecules instead of five and on the basis of former study, Dahan put forward the topic of “the crystal structure of the magnesium dichromate hmta hexahydrate complex” in 1973 (14). In Dahan’s study, the
structure of the Mg dichromate hmta hexahydrate complex can be regarded as composed of two CrO₄ tetrahedra joined through a shared oxygen atom, a slightly distorted octahedron around Mg and two hmta molecules. There were no coordination bonds between these groups. They were linked by hydrogen bonds, thus determining the packing and controlling the stability.

Sieranski and Kruszynski (15) studied complexes of Mg and hmta in 2011. Sieranski chose hmta and 1,10-phenanthroline as ligands complexed with Mg sulfate. Coordination compounds \([\text{Mg(H}_2\text{O)}_8]^{2+}\cdot2(\text{hmta})\cdot\text{SO}_4^{2-}\cdot5(\text{H}_2\text{O})\) and \(\text{Mg(C}_2\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2\text{SO}_4\) were synthesised and characterised by elemental and thermal analysis, infrared (IR) spectroscopy, ultraviolet-visible (UV-vis) spectroscopy, fluorescence spectroscopy and X-ray crystallography. The compounds were found to be air stable and well soluble in water.

Mg and calcium have been most studied but heavier alkaline earth metals have also been investigated. For instance, after the development of the strontium-based drug, strontium renelate, which reduces the incidence of fractures in osteoporotic patients, there has been an increasing awareness of this metal’s role in humans.

Khandolkar et al. (16) studied the synthesis, crystal structure, redox characteristics and photochemistry of a new heptamolybdate supported coordination compound \((\text{hmta})_2\{\text{Mg(H}_2\text{O)}_5\}_2(\text{Mo}_7\text{O}_{24})\}_2\cdot3\text{H}_2\text{O}\) in 2015. In their study, the synthesis, characterisation and photochemistry of a new heptamolybdate supported Mg-aqua coordination complex using hmta as structure directing agent was reported.

Tanco Salas (17) studied a complex of aluminium and hmta (‘Al-hmta’) in 2004. The Al-hmta complex was found to have deodorant and therapeutic properties with potential applications in cosmetic and pharmaceutical compositions. Furthermore, the Al-hmta complex had the capacity to trap substances which could subsequently be released, therefore being useful as a carrier of those substances.

1.2 Coordination with Salts of Main Group Elements and Subgroup B Elements

Different metal salts have different coordination abilities and properties. Usually, the complex is made up of the main group element as the central atom, and the subgroup elements appear in the ligands. The combination of two metals may lead to new materials such as polyoxometalates (POMs) with different properties and more stable structures.

Chen et al. synthesised two new extended frameworks based on two different sandwich-type polytungstoarsenates under routine conditions in 2009. They found an advance on the sandwich-type POMs, which had larger volumes and more negative charges than commonly used POMs, allowing the formation of higher coordination numbers with metal cations. Thus, sandwich-type POMs should be excellent building blocks for constructing extended networks (28).

1.3 Coordination with Different Metal Salts of Subgroup B Elements

Allan et al. (30) studied transition metal halide complexes of hmta in 1970. Complexes of hmta have been prepared with the halides of manganese(II), cobalt(II), nickel(II), zinc(II), cadmium(II), iron(II) and copper(II) and also with the thiocyanates of Co(II), Ni(II) and Zn(II). These complexes have been characterised by elemental analysis, vibrational and electronic spectra and magnetic moments.

Ahuja et al. (31) studied hmta complexes with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) thiocyanates. As a potentially tetradentate ligand, hmta complexes with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) thiocyanates were prepared and characterised by their elemental analyses, magnetic susceptibilities, electronic and IR spectral studies down to 200 cm⁻¹, 611 cm⁻¹ as well as X-ray powder diffraction patterns in the solid state. It was shown that hmta, though a potentially tetradentate ligand, acts only as a terminally bonded monodentate ligand or a bidentate ligand bridging between two metal atoms, retaining the chair configuration of the uncoordinated molecule in all these complexes. The tentative stereochemistries of the complexes were discussed.

Agwara et al. (32) studied the physicochemical properties of hmta complexes with Mn(II), Co(II) and Ni(II) in 2004, and in 2012 these complexes had been synthesised in water and ethanol (33). All the complexes were hydrogen-bonded, except the Co complex \([\text{Co(hmta)}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]\] which was polymeric. These complexes were characterised by elemental analysis, IR and visible spectroscopy as well as conductivity measurements. The results suggest octahedral coordination in which the central metal ion is bonded to aqua ligands and the hmta is bonded to the aqua ligands through
<table>
<thead>
<tr>
<th>Formula (M:hmta)</th>
<th>Serial No.</th>
<th>Crystal system, space group</th>
<th>Z, d, Mg m⁻³</th>
<th>R indices (all data)</th>
<th>F (000)</th>
<th>CCDC No.</th>
<th>Reference No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Li(H₂O)₄]⁺⁺•2(hmta)•ClO₄⁻ (1:2)</td>
<td>1a</td>
<td>Orthorhombic, Pn2₁ (No. 33)</td>
<td>4, 1.416</td>
<td>R₁ = 0.0384, wR₂ = 0.0964</td>
<td>976</td>
<td>1003176</td>
<td>(19)</td>
</tr>
<tr>
<td>[Na(ClO₄)(H₂O)(hmta)]₃⁺ (1:1)</td>
<td>1b</td>
<td>Orthorhombic, Pnma (No. 62)</td>
<td>4, 1.625</td>
<td>R₁ = 0.0284, wR₂ = 0.0867</td>
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<td>1003177</td>
<td>(19)</td>
</tr>
<tr>
<td>[Na(hmta)(H₂O)₄]²⁺•2SCN⁻ (1:1)</td>
<td>2b</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>2, 1.366</td>
<td>R₁ = 0.0378, wR₂ = 0.0900</td>
<td>624</td>
<td>802360</td>
<td>(20)</td>
</tr>
<tr>
<td>[K₂(hmta)(SCN)₃]₂⁺ (2:1)</td>
<td>1c</td>
<td>Monoclinic, C2/c (No. 15)</td>
<td>4, 1.559</td>
<td>R₁ = 0.0339, wR₂ = 0.0877</td>
<td>688</td>
<td>833296</td>
<td>(20)</td>
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<tr>
<td>[NaNO₃(hmta)]₃⁻ (1:1)</td>
<td>3b</td>
<td>Trigonal, R3c (No. 161)</td>
<td>6</td>
<td>R₁ = 0.0268, wR₂ = 0.0777</td>
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<td>266846</td>
<td>(8)</td>
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<td>[Li(H₂O)₄]⁺⁺•(hmta)•Cl⁻ (1:1)</td>
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<td>Trigonal, R32 (No. 155)</td>
<td>18, 1.289</td>
<td>R₁ = 0.0339, wR₂ = 0.0881</td>
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<td>859820</td>
<td>(21)</td>
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<td>[Li(H₂O)₄]⁺⁺•(hmta)•I⁻ (1:1)</td>
<td>3a</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>4, 1.629</td>
<td>R₁ = 0.0546, wR₂ = 0.1321</td>
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<td>859821</td>
<td>(21)</td>
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<td>[Na(H₂O)₄]⁺⁺•(hmta)²⁺•2H₂O•2Br⁻ (1:1)</td>
<td>4b</td>
<td>Orthorhombic, Pbca (No. 61)</td>
<td>4, 1.522</td>
<td>R₁ = 0.0388, wR₂ = 0.0806</td>
<td>1376</td>
<td>859822</td>
<td>(21)</td>
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<td>[Na(H₂O)₄]⁺⁺•(hmta)²⁺•2H₂O•2I⁻ (1:2)</td>
<td>5b</td>
<td>Orthorhombic, Pbca (No. 61)</td>
<td>4, 1.649</td>
<td>R₁ = 0.0450, wR₂ = 0.1192</td>
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<tr>
<td>[K(H₂O)(hmta)]₁⁻ (1:1)</td>
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<td>Monoclinic, C2/m (No. 12)</td>
<td>4, 1.913</td>
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<td>859824</td>
<td>(21)</td>
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<tr>
<td>[Rb(H₂O)(hmta)]₁⁻ (1:1)</td>
<td>1d</td>
<td>Monoclinic, C2/m (No. 12)</td>
<td>4, 2.095</td>
<td>R₁ = 0.0234, wR₂ = 0.0639</td>
<td>704</td>
<td>859825</td>
<td>(21)</td>
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<tr>
<td>(hmta)₃•{[Mg(H₂O)₃]₂⁺•[Mo₇O₂₄]³⁻•3H₂O (1:2)}</td>
<td>1e</td>
<td>Monoclinic, C2/c (No. 15)</td>
<td>4, 2.493</td>
<td>R₁ = 0.0382, wR₂ = 0.0829</td>
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<td>(16)</td>
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<td>MgCrO₄•2(hmta)•6H₂O (1:2)</td>
<td>2e</td>
<td>Triclinic P1 (No. 2)</td>
<td>2, 1.595</td>
<td>–</td>
<td>654</td>
<td>–</td>
<td>(14)</td>
</tr>
<tr>
<td>[Mg(H₂O)₆]²⁺•2(hmta)•SO₄²⁻•5(H₂O) (1:2)</td>
<td>3e</td>
<td>Triclinic, P1 (No. 1)</td>
<td>1, 1.446</td>
<td>R₁ = 0.0317, wR₂ = 0.0761</td>
<td>322</td>
<td>813464</td>
<td>(15)</td>
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<tr>
<td>[Mg(H₂O)₆]²⁺•2(hmta)•2NO₃⁻•4H₂O (1:2)</td>
<td>4e</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>4, 1.3782</td>
<td>R₁ = 1.0538, wR₂ = 0.1334</td>
<td>1304</td>
<td>865230</td>
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<tr>
<td>[Ca₂(H₂O)₆(NO₃)₄]²⁺•2(hmta) (1:1)</td>
<td>1f</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>2, 1.580</td>
<td>R₁ = 0.0401, wR₂ = 0.1214</td>
<td>752</td>
<td>865231</td>
<td>(18)</td>
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<td>[Sr₂(H₂O)₆(NO₃)₄]²⁺•2(hmta) (1:1)</td>
<td>1g</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>2, 1.733</td>
<td>R₁ = 0.0304, wR₂ = 0.0735</td>
<td>864</td>
<td>865232</td>
<td>(18)</td>
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### Table II Major Crystal Data and Refinement for Compounds of hmta with Different Metal Salts

<table>
<thead>
<tr>
<th>Formula (M:hmta)</th>
<th>Crystal system, space group</th>
<th>Z, d, Mg m⁻³</th>
<th>R indices (all data)</th>
<th>F (000)</th>
<th>CCDC No.</th>
<th>Reference No.</th>
</tr>
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<tbody>
<tr>
<td>Li₃[Fe(CN)₆]₂(hmta)•5H₂O (3:1:2)</td>
<td>Orthorhobic, Imm2 (No. 44)</td>
<td>2, 1.43</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(22)</td>
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<tr>
<td>Na₃[Fe(CN)₆]₂(hmta)•5H₂O (3:1:2)</td>
<td>Orthorhombic, Pca2₁ (No. 29)</td>
<td>4, 1.50</td>
<td>R₁ = 0.044, wR₂ = 0.043</td>
<td>–</td>
<td>–</td>
<td>(23)</td>
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<tr>
<td>K₃[Fe(CN)₆]₂(hmta)•4H₂O (3:1:2)</td>
<td>Triclinic, P1 (No. 1)</td>
<td>4, 1.48</td>
<td>R₁ = 0.042, wR₂ = 0.045</td>
<td>–</td>
<td>–</td>
<td>(23)</td>
</tr>
<tr>
<td>Ca₂[Fe(CN)₆]₂(hmta)•6H₂O (2:1:2)</td>
<td>Monoclinic, P2₁ (No. 4)</td>
<td>4, 1.72</td>
<td>R₁ = 0.055, wR₂ = 0.055</td>
<td>–</td>
<td>–</td>
<td>(24)</td>
</tr>
<tr>
<td>Cr₂O₃Ca•2(hmta)•7H₂O (1:2:1)</td>
<td>Monoclinic, C2/c (No. 15)</td>
<td>4, 1.676</td>
<td>R₁ = 0.038, wR₂ = 0.036</td>
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<td>–</td>
<td>(25)</td>
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<tr>
<td>Sr₃[Fe(CN)₆]₂•3(hmta)•18H₂O (3:2:3)</td>
<td>Tetragonal, P4₂/mnc (No. 137)</td>
<td>4, 1.83</td>
<td>R₁ = 0.066, wR₂ = 0.062</td>
<td>–</td>
<td>–</td>
<td>(26)</td>
</tr>
<tr>
<td>Ba₃[Fe(CN)₆]₂•2(hmta)•11H₂O (3:2:2)</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>2, 1.76</td>
<td>R₁ = 0.057</td>
<td>–</td>
<td>–</td>
<td>(26)</td>
</tr>
<tr>
<td>[(hmta)-CH₃]K₃₅Na₈₅[K₉₆Ce(AsW₁₀O₃₈)(H₂O)₂]₃•36H₂O</td>
<td>Triclinic, P1 (No. 1)</td>
<td>2, 4.047</td>
<td>R₁ = 0.0591, wR₂ = 0.1743</td>
<td>8504</td>
<td>660692</td>
<td>(27)</td>
</tr>
<tr>
<td>[[(hmta)-CH₃]K₅Na₆Ce(AsVW₁₄O₄₂)]•19H₂O</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>4, 3.681</td>
<td>R₁ = 0.0863, wR₂ = 0.2071</td>
<td>11708</td>
<td>705356</td>
<td>(28)</td>
</tr>
<tr>
<td>[[(hmta)-CH₃]H•H₂O] [(hmta)-CH₃-2OH] [H₃V₁₀O₂₈(Na(H₂O)₄)]•4H₂O</td>
<td>Triclinic, P1 (No. 1)</td>
<td>1, 2.329</td>
<td>R₁ = 0.0389, wR₂ = 0.1141</td>
<td>725</td>
<td>–</td>
<td>(29)</td>
</tr>
</tbody>
</table>
hydrogen-bonding. Antibacterial activities of the ligand and its complexes show that the ligand was active against one out of 10 tested bacteria species; the Co complexes [Co(H₂O)₆](hmta)₂(NO₃)₂•4H₂O and [Co(hmta)₂(NO₃)₂(H₂O)₂] were the most active, showing activity against all the microorganisms. These Co complexes also show greater activity than the reference antibiotic gentamycin against Klebsiella pneumoniae.

