Catalytic upgrading of bio-oils by esterification

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ABSTRACT

Biomass is the term given to naturally-produced organic matter resulting from photosynthesis, and represents the most abundant organic polymers on Earth. Consequently, there has been great interest in the potential exploitation of lignocellulosic biomass as a renewable feedstock for energy, materials and chemicals production. The energy sector has largely focused on the direct thermochemical processing of lignocellulose via pyrolysis/gasification for heat generation, and the co-production of bio-oils and bio-gas which may be upgraded to produce drop-in transportation fuels. In this mini-review we describe recent advances in the design and application of solid acid catalysts for the energy efficient upgrading of pyrolysis biofuels.

1. INTRODUCTION

Mounting concerns over dwindling petroleum oil reserves, in concert with growing governmental and public acceptance of the anthropogenic origin of rising CO_2 emissions and associated climate change, is driving academic and commercial routes to utilise renewable feedstocks as sustainable sources of fuel and chemicals. The quest for such sustainable resources to meet the demands of a rapidly rising global population represents one of this century's grand challenges [1]. Waste biomass, sourced from non-food lignocellulose, sugars, and triglycerides is the only sustainable source of carbon that can provide low cost solutions for transportation fuels [2]. Popular approaches to lignocellulosic biomass utilisation for fuels production encompass sugar fermentation to ethanol, gasification to syngas (CO/H_2), and liquefaction or pyrolysis to bio-oils (**Figure 1**).
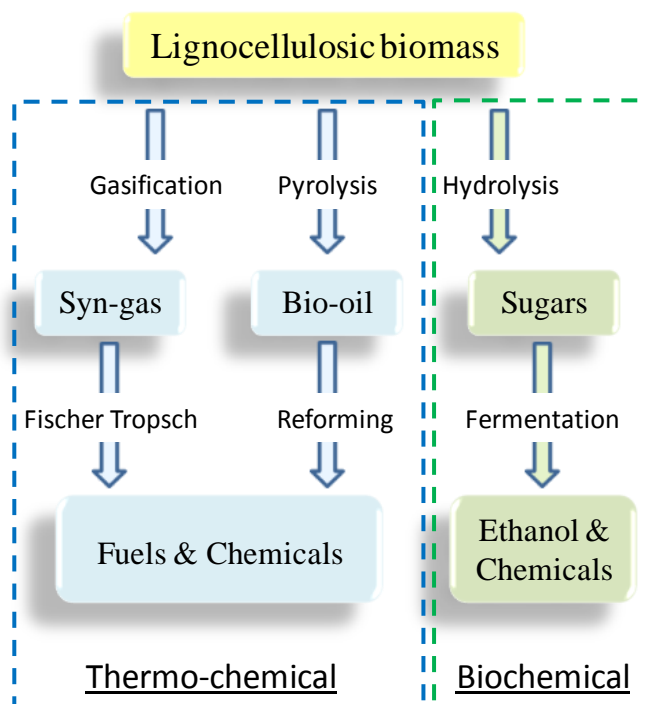

Figure 1. Biochemical and thermochemical routes for lignocellulose conversion to chemicals and fuels.

Pyrolytic thermal decomposition of biomass in the absence of oxygen yields a broad product distribution which is sensitive to the feedstock, reaction temperature and residence time [3]. Intermediate pyrolysis employing low temperatures and long residence times favours charcoal formation, while fast pyrolysis using moderate temperatures and short vapour residence time are optimal for liquids production [4]. High temperatures and longer residence times favour gasification [5], with the resulting (purified) syngas available for well-established catalytic processes such as Fischer Tropsch and methanol synthesis for the conversion of CO/H_2 mixes to fuels and methanol. While fast pyrolysis of agricultural waste and short rotation crops [6-8] shows great promise in producing bio-oils that retain up to 70 % of the energy of the raw biomass, the resulting oil has a high oxygen content and relatively low heating value (16-19 MJ/Kg, i.e. less than half that of petroleum-derived fuels). Pyrolysis oil is also highly acidic and corrosive (pH 2–3), and as a result fresh bio-oil is inherently unstable at room temperature, deteriorating via polymerization and condensation reactions on storage with attendant increased viscosity and poorer combustion. Typical bio-oils are a mixture of acids, alcohols, furans, aldehydes, esters, ketones, sugars and multifunctional compounds such as hydroxyacetic acid, hydroxyacetaldehyde and hydroxyacetone (derived from cellulose and hemicellulose), together with 3-hydroxy- 3-methoxy benzaldehyde, phenols, guaiacols and syringols derived from the lignin component. Representative compositions are shown in **Figure 2** [9-11].
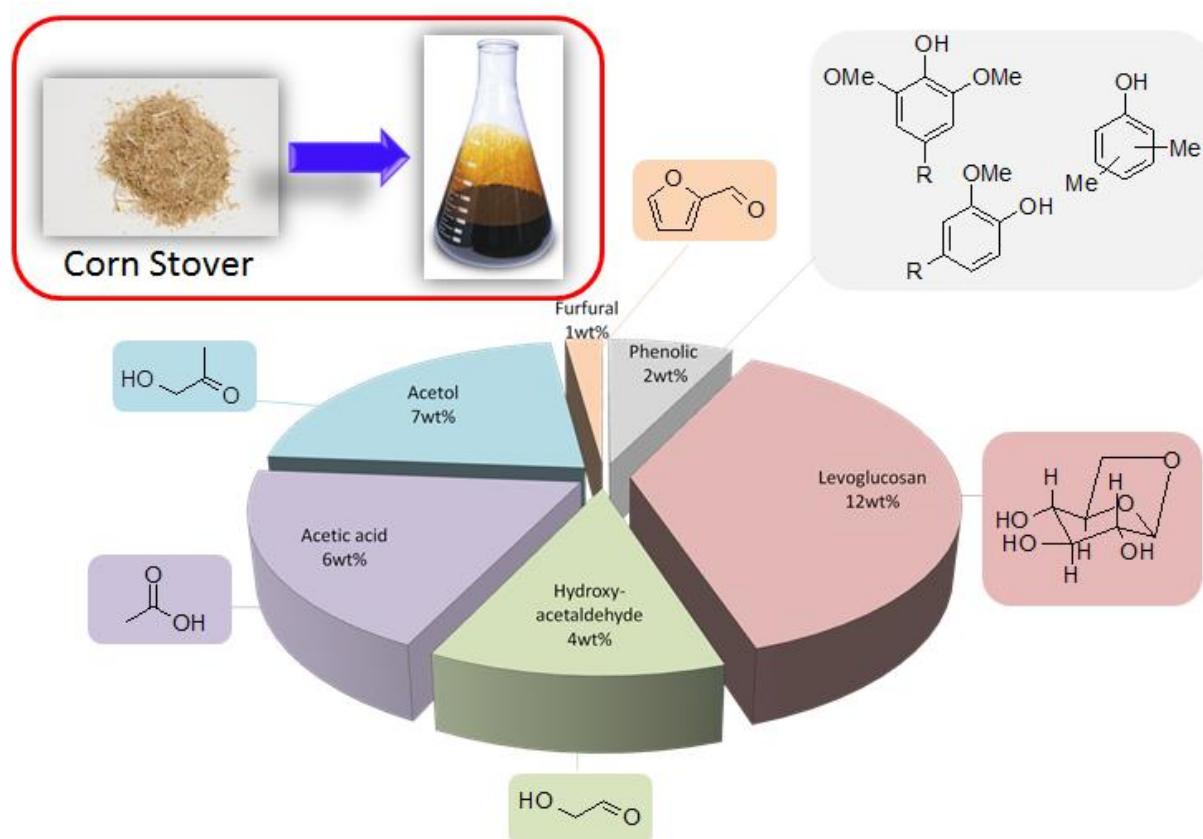

Figure 2. Representative wt% composition of bio-oil derived from the fast pyrolysis of corn stover. Adapted from reference [11], with permission from Elsevier.

Biomass pyrolysis routes to transportation fuels are therefore only economically viable if the bio-oil is subjected to upgrading treatments to improve their physicochemical properties [6, 12-14]. There are several promising catalytic processes for bio-oil upgrading/pre-treatment, including ketonisation, aldol condensation and hydro-deoxygenation. This review focuses on catalytic upgrading by esterification over solid acids which offers a low energy route to oil stabilisation. Esterification of the corrosive acidic components in bio-oil is proposed as a simple pre-treatment to improve the stability of oils during storage and transportation prior to subsequent upgrading. Indeed, the addition of small concentrations of ethanol or methanol (<10 %) has been observed to improve bio-oil stabilisation [15-17], drastically reducing the ageing rate of the bio-oil via homogeneous reactions initiated by the organic acid itself. Methanol addition alone can induce a 20-fold improvement in oil stability (as judged by viscosity changes) through the formation esters (1) and acetals (2) via non-catalytic reaction with carboxylic acids and aldehydes respectively.

$$(1)\ R_1COOH + R\text{–}OH \leftrightarrow R_1COOR + H_2O,$$

$$(2)\ R_1CHO + 2R\text{–}OH \leftrightarrow R_1CH(OR)_2 + H_2O.$$
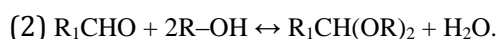
While the use of strong mineral acids such as H_2SO_4 is effective at catalysing esterification, this is not recommended due to the corrosive and hazardous nature of the acid, and also the requirement for subsequent neutralisation which generates vast quantities of aqueous waste for clean-up. The use of solid acids circumvents these problems; however, there is a need to develop new, tailored solid acids with superior acid site accessibility and stability in aqueous environments compared with those commercially available. In particular, consideration must be made of the impact of high molecular weight hydrocarbons present in bio-oil that may lead to pore-blockage in conventional, commercial microporous solid acids such as zeolites [18, 19].

2. SOLID ACID CATALYSTS FOR BIO-OIL ESTERIFICATION

Bio-oils derived via pyrolysis (particularly catalytic fast pyrolysis [20]) possess relatively high concentrations of acetic acid typically spanning 1-10 %, [21, 22] in addition to trace formic and propanoic acids, with their attendant low pH 2-3 a source of vessel corrosion and fuel instability [23]. Esterification of such organic acids can occur with either alcohol components intrinsic to bio-oils, notably phenolics such as guaiacol and cresols and oxygenates such as acetol and levoglucosan,[24] or via external sources such as methanol, ethanol or butanol [25-30]. The latter are advantageous in terms carbon neutrality as they may be derived through fermentation of biomass from renewable resources. Since the boiling points of esters are lower than their parent acids, upgrading via esterification offers the possibility for reactive distillation to remove water, unreacted alcohols and volatile esters, resulting in light and heavy oil fractions with weaker acidity and superior chemical stability and viscosity to conventional fast pyrolysis bio-oils. [31]

The mechanism of acid catalysed esterification with alcohols is well established, and believed to proceed via a similar pathways for solid and homogeneous mineral acids, although heterogeneously catalysis esterification is generally held to be solely driven by Brönsted acid sites [32]. Formation of a strongly adsorbed, protonated acid

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intermediate [32, 33] is followed by rate-limiting step nucleophilic attack by the alcohol to yield a protonated carbonyl (**Figure 3**), through either a single- (Eley-Rideal) or double-site mechanism (Langmuir-Hinshelwood) mechanism [33, 34]. Various solid acid catalysts have been investigated for the esterification of bio-oils and associated model acid components, and are discussed by classification below.
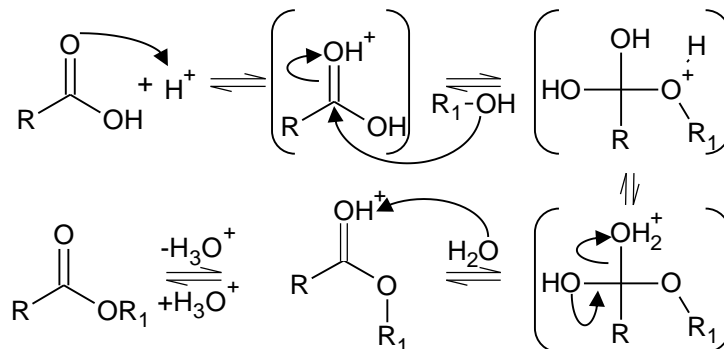

Figure 3. Proposed reaction mechanism for solid acid catalysed esterification. Adapted from reference [34], with permission from Elsevier.

2.1 SULFATED ZIRCONIAS

Sulphated zirconias have received a great deal of attention of the last couple of decades due to their unique balance between acid and base sites and the ability to easily and controllably tune this character of their surface [35-43]. The inductive effect of the S=O bond in sulphate species on the surface of SZ increases the Lewis acid strength of the Zr^{4+} [44-46] (**Figure 4**). In the presence of water these Lewis acid sites were converted to Brönsted acid sites via proton donation from the adsorbed water molecule [46]. One complication in the use of sulphated zirconias is the low surface area and pore volumes of the zirconia itself, thus a great deal of effort has been focused on development of structured zirconia materials [47-51] employing surfactant templating methods to introduce mesoporosity [51-55].
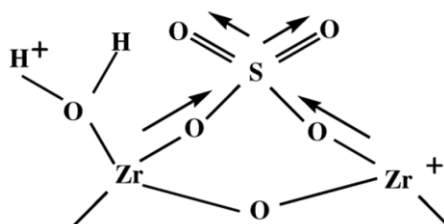

Figure 4. A simplified structure of sulphated zirconia showing Brönsted and Lewis acid sites. Reprinted from reference [46] with permission from Elsevier.

Modified zirconias, including tungstated [56], ZnO, TiO_2 and Nd_2O_3 doped [57] and sulfated zirconia (SZ) [58-60] have been widely employed for the esterification of free fatty acids pertinent to the processing of plant and waste oils for biodiesel production, however they have more recently found application in the removal of short chain carboxylic acids from bio-oil. Deveulapelli *et al* investigated the performance of mesoporous SZ on the esterification of 4-methoxyphenylacetic acid (4-MPAA) with dimethyl carbonate at 403-443 K [61], noting that mesopore incorporation increased the surface acid site density and mass-transport properties, resulting in