Kumar et al. (34) studied Cd hmta nitrate in 2012. The crystal structure analysis of the complex revealed a zig-zag polymeric network in which the Cd(II) ions are linked via the nitrogen atom of the hmta ligand. The complex has a network of hydrogen bonds. For isothermal thermogravimetry (TG) data, use of the isoconversional method was an effective means of unmasking complex kinetics.

Salem (35), of Tanta University, Egypt, studied the catalytic effect of some transition metal hmta complexes in hydrogen peroxide decomposition. The kinetics of the catalytic decomposition of H₂O₂ with Wofatit KPS resin (4% divinylbenzene), (40–80 μm) in the form of 1: 1 Cu(II)-, Mn(II)-, and the rate constant, k (per gram of dry resin) increased in the following sequence: Mn(II) > Co(II) > Cu(II) > Ni(II). The active species, formed as an intermediate at the beginning of the reaction, had an inhibiting effect on the reaction rate. An anionic surfactant, sodium dodecyl sulfate (SDS), considerably inhibited the reaction rate. A probable mechanism for the decomposition process was suggested, which was consistent with the results obtained.

Paboudam et al. (36), reported the results of a study on the influence of solvent on the electronic and structural properties of metal-hmta complexes in aqueous and non-aqueous solvents. Their goal was to study the effect of aqueous and non-aqueous media on the coordination of hmta to metal ions. The protometric studies of the hmta ligand had confirmed that only one basic site was protonated in acidic medium and this ligand was decomposed in acidic medium. In aqueous medium, hmta ligand does not coordinate directly to the metal ions but rather through the H-bonded species. In non-aqueous solvents, hmta coordinates to metal ions displaying diversity in the resulting structures in which hmta can either be monodentate, bridged, tridentate or tetradeutate.

Cai et al. (37) studied a Co(II)-hmta complex prepared using jet milling. An organic metal complex may exhibit different structures when synthesised by different methods. For instance, the Co(II)-hmta complexes Co(hmta)₂Cl₂•10H₂O and Co(hmta)₂Cl₂•6H₂O could be obtained using solution synthesis and mechanical grinding, respectively. The thermogravimetric analysis (TGA) result further confirmed that the structure of the Co(II)-hmta complex obtained by grinding was Co(hmta)₂Cl₂•6H₂O. In addition, there were also studies on complexes of hmta with Cu and silver ion salts.

Stocker (38) studied the crystal structure of a novel Cu(I) cyanide complex with hmta, (CuCN)₃(hmta)₂ in 1990. Grodzicki et al. (39) studied a complex of Cu(II) chloride with hmta in 1991. Their study included spectroscopic and magnetic investigations which indicated that, in the crystal structure of this compound, polymeric chains, 3CuCl₂+hmta•2H₂O and hmta•HCl groups occurred.

Hazra et al. (40) studied four new Cu(II)-hmta complexes synthesised and structurally characterised by X-ray crystallography in 2013. The unique feature of the study was that it had been possible to construct all probable architectures that can be assembled by utilising linear dinuclear Cu(II) carboxylate as a node and hmta as a spacer (angular, pyramidal and tetrahedral) varying only slightly the nonfunctional part of the aromatic carboxylic acids.

A thesis by Degagsa et al. (41) showed that [Cu(hmta)₃(H₂O)]SO₄ had been synthesised by direct reaction of hmta and penta-hydrated Cu sulfate (CuSO₄•5H₂O) and was characterised by magnetic susceptibility measurements, atomic absorption spectroscopy, IR and UV-vis spectroscopic analysis as well as conductivity measurements. Sulfate ion and hmta composition of the complex were also determined using gravimetric and volumetric analysis respectively. The structure of the complex was then proposed to be distorted octahedral in which a single Cu ion is bonded to three water and three hmta molecules. The antimicrobial activity of hmta was enhanced upon complexation due to the increase in lipo-solubility of the complex upon coordination with the ligands. It can also be concluded that the complexes show greater antibacterial activity than the reference antibiotic, gentamycin, towards Staphylococcus aureus and Salmonella typhi. Thus, with further investigation and exploitation this complex could be developed as an antibacterial drug for the treatment of infections caused by these bacteria.

Carlucci et al. (42) studied [Ag₆(hmta)₆]⁶⁺ in 1997. When solutions of AgPF₆ and hmta in
ethanol/dichloromethane were evaporated to dryness, a polymeric species was obtained, \([\text{Ag(hmta)}][\text{PF}_6]_2\cdot\text{H}_2\text{O}\), containing a three-dimensional (3D) triconnected network topologically related to the prototypical SrSi_2.

Plotnikov et al. (43) studied antibacterial and immunomodulatory effects of hmta Ag nitrate in 2016. The antibacterial properties and influence on immune blood cells of the Ag-based compound with general formula \([\text{Ag(hmta)}]_n\text{NO}_3\) were investigated. A noticeable inhibitory effect of the drug was observed only at high concentration in phytohemagglutinin (PHA)-stimulated reaction of blast transformation of lymphocytes (RBTL). Based on this result, the tested Ag complex could be considered as a potential candidate for an antibacterial drug with low toxicity.

1.4 Coordination with Metal Salts of Lanthanide Elements

Zalewicz (82) carried out thermal analysis of complex salts of lanthanide chlorides with hmta in 1989. Thermal decomposition of lanthanide chloride complex salts with hmta of the general formula \(\text{LnCl}_2\cdot2\text{hmta}\cdot\text{nH}_2\text{O}\) (Ln = lanthanum, praseodymium, neodymium, samarium, dysprosium, erbium; \(n = 8, 10, 12\)) was examined. Mechanisms of the thermal dehydration reaction of these salts were established and kinetic parameters of the first state of the dehydration reaction were determined. The following year, the same survey was carried out for lanthanide bromine salts (83). Zalewicz et al. (84) carried out coupled thermogravimetry-mass spectrometry (TG-MS) investigations of lanthanide(III) nitrate complexes with hmta in 2004. New transition metal compounds of the general formula \(\text{Ln(NO}_3)_2\cdot2[\text{hmta}]\cdot\text{nH}_2\text{O}\), where \(\text{Ln} = \text{La, Nd, Sm, gadolinium, terbium, Dy, Er, lutetium; n = 7–12}\), were obtained. The compounds and the gases evolved in the course of their thermal decomposition were characterised by TGA. The measurements were carried out in air and argon environments in order to compare the intermediate products, final products and the mechanism of the thermal decomposition. The combined TG-MS system was used to identify the main volatile products of thermal decomposition and fragmentation processes of the obtained compounds.

Singh et al. (85) studied the kinetics of thermolysis of La nitrate with hmta in 2014. The highlights were the confirmation of the crystal structure of this complex by X-ray crystallography, its thermal analysis by TG and thermogravimetry coupled with differential scanning calorimetry (TG-DSC), the discovery that the complex is insensitive towards impact and friction and the evaluation of its kinetics by model fitting. The preparation, characterisation and thermolysis of the La nitrate complex with hmta were investigated.

Trzesowska et al. (86) studied the synthesis, crystal structure and thermal properties of a mixed ligand 1,10-phenanthroline and hmta complex of La nitrate, providing insight into the coordination sphere geometry changes of La(III) 1,10-phenanthroline complexes. Geometry optimisation was carried out using a density functional theory (DFT) method using the Becke, three-parameter, Lee-Yang-Parr (B3LYP) functional by means of the Gaussian 03 program package. The minimal basis set CEP-4G was used on La and 6-31G(d’) on oxygen, nitrogen, carbon and hydrogen atoms.

1.5 Coordination with Metal Salts of Quaternary Nitrogen

In Table IV, the grey background compounds are made up of hmta coordinated with quaternary nitrogen, while those on a white background are formed by coordination of hmta molecules. In other words, the hmta molecule links to other small atoms or molecules directly, to form new molecules with different properties. This particular mode of coordination makes it easier for molecules in such complexes to be connected and form mesh structures (Scheme I).

Interestingly, it was found that when the hmta is changed into a \([\text{hmta-CH}_3]^+\) cation during reaction, acid-catalysed decomposition of some hmta molecules resulted and led to a subsequent alkylation of hmta in solution (27).