significant rate enhancements over conventional low area SZ. However, neither the Brönsted/Lewis acid character nor sulfur content of the mesoporous and conventional SZ materials were characterised in this study, and since the former are known to be highly sensitive to the latter,[42] the mesoporous SZ may simply have contained a higher sulfur loading and concomitant proportion of Brönsted sites. Yu and co-workers explored acetic acid esterification with ethanol (2:1 molar ratio of alcohol:acid) over rare earth oxide and alumina promoted SZ at 340 K [62]. Pyridine adsorption studies indicated that the total number of Brönsted and Lewis acid sites on the oxide promoted SZs was less than the non-promoted SZ, although the fraction of superacid sites was increased, the highest being observed for doubly promoted Yb_2O_3-Al_2O_3 SZ catalysts (SZYA). The number and strength of acid sites correlated well with ethyl acetate yield, with the SZYA material conferring the highest yield of 60 %, but also possessing the highest surface area. Unfortunately this SZYA catalyst exhibited significant sulphur leaching during reaction, resulting in considerable deactivation and poor acetate yields after multiple recycles. Surface area normalised esterification rates were not reported in this work. An extensive comparison of solid acid catalysts for acetic acid esterification with butanol was undertaken at 348 K over SZ, Nb_2O_5 and a series of zeolites (H-USY-20, H-BETA-12.5, H-MOR-45 and H-ZSM-5-12.5) [63]. SZ catalysts exhibited the highest activity, however water adsorption resulted in progressive blocking of active sites or sulphur leaching. Higher temperature calcination improved the activity and stability up to 550 °C, possibly reflecting the formation of crystalline tetragonal zirconia; higher temperatures promoted monoclinic zirconia and lower activity (**Figure 5**).
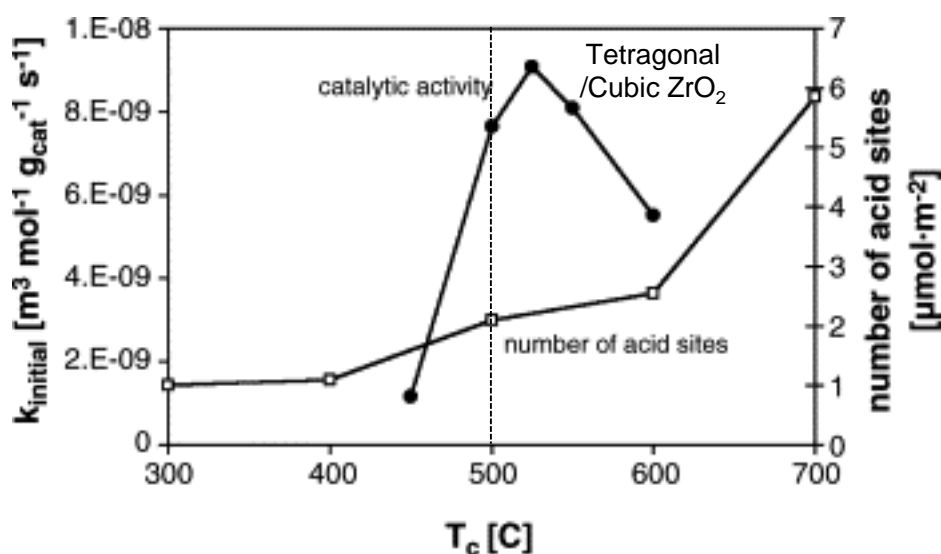

Figure 5. Effect of calcination temperature on the acid site density of SZ and associated impact on activity towards acetic acid esterification with butanol. Reprinted from reference [63], with permission from Elsevier.

Junming et al [31] compared the performance of SZ, SO_4/TiO_2 and SO_4/SnO_2 for the reactive distillation of pyrolysed rice husk bio-oil with ethanol under ambient pressure and 330 K, resulting in light and heavy upgraded oil fractions with higher pH (5-7) and significantly lower water content (**Table 1**). The light oil fraction contained predominantly ethyl esters of organic acids. SZ outperformed the other sulfated metal oxides in terms of the light oil yield, however the physicochemical properties of the different catalysts were not characterised, nor the compositions of light oils obtained for the titania and tin oxide supports, hence the superiority of zirconia is qualitative and rather ill-defined. Upgrading of flash pyrolysis rice husk bio-oil has also been reported via

simultaneous hydrotreatment, esterification, and cracking in supercritical ethanol under hydrogen pressures between 5 and 20 bar over a palladium doped SZ/SBA-15 catalyst at 280 °C.[64] The majority of organic acids were converted into their corresponding esters (notably a ten-fold drop in acetic acid), inducing a rise in pH and heating value and in parallel with a fall in kinematic viscosity and density compared to the parent bio-oil. Palladium was essential to prevent tar and coke formation observed over the unpromoted SZ/SBA-15. It is important to note that similar improvements in bio-oil properties were observed following non-catalytic upgrading by this method, partly reflecting the large excess of ethanol employed which hindered quantitative analysis of the upgraded oil fraction.

Table 1. Comparison of raw oil and upgraded oil after ageing. Reprinted from reference [31], with permission from Elsevier.

Properties	Original oil[a]	Light oil[a]	Heavy oil[a]
pH	2.86	7.08	5.69
Density (g cm^{-3})	1.15	0.91	0.95
H$_2$O content	33.2	0.53	5.03
Calorific value (kJ g^{-1})	14.2	21.6	24.6
Dynamic viscosity (mm^2 s^{-1})[b]	13.4	0.47	3.82
Appearance	Dark brown	Colorless	Dark

[a]Upgraded bio-oil after 3 months of aging storage.
[b]Measured at a temperature of 303 K.

Sulfated ZrO$_2$/TiO$_2$ nanocomposites have shown promise in the esterification of longer chain acid components of pyrolysis bio-oils, namely levulinic acid, with ethanol.[65] Li et al prepared ZrO$_2$-modified TiO$_2$ nanorods via hydrothermal synthesis and subsequent deposition-precipitation, comprising 20-200 nm diameter rods up to 5 μm long, uniformly decorated with 10 to 20 nm ZrO$_2$ nanoparticles (**Figure 6**). The sulfated nanocomposite contained around 14 atom% S and exhibited excellent ethyl levulinate yields of 90 % at a mild temperature of 105 °C after 3 h reaction, crucially utilising the ideal ethanol:acid ratio of 1:1.
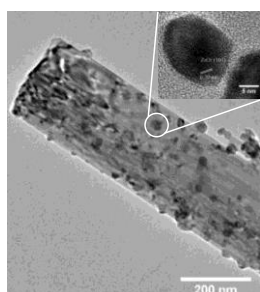

Figure 6. SEM image of ZrO$_2$/TiO$_2$ nanocomposites. Inset shows HRTEM image of a deposited tetragonal ZrO$_2$ nanoparticle. Reprinted with permission from reference [65]. Copyright 2012 American Chemical Society.

Chen et al compared the rate of acetic acid esterification with cyclohexanol versus n-butanol over SZ/SBA-15 prepared via a two-step impregnation.[66] Higher ester yields were obtained for n-butanol (86 %) than for

cyclohexanol (62 %), and the same trends were noted for selectivity to the ester with the principal by-products derived from intramolecular or intermolecular dehydration and subsequent hydrogenation. The faster rate of n-butanol esterification was attributed to its more efficient mass-transport into the SBA-15 mesopores.

2.2 ZEOLITES

Zeolites are naturally occurring alumino-silicates that have been using in catalysis for over half a century, with many varieties of synthetic zeolites available. Zeolites are capable of possessing both Brönsted and Lewis acid sites, the latter arising from aluminium defects present in the structure, and as such there has been a great deal of research focused on tailoring the Lewis acidity of zeolites through de-alumination [33, 67, 68]. Furthermore, the acid character of the zeolites is maintained upon addition of active metal phases, through ion-exchange, allowing for a great deal of flexibility [33, 69] and bifunctional behaviour. **Figure 7** shows a schematic of the pore structure of four common zeolite classes, showing how the $SiO_{4/2}$ and $AlO^-_{4/2}$ tetrahedra crystallise as pentasil or sodalite units to form the 3D zeolite network.
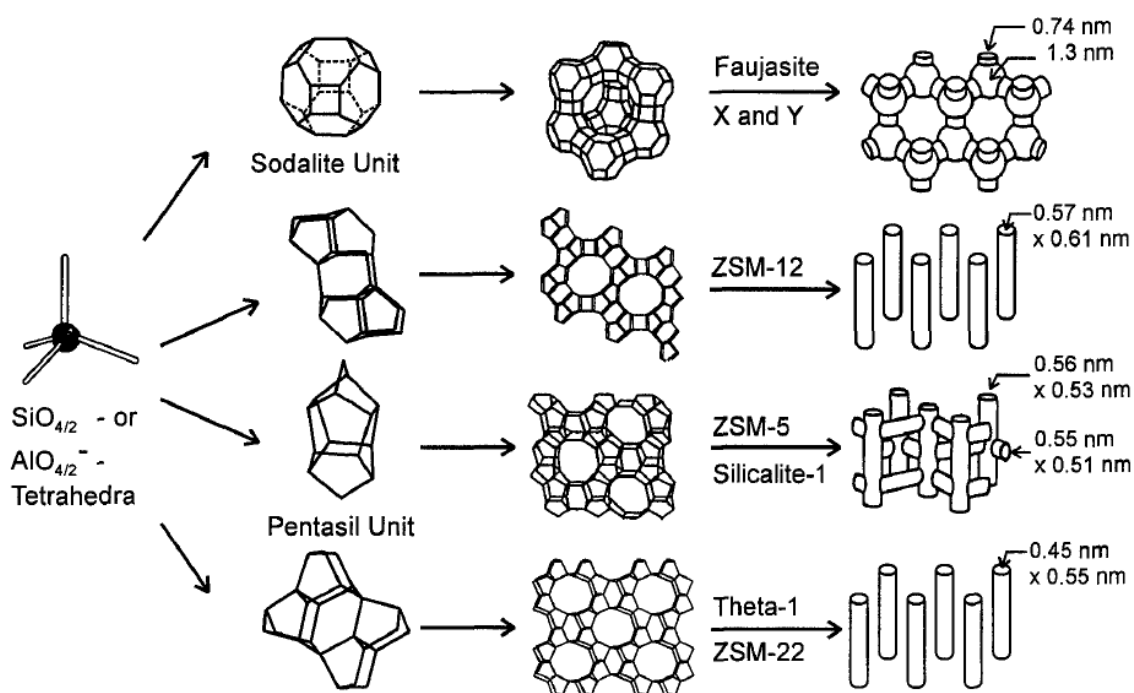