2. Discussion of the Coordination Mode of hmta with Metal Salts

2.1 Effect of Different Metal Cations

The reaction of main group metal salts with hmta leads to the formation of coordination compounds, mononuclear in case of lithium compounds, dinuclear in other element compounds. The electronic properties of the cations strongly influence the coordination modes of both hmta molecules and anions. Li ions are four-coordinated, Na, potassium and rubidium ions are six-coordinated, and Mg, Ca, Sr and barium ions are six or more. Thus the
<table>
<thead>
<tr>
<th>Formula (M:hmta)</th>
<th>Crystal system, space group</th>
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<th>R indices (all data)</th>
<th>F (000)</th>
<th>CCDC No.</th>
<th>Reference No.</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="NO%E2%82%83">Fe(H₂O)₆</a>₂•2(hmta)•4H₂O (1:2)</td>
<td>Triclinic, P1 (No. 1)</td>
<td>1, 1.523</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(44)</td>
</tr>
<tr>
<td><a href="NO%E2%82%83">Fe(H₂O)₆{(H₂O-(hmta)})₂</a>₂•4H₂O (1:2)</td>
<td>Triclinic, P1 (No. 2)</td>
<td>1, 1.562</td>
<td>R₁ = 0.039, wR₂ = 0.088</td>
<td>976</td>
<td>–</td>
<td>(45)</td>
</tr>
<tr>
<td>H₂V₁₀O₂₈•2(hmta)•8H₂O (5:1)</td>
<td>Monoclinic, C2/m (No. 12)</td>
<td>2, 2.252</td>
<td>R₁ = 0.0396, wR₂ = 0.1068</td>
<td>1384</td>
<td>729399</td>
<td>(46)</td>
</tr>
<tr>
<td>H₂V₁₀O₂₈•{(hmta)•CH₂OH}₂•6H₂O (5:1)</td>
<td>Triclinic, P1 (No. 1)</td>
<td>1, 2.294</td>
<td>R₁ = 0.0295, wR₂ = 0.0792</td>
<td>704</td>
<td>685560</td>
<td>(47)</td>
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<tr>
<td>H₂V₁₀O₂₈•{(hmta)•CH₂OH}₂•4H₂O (5:1)</td>
<td>Monoclinic, C2/m (No. 12)</td>
<td>2, 2.275</td>
<td>R₁ = 0.0352, wR₂ = 0.0932</td>
<td>1368</td>
<td>746415</td>
<td>(47)</td>
</tr>
<tr>
<td>[(hmta)•CH₃][H₂V₁₀O₂₈]</td>
<td>Monoclinic, C2/m (No. 12)</td>
<td>2, 2.247</td>
<td>R₁ = 0.0358, wR₂ = 0.0896</td>
<td>1348</td>
<td>–</td>
<td>(48)</td>
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<tr>
<td>[(hmta)•H][{(hmta)•CH₂OH}₂][H₂V₁₀O₂₈]•6H₂O (10:3)</td>
<td>Orthorhombic, Pna2¹ (No. 33)</td>
<td>4, 2.077</td>
<td>R₁ = 0.0573, wR₂ = 0.1052</td>
<td>3112</td>
<td>–</td>
<td>(48)</td>
</tr>
<tr>
<td>Mn(hmta)₆(H₂O)₁₂(NO₃)₂•4H₂O (1:2)</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>4, 1.42</td>
<td>R₁ = 0.046, wR₂ = 0.118</td>
<td>1355.7</td>
<td>211785</td>
<td>(49)</td>
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<tr>
<td>[Mn(H₂O-(hmta)-H₂O)₂{(H₂O-CIO₄)₂}(H₂O)₂] (1:1)</td>
<td>Triclinic, P1 (No. 2)</td>
<td>1, 1.583</td>
<td>R₁ = 0.056, wR₂ = 0.126</td>
<td>355</td>
<td>658325</td>
<td>(45)</td>
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<tr>
<td>[Mn(H₂O)₆(NO₃)₂•2(hmta)•4H₂O (1:2)</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>4, 1.416</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(50)</td>
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<tr>
<td>(hmta)₃Mn(OH₂)₂(Br)₂ (1:2)</td>
<td>Orthorhombic, Pna2₁ (No. 33)</td>
<td>4, 1.865</td>
<td>R₁ = 0.0241</td>
<td>1068</td>
<td>293765</td>
<td>(51)</td>
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<td>[Mn₂O₂(CCCMe)₆(hmta)₃]•(n-C₃H₇OH) (1:1)</td>
<td>Hexagonal, P6₃/m (No. 176)</td>
<td>2, 1.224</td>
<td>R₁ = 0.0702, wR₂ = 0.1783</td>
<td>1350</td>
<td>837612</td>
<td>(52)</td>
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<tr>
<td>[Mn₂O₂(CCCMe)₆(hmta)₃]•(C₆H₅CH₃) (1:1)</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>4, 1.349</td>
<td>R₁ = 0.0482, wR₂ = 0.0997</td>
<td>2764</td>
<td>837613</td>
<td>(52)</td>
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<tr>
<td>[MnFe₂O(O₂CCMe)₃(hmta)]₂•0.5MeCN (1:2:2)</td>
<td>Orthorhombic, Aea₂ (No. 41)</td>
<td>8, 1.300</td>
<td>R₁ = 0.0867, wR₂ = 0.15156</td>
<td>4624</td>
<td>837614</td>
<td>(52)</td>
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<td>[MnFe₂O(O₂CCMe)₃(hmta)]₂•Me₃CCO₂H•(n-C₆H₁₄) (1:2:2)</td>
<td>Orthorhombic, Pbcn (No. 60)</td>
<td>8, 1.306</td>
<td>R₁ = 0.1273, wR₂ = 0.2047</td>
<td>5184</td>
<td>837615</td>
<td>(52)</td>
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<tr>
<td>[MnFe₂O(O₂CCMe)₃(hmta)₁.₅]•(C₆H₅CH₃)</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>4, 1.342</td>
<td>R₁ = 0.0731, wR₂ = 0.1366</td>
<td>4632</td>
<td>837616</td>
<td>(52)</td>
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<th>R indices (all data)</th>
<th>F (000)</th>
<th>CCDC Reference No.</th>
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<tr>
<td>Triclinic, P1 (No. 1)</td>
<td>[Ni(hmta)(ClO₄)₂(H₂O)₂]·2(hmta)·2H₂O</td>
<td>R₁ = 0.056, wR₂ = 0.074</td>
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<td>1.1619 (58)</td>
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<td>Orthorhombic, C2/c (No. 15)</td>
<td>[Ni(hmta)(ClO₄)₂(H₂O)₂]·2(hmta)·2H₂O</td>
<td>R₁ = 0.055, wR₂ = 0.076</td>
<td>4</td>
<td>28.1949 (61)</td>
</tr>
<tr>
<td>Monoclinic, C2/c (No. 15)</td>
<td>[Ni(hmta)(ClO₄)₂(H₂O)₂]·2(hmta)·2H₂O</td>
<td>R₁ = 0.054, wR₂ = 0.074</td>
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<td>1.1619 (58)</td>
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<tr>
<td>Orthorhombic, P1 (No. 1)</td>
<td>[Ni(hmta)(ClO₄)₂(H₂O)₂]·2(hmta)·2H₂O</td>
<td>R₁ = 4.135, wR₂ = 0.076</td>
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<td>28.1949 (61)</td>
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<td>Orthorhombic, P1 (No. 1)</td>
<td>[Ni(hmta)(ClO₄)₂(H₂O)₂]·2(hmta)·2H₂O</td>
<td>R₁ = 4.135, wR₂ = 0.076</td>
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<td>28.1949 (61)</td>
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<td>R₁ = 4.135, wR₂ = 0.076</td>
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<td>R₁ = 4.135, wR₂ = 0.076</td>
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<td>28.1949 (61)</td>
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<td>Orthorhombic, P1 (No. 1)</td>
<td>[Ni(hmta)(ClO₄)₂(H₂O)₂]·2(hmta)·2H₂O</td>
<td>R₁ = 4.135, wR₂ = 0.076</td>
<td>4</td>
<td>28.1949 (61)</td>
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<td>Formula (M:hmta)</td>
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<td>([\text{Ni}(\text{H}_2\text{O})_6]<em>3 \text{C}</em>{20} \cdot 2(\text{hmta}) \cdot 4\text{H}_2\text{O}) (1:2)</td>
<td>Triclinic (P1) (No. 1)</td>
<td>1, 1.412</td>
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<td>Triclinic, (P1) (No. 1)</td>
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<td>(\text{Ni}(\text{btc})_2(\text{hmta})_2(\text{H}_2\text{O})) (1:2)</td>
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<td>([\text{Ni}(2\text{-nbz})_2(\mu_2\text{-hmta})(\text{H}_2\text{O})_2]_n) (1:1)</td>
<td>Triclinic, (P1) (No. 1)</td>
<td>2, 1.639</td>
<td>–</td>
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<td>([\text{Ni}(4\text{-nbz})_2(\mu_2\text{-hmta})(\text{H}_2\text{O})_2]_n) (1:1)</td>
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<td>(\text{Cu}(\text{NCO})_2(\text{hmta})_2) (1:2)</td>
<td>Triclinic, (P1) (No. 1)</td>
<td>–</td>
<td>(R_1 = 0.048), (wR_2 = 0.062)</td>
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<td>((\text{CuCN})_2(\text{hmta})_2) (1:2)</td>
<td>Monoclinic, (C2/c) (No. 15)</td>
<td>4, 1.817</td>
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<td>(\text{Cu}_3(\text{hmta})(\text{H}_2\text{O})_2(\text{mal})_2) (2:1)</td>
<td>Orthorhombic, (Imm2) (No. 44)</td>
<td>2, 2.047</td>
<td>(R_1 = 0.0572), (wR_2 = 0.1577)</td>
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<td>([\text{Cu}_3(2\text{-nbz})_6(\mu_2\text{-hmta})]_n) (3:1)</td>
<td>Tetragonal, (I_{4}d) (No. 122)</td>
<td>16, 1.624</td>
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<td>–</td>
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<td>([\text{Cu}_3(\text{pa})_6(\mu_3\text{-hmta})]_n) (3:1)</td>
<td>Triclinic, (P1) (No. 1)</td>
<td>2, 1.491</td>
<td>–</td>
<td>–</td>
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<td>([\text{Cu}_3(4\text{-nbz})_6(\mu_3\text{-hmta})]_n) (3:1)</td>
<td>Trigonal, (P3) (No. 143)</td>
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<td>([\text{Cu}(3\text{-nbz})_2(\mu_4\text{-hmta}) \cdot 6\text{H}_2\text{O}]_n) (1:1)</td>
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<td>([\text{Zn}(\text{H}_2\text{O})_2(\text{hmta}) \cdot 6\text{H}_2\text{O}]_2(\text{H}_2\text{O} \cdot \text{ClO}_4)_2(\text{H}_2\text{O})_2) (1:1)</td>
<td>Triclinic, (P1) (No. 2)</td>
<td>1, 1.639</td>
<td>(R_1 = 0.047), (wR_2 = 0.120)</td>
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<td>([\text{Zn}(\text{hmta})_2(\text{H}_2\text{O})_4]^{2+} \cdot [\text{Zn}(\text{H}_2\text{O})_6]^{2+} \cdot 2\text{SO}_4^{2-} \cdot 6\text{H}_2\text{O}) (1:1)</td>
<td>Triclinic, (P1) (No. 2)</td>
<td>2, 1.634</td>
<td>(R_1 = 0.0792), (wR_2 = 0.2011)</td>
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<td>([\text{Zn}(\text{H}_2\text{O})_6]^{2+} \cdot 2(\text{hmta}) \cdot 2\text{NO}_3^{-} \cdot 4\text{H}_2\text{O}) (1:2)</td>
<td>Triclinic, (P1) (No. 2)</td>
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<td>(R_1 = 0.0324), (wR_2 = 0.0888)</td>
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<td>2, 1.702</td>
<td>(R_1 = 0.0714), (wR_2 = 0.1165)</td>
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<th>F (000)</th>
<th>Z</th>
<th>d, Mg m⁻³</th>
<th>R indices (all data)</th>
<th>wR²</th>
<th>R₁</th>
<th>wR₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn₂(2-nbz)₂(hmta)]</td>
<td>Triclinic, P1 (No. 1)</td>
<td>[Zn₁(3-nbz)₂(hmta)]</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>2, 1.658</td>
<td>4, 1.782</td>
<td>4, 1.913</td>
<td>4, 2.094</td>
<td>4, 2.072</td>
<td>8, 1.815</td>
<td>-</td>
</tr>
<tr>
<td>[Zn₃(3-nbz)₄(hmta)(OH)₂]·2nH₂O</td>
<td>Monoclinic, C2/c (No. 15)</td>
<td>[Cd(hmta)₃(NO₃)₄(H₂O)]·2nH₂O</td>
<td>Monoclinic, C2/c (No. 15)</td>
<td>4, 1.782</td>
<td>4, 1.816</td>
<td>4, 2.072</td>
<td>4, 2.072</td>
<td>4, 2.072</td>
<td>8, 1.185</td>
<td>-</td>
</tr>
<tr>
<td>[Cd(C₂O₄)₆(hmta)(DMF)]</td>
<td>Orthorhombic, Pbca (No. 22)</td>
<td>[Cd(SCN)₂(hmta)₀.₅(H₂O)]·H₂O</td>
<td>Orthorhombic, Pnma (No. 63)</td>
<td>4, 1.782</td>
<td>4, 1.816</td>
<td>4, 2.072</td>
<td>4, 2.072</td>
<td>4, 2.072</td>
<td>8, 1.185</td>
<td>-</td>
</tr>
<tr>
<td>[Cd(H₂O)₄(hmta)]</td>
<td>Orthorhombic, Fdd₂ (No. 43)</td>
<td>{[Cd(H₂O)₄(hmta)]₃·4H₂O}·Cl₂·4H₂O·68DMF</td>
<td>Orthorhombic, P2₁/c (No. 14)</td>
<td>4, 1.782</td>
<td>4, 1.782</td>
<td>4, 1.861</td>
<td>4, 1.861</td>
<td>4, 1.861</td>
<td>8, 1.861</td>
<td>-</td>
</tr>
<tr>
<td>[Cd(H₂O)₄(hmta)]</td>
<td>Cubic, Fd3m (No. 227)</td>
<td>{[Cd(H₂O)₄(hmta)]₃·4H₂O}·Cl₂·4H₂O·68DMF</td>
<td>Cubic, Fd3m (No. 227)</td>
<td>4, 1.782</td>
<td>4, 1.782</td>
<td>4, 1.861</td>
<td>4, 1.861</td>
<td>4, 1.861</td>
<td>8, 1.861</td>
<td>-</td>
</tr>
</tbody>
</table>

Continued
<table>
<thead>
<tr>
<th>Formula (M:hmta)</th>
<th>Crystal system, space group</th>
<th>CCDC No.</th>
<th>Reference No.</th>
<th>Z, d, Mg m⁻³</th>
<th>R indices (all data)</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="H%E2%82%82O">Ag(L₃)(hmta)</a></td>
<td>Orthorhombic, Pca₂₁ (No. 29)</td>
<td>782488</td>
<td>(72)</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>[Ag₂(L₄)(hmta)₂(H₂O)]</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>782489</td>
<td>(72)</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>[Ag₆(L₅)₆(hmta)₆]</td>
<td>Monoclinic, P2₁ (No. 4)</td>
<td>782490</td>
<td>(72)</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>[Ag₆(L₆)₆(hmta)₆]</td>
<td>Monoclinic, P2₁ (No. 4)</td>
<td>782491</td>
<td>(72)</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td><a href="abs">Ag(μ₃-hmta)</a></td>
<td>Orthorhombic, Pmn2₁ (No. 31)</td>
<td>169729</td>
<td>(73)</td>
<td>2, 1.863</td>
<td>-</td>
</tr>
<tr>
<td><a href="ns">Ag(μ₃-hmta)</a></td>
<td>Orthorhombic, Pmn2₁ (No. 31)</td>
<td>169730</td>
<td>(73)</td>
<td>4, 1.675</td>
<td>-</td>
</tr>
<tr>
<td>[Ag(μ₃-hmta)]</td>
<td>Orthorhombic, Pna2₁ (No. 33)</td>
<td>169731</td>
<td>(74)</td>
<td>2, 2.248</td>
<td>R₁ = 0.0670, wR₂ = 0.1624</td>
</tr>
<tr>
<td>[Ag₃(μ₄-hmta)²(H₂O)]</td>
<td>Orthorhombic, Pna2₁ (No. 33)</td>
<td>169732</td>
<td>(74)</td>
<td>4, 2.170</td>
<td>-</td>
</tr>
<tr>
<td>[Ag₈(μ₃-hmta)²(μ₄-hmta)²(m-pma)²(m-H₂O)₃]</td>
<td>Monoclinic, C2/c (No. 15)</td>
<td>169733</td>
<td>(75)</td>
<td>4, 2.148</td>
<td>R₁ = 0.0478, wR₂ = 0.2012</td>
</tr>
<tr>
<td>[Ag(μ₃-hmta)(p-nba)]</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>169734</td>
<td>(75)</td>
<td>4, 1.828</td>
<td>R₁ = 0.0376, wR₂ = 0.1263</td>
</tr>
<tr>
<td>[Ag(μ₃-hmta)(m-nba)]</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>169735</td>
<td>(75)</td>
<td>4, 1.885</td>
<td>R₁ = 0.0380, wR₂ = 0.0848</td>
</tr>
<tr>
<td>[Ag(μ₃-hmta)(dnba)]</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>169736</td>
<td>(75)</td>
<td>4, 1.939</td>
<td>R₁ = 0.0414, wR₂ = 0.1110</td>
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<tr>
<td>[Ag(μ₃-hmta)(α-hna)]</td>
<td>Monoclinic, Pca₂₁ (No. 29)</td>
<td>169737</td>
<td>(75)</td>
<td>4, 1.577</td>
<td>-</td>
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</table>

(Continued)
<table>
<thead>
<tr>
<th>Formula (M:hmta)</th>
<th>Crystal system, space group</th>
<th>CCDC No.</th>
<th>Z, d, Mg m⁻³</th>
<th>R indices (all data)</th>
<th>F (000)</th>
<th>Reference No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(<a href="C_2H_5OH">Ag(\mu^3-hmta)(\beta-hmta)(\beta-hna)</a>)</td>
<td>Orthorhombic, Pca2₁ (No. 29)</td>
<td>-</td>
<td>4, 1.576</td>
<td>-</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td>(<a href="H_2O">Ag(\mu^3-hmta)(noa)</a>(C_2H_5OH))</td>
<td>Orthorhombic, Pbcn (No. 60)</td>
<td>-</td>
<td>8, 1.509</td>
<td>-</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td>([Ag_2(\mu^3-hmta)_2(fa)]\cdot4H_2O)</td>
<td>Orthorhombic, Pbcn (No. 60)</td>
<td>-</td>
<td>4, 1.965</td>
<td>-</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td>([Ag_2(\mu^3-hmta)_2(adp)]\cdot8H_2O)</td>
<td>Orthorhombic, Pbcn (No. 60)</td>
<td>-</td>
<td>8, 1.970</td>
<td>-</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td>([Ag(hmta)(fma)_{0.5}]\cdot2H_2O)</td>
<td>Orthorhombic, Pbcn (No. 60)</td>
<td>-</td>
<td>8, 1.970</td>
<td>-</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td>(<a href="PF_6">Ag_5(hmta)_6</a>\cdot3CH_2Cl_2)</td>
<td>Hexagonal, P6₃/m (No. 176)</td>
<td>-</td>
<td>2, 2.101</td>
<td>-</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td>([Ag_4(hmta)_3(H_2O)]_4(PF_6)\cdot3C_2H_5OH)</td>
<td>Cubic, Pa₃ (No. 205)</td>
<td>-</td>
<td>8, 2.022</td>
<td>-</td>
<td>-</td>
<td>75</td>
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<tr>
<td>([Ag_2(\mu^4-hmta)(Tos)]_2)</td>
<td>Monoclinic, C2/c (No. 15)</td>
<td>-</td>
<td>4, 2.014</td>
<td>-</td>
<td>-</td>
<td>75</td>
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<tr>
<td>([Ag_2(\mu^3-hmta)_2(CF_3SO_3)(H_2O)]_2\cdotH_2O)</td>
<td>Monoclinic, C2/c (No. 15)</td>
<td>-</td>
<td>4, 2.103</td>
<td>-</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td>([Ag_3(hmta)_2(H_2O)]_4(PF_6)\cdot3PF_6)</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>-</td>
<td>4, 2.321</td>
<td>-</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td>([Ag(NO_3)(hmta)])</td>
<td>Orthorhombic, Pca2₁ (No. 29)</td>
<td>-</td>
<td>4, 2.33</td>
<td>-</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td>([Ag(hmta)Br]_2)</td>
<td>Orthorhombic, Cmc2₁ (No. 36)</td>
<td>-</td>
<td>8, 3.850</td>
<td>-</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td>([Hg(hmta)Br]_2\cdot2Hg(SCN))</td>
<td>Orthorhombic, P2₁/m (No. 15)</td>
<td>-</td>
<td>2, 2.830</td>
<td>-</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td>(<a href="hmta">HgCl_2</a>_2\cdot2HgCl_2)</td>
<td>Orthorhombic, Fdd (No. 70)</td>
<td>-</td>
<td>8, 3.548</td>
<td>-</td>
<td>-</td>
<td>75</td>
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### Table IV Major Crystal Data and Refinement for Compounds of hmta with Metal Salts