Figure 7. Structures of select zeolites highlighting their micropore networks. Reprinted from reference [70], with permission from Elsevier.

The majority of zeolites are highly microporous [71], which raises issues pertaining to mass transport limitations for bulky substrates imposed by their lack of porosity beyond the micropore region. There has been much interest in the development of zeolites with either hierarchical pore networks [72-76] or larger more accessible pore diameters [77]. Introduction of a hierarchical pore structure within zeolites can be achieved via one of two methods, templating and/or desilication; the former being part of the synthetic procedure for making the zeolite, the latter being a post-synthetic modification [71]. Desilication through treatment with alkaline solutions of Na_2CO_3 or NaOH selectively removes Si over other components of zeolites [73, 75, 78]. In a paper by Čimek et al, the importance of the removal of

alumina as a prerequisite to desilication was investigated by varying the dissolution conditions [78]. Detailed reviews on the synthesis of hierarchical and large pore zeolites can be found in the following references [71, 77].

Despite their potential limitations, zeolites are the most extensively explored class of solid acid for bio-oil upgrading via esterification, with considerable efforts focused on elucidating the reaction pathways and relationships between zeolite structure, acidity and corresponding catalytic performance. In an early related investigation, Corma and co-workers studied the influence of cation exchange over NaHY zeolites upon phenylacetic and benzoic acid esterification with ethanol [33] between 298-383 K. The threshold temperature for esterification was related to the degree of cation exchange (333 K for HY-21, falling to 315 K for HY-50 and HY-90). Titration of the acid site strength and density via pyridine adsorption indicated that esterification required strong acid sites, with Brönsted acid strength inversely proportional to the number of Al atoms in the secondary coordination sphere. Acid pre-adsorption revealed that protonation of the carbonyl group of phenylacetic acid was rate-limiting. This was consistent with the lack of weak Brönsted acid sites required for ethanol adsorption over the HY-50 and HY-90 materials. Dealumination increased surface hydrophobicity, displacing reactively-formed water from the active sites during esterification and displacing the equilibrium towards the ester. Phenylacetic acid esterification with p-cresol was also briefly investigated, with the strong Brönsted acidic HY-50 and HY-90 zeolites most active.

More recent studies of vapour phase acetic acid and ethanol esterification under steady state conditions identified co-adsorbed acetic acid/ethanol dimers as critical surface intermediates over protonated BEA, FER, MFI, and MOR zeolites [79]. Detailed kinetic analyses suggested a reaction mechanism involving two dominant surface species, an inactive ethanol dimer whose strong adsorption on Brönsted sites inhibited ester formation, and a co-adsorbed acetic acid/ethanol complex able to react and form ethyl acetate over a wide range of temperature and acetic acid:ethanol partial pressure (**Figure 8**). The intrinsic rate constant for activation of the co-adsorbed complex increased in the order FER < MOR < MFI < BEA.
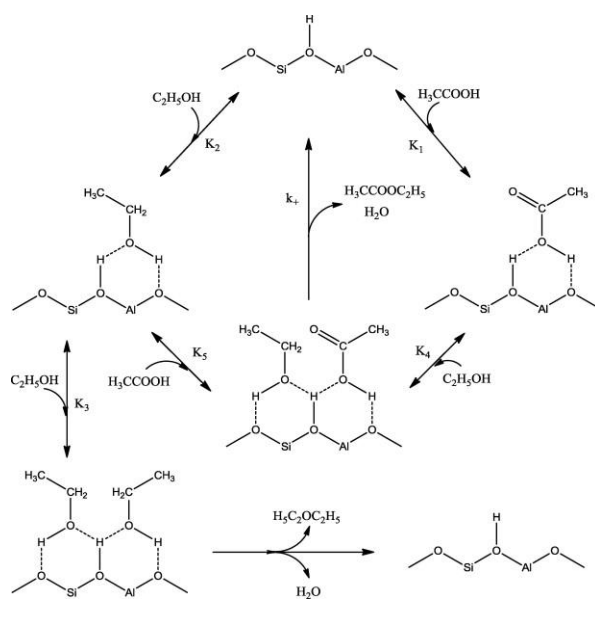
Figure 8. Reaction network for acetic acid esterification with ethanol over protonated zeolites highlighting co-adsorbed acid/alcohol dimer as key reactive intermediate to ester formation (k_+). Reprinted from reference [79], with permission from Elsevier.

A very recent investigation of acetic acid esterification with o-cresol, the latter commonly found in pyrolysis bio-oils, was undertaken over different zeolite framework types (FER, MFI, MOR, BEA and FAU) and hierarchical mesoporous-microporous architectures. [80] Large pore beta and faujasite zeolites catalysed efficient ester formation at 453 K with yields up to 25 %, whereas smaller pore frameworks such as mordenite, ZSM-5 and ferrierite were only active at 473 K with the reactively-formed cresol acetate apparently retained within the pore network due to its relatively large molecular size contributing to subsequent carbon laydown over strong Brönsted acid sites. Hierarchical faujasite and MFI zeolites synthesised through alkaline-mediated desilication exhibited significantly improved acid conversion and ester yields over their conventional microporous counterparts (**Figure 9**), attributed to superior mass-transport associated with intracrystalline mesopores and lower coking, notably for access-limited ZSM-5. While such simple post-synthetic modification of commercially available zeolites enhanced acetic acid esterification, it also results in lower Brönsted acid site densities and relatively poor recycling performance.
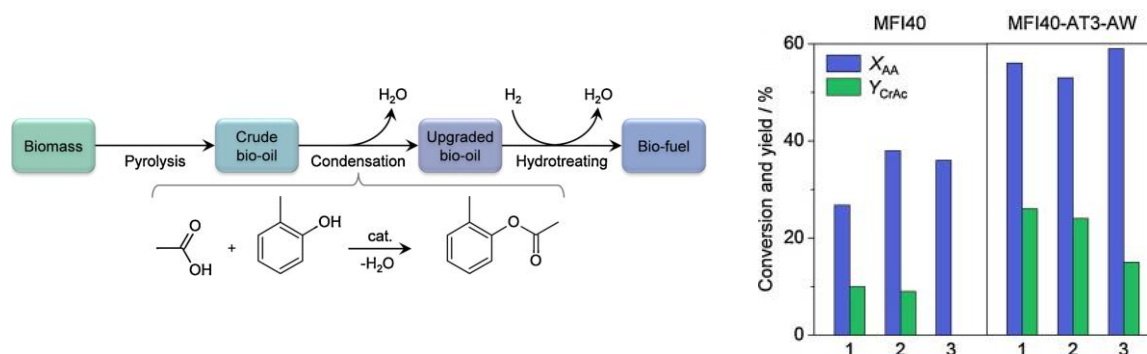

Figure 9. (left) Potential application of acetic acid esterification with o-cresol in bio-oil upgrading; (right) superior performance of hierarchical versus conventional MFI zeolites in cresol acetate production. Reprinted from reference [80], with permission from Elsevier.