<table>
<thead>
<tr>
<th>Formula (M:hmta)</th>
<th>Crystal system, space group</th>
<th>Z, d, Mg m⁻³</th>
<th>R indices (all data)</th>
<th>F (000)</th>
<th>CCDC No.</th>
<th>Reference No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[La(NO₃)₂•C₁₂H₂₈N₄•(H₂O)₄]⁺•NO₃⁻•(hmta)•2H₂O (1:1)</td>
<td>Monoclinic, P2₁/n (No. 14)</td>
<td>4, 1.731</td>
<td>R₁ = 0.0504, wR₂ = 0.0396</td>
<td>1520</td>
<td>269659</td>
<td>(86)</td>
</tr>
<tr>
<td>[La(NO₃)₂(H₂O)₆]⁺•2(hmta)•NO₃⁻•H₂O (1:2)</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>4, 1.686</td>
<td>R₁ = 0.0697, wR₂ = 0.1239</td>
<td>-</td>
<td>993310</td>
<td>(85)</td>
</tr>
<tr>
<td>[Nd(H₂O)₆]Cl⁺•2(hmta)•4H₂O (1:2)</td>
<td>Triclinic, P1 (No. 1)</td>
<td>2, 1.638</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(87)</td>
</tr>
<tr>
<td>La(NCS)₃•2(hmta)•9H₂O (1:1)</td>
<td>Orthorhombic, Pnma (No 62)</td>
<td>-</td>
<td>R₁ = 0.0281, wR₂ = 0.0634</td>
<td>-</td>
<td>1003/4553</td>
<td>(88)</td>
</tr>
<tr>
<td>[Ln(H₂O)₆]<a href="hmta">M(CN)₆</a>[FeDy] (1:2)</td>
<td>Cubic, Fm3m (No. 225)</td>
<td>4, 1.655</td>
<td>R₁ = 0.0307, wR₂ = 0.0634</td>
<td>1528</td>
<td>258316</td>
<td>(90)</td>
</tr>
<tr>
<td>[La(NO₃)₂(H₂O)₆]⁺•NO₃⁻•2(hmta)•2H₂O (1:2)</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>4, 1.707</td>
<td>R₁ = 0.0307, wR₂ = 0.0634</td>
<td>1528</td>
<td>258316</td>
<td>(90)</td>
</tr>
<tr>
<td>[Ce(NO₃)₂(H₂O)₆]⁺•NO₃⁻•2(hmta)•2H₂O (1:2)</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>4, 1.712</td>
<td>-</td>
<td>1532</td>
<td>266394</td>
<td>(90)</td>
</tr>
<tr>
<td>[Pr(NO₃)₂(H₂O)₆]⁺•NO₃⁻•2(hmta)•2H₂O (1:2)</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>4, 1.721</td>
<td>-</td>
<td>1536</td>
<td>266395</td>
<td>(90)</td>
</tr>
<tr>
<td>[Nd(NO₃)₂(H₂O)₆]⁺•NO₃⁻•2(hmta)•2H₂O (1:2)</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>4, 1.793</td>
<td>-</td>
<td>1580</td>
<td>-</td>
<td>(90)</td>
</tr>
<tr>
<td>[Sm(NO₃)(H₂O)₃]⁺•2NO₃⁻•2(hmta)•3H₂O (1:2)</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>4, 1.730</td>
<td>-</td>
<td>1628</td>
<td>266396</td>
<td>(90)</td>
</tr>
<tr>
<td>[Eu(NO₃)(H₂O)₃]⁺•2NO₃⁻•2(hmta)•3H₂O (1:2)</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>4, 1.740</td>
<td>R₁ = 0.0333, wR₂ = 0.0879</td>
<td>1632</td>
<td>258317</td>
<td>(90)</td>
</tr>
<tr>
<td>[Gd(NO₃)(H₂O)₃]⁺•2NO₃⁻•2(hmta)•3H₂O (1:2)</td>
<td>Monoclinic, P2₁/c (No. 14)</td>
<td>4, 1.75</td>
<td>-</td>
<td>1636</td>
<td>266397</td>
<td>(90)</td>
</tr>
<tr>
<td>[Dy(H₂O)₃]³⁺•3NO₃⁻•2(hmta)•2H₂O (1:2)</td>
<td>Triclinic, P1 (No. 1)</td>
<td>2, 1.756</td>
<td>R₁ = 0.0287, wR₂ = 0.0754</td>
<td>822</td>
<td>258318</td>
<td>(90)</td>
</tr>
<tr>
<td>[Ho(H₂O)₃]³⁺•3NO₃⁻•2(hmta)•2H₂O (1:2)</td>
<td>Triclinic, P1 (No. 1)</td>
<td>2, 1.767</td>
<td>-</td>
<td>824</td>
<td>266389</td>
<td>(90)</td>
</tr>
</tbody>
</table>

(Continued)
### 2.2 Effect of Different Anions

In the studied compounds, unshared electrons were not only provided by ligands, but also by anions such as Cl\(^-\), Br\(^-\), I\(^-\), NO\(_3\)^-, ClO\(_4\)^-, Cr\(_2\)O\(_7\)^2- and SCN\(^-\). Different anions are mainly used for regulating the electric charge and sometimes make the overall molecule slightly distorted. Among the inorganic anions serving as ligands the most popular is SCN\(^-\) due to its great tendency to link metal ions.

### 2.3 Effect of Water Molecules

Among these compounds, water molecules also play a very important role, providing oxygen atoms or hydrogen bonds and making the overall structure more stable. Thermal analyses show that the water molecules in the investigated compounds were totally removed during thermal decomposition and further heating.

### 2.4 Coordination Positions and Crystal System

The hmta molecule is a tetrafunctional neutral organic ligand which can be used as an outer coordination sphere modulator of an inner coordination sphere or as a crosslinking agent building block in di- and multinuclear compounds. It has been used to assemble new supramolecular structures with metal ions, via various coordination modes, involving one to four N atoms of the hmta molecule.

The ions and molecules appear in different positions, called the inner and outer coordination spheres. For example, main group metal salts coordinate with hmta in the inner coordination

---

**Scheme I. Schematic diagram of alkylation reaction**

<table>
<thead>
<tr>
<th>Formula (M:hmta)</th>
<th>CCDC No.</th>
<th>Reference No.</th>
<th>Z, d, Mg m(^{-3})</th>
<th>R indices (all data)</th>
<th>F (000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Tm(H(_2)O)(_8)](^{3+}) • 3NO(_3) – 2(hmta) • 2H(_2)O</td>
<td>266391</td>
<td>(90)</td>
<td>828</td>
<td>2, 1.781</td>
<td>3192</td>
</tr>
<tr>
<td>[Yb(H(_2)O)(_8)](^{3+}) • 3NO(_3) – 2(hmta) • 2H(_2)O</td>
<td>266392</td>
<td>(90)</td>
<td>830</td>
<td>2, 1.801</td>
<td>3192</td>
</tr>
<tr>
<td>[Lu(H(_2)O)(_8)](^{3+}) • 3NO(_3) – 2(hmta) • 2H(_2)O</td>
<td>266393</td>
<td>(90)</td>
<td>832</td>
<td>2, 1.807</td>
<td>3192</td>
</tr>
<tr>
<td>{H-(hmta)}(^2) (H(_3)O)[Ce(H(_2)O)(_5)Mo(_7)O(_24)] • 4H(_2)O</td>
<td>3192</td>
<td>(91)</td>
<td>4, 2.798</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>{H-(hmta)}(^2) [(UO(_2))(_2) (\text{(C}_4\text{H}_4\text{O}_5))(_2) (\text{OH})] (\text{2H}_2)O</td>
<td>-</td>
<td>(92)</td>
<td>4, 1.5478</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

---

**Table 1. Crystal system, space group, and R indices for the studied compounds.**
sphere in the case of Na, K and Rb compounds, and in the outer coordination sphere in the case of Li, Mg, Ca and Sr compounds. This phenomenon may be affected by many factors, the electronic properties of the cation being the most important. 

Under the action of hmta, different ions and water molecules form different crystal systems: orthorhombic, monoclinic, triclinic, hexagonal, cubic or parallelepiped. Among them, monoclinic and triclinic crystal structures are the most common. There are also some rare 3D hybrid compounds, such as [Na(ClO₄)(H₂O)(hmta)]ₙ, [NaNO₃•hmta]ₙ, [K₂(hmta)(SCN)₂]ₙ, [K(H₂O)(hmta)]Iₙ and [Rb(H₂O)(hmta)]Iₙ. It is thereby demonstrated that simple inorganic anions and organic molecules can be used to construct 3D networks possessing high complexity (multinodal nets with complicated stoichiometry) after proper selection of the molecular species for net self-assembly.

2.5 A Discussion on Synthetic Methods

As the ligands, salts and hmta are soluble in water almost all of the synthetic methods are similar: make the solution at a certain proportion and stir them together for a number of hours, followed by treatment for several days or weeks at either room temperature or a specific temperature. So far, most complexes were prepared by virtue of this method. When the molecules are larger or ligand types are more complex, the synthesis conditions should manipulate a number of variables such as pH, ligand and cation size and type.

2.6 The Similarities and Differences of Transition Metal Complexes

Compared to transition metal coordination compounds, those of alkaline earth metals have not been widely studied. Such materials should be environmentally friendly and their syntheses should be simple and economical. Thus, investigation of alkaline earth metal coordination chemistry is indispensable for obtaining new compounds and new materials.

There has been much research on transition metal complexes with hmta as well as comparison of their performance in a range of potential applications. Among the most studied are complexes with Ni, Mn, Cu or Zn. As a transition metal centre, Ni is well suited for the construction of various coordination polymers with N- and/or O-ligands on account of its variable oxidation states, different geometries, spectral and magnetic features and ligand field effects.

Organometallic complexes of lanthanide metals are mainly used to catalyse organic reactions. Some other functional studies are still in progress.

3. Applications of hmta with Metal Salts

3.1 Military Applications

Complexes of hmta have been investigated for military applications as explosives. Singh et al. (45) characterised a complex of lanthanum nitrate with hmta by X-ray crystallography. Thermolysis of the complex was undertaken using TG and TG–DSC, a micro-destructive technique which does not require any pretreatment before analysis and can provide useful information about thermal and chemical reaction processes in a relatively short time. In order to establish safe handling procedures, sensitivity of explosives towards mechanical destructive stimuli such as impact and friction are measured. The development of highly energetic materials includes processability and the ability to attain insensitive munitions (IM). The paper investigated the preparation of a lanthanum nitrate complex of hmta in water at room temperature. The complex, of molecular formula [La(NO₃)₃(H₂O)₆](2hmta)(NO₃)₂(H₂O), was characterised by X-ray crystallography. Thermal decomposition was investigated using TG, TG–DSC and ignition delay measurements. Kinetic analysis of isothermal TG data was carried out using model fitting methods as well as model free iso-conversional methods. The complex was found to be insensitive towards mechanical destructive stimuli such as impact and friction.

In order to identify the end product of thermolysis, the X-ray diffraction (XRD) patterns were examined which proved the formation of La₂O₃. The crystal structure reveals that the lanthanum metal had a coordination number of 10. TG–DSC studies showed a three-step decomposition of the complex. The oxidation-reduction reaction between oxidiser (NO₃) and fuel (hmta) led to ignition yielding La₂O₃ and gaseous products. The oxide residue was confirmed by the XRD pattern. The impact and friction sensitivity measurements showed that this compound exhibited remarkably low sensitivity towards impact (>73 J) and friction (>360 N). This nitrogen-rich metal complex may be a good candidate as a ‘green’ metal energetic.
material for potential applications in propellants, explosives and pyrotechnics.

4. Conclusion

Through studies of the synthesis, preparation, structure analysis and applications of complexes of hmta with different metal salts, a rough understanding of these materials has been gained. From the earliest synthetic and structural analyses, the physical and chemical properties and a range of applications have been investigated. The understanding gained from this provides a basis for the study of other organic ligands. With the development of computer technology, future research can also be carried out by theoretical calculation to select better metal complexes.

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Recent Advances in Controlled and Modified Atmosphere of Fresh Produce

Postharvest technologies to reduce food waste and maintain fresh produce quality

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World trade has transformed food retailing and driven the development of technology for the transportation and storage of horticultural products, providing year-round supply of fruit and vegetables. Horticultural produce is highly perishable, as fruit and vegetables continue their metabolic processes that lead to ripening and senescence after harvest, making them ultimately unmarketable. Advanced postharvest technologies are essential for reducing food waste while maintaining high standards of safety and quality. Together with cold storage, controlled atmosphere (CA) and modified atmosphere packaging (MAP) have been applied to alter the produce’s internal and external environment, decreasing its metabolic activity and extending shelf-life. Both CA and MAP have benefitted from technological innovation. Respiratory quotient control has improved the management of conventional and recently developed CA systems; gas scavengers have made MAP more efficient; and the inclusion of natural additives has enhanced food safety across the supply chain. This paper critically reviews the application of new postharvest techniques to manipulate gaseous environments and highlights areas that require further study.

Introduction

Over the past decades, the nature of food retailing has been transformed by worldwide trade. The development of infrastructure, facilities and technology across the supply chain, together with the liberalisation of the global economy, have driven consumers’ expectations for year-round availability of fresh fruit and vegetables (1). Maintaining freshness requires the efficient transport and storage of highly perishable horticultural produce. After harvest, fruit and vegetables maintain their physiological systems and continue with their metabolic activity. Respiration and transpiration lead to the consumption of substrates, such as sugars and organic acids, and the loss of water, which accompanies ripening and senescence, eventually making the produce non-marketable. Food waste is a global problem that has increased in the last ten years.

In developed countries, access to advanced postharvest technology is essential for reducing loss and waste while maintaining food safety and quality. Historically, cold storage such as cellars, basements, caves and ice houses have been used to preserve fresh produce (2). The technology has
advanced since the recognition of microbial food spoilage in the 18th century. Fruit and vegetables must be cooled to remove heat: before processing, transporting and storing (3). Nowadays, refrigeration units are more cost-effective, sustainable and consume less energy. They can be used as centralised systems that operate at a wide range of temperatures and respond quickly to changes in working temperature. Reducing storage temperature decreases enzymatic activity, respiratory and metabolic processes, and hence can extend shelf-life. Yet, current market requirements are more demanding, having longer postharvest periods where high quality and food safety standards must be maintained. Because of this, other techniques such as CA storage and MAP are used to enhance and augment cold storage. These, either actively or passively, alter the atmosphere composition surrounding and within the produce in order to influence cellular metabolism, causing a reduction in catabolism in climacteric fruit and vegetables (4), and an inhibition of enzymatic reactions (5). Each commodity has its own optimal CA and MAP conditions which, together with controls on storage duration, relative humidity and ethylene concentration, may influence shelf-life and flavour-life. An important feature of the technologies is that they are innocuous and can be applied to organic fruit and vegetables. CA and MAP techniques have been evolving because of the development of new technology and improved knowledge of fresh produce physiology. This review outlines the most recent approaches in CA and MAP techniques highlighting their advantages, disadvantages and main applications.

**Controlled Atmosphere Storage**

CA technology is one of the most successful techniques developed by the postharvest industry in the 20th century. However, ca. 100 BC the Romans already stored grain in sealed underground pits (6, 7). Jacques Etienne Berard observed in the early 1800s in France that fruit did not ripen in a low oxygen atmosphere (8). In 1927, Kidd and West found that a reduction in respiration rate in apples was correlated to an extension of storage life (9). Since this time, postharvest scientists have progressively studied the effect of different atmospheres on most horticultural produce to obtain optimal concentrations of gases (10–13). The application of conventional CA generally consists of increasing carbon dioxide levels and decreasing the oxygen concentration. It has been shown that CA alters the atmosphere surrounding the product and thus the internal gas composition, reducing the fruit or vegetable metabolic activity and delaying senescence. Some controversy exists around the use of CA. This is because the consumer may think that CA storage confers a counterfeit freshness to the produce they buy. The reality is that CA extends the seasonal availability of produce, maintains the physicochemical and functional quality and can reduce the cost to the consumer. On top of these advantages, the reduction of storage disorders such as chilling injury (14–16) help reduce food waste, which lowers economic, social and environmental impact (17). Furthermore, its potential as an alternative to using postharvest chemicals is a subject of high interest (18, 19).

The effectiveness of CA depends on: cultivar, climacteric nature, storage temperature, selected concentration of gases, stage of maturity, commodity quality at harvest and pre-storage treatments. If the conditions are optimal for the chosen crop, senescence will be delayed by: reducing respiration rate and substrate oxidation, delaying ripening of climacteric fruit and reducing the rate of ethylene production (20). Also, CA reduces the pathogen respiration rate, and can maintain natural disease resistance. In summary, CA prolongs storage life. However, inappropriate CA store management can provoke the development of off-odours, off-flavours and physiological disorders. To obtain the best results, it is essential to have a deep knowledge about the produce physiology and adapt the technology to each scenario. It is generally accepted that applying CA as soon as possible is the best option to maximise efficacy. Yet this causes a dramatic change in the surrounding environment that can elicit abiotic stress in the product (21). Recent studies propose CA scheduling as a means to better adapt to produce metabolism. Chope et al. (22) reported that delaying the start of CA on onions for three weeks was as effective at controlling sprout growth using continuous CA. Alamar et al. (13) applied different CA timings on strawberry, finding that the application of CA for 2.5 days midway through storage at 5°C (2.5 days; 15 kPa CO₂ + 5 kPa O₂ after 2 days in air) increased shelf-life by 3 days. Likewise, it is recommended to use low-temperature conditions during pre-storage. The equipment and the methods used are under constant development. However, the following key components should be installed for an efficient CA facility: gas tight stores or cabins, a refrigeration system, gas control instrumentation and robust
monitoring systems (for example oxygen, carbon dioxide, ethylene, temperature and humidity sensors).

The optimal gas concentrations should be adapted to each commodity. Preferably, fruit and vegetables must be stored under low oxygen concentrations, close to the anaerobic compensation point (ACP); taking into account that oxygen levels above the ACP quickly increase respiration rate, and when below, fermentation will adversely affect fruit metabolism (23). In the 1990s, it was demonstrated that fruit like apples can be stored at oxygen levels as low as 0.5% (24–26). If the storage is carried out below 2.5 kPa of oxygen, it is considered ultra-low oxygen (ULO) storage. Although applying ULO is more expensive than conventional CA methods, its use has resulted in better firmness and quality retention (27).

Another option is reducing the initial oxygen concentration with the objective of conditioning the fruit to resist further abiotic stresses. This technique is known as initial low oxygen stress (ILOS) and it has been found to be effective against superficial scald, avoiding the use of chemical treatments (28). CA and ULO storage are static systems, which means that the atmosphere is set to an optimal level and does not vary according to the product response (29). This has several disadvantages: the lowest optimal oxygen content must be adjusted for each produce and condition (such as cultivar and seasonal variation) and it is difficult to access fruit within a container without disturbing the atmosphere, which gives no access to real-time information (30).

The CA technique has evolved with the development of more accurate control systems, to dynamic controlled atmosphere (DCA storage). DCA storage aims for the lowest possible oxygen level, as per ULO, but adapts the gas concentrations dynamically on the basis of the changing physiological response of the produce (31). If the system detects low-oxygen stress, it increases the oxygen level until the commodity response is back to the optimal threshold (23). This method is attractive because it uses existing CA technology that is improved by controlling parameters in near real-time, extending the produce storage life longer than traditional CA. It can also reduce the impact of storage disorders such as superficial scald in apples and pears. Until recently, superficial scald was prevented by using the postharvest antioxidant diphenylamine (DPA) or ethoxyquin (only for pears), but their use is no longer permitted within the European Union (32).

In order to achieve an accurate gas control, CA rooms are continuously monitored to detect the aforementioned stress. Ethanol production (dynamic control system (DCS)), chlorophyll fluorescence (DCA-CF), and the assessment of the respiratory quotient (RQ) are the main parameters measured. DCS uses ethanol, the final product of fermentation, as the stress signal for anaerobic conditions. It is determined in the headspace of a sample box placed in the storage room with sensors such as a quartz crystal microbalance (33, 34). The main issue with this method is that most of the ethanol produced during fermentation remains in the cells, making its detection difficult (23).

DCA-CF is another non-destructive method for measuring the primary processes of photosynthesis such as light absorption, excitation energy transfer and the photochemical reaction in photosystem II (35). These processes are affected by factors such as light intensity, temperature, humidity and gas composition. In this sense, changes in CF measurements are indicators to stress, such that CF can detect cellular injury in advance of symptom development (36). It has been successfully used to perceive low oxygen stress in CA environments for storage of apple, avocado, pear and kiwifruit (30, 36, 37). The limitations of this system are: that sensors can only measure a small portion of an individual fruit, extrapolating the results; they cannot repeatedly measure at the same point; the sensors are still expensive; they need to be calibrated; and peaks in CF can also be caused by other kind of stress, for example abiotic stress (drought, chilling injury). The most popular system for DCA-CF is based on fluorescence interactive response monitor (FIRM) sensors, which detect fluoresced light (Isolcell, s.P.a., Italy).

An alternative to these methods is the RQ measurement of stored produce, which can be used as a stress signal to adapt gas levels in the storage facility (23). RQ is the ratio of the carbon dioxide production rate to the oxygen consumption rate of the stored fruit or vegetable (Figure 1). The RQ will remain under one in aerobic conditions and increase exponentially over unity if oxygen concentration approaches zero, caused by a shift from aerobic respiration to fermentation, which implies low oxygen stress (5, 38). In this case, the limitation when applied to DCA systems is the leakage of the storage facility, which introduces noise to the results. A new automatic DCA control system based on online real-time RQ measurements has been recently developed that is
integrated into the control system of the CA facility (39). This enables the CA system to adjust the gas concentrations immediately according to RQ readings, avoiding the mentioned noise as it takes into account the leakage in a predictive model (23). This technology can be applied in individual sample containers that are representative of the conditions of the storage facility. An example of this option is the LabPod (Storage Control Inc, USA), a hermetically water-sealed container with a stainless steel base and a transparent plastic cover (Figure 2). Each pod has oxygen, carbon dioxide and temperature sensors with digital communication to a central operating panel. In it, RQ is periodically and automatically measured and used to set the gas concentrations in the storage room. It is recommended for products that are kept in long-term storage, such as apples, kiwifruit and pear, as, at this moment, it requires a capital investment and is expensive to operate (40). Novel biosensors and photonics are now being developed to better understand physiologically-targeted CA interventions to control ripening. They will also allow real-time phenotyping, which offers new insight into fruit and vegetable quality and safety aspects (41). Apart from the factors already mentioned, the action of ethylene (\(\text{C}_2\text{H}_4\)) has to be carefully considered. Ethylene is a natural plant hormone which works at trace levels stimulating or regulating fruit ripening (especially in climacteric fruit) (42). CA storage implies the increase of carbon dioxide and the reduction of oxygen. Low oxygen and/or elevated carbon dioxide concentrations inhibit the ethylene production rate by suppressing 1-aminocyclopropane-1-carboxylic acid synthase transcripts, the key enzyme in the synthesis pathway of ethylene (43). Another effective option to inhibit ethylene is the application of 1-methylcyclopropene (1-MCP) (Figure 3). 1-MCP is a gaseous cyclic olefin which binds irreversibly to ethylene receptors avoiding ethylene-dependent responses (44–46). 1-MCP is very efficient because its affinity for the receptor is around ten
times greater than that of ethylene (44). Some recent studies show that the effects of 1-MCP are comparable to CA in maintaining fresh produce quality (47). However, DCA is the solution that can allow optimal results during postharvest storage (48).

Research has been focused on inhibiting ethylene action in the last decade. However, scrubbing technologies are also available and their efficiency has been widely proven. These techniques include high-temperature catalytic degradation, oxidation of ethylene through potassium permanganate (KMnO₄)-based mechanisms, activated carbon and impregnated zeolite (42). The most commercially used technique to remove ethylene is simple ventilation but it is not compatible with environments which require sealing such as CA or some MAP solutions and ethylene adsorption materials.

**Modified Atmosphere Packaging**

Packaging should be designed according to the marketing and distribution needs of the product. It should do the following: protect the product from mechanical damage, avoid moisture loss and modify the internal atmosphere to prolong shelf-life. Physical injuries (vibration and compression bruises or abrasion damage) can be reduced by proper package design which acts as a shock-absorber. Packages must also allow the product to reach the optimal storage temperature quickly.

MAP is a technology that alters the atmosphere within the package according to the interaction between the product respiration rate and the transfer of gases through the package (49). Diffusion through the package depends on the film characteristics (permeability, area and thickness) and the temperature of the surrounding environment (50). When the packaging technology is adapted to the produce respiration rate, an equilibrium modified atmosphere (EMA) can be established in the package, leading to a reduction in the respiration rate and metabolic processes, and with it, increased product shelf-life. The most used gases in MAP are oxygen, carbon dioxide and nitrogen. As previously mentioned, whilst oxygen is consumed during storage life, carbon dioxide is generated through respiration. This process, as well as the interchange with the surrounding environment, will help to achieve EMA.

Packaging systems delay senescence by decreasing respiration rate, metabolic activity and microbial growth (51). There are two types of MAP based on gaseous transmission rates: passive and active. The former uses the natural permeability and thickness of the packaging film to establish the desired atmosphere for the product as a result of its respiration (52). Despite the promise of MAP, it is not yet used ubiquitously in the food industry (53) for the following reasons: the cost of the technology packaging machinery and materials, the analytical equipment necessary to ensure the correct gas mixture, and the fact that some benefits of MAP are lost once the package is opened or where there are leaks. The most common polymers used are polyamide (PA), polypropylene (PP, oriented or not), polyethylene (PE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), polystyrene (PS), polyester (PES), polyethylene terephthalate (PET), ethylene vinyl alcohol (EVOH) and polyvinylchloride (PVC) (54, 55).

The technique has been successfully applied to whole and fresh-cut products such as artichokes (56), lettuce (57) and strawberry (58). In order for the produce to create the optimal atmosphere the packaging material must be permeable. These packaging films can be microperforated to enable gas interchange between the inside and the outside of the packaging. Xtend® packaging (Johnson Matthey, UK) helps equilibrate the packed produce atmosphere within the optimal range of oxygen and carbon dioxide for a specific fruit or vegetable. It is also able to retain humidity within the package, reducing weight loss during storage. Another example is PerfoTec® (PerfoTec BV, The Netherlands). The film permeability for a particular product is determined and the PerfoTec® laser system carries out the required microperforations.