The influence of Pd doping upon Brönsted acidity and concomitant acetic acid esterification with methanol was studied by Koo et al at 373 K over H-ZSM-5 and H-ferrierite zeolites. [32] Both parent protonated zeolites exhibited modest acetic acid conversion but excellent selectivity to methyl acetate (~15 % and 90 % respectively), with palladium addition increasing conversion to ~25 % and methyl acetate to ~95 %. DRIFTS vibrational studies revealed that strong Brönsted sites (prevalent in the lower Si:Al ratio ferrierite) facilitated strong methanol adsorption and the production of undesired alcohol dimers in competition with acid esterification. Ammonia TPD studies indicated that Pd^{2+} cations selectively bind to stronger Brönsted acid sites, thus preventing the formation of alcohol dimers, consistent with the smaller observed promotion of the H-ZSM-5 zeolite which possessed fewer strong Brönsted sites. H-ZSM-5 has also been exploited for upgrading high acetic acid content (~18 %) pyrolysis bio-oil from rice husk under conventional (100 °C), sub- (238 °C) and super-critical (260 °C) conditions employing ethanol.[28] Super-critical conditions proved the most effective, lowering the acetic content to around 4 %, and resulting in approximately half of the residual heavy oil component than present after sub-critical treatment. Brönsted acid site density and strength distribution proved a good indicator of esterification, and in contrast to the preceding study, lower Si:Al ratios proved superior to higher values, with Si:Al =22 > 100 > 300

(at least in regard to the heavy oil fraction, though it should be noted that ester compositions and yields were not quantified). Microwave irradiation has also been employed to enhance esterification of phenylacetic acid with p-cresol over H-β zeolite, functionalities encountered in bio-oil components,[81] revealing a striking rate enhancement compared with the conventional thermal reaction (**Figure 10**). Phenylacetic acid conversion was highly sensitive to temperature, increasing from 9 to 60 % between 403 to 463 K, and acid:alcohol ratio, rising from 34 to 60 % with increasing molar ratios from 1:1 to 1:3, but remained 100 % to p-cresyl phenylacetate (a valuable ester used in personal care products) at all temperatures. Kinetic modelling supported a Langmuir-Hinshelwood-Hougen-Watson indicative of a bimolecular surface process. Unfortunately the H-β zeolite catalyst was prone to poisoning by reactively-formed water, indicating the requirement for reactive distillation to displace the reaction equilibrium to 90 % conversion.
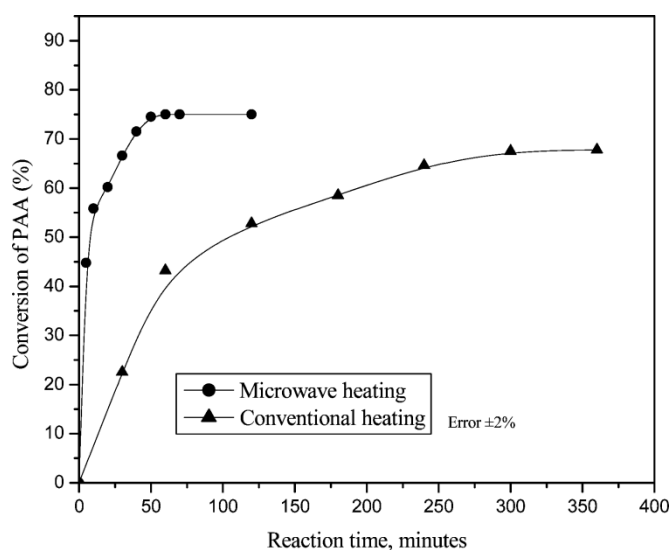

Figure 10. Superior performance of microwave heating in the esterification phenylacetic acid with p-cresol over H-β zeolite. Reprinted with permission from reference [81]. Copyright 2011 American Chemical Society.

Desilicated H-ZSM-5 has found application as a functional support for phosphotungstic acid (HPW) in the esterification of levulinic acid with ethanol,[82] wherein the desilication protocol imparted intercrystalline mesopore voids within which to incorporate the superacidic heteropoly acid, thereby overcoming the mass-transport barriers intrinsic to the microporous zeolite. The bifunctional HPW/ZSM-5 material exhibited significantly higher acid site loadings than the parent H-ZSM-5 (0.5 versus 0.9 mmol.g^{-1} respectively), proportional to the HPW loading upto 15 wt%, and concomitant superior activity resulting in an increase in levulinic acid conversion from 28 % to 94 % at 351 K, albeit under a 6:1 excess of ethanol:levulinic acid and substrate:catalyst ratio of only 5:1.

2.3 FUNCTIONALISED MESOPOROUS SILICAS

As previously discussed, poor accessibility of the active site within the micropore networks of zeolitic systems and associated mass transport/diffusion limitations hinders their performance in liquid phase catalysed processes. Further catalyst development and improved activity should prove possible through utilising tailored porous solids as high area supports to enhance accessibility of the active acid groups [83, 84]. Templating methods are commonly divided into one of two classes on the basis of the template used, and classed as either soft or hard templates. Soft

templating methods have commonly been used in the development of mesoporous [54, 85-88], which when coupled with hard templating approaches can be used to generate hierarchical macro-mesoporous materials [88-90]. Hard templating techniques have also been used in the synthesis of mesoporous carbons [91-93]. Since the discovery of the M41S class of mesoporous materials by Mobil, there has been an explosion of interest in the preparation of soft-templated porous solids, and these have been extensively reviewed [94-97]. In the case of silicates, the most widely investigated mesoporous inorganic supports, network morphology and stability reflect the templating conditions (ionic or neutral surfactant), silica precursor (e.g. fumed silica, tetraethylorthosilicate (TEOS), Ludox or sodium silicate) and whether hydrothermal synthesis or co-solvents are employed. Subsequent calcination, to burn out the organic template, yields materials with well-defined meso-structured pores of 2-10 nm and surface areas up to 1000 m^2g^{-1}. The SBA family of materials generated from block copolymer surfactants (e.g. P123 ($PEO_{20}PPO_{70}PEO_{20}$) typically give rise to larger pore diameters than those achieved with alkyl amines or ammonium surfactants. Upon template removal the resulting material possesses excellent long and short range structure (**Figure**).
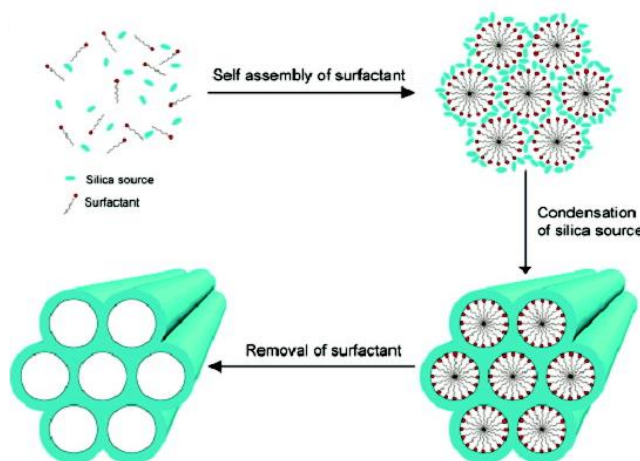

Figure 11. Soft-templating route in the synthesis of mesoporous silicas. 2008 Canadian Science Publishing or its licensors. Reproduced with permission from reference [98].