New structural polymers are now available to improve packaging materials towards bio-based and bio-degradable, non-petroleum sustainable...
packaging materials such as polylactic acid (PLA; for example, NATIVIA®, UAE) made from corn or other starch or sugar sources (59), polylactide aliphatic copolymer (CPLA) (60) and polymers derived from high proportions of recycled plastics (61). At this point, these new materials have limitations in terms of their cost and technical performance. MAP is highly dependent on respiration and temperature. To overcome this, membranes like BreatheWay® contain thermostresponsive crystalline polymers that allow high gas transmission rates at high temperatures (62).

One of the current challenges of MAP is the control of transpiration rate (TR) in fresh produce storage (63). TR is related to the mass transfer process from the stored product to the surrounding atmosphere (64) and is affected by fresh produce factors such as maturity stage, and environmental factors such as water vapour pressure deficit gradient (65). Water loss after harvest leads to weight loss and quality reduction of the produce while an accumulation of water at the product surface will help the growth of spoilage microorganisms (63). Nowadays macroperforations are used to diminish the impact of this problem, yet their presence precludes the creation of a modified atmosphere.

Microbial growth within the package is one of the challenges for MAP. Nanotechnology can enhance packaging functionality by adding antimicrobial, structural and barrier properties (66). This technology can also improve mechanical properties of films and reduce oxygen transmission rates (61). Other gases have also enriched MAP: helium, argon, xenon and nitrous oxide (N₂O). They are also reported to reduce microbial growth and maintain quality (67–69), but are yet to be widely used commercially.

Active MAP is based on the alteration of gases within the package to achieve the ideal gas equilibrium earlier than passive MAP. The techniques used include flushing pre-set gas mixtures into the package; introducing gas scavengers, such as oxygen and carbon dioxide scavengers, moisture absorbers, and ethylene scrubbers; and inserting gas emitters, such as carbon dioxide emitters (70). In the case of flushing gas mixtures, it is proven that high initial concentrations of oxygen (above 70 kPa) have an antimicrobial effect on aerobic and anaerobic microorganisms (71–73). This is also effective for helping inhibit enzymatic browning (74, 75) and avoiding loss of firmness (74, 76). However, operating in high oxygen environments carries the risk of fire. High carbon dioxide concentrations inhibit several enzymes of the Krebs’ cycle (77), slowing down ripening processes and decay. However, their efficacy will depend on cultivar, maturity stage and storage conditions. With respect to active inserts, oxygen scavengers are traditionally based on a metal powder (generally iron, ferrous carbonate or metallic platinum), ascorbic acid and enzymes (glucose oxidase and alcohol oxidase).

Active inserts are defined according to their scavenging reaction (such as enzyme mediated oxidation and oxidation speed), and their scavenging capacity (millilitres of oxygen removed). They can lower oxygen concentrations within the sealed packs, slowing deterioration caused by oxidation (78). The use of sulfites, such as potassium sulfite, and natural antioxidants, including tocopherols, lecithin, organic acids and plant extracts, are currently being explored (79) to reduce the oxidation of the fresh produce and delay denaturation of proteins (80). Currently they are applied to breads, nuts, candies and confectioneries, coffee and tea and processed, smoked and cured meats, among others, to improve storage conditions. Generally these scavengers are designed for oxygen removal from sealed food packaging and not semi-permeable fresh produce EMA packaging. More research is needed as existing oxygen scavenger formats are typically cumbersome and not appropriate for fresh produce storage conditions.

Carbon dioxide scavengers (chemical absorbers such as calcium hydroxide, sodium carbonate, calcium oxide; physical absorbers such as zeolite and activated carbon) can similarly delay senescence and reduce browning and mould decay (81). This is particularly interesting for climacteric products, which produce high concentrations of carbon dioxide affecting their organoleptic characteristics.

Another option is the removal of ethylene from the package. Ethylene scrubbers, such as potassium permanganate pellets (Ryan Co, USA) and clay mineral coated strips (It’s Fresh, UK) (42), can slow down senescence and reduce decay by neutralising the effect of the plant hormone. Carbon dioxide emitters increase carbon dioxide concentration within the package, helping achieve the optimal gas mixture for each product (70).

A recent trend, known as smart or intelligent packaging, is to fit packaging with sensors able to monitor quality, microbiological growth or temperature along the supply chain (82, 83). Intelligent packaging components include radio frequency identification sensors (84),...
time-temperature and ripeness indicators (for example, ripeSense®, New Zealand), and biosensors (85). Also, carbon dioxide and oxygen gas sensors are being developed for real-time monitoring of produce quality (86). Some low cost intelligent packaging options are available to provide visual information on freshness: fluorescent dyes or molybdenum ions (87, 88). These can inform not only about food quality, but also food safety (89).

It is possible to create physical barriers on the fruit surface which provide protection against moisture loss and can help control oxygen and carbon dioxide concentrations, in a similar way to MAP as they are able to change the internal atmosphere of the produce. This technique is known as edible coating (90). The ideal edible coating should be able to extend storage life without causing anaerobiosis and reduce decay and water loss (90), acting also as antimicrobial agents. The development of this technique began with the application of wax coatings on fruit using dipping methods. The material used to formulate them has to be generally regarded as safe (GRAS) and has evolved with time. According to Arvanitoyannis and Gorris (91), the edible coating must: be water resistant and cover the product completely when applied, reduce water vapour permeability, generate the optimal atmosphere, improve the produce appearance, melt over 40°C without decomposition, dry with high efficiency, have low viscosity, be easily emulsifiable, be economical, be translucent and not interfere with produce quality. The composition of edible coatings has advanced to be based on natural compounds. Some of the latest examples are: Aloe vera gel (92), alginate-based edible coatings (93), shellac (94) or silk fibroin (95).

At a commercial level, AgriCoat NatureSeal Ltd, UK, provides a sucrose ester based edible coating for whole fruit, mainly melon (Semperfresh®, UK) and fresh-cut produce (NatureSeal®, UK), which are sulfite-free (GRAS) and delay ripening effects. Edible coatings are able to extend the shelf-life of perishable products, maintain initial appearance, including colour and gloss, and delay decay. The correct formulation should not affect flavour or appearance. To maintain safety within the packaging an application of solutions such as natural antimicrobial like cinnamon or vanillin (93), and essential oils (96) can be used within the edible coating or on their own. Films can also be coated with inhibitors such as titanium dioxide (TiO₂), which is able to inactivate pathogens like Escherichia coli (97, 98). These packaging options are required to respond to consumers’ demand for ready to eat fruit and vegetables. The fresh-cut industry has to face not only physiological issues that lead to ripening and senescence of fresh produce, but also the likely microbial growth caused by the exposure of tissues to the environment. Mechanical wounding, due to minimal processing, damages cells making it easier for pathogens to contaminate the produce and for enzymes to catalyse non-desirable processes such as browning. Hence, the application of the correct gas mixture environment, edible coatings and natural antimicrobials are critical in this case (99).

Other postharvest technologies can complement MAP. In order to control microbial growth, non-ionising, germicidal and artificial ultraviolet C (UV-C) light (100) can be applied. Some studies show an enhancement of bioactive compounds when this technique is used (100, 101). There are no residues left in the fruit or vegetable after UV-C treatment, which is an advantage in meeting new consumer requirements. A promising technique to improve food safety is cold plasma technology (NSW Department of Primary Industries, Australia). It is created by applying an electric current to normal air or a gas to generate reactive gaseous species with antimicrobial activity. It involves no chemicals, and therefore, no residues.

**Future Prospects**

The growing demand to decrease postharvest use of chemicals and the need for more sustainable technologies has led to the development of improved CA and MAP storage methods. More research is needed to understand the dynamic physiological responses of fresh produce to CA and MAP in order to determine the optimal conditions for each cultivar and scenario. Critically, a better understanding of how flavour can be extended is required; one of the most repeated consumers’ complaints is the lack of fresh fruit and vegetable flavour. With respect to MAP, the structure and functionality of film polymers should be improved, and new sustainable materials developed and deployed. Moreover, a reduction of cost will make these technologies accessible to a wider number of companies within the sector, improving the adoption of MAP and reducing food waste.

Research should focus on optimising gas concentrations by selection of appropriately permeable packaging materials, and on improving their interaction with active materials such as scavengers, emitters, and nanoparticles. In this case, a modelling approach taking into account
different materials, gas compositions and temperatures will enhance results in the short term. Studies on consumer response to active materials and the information presented by intelligent packaging is needed. Finally, these advances will drive the development of microbiologically safe products, with high functional and sensory quality.

Concluding Remarks

In conclusion, CA storage and MAP serve as important tools to maintain fruit and vegetable quality along the supply chain, reducing food waste and extending fresh produce availability all year round. They need however to be adapted to the new requirements of consumers, being innocuous and applicable to ‘residue free’ produce. Thanks to recent technological developments, it is possible to create storage environments that adjust their settings to the physiological response of the commodity, further extending postharvest life while maintaining quality. The advances in CA and MAP will drive the development of more sustainable materials and more efficient gas control, which are essential instruments for postharvest management. However, these technologies have the following main limitations: imprecise monitoring of fruit and vegetable response, high energy requirements, high cost of materials and reduced retention of initial quality (such as flavour-life). These problems can be overcome through physiologically-targeted CA and MAP.

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Challenges and Opportunities in Fast Pyrolysis of Biomass: Part I

Introduction to the technology, feedstocks and science behind a promising source of fuels and chemicals

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Fast pyrolysis for liquids has been developed in recent decades as a fast and flexible method to provide high yields of liquid products. An overview of this promising field is given, with a comprehensive introduction as well as a practical guide to those thinking of applying fast pyrolysis liquids (bio-oil) in various applications. It updates the literature with recent developments that have occurred since the reviews cited herein. Part I contains an introduction to the background, science, feedstocks, technology and products available for fast pyrolysis. Part II will detail some of the promising applications as well as pre-treatment and bio-oil upgrading options. The applications include use of bio-oil as an energy carrier, precursor to second generation biofuels, as part of a biorefinery concept and upgrading to fuels and chemicals.

1. Introduction

1.1 Background

Pyrolysis has become of major interest due to the flexibility in operation, versatility of the technology and adaptability to a wide variety of feedstocks and products. Pyrolysis operates in anaerobic conditions where the constituents of biomass are thermally cracked to gases and vapours which usually undergo secondary reactions thereby giving a broad spectrum of products. There are a number of conditions and circumstances that have a major impact on the products and the process performance. These include feedstock, technology, reaction temperature, additives, catalysts, hot vapour residence time, solids residence time, and pressure.

Pyrolysis has been applied for thousands of years for charcoal and chemicals production but it is only in the last 40 years that fast pyrolysis for liquids has been developed. This operates at moderate temperatures of around 500°C and very short hot vapour residence times of less than 2 seconds. Fast pyrolysis is of considerable interest because this directly gives high yields of liquids of up to 75 wt% which can be used directly in a variety of applications (1) or used as an efficient energy carrier. Intermediate and slow pyrolysis focus on production of solid char as the main product with the liquids and gases usually as byproducts, although increasing attention is being paid to maximising the value of these byproducts. Pyrolysis has also been used for many years to reduce quantities of waste that require disposal as well as making the residues less harmful to the environment. These processes have traditionally employed slow pyrolysis as the core technology.
1.2 Science of Pyrolysis

Pyrolysis is thermal decomposition occurring in the absence of oxygen. Lower process temperatures and longer hot vapour residence times favour the production of charcoal. Higher temperatures and longer hot vapour residence times increase biomass conversion to gas, and moderate temperatures and short hot vapour residence time are optimal for producing liquids. Three products are always produced, but the proportions can be varied over a wide range by adjustment of the process parameters. Table I indicates the product distribution obtained from different modes of pyrolysis, showing the considerable flexibility achievable by changing process conditions. Fast pyrolysis for liquids production is currently of particular interest commercially as the liquid can be stored and transported, and used for energy, transport fuels, chemicals or as an energy carrier.

2. Fast Pyrolysis

In fast pyrolysis, biomass decomposes very quickly to generate mostly vapours and aerosols and some charcoal and gas. After cooling and condensation, a dark brown homogenous mobile liquid is formed if wood or a low ash feed is used. The liquid has a heating value about 40% that of conventional fuel oil on a weight basis or 60% that of fuel oil on a volume basis due to the high density. This liquid is referred to as bio-oil and is the basis of the recent ASTM standard (2). A high yield of liquid is obtained with most low ash biomass of up to 75 wt% on dry biomass feed. The essential features of a fast pyrolysis process for producing liquids are:

- Feed moisture content of less than 10 wt% since all the feed water reports to the liquid phase along with water from the pyrolysis reactions. High water contents in the liquid product can lead to phase separation.
- Very high heating rates and very high heat transfer rates at the biomass particle reaction interface usually require a finely ground biomass feed of typically less than 3 mm as biomass generally has a low thermal conductivity. As fast pyrolysis for liquids occurs in a few seconds or less, heat and mass transfer processes and phase transition phenomena, as well as chemical reaction kinetics, play important roles. The rate of particle heating is usually the rate-limiting step in most fast pyrolysis processes other than ablative pyrolysis where biomass directly contacts the hot reactor surface (3).
- Carefully controlled fast pyrolysis reaction temperature of around 500°C for most biomass maximises the liquid yield. Ash, particularly alkali metals, catalyses secondary reactions.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Conditions</th>
<th>Liquid</th>
<th>Solid</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast</td>
<td>~500°C Short hot vapour residence time &lt;2 s</td>
<td>75 wt% (bio-oil)</td>
<td>12 wt% char</td>
<td>13 wt%</td>
</tr>
<tr>
<td></td>
<td>Short solid residence time up to 10 s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intermediate</td>
<td>~400°C Moderate hot vapour residence time 5–20 s</td>
<td>40 wt% in two phases</td>
<td>40 wt% char</td>
<td>20 wt%</td>
</tr>
<tr>
<td></td>
<td>Moderate solid residence time up to 20 minutes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slow pyrolysis (Carbonisation)</td>
<td>~400°C Long hot vapour residence time up to</td>
<td>30 wt% in two phases</td>
<td>35 wt% char</td>
<td>35 wt%</td>
</tr>
<tr>
<td></td>
<td>Long solid residence time depending on technology</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasification (allothermal)</td>
<td>~750–900°C Short hot vapour residence time 5 s</td>
<td>Minimal</td>
<td>Up to 2 wt% char</td>
<td>Up to 98 wt%</td>
</tr>
<tr>
<td></td>
<td>Short solid residence time</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Torrefaction (slow)</td>
<td>~250–300°C Solids residence time up to 30 mins</td>
<td>0 wt% unless vapours are</td>
<td>70–80 wt% solid</td>
<td>15 wt%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>condensed, then up to 15 wt%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
of the pyrolysis vapours to carbon dioxide and water resulting in lower liquid yields with a higher water content. In extreme cases (at ash levels typically above around 2.5 wt%) so much water is formed that phase separation of the liquid occurs. Therefore, short hot vapour residence times are required of typically less than 2 seconds to minimise secondary reactions.