Organic modification of resulting mesoporous silicas via grafting of thiol-functionalised organic tethers offers a facile route to prepare solid sulfonic acid catalysts, which have found a wide range of applications in acid catalysis as a clean alternative to H_2SO_4. Phenyl and propyl sulfonic acid SBA-15 catalysts are particularly attractive solid acid materials with activities comparable to Nafion and Amberlyst resins in esterification reactions [99]. Phenylsulfonic acid functionalised silicas are reportedly more active than their corresponding propyl analogues, in line with their respective acid strengths but are more difficult to prepare.

Organo-functionalised silicas have received considerable attention as versatile solid acid catalysts, commonly employing (3-mercaptopropyl) trimethoxysilane (MPTMS) as a precursor to covalently tethered sulfonic acid moities. Cano-Serrano et al explored the application of MPTS, the dimethoxy equivalent (3-mercaptopropyl)methyldimethoxysilane (MPMDMS), and/or phenyltrimethoxysilane (PTS) via grafting over amorphous silica and subsequent thiol oxidation for acetic acid esterification with methanol at a 1:1 molar ratio at 333 K [100]. MPMDMS alone exhibited the poorest activity due to incomplete oxidation of the thiol precursor, with MPTMS/PTMS, and MPTMS alone affording the highest acid conversion of 30 % after 3 h reaction,

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outperforming a Nafion/silica composite. Ageing studies indicated that these sulfonic acid silicas were generally stable to sulfur leaching in methanol.

A subsequent investigation by Lohitharn and Shanks employed a one-pot co-condensation synthetic route to preparing propylsulfonic acid functionalised SBA-15 (PrSO$_3$H/SBA-15) for acetic acid esterification with ethanol in 1,4-dioxane solvent [101]. In particular this work explored the impact of aldehydes upon esterification to simulate real bio-oil feedstocks [102, 103]. At 323 K acetic acid conversion was 42 % in the absence of aldehyde, falling to 30 % after 50 h reaction in the presence of acetaldehyde or propionaldehyde for an ethanol:acetic acid molar ratio of 2.7. This fall was attributed to ethanol consumption through rapid acetalization resulting in the production of aldehyde diethyl acetal. The impact of aldehydes was ameliorated at higher temperature, attributed to the exothermic nature of acetalizations.

In a subsequent study, Miao and co-workers compared the kinetics of acetic acid esterification with methanol over PrSO$_3$H/SBA-15 with homogeneous propane sulfonic acid at 323 K. The esterification reaction at 323 K was lower than predicted, attributed to association of the PrSO$_3$H groups with surface silanols on the SBA-15 support, hindering their interaction with the reactants and correspondingly higher activation energy of 42.6 kJ.mol^{-1} relative to propane sulphonic acid of 36.4 kJ.mol^{-1}. Kinetic studies indicated a dual-site Langmuir-Hinshelwood mechanism operated over PrSO$_3$H/SBA-15, with esterification requiring co-adsorption of acetic acid and ethanol. In contrast the homogeneous reaction followed Eley-Rideal kinetics. Density functional theory calculations of Si-tethered propylsulfonic acid complexes suggest sulfonic acid sites bind acetic acid significantly more strongly than methanol and water (142 kJ.mol^{-1} versus ~59 kJ.mol^{-1} respectively) in qualitative agreement with adsorption studies wherein acetic acid pre-adsorption supressed methyl acetate production whereas methanol pre-adsorption had little impact. This conclusion is in accordance with literature reports for other solid acids, for which the reaction proceeds via protonation of the carboxylic acid [32, 34, 37] (**Figure 12**).
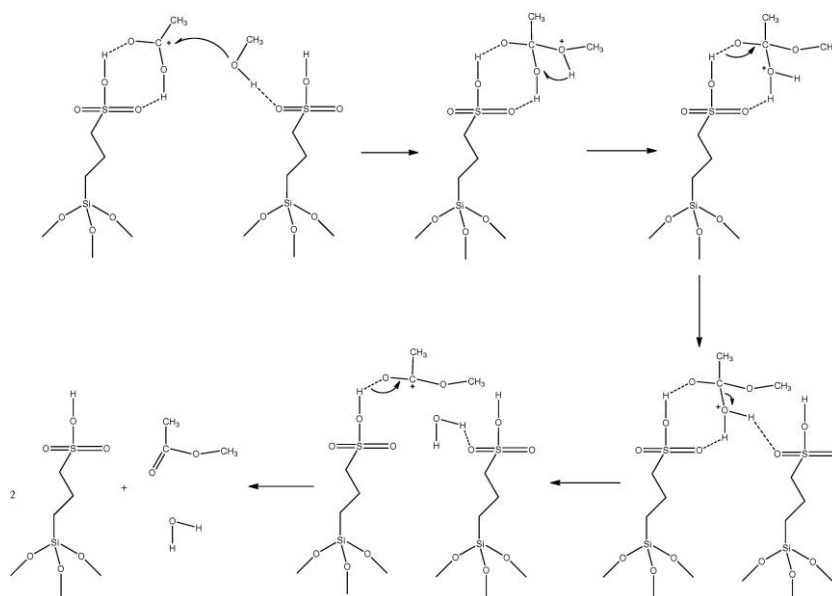

Figure 12. Postulated reaction mechanism for acetic acid esterification with methanol over PrSO$_3$H/SBA-15. Reprinted from reference [104], with permission from Elsevier.

Dacquin and co-workers studied the effect of surface hydrophobicity via co-grafting of alkyl and sulfonic acid groups onto a MCM-41 surface [105]. Products such as water will associate strongly or weakly with the surface depending on their polarity and that of the surface, and by controlling the relative coverage of parent propyl thiol groups the surface properties can easily be tailored as shown in **Figure** .
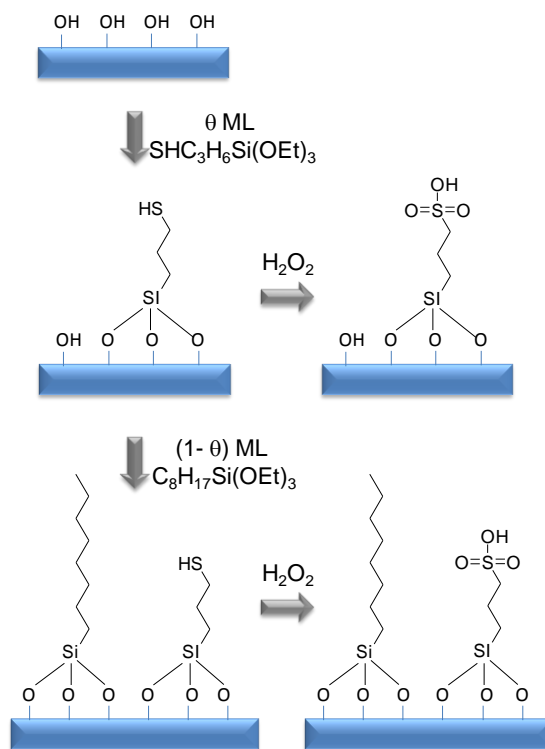

Figure 13. Sulphonic acid and alkyl silane grafted onto an MCM-41 surface. Reproduced from reference [105] with permission from The Royal Society of Chemistry.