- Rapid removal of product char is necessary to minimise catalytic cracking of hot vapours since all the biomass ash is retained by the char. Failure to minimise contact with char results in cracking as above.
- Rapid cooling of the pyrolysis vapours to minimise thermal cracking to give the bio-oil product, for similar reasons as for effective char removal. This is usually achieved in a quench system often employing a non-miscible liquid such as a hydrocarbon or cooled product bio-oil.

Several comprehensive reviews of fast pyrolysis for liquids production are available (4–10).

### 2.1 Feedstocks

Biomass is usually made up of three main components – cellulose, hemicellulose and lignin with water and ash. Cellulose is a polymer of glucose, a six-carbon molecule, which can be thermally and catalytically cracked to monomers and decomposition products. Hemicellulose is a polymer of five-carbon rings that can also be cracked to smaller organic molecules. Lignin is a complex polymer built up of phenolic units that can be cracked to a wide range of phenolic products. Other components of biomass include water at up to 60 wt% in freshly grown biomass; and ash, mostly alkali metals from nutrients, which is catalytically active and causes cracking of organic molecules. This is beneficial in gasification where they help to crack tars, but not beneficial in pyrolysis where they crack the organics in the vapour resulting in lower liquid yields with an adverse effect on liquid properties. The alkali metals that form ash which are essential for nutrient transfer and growth of the biomass are significant in fast pyrolysis. The most active is potassium followed by sodium and calcium. These act by causing secondary cracking of vapours and reducing liquid yield and liquid quality. The vast majority of these alkali metals report to the char which results in the char byproduct acting as a cracking catalyst thus requiring rapid and effective removal of char within the fast pyrolysis process.

Ash can be managed to some extent by selection of crops and harvesting time especially with rhizome crops like Miscanthus which senesces over winter with alkali metals returning to the rhizome, however it cannot be eliminated from growing biomass. Ash can be reduced by washing in water or dilute acid and the more extreme the conditions in temperature or concentration respectively, the more complete the ash removal. Recent work has shown that surfactants are the most effective (11). However as washing conditions become more extreme firstly hemicellulose and then cellulose is lost through hydrolysis. This reduces liquid yield and quality. In addition, washed biomass needs to have any acid removed as completely as possible and recovered or disposed of and the wet biomass has to be dried.

So washing is not often considered a viable possibility, unless there are some unusual circumstances such as removal of contaminants. Another consequence of high ash removal is the increased production of levoglucosan and levoglucosenone which can reach levels in bio-oil where recovery becomes an interesting proposition.

### 2.2 Technology

A conceptual fast pyrolysis process is depicted in Figure 1 from biomass feed to collection of a liquid product. Each process step has several alternatives such as the reactor and liquid collection but the underlying principles are similar.

At the heart of a fast pyrolysis process is the reactor. Although it probably represents only about 10–15% of the total capital cost of an integrated system, most research and development has focused on developing and testing different reactor configurations on a variety of feedstocks, although increasing attention is now being paid to improvement of liquid collection systems and improvement of liquid quality. The rest of the fast pyrolysis process consists of biomass reception, storage and handling, biomass drying and grinding, product collection, storage and, when relevant, upgrading.

The byproduct char is typically about 15 wt% of the products but about 25% of the energy of the biomass feed. In commercial processes, it is used within the process to provide the process heat requirements by combustion or it can be separated and exported, in which case an alternative fuel is required to provide the heat for pyrolysis. Depending on the reactor configuration and gas velocities, a large part of the char will be of a
Fig. 1. Conceptual fast pyrolysis process

comparable size and shape as the biomass feed. Fresh char is pyrophoric i.e. it spontaneously combusts when exposed to air so careful handling and storage is required. This property deteriorates with time due to oxidation of active sites on the char surface.

2.2.1 Bubbling Fluid Bed Reactors

Bubbling fluid beds have the advantages of a well understood technology that is simple in construction and operation, has good temperature control and very efficient heat transfer to biomass particles arising from the high solids density. The usual fluidising medium is sand, but increasing attention is paid to catalysts acting as the fluidising medium, but care is needed to manage deactivation of the catalysts. Heating can be achieved in a variety of ways and scaling is well understood. However, heat transfer to the fluid bed at large scales of operation has to be considered carefully because of the scale-up limitations of different methods of heat transfer. Bubbling fluid-bed pyrolysers give good and consistent performance with high liquid yields of typically 70–75 wt% from wood on a dry-feed basis, and for this reason, are widely used for smaller scale or laboratory experiments, such as the pioneering work at the University of Waterloo (12). Small biomass particle sizes of less than 2–3 mm are needed to achieve high biomass heating rates, and the rate of particle heating is usually the rate-limiting step. This technology is ideal for laboratory units due to the ease of operation and control, when heating is usually achieved by electrical heaters. At a commercial scale Dynamotive built two fluid bed systems in Canada, one of which ran for a few years and has now been dismantled, and the second larger unit is not believed to have been commissioned before dismantling. Heat transfer to the reactor is understood to have been a cause for concern.

Vapour and solid residence time is controlled by the fluidising gas flow rate and is higher for char than for vapours. As char acts as an effective vapour cracking catalyst at fast pyrolysis reaction temperatures, rapid and effective char separation is important. This is usually achieved by ejection and entrainment followed by separation in one or more cyclones so careful design of sand and biomass/char hydrodynamics is important. The high level of inert gases arising from the high permanent gas flows required for fluidisation result in very low partial pressure for the condensable vapours and thus care is needed to design and operate efficient heat exchange and liquid collection systems. In addition the large inert gas flowrates result in relatively large equipment thus increasing cost. Liquid collection is either by indirect heat exchange or quenching in recycled bio-oil or an immiscible hydrocarbon such as Isopar – a proprietary mix of isoparaffins with a high boiling point to minimise evaporation and produce a high flash point.

Aerosols are a significant part of the liquid yield and are collected either by electrostatic precipitation or coalescence on demisters. These are incompletely depolymerised lignin fragments which seem to exist as a liquid with a substantial molecular weight. Evidence of their liquid basis is found in the
accumulation of liquid in the ESP which runs down the plates to accumulate in the bio-oil product. Demisters for agglomeration or coalescence of the aerosols have been used but published experience suggest that this is less effective.

2.2.2 Circulating Fluid Beds and Transported Beds Reactors

Circulating fluid bed (CFB) such as Empyro and transported bed reactor systems such as Ensyn have many of the features of bubbling beds described above, except that the residence time of the char is almost the same as for vapours and gas, and the char is more attritted due to the higher gas velocities. This can lead to higher char contents in the collected bio-oil unless more extensive char removal is included. An added advantage is that CFBs are potentially suitable for larger throughputs even though the hydrodynamics are more complex, as this technology is widely used at very high throughputs in the petroleum and petrochemical industry.

Heat supply is usually from recirculation of heated sand from a secondary char combustor, which can be either a bubbling or circulating fluid bed. In this respect the process is similar to a twin fluid-bed gasifier except that the reactor (pyrolyser) temperature is much lower and the closely integrated char combustion in a second reactor requires careful control to ensure that the temperature, heat flux and solids flow match the process and feed requirements. Heat transfer is a mixture of conduction and convection in the riser. One of the unproven areas is scale up and heat transfer at high throughputs.

All the char is burned in the secondary reactor to re-heat the circulating sand, so there is no char available for export unless an alternative heating source is used. If separated the char would be a fine powder that would require careful handling due to its pyrophoric nature.

2.2.3 Ablative Pyrolysis

Ablative pyrolysis is substantially different in concept compared with other methods of fast pyrolysis (13). In all the other methods, the rate of reaction is limited by the rate of heat transfer through the biomass particles, which is why small particles are required. The mode of reaction in ablative pyrolysis is like melting butter in a frying pan: the rate of melting can be significantly enhanced by pressing the butter down and moving it over the heated pan surface. In ablative pyrolysis, heat is transferred from the hot reactor wall to ‘melt’ wood that is in contact with it under pressure. As the wood is moved away, the molten layer then vaporises to a product very similar to that derived from fluid bed systems. Some of the extensive fundamental work was carried out in Nancy, France (14) and this concept was scaled to laboratory processing (15).

The pyrolysis front thus moves unidirectionally through the biomass particle. As the wood is mechanically moved away, the residual oil film both provides lubrication for successive biomass particles and also rapidly evaporates to give pyrolysis vapours for collection in the same way as other processes. There is an element of cracking on the hot surface from the char that is also deposited. The rate of reaction is strongly influenced by pressure of the wood onto the heated surface; the relative velocity of the wood and the heat exchange surface; and the reactor surface temperature. The key features of ablative pyrolysis are therefore as follows:

- High pressure of particle on hot reactor wall, achieved by centrifugal force or mechanically
- High relative motion between particle and reactor wall
- Reactor wall temperature less than 600°C.

As reaction rates are not limited by heat transfer through the biomass particles, larger particles can be used and in principle there is no upper limit to the size that can be processed. The process, in fact, is limited by the rate of heat supply to the reactor rather than the rate of heat absorption by the pyrolysing biomass, as in other reactors. There is no requirement for inert gas, so the processing equipment is smaller and the reaction system is thus more intensive. In addition the absence of fluidising gas substantially increases the partial pressure of the condensable vapours leading to more efficient collection and smaller equipment. However, the process is surface-area-controlled so scaling is less effective and the reactor is mechanically driven, and is thus more complex. The char is a fine powder which can be separated by cyclones and hot vapour filters as for fluid bed reaction systems.

2.2.4 Screw and Augur Kiln Reactors

There have been a number of developments that mechanically move biomass through a hot reactor rather than using fluids, including screw and augur reactors. Heating can be with recycled hot sand as at the Bioliq plant at Karlsruhe Institute of
Technology (KIT), Germany, (Forschungszentrum Karlsruhe (FZK) until 2009) (16), or with heat carriers such as steel or ceramic balls as in Haloclean, also at KIT (17), or external heating. The nature of mechanically driven reactors is that very short residence times comparable to fluid and circulating fluid beds are difficult to achieve, and hot vapour residence times can range from 5 to 30 seconds depending on the design and size of reactor. Examples include screw reactors and more recently the Lurgi LR reactor at KIT (10, 11) and the Bio-oil International reactors which have been studied at Mississippi State University, USA (18).

Screw reactors are particularly suitable for feed materials that are difficult to handle or feed, or are heterogeneous. The liquid product yield is lower than fluid beds and is usually phase separated due to the longer residence times and contact with byproduct char. Also the char yields are higher. KIT has promoted and tested the concept of producing a slurry of the char with the liquid to maximise liquid yield in terms of energy efficiency (19), but this would require an alternative energy source to provide heat for the process.

### 2.2.5 Microwave Pyrolysis

There is growing interest in microwave pyrolysis as a more direct way of heating biomass quickly (20, 21). This offers the advantage of avoiding or reducing the low thermal conductivity of biomass encountered in conventional thermal pyrolysis, but requires premium energy to drive the process and needs careful design to overcome the potentially poor penetration of microwaves through organic material. The uniform heating resulting from use of microwaves is likely to reduce secondary reactions as reaction products are less likely to interact with pyrolysed biomass. There are some interesting challenges in scale up and comparisons of products between microwave and conventional fast pyrolysis will be interesting.

### 2.2.6 Heat Transfer in Fast Pyrolysis

There are a number of technical challenges facing the development of fast pyrolysis, of which the most significant is heat transfer to the reactor. Pyrolysis is an endothermic process, requiring a substantial heat input to raise the biomass to reaction temperature, although the heat of reaction is insignificant. Heat transfer in commercial reactors is a significant design feature and the energy in the byproduct charcoal would typically be used in a commercial process by combustion of the char in air. Typically the char contains about 25% of the energy of the feedstock, and about 75% of this energy is required to drive the process. The byproduct gas only contains about 5% of the energy in the feed and this is not sufficient for pyrolysis. The main methods of providing the necessary heat are listed below:

- Through heat transfer surfaces located in and/or on suitable positions in the reactor such as in-bed heating tubes and/or concentric annular heater around the bed
- By heating the fluidisation gas in the case of a fluid bed or circulating fluid bed reactor, although excessive gas temperatures may be needed to input the necessary heat that could result in local overheating and reduced liquid yield, or alternatively very high gas flows may be needed resulting in unstable fluid dynamics. Partial heating is usually satisfactory and desirable to optimise energy efficiency
- By removing and re-heating the bed material in a separate reactor as used in most CFB and transported bed reactors
- By the addition of some air, although this can create localised hot spots and increase cracking of the liquids to tars
- By use of microwaves (see Section 2.2.5).

There are a variety of ways of providing the process heat from byproduct char or gas or from fresh biomass. This facet of pyrolysis reactor design and optimisation is most important for commercial units and will attract increasing attention as plants become bigger. Examples of options include:

- Combustion of byproduct char, all or part
- Combustion of byproduct gas which normally requires supplementation for example with natural gas
- Combustion of fresh biomass instead of char, particularly where there is a lucrative market for the char
- Gasification of the byproduct char and combustion of the resultant producer gas to provide greater temperature control and avoid alkali metal problems such as slagging in the char combustor
- Use of byproduct gas with similar advantages as above, although there is unlikely to be sufficient energy available in this gas without some supplementation
- Use of bio-oil product
- Use of fossil fuels where these are available at low cost, do not affect any interventions allowable on the process or product, and the byproducts have a sufficiently high value.
2.3 Products

The liquid bio-oil is formed by rapidly quenching and thus ‘freezing’ the intermediate products of flash degradation of hemicellulose, cellulose and lignin. The liquid thus contains many reactive species, which contribute to its unusual attributes. Bio-oil can be considered a micro-emulsion in which the continuous phase is an aqueous solution of holocellulose decomposition products, that stabilises the discontinuous phase of pyrolytic lignin macro-molecules through mechanisms such as hydrogen bonding. One theory is that a surfactant is formed in fast pyrolysis that creates a stable micro-emulsion with the pyrolytic lignin. Aging or instability is believed to result from a breakdown in this emulsion.

Bio-oil typically is a dark brown, free-flowing liquid and approximates to biomass in elemental composition. Depending on the initial feedstock and the mode of fast pyrolysis, the colour can be almost black through dark red-brown to dark green, being influenced by the presence of micro-carbon in the liquid and chemical composition. Hot vapour filtration gives a more translucent red-brown appearance owing to the absence of char. High nitrogen content can impart a dark green tinge to the liquid.

It is composed of a very complex mixture of oxygenated hydrocarbons with an appreciable proportion of water from both the original moisture and reaction product. Some solid char may also be present. Typical organics yields from different feedstocks and their variation with temperature are shown in Figure 2 and Figure 3 shows the temperature dependence of the four main products from a representative feedstock (22). Similar results are obtained for most biomass feedstocks, although the maximum yield can occur between 480°C and 525°C depending on feedstock. Grasses, for example, tend to give maximum liquid yields of around 55–60 wt% on a dry feed basis at the lower end of this temperature range, depending on the ash content of the grass. Liquid yield depends on biomass type, temperature, hot vapour residence time, char separation and biomass ash content, the last two having a catalytic effect on vapour cracking. It is important to note that maximum yield is not the same as maximum quality, and quality needs careful definition if it is to be optimised. Bio-oil quality and quality management and improvement have also been reviewed (23).

The liquid typically contains about 25 wt% water which forms a stable single-phase mixture, but it can range from about 15 wt% to an upper limit of about 30–50 wt% water, depending on the feed material, how it was produced and subsequently collected. Above 50 wt% water (and sometimes lower) the liquid phase separates. A typical feed material specification is a maximum of 10% moisture in the dried feed material, as both this feed moisture and the water of reaction from pyrolysis, typically about 12% based on dry feed, both report to the liquid product. Pyrolysis liquids can tolerate the addition of some water, but there is a limit to the amount of water which can be added to the liquid before phase separation occurs, in other words the liquid cannot be dissolved in water. Water addition reduces viscosity, which is useful; reduces heating value which means that more liquid is required to meet a given duty; and can improve stability. The effect of water is therefore complex and important. Bio-oil is miscible with polar solvents such as methanol, acetone, but...
totally immiscible with petroleum-derived fuels. This is due to the high oxygen content of around 35–40 wt%, which is similar to that of biomass, and provides the chemical explanation of many of the characteristics reported. Removal of this oxygen by upgrading requires complex catalytic processes which are described in Part II.

The density of the liquid is very high at around 1200 kg t⁻¹, compared with light fuel oil at around 0.85 kg l⁻¹. This means that the liquid has about 42% of the energy content of fuel oil on a weight basis, but 61% on a volumetric basis. This has implications for the design and specification of equipment such as pumps and atomisers in boilers and engines.

Viscosity is important in many fuel applications (24). The viscosity of the bio-oil as produced can vary from as low as 25 m² s⁻¹ to as high as 1000 m² s⁻¹ (measured at 40°C) or more depending on the feedstock, the water content of the bio-oil, the amount of light ends collected and the extent to which the oil has aged.

Pyrolysis liquids cannot be completely vaporised once they have been recovered from the vapour phase. If the liquid is heated to 100°C or more to try to remove water or distil off lighter fractions, it rapidly reacts and eventually produces a solid residue of around 50 wt% of the original liquid, some distillate containing volatile organic compounds that have been cracked and water. While bio-oil has been successfully stored for several years in normal storage conditions in steel and plastic drums without any deterioration that would prevent its use in any of the applications tested to date, it does change slowly with time, most noticeably there is a gradual increase in viscosity. More recent samples that have been distributed for testing have shown substantial improvements in consistency and stability, demonstrating the improvement in process design and control as the technology develops.

Ageing is a well known phenomenon caused by continued slow secondary reactions in the liquid which manifests as an increase in viscosity with time. It can be reduced or controlled by the addition of alcohols such as ethanol or methanol. In extreme cases phase separation can occur. It is exacerbated or accelerated by the presence of fine char. This has been reviewed by Diebold (25, 26).

Fast pyrolysis liquid has a higher heating value (HHV) of about 17 MJ kg⁻¹ as produced with about 25 wt% water that cannot readily be separated. While the liquid is widely referred to as ‘bio-oil’, it will not mix with any hydrocarbon liquids. It is composed of a complex mixture of oxygenated compounds that provide both the potential and challenge for utilisation. There are some important properties of this liquid that are summarised in Table II and Table III. There are many particular characteristics of bio-oil that require consideration for any application (6). Oasmaa and Peacocke have reviewed physical property characterisation and methods (27, 28).

### Table II Typical Properties of Wood-Derived Crude Bio-Oil

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Typical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>25%</td>
</tr>
<tr>
<td>pH</td>
<td>2.5</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.20</td>
</tr>
<tr>
<td>Elemental analysis C</td>
<td>56%</td>
</tr>
<tr>
<td>H</td>
<td>6%</td>
</tr>
<tr>
<td>O</td>
<td>38%</td>
</tr>
<tr>
<td>N</td>
<td>0–0.1%</td>
</tr>
<tr>
<td>HHV as produced</td>
<td>17 MJ kg⁻¹</td>
</tr>
<tr>
<td>Viscosity (40°C and 25% water)</td>
<td>40–100 mPa s</td>
</tr>
<tr>
<td>Solids (char) which also includes ash</td>
<td>0.1%</td>
</tr>
<tr>
<td>Vacuum distillation residue</td>
<td>up to 50%</td>
</tr>
<tr>
<td>Characteristic</td>
<td>Cause</td>
</tr>
<tr>
<td>-------------------------</td>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td><strong>Acidity or low pH</strong></td>
<td>Organic acids from biopolymer degradation</td>
</tr>
<tr>
<td><strong>Ageing</strong></td>
<td>Continuation of secondary reactions including polymerisation</td>
</tr>
<tr>
<td></td>
<td><strong>Continuation of secondary reactions including polymerisation</strong></td>
</tr>
<tr>
<td><strong>Alkali metals (ash)</strong></td>
<td>Virtually all alkali metals report to char so this not a big problem</td>
</tr>
<tr>
<td></td>
<td>High ash feed</td>
</tr>
<tr>
<td></td>
<td>Incomplete solids separation</td>
</tr>
<tr>
<td></td>
<td><strong>Incomplete solids separation</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Slag formation</strong></td>
</tr>
<tr>
<td><strong>Char</strong></td>
<td>Incomplete char separation in process</td>
</tr>
<tr>
<td></td>
<td><strong>Ageing of oil</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Sedimentation</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Filter blockage</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Catalyst blockage</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Engine injector blockage</strong></td>
</tr>
<tr>
<td><strong>Chlorine</strong></td>
<td>Contaminants in biomass feed</td>
</tr>
<tr>
<td><strong>Colour</strong></td>
<td>Cracking of biopolymers and char</td>
</tr>
<tr>
<td><strong>Contamination of feed</strong></td>
<td>Poor harvesting practice</td>
</tr>
<tr>
<td><strong>Distillability is poor</strong></td>
<td>Reactive mixture of degradation products of biomass</td>
</tr>
<tr>
<td></td>
<td><strong>Bio-oil cannot be distilled – maximum 50% typically</strong></td>
</tr>
<tr>
<td><strong>High viscosity</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Gives high pressure drop increasing equipment cost</strong></td>
</tr>
<tr>
<td></td>
<td><strong>High pumping cost</strong></td>
</tr>
<tr>
<td><strong>Low H:C ratio</strong></td>
<td>Biomass has low H:C ratio and thermal degradation products replicate this ratio</td>
</tr>
<tr>
<td><strong>Materials incompatibility</strong></td>
<td>Phenolics and aromatics</td>
</tr>
<tr>
<td><strong>Miscibility with hydrocarbons is very low</strong></td>
<td>Highly oxygenated nature of bio-oil</td>
</tr>
<tr>
<td><strong>Nitrogen</strong></td>
<td>Contaminants in biomass feed</td>
</tr>
<tr>
<td></td>
<td>High nitrogen feed such as proteins in wastes</td>
</tr>
<tr>
<td></td>
<td><strong>Catalyst poisoning in upgrading</strong></td>
</tr>
<tr>
<td><strong>Oxygen content is very high</strong></td>
<td>Biomass composition has high oxygen so thermal degradation products have high oxygen</td>
</tr>
<tr>
<td></td>
<td><strong>Poor stability</strong></td>
</tr>
<tr>
<td><strong>Phase separation or inhomogeneity</strong></td>
<td>High feed water</td>
</tr>
<tr>
<td></td>
<td>High ash in feed</td>
</tr>
<tr>
<td></td>
<td>Poor char separation in process</td>
</tr>
<tr>
<td></td>
<td><strong>Layering</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Poor mixing</strong></td>
</tr>
<tr>
<td><strong>Smell or odour</strong></td>
<td>Aldehydes and other volatile organics, many from hemicellulose</td>
</tr>
</tbody>
</table>

(Continued)
<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Cause</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solids</strong></td>
<td>Particulates from reactor such as sand Particulates from feed contamination Small particles of char</td>
<td>Sedimentation Erosion and corrosion Blockage</td>
</tr>
<tr>
<td><strong>Structure</strong></td>
<td>The unique structure is caused by the rapid de-polymerisation and rapid quenching of the vapours and aerosols</td>
<td>Susceptibility to ageing such as viscosity increase and phase separation</td>
</tr>
<tr>
<td><strong>Sulfur</strong></td>
<td>Contaminants in biomass feed</td>
<td>Catalyst poisoning in upgrading</td>
</tr>
<tr>
<td><strong>Temperature sensitivity</strong></td>
<td>Incomplete or ‘frozen’ degradation reactions</td>
<td>Irreversible decomposition of liquid into two phases above 100°C Irreversible viscosity increase above around 60°C Potential phase separation above around 60°C</td>
</tr>
<tr>
<td><strong>Toxicity</strong></td>
<td>Biopolymer degradation products</td>
<td>Human toxicity is positive but small Ecotoxicity is negligible</td>
</tr>
<tr>
<td><strong>Viscosity</strong></td>
<td>Chemical composition of bio-oil gives high viscosity, which tends to increase with time due to ageing</td>
<td>Fairly high and tends to increase with time Greater temperature effect on viscosity change than for hydrocarbons Increasing temperature to lower viscosity requires care due to thermal sensitivity</td>
</tr>
<tr>
<td><strong>Water content</strong></td>
<td>Pyrolysis reactions Feed water</td>
<td>Complex effect on viscosity and stability: increased water lowers heating value, density and stability; and raises pH Affects catalysts for example through hydrolysis</td>
</tr>
</tbody>
</table>

### 2.4 Liquids Collection

The gaseous products from fast pyrolysis consist of aerosols, true vapours and non-condensable gases. These require rapid cooling to minimise secondary reactions and condense the true vapours, while the aerosols require additional coalescence or agglomeration. Simple indirect heat exchange can cause preferential deposition of lignin-derived components leading to liquid fractionation and eventually blockage in pipelines and heat exchangers. Quenching in product bio-oil or in an immiscible hydrocarbon solvent is widely practised.

Orthodox aerosol capture devices such as demisters and other commonly used impingement devices are not reported to be as effective as electrostatic precipitation, which is currently the preferred method at both laboratory and commercial scale units. The vapour product from fluid bed and transported bed reactors has a low partial pressure of condensable products due to the large volumes of fluidising gas, and this is an important design consideration in liquid collection. This disadvantage is reduced in the rotating cone and ablative reaction systems, both of which exclude inert gas which leads to more compact equipment and lower costs (29).

### 2.5 Byproducts

Char and gas are byproducts, typically containing about 25% and 5% of the energy in the feed material respectively. The pyrolysis process itself requires about 15% of the energy in the feed, and of the byproducts, only the char has sufficient energy to provide this heat. The heat can be derived by burning char in orthodox reaction system design, which makes the process energy self-sufficient. More advanced configurations could gasify the char to a lower heating value (LHV) gas and then burn the resultant gas more effectively...
to provide process heat with the advantage that the alkali metals in the char can be much better controlled. The waste heat from char combustion and any heat from surplus gas or byproduct gas can be used for feed drying and in large installations could be used for export or power generation. An important principle of fast pyrolysis is that a well-designed and well-run process should not produce any emissions other than clean flue gas i.e. CO₂ and water, although they will have to meet local emissions standards and requirements.

2.5.1 Char

Char acts as a vapour cracking catalyst, so rapid and effective separation from the pyrolysis product vapours is essential, although it is not clear to what extent cracking is caused by the alkali metals in the char. Cyclones are the usual method of char removal, however some fines always pass through the cyclones and collect in the liquid product where they accelerate ageing and exacerbate the instability problem which is described below. Some success has been achieved with hot vapour filtration which is analogous to hot gas cleaning in gasification systems (30–33). Problems arise with the sticky nature of fine char and disengagement of the filter cake from the filter.

Pressure filtration of the liquid for substantial removal of particulates (down to <5 µm) can be difficult because of the complex interaction of the char and pyrolytic lignin, which appears to form a gel-like phase that rapidly blocks the filter. Modification of the liquid microstructure by addition of solvents such as methanol or ethanol that solubilise the less soluble constituents can improve this problem and contribute to improvements in liquid stability. However the suitability of this approach depends on the application for the bio-oil.

2.5.2 Gas

The gas contains only a small proportion (around 5%) of the initial energy of the biomass feed and is insufficient to provide all the necessary process heat. The heating value depends on the process technology and the extent to which the off gas is diluted by inert and/or recycle gas.

2.6 Environment, Health and Safety

As bio-oil becomes more widely available, attention will be increasingly placed on environment, health and safety aspects. A study was completed in 2005 to assess the ecotoxicity and toxicity of 21 bio-oils from most commercial producers of bio-oil around the world in a screening study, with a complete assessment of a representative bio-oil (34). The study includes a comprehensive evaluation of transportation requirements as an update of an earlier study (35) and an assessment of the biodegradability (36). The results are complex and require more comprehensive analysis but the overall conclusion was that bio-oil offers no significant health, environment or safety risks.

Acknowledgement

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