Furthermore, sulphonic acid moieties can strongly associate with the hydroxyl groups of the silica surface, making the active sites for catalysis unavailable to bind with reactants. In such a situation the alkyl grafting would inhibit these associations with the surface and force the sulphonic acid moieties into the correct conformation. From **Figure 14** it can be seen that for esterification of acetic acid with butanol the TOF of the materials increased both with sulphonic acid group density and more significantly with increases in the density of alkyl group.
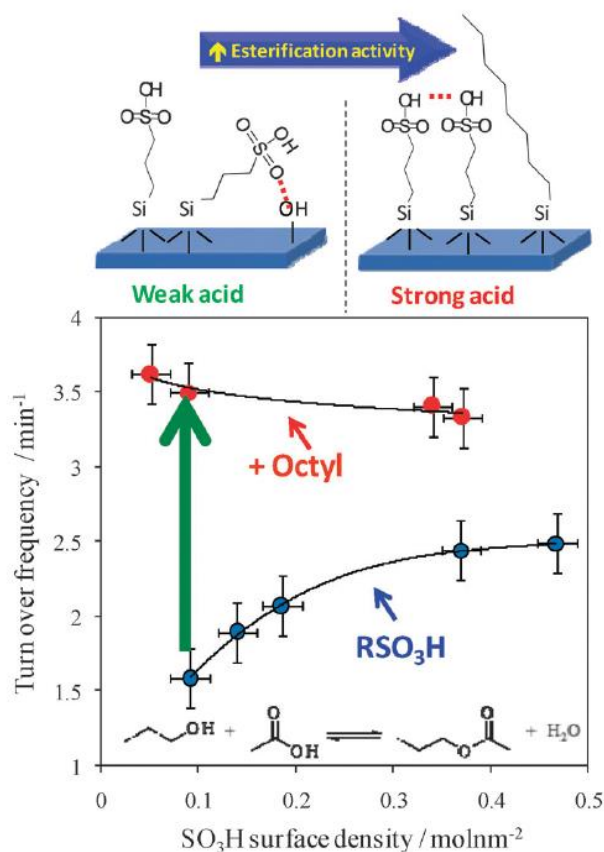
Figure 14. Catalytic activity of sulphonic acid functionalised MCM-41 in the esterification of butanol with acetic acid. Increased acid site density and hydrophobicity increases the turnover frequencies of the catalysts. Adapted from reference [105] with permission from The Royal Society of Chemistry.

2.4 HETEROPOLY ACIDS

Heteropoly acids (HPAs) are unique strong Brönsted acids that have been widely used as both heterogeneous and homogeneous catalysts for several decades. The basic structural units of HPAs are metal-oxygen octahedra, which assemble to form a polyoxometalate anions. The most stable, easily synthesised and widely studied HPAs are built upon the Keggin unit which is of general formula $XM_{12}O_{40}^{x-8}$, comprising a central p-block atom, X, of oxidation state x (eg. Si^{4+}, Ge^{4+}, P^{5+}, As^{5+}), metal ions, M, (eg. W^{6+}, Mo^{6+}) and oxygen atoms. At the centre of the Keggin structure is a XO_4 tetrahedra surrounded by 12 MO_6 octahedra, (Figure 6, α-$PM_{12}O_{40}^{3-}$). Two examples of frequently used Keggin-type HPAs are $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$. Solid HPAs also contain hydration water molecules, which may be removed to increase the acidity of the material. A major advantage of HPAs is that their acidity and redox properties are highly tuneable through modification of their chemical composition [106]. The structure and chemical properties of HPAs are reviewed in detail in the following references,[107-109] however, in summary by changing the metal and the p-block element, a wide range of different heteropoly acid structures may be prepared, such as Wells-Dawson ($H_nX_2M_{18}O_{62}$), Dexter-Silverton ($H_nXM_{12}O_{42}$), and Strandberg ($H_nX_2M_5O_{23}$) types. Examples of several heteropoly anions of assorted shape and composition are shown in **Figure 15**.
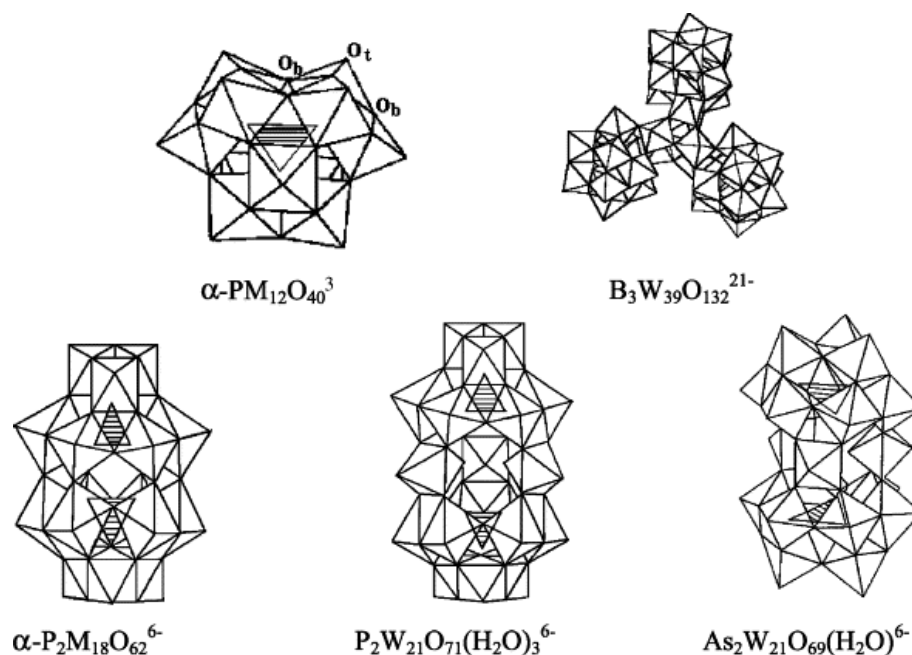
Figure 15. Structures of heteropoly acid anions (M=M^{6+}, W^{6+}). Reprinted from reference [109], with permission from Elsevier.

The Keggin anion has terminal M=O sites and both edge and corner bridging M-O-M sites. In the solid state, the protons act to link adjacent anions but the anions and counterions are relatively mobile within the structure compared to the building blocks of other solid acid structures, such as metal oxides or zeolites. HPAs are soluble in polar solvents and in solution they are fully dissociated and are stronger acids than typical inorganic acids (eg. HCl, H_2SO_4).[109] The dissociation constants for each successive proton do not increase significantly for HPAs in solution. This is in contrast to inorganic acids such as H_3PO_4, for which pK_1 is significantly lower than pK_2 and pK_3 at 2, 7 and 12 respectively in aqueous solution at 25 ºC.[110] HPA acidity is affected by the chemical composition of the anion, with tungsten-based Keggin-type HPAs being stronger acids than molybdenum ones, and phosphorous-based HPAs are also more acidic than their silicon-based analogues.[111] Also, for a given metal, the acidity of the HPA increases with increasing charge on the central atom (P^{5+}>Si^{4+}, Ge^{4+}>B^{3+} etc).[112]

The high acidities are also observed for solid phase HPAs, which are reported to be stronger acids than conventional solid oxides such as SiO_2-Al_2O_3 and also zeolites and sulphated zirconia [113]. Although the majority of HPAs, such as $H_3PW_{12}O_{40}$ are pure Brønsted acids, [113] Lewis acidity can be generated through the addition of metals such as Ti, Zr and Th.[114] The activity HPAs as solid acid catalysts is improved by the presence of these Lewis sites, with Zr offering a greater increase than Ti.[114] The relationship between the acidity and increasing charge on the anion's central atom is the same as for solid HPAs as those in solution, with $H_3PW_{12}O_{40}$ > $H_4SiW_{12}O_{40}$ for example. The structure of the heteropoly anion also affects the acidic strength, with Keggin-type HPAs being stronger acids than Dawson-types (eg. $H_3PW_{12}O_{40}$ > $H_6P_2W_{18}O_{62}$).[115]

One limiting factor of HPAs is their relatively low intrinsic surface area and corresponding low activity. This issue may be overcome by dispersing the HPA over a high surface area support material and it has been demonstrated that this can yield a superior catalyst than the unsupported equivalent. As a result of the desirable

catalytic properties of supported HPAs, there are now a wide range of reports of the preparation of such solid acid materials and their performance in reactions such as alkylation,[116-118] dehydration,[119-121] esterification[122, 123] and hydroxylation.[124, 125] The most suitable wt.% loading of HPA varies with the nature of the reaction, since non-polar substrates may only react at the surface of the solid acid, whereas polar reagents may be absorbed into the bulk of the material and therefore may benefit from higher wt.% loadings of supported heteropolyacid.[126] The HPAs may be incorporated into the pore networks of structured mesoporous supports such as SBA-15, which increases the hydrophilicity of the channels and may lead to improved product selectivity in certain reaction systems.[127] The channels may be further tuned by altering the chemical composition of the anchoring group, with the presence of an amino group leading to increased hydrophilicity (**Figure 16**).
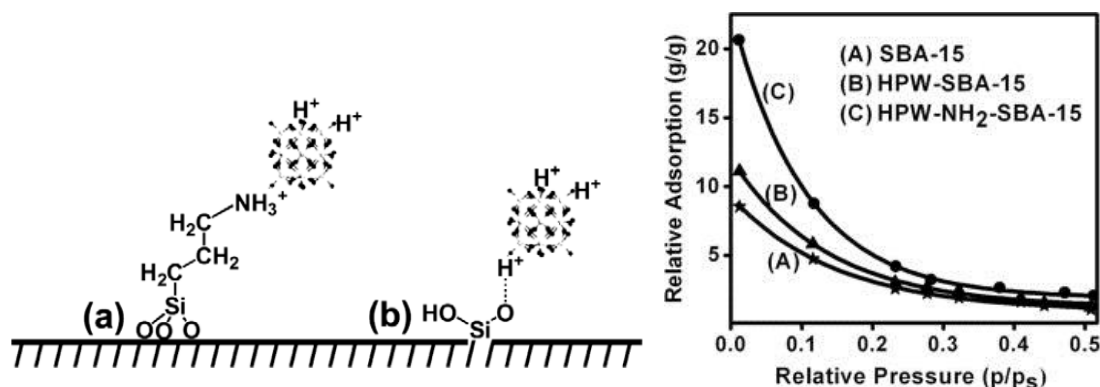

Figure 16. Schematic structure of the heteropoly acid ($H_3PW_{12}O_{40}$) anchored to an SBA-15 surface **(a)** HPW-NH$_2$-SBA-15, and **(b)** HPW-SBA-15 and their relative adsorptions (ratio of water to n-hexane adsorbed), Reprinted from reference [127], with permission from Elsevier.

While heteropoly acids have not been studied in great detail in the context of catalytic upgrading of bio-oil they are effective catalysts for acetic acid esterification. Liu et al have shown that amine tethered phosphotungstic acid (HPW) on SBA-15 is effective for the esterification of acetic acid with butanol at 360 K (**Figure 17**) [127]. Surface hydrophilic/hydrophobic character of the HPW/SBA-15 and unfunctionalised parent SBA-15 was assessed via isothermal water and n-hexane adsorption, which indicated their hydrophobicity followed the order SBA-15 > HPW-SBA-15 > HPW-NH$_2$-SBA-15. All three catalysts were almost 100 % selective to n-butyl acetate, however the more hydrophilic HPW-NH$_2$-SBA-15 was more active than the HPW-SBA-15 material, which in turn outperformed the parent silica, although n-butyl acetate yields after 15 h reaction only between 80-90 %. This small difference was atttributed to the greater hydrophilicity of the HPW functionalised silica preferentially expelling the relatively more hydrophobic n-butyl acetate from within the pore network, maintaining a high local concentration of the more hydrophilic acetic acid and n-butanol at the acid sites. In light of the high background esterification rate (60 % conversion without any catalyst), it seems most likely that the superior performance of the HPW functionalised silicas simply reflects their strong acidity with respect to SBA-15 (acid properties were not determined in this work), rather than any significant hydrophilic effect. The amine coordinated HPW proved less prone to leaching during reaction.
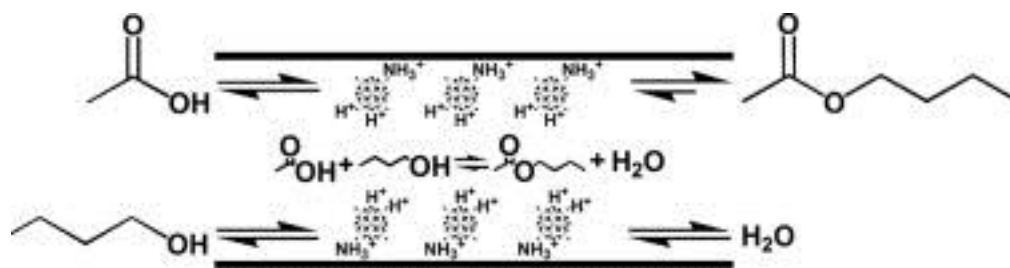
Figure 17. Proposed expulsion of 'hydrophobic' n-butyl acetate from hydrophilic pores of HPW functionalised SBA-15. Reprinted from reference [127], with permission from Elsevier.

A recent investigation on smaller mesopore MCM-41 silica investigated the effect of introducing Brönsted acidity via modification with framework Al or post-synthetic impregnation with HPW at loadings between 10-40 wt% [128]. The resultant materials were screened towards acetic acid esterification with several alcohols pertinent to bio-oils upgrading (ethanol, propanol, butanol and benzyl alcohol). The monoester yields spanned 73-95 % after 8 h over fresh Al-MCM-41 (30:1 Si:Al) and HPW-MCM-41 (20 wt% HPW) catalysts, with yields increasing in the order butanol < propanol < ethanol < benzyl alcohol, although detailed control experiments were not reported to establish the background rates of acetic acid esterification, known to be high for benzyl alcohol [129]. FTIR identified the presence of both weak and superacidic sites on the HPW-MCM-41 catalysts, with the number of strong acid sites reaching a maximum for the 20 wt% 12-TPA material. The impact of alcohol: acid ratio was explored over a narrow range (1:1.5 to 1.5:1), with the ester yield found to increase with acid molar ratio, attributed to preferential adsorption of alcohol and site-blocking. Recycling studies evidenced steady deactivation of HPW-MCM-41 (and Al-MCM-41) during esterification for all the alcohols due to leaching of the heteropoly acid.

HPW supported on montmorillonite K10 was also utilised by Gurav et al for acetic acid esterification with different alcohols (predominantly ethanol) [130]. At 373 K and 8 h on stream, good conversion and 100 % selectivity to ethyl acetate was achieved over all HPW impregnated K10 catalysts, resulting in ester yields increasing from 77.1 % to 90 % with increasing HPW loading from 10-30 mol% mirroring the total acid site density determined by ammonia TPD, though even the parent K10 support achieved 63.9 % acetic acid conversion. In contrast to the preceding work on HPW-MCM-41, acetic acid conversion increased from 45 % to 94 % over 20 mol% HPW/K10 with increasing alcohol carbon length from methanol to butanol at a common 2:1 acid: alcohol molar ratio. This is contradictory to oleic acid esterification wherein ethanol was superior to butanol [131], and butyric acid esterification for which a continuous decrease in rate with alcohol chain length was observed, methanol significantly outperforming ethanol [132].

2.5 CARBON BASED SOLID ACID CATALYSTS

Activated carbons (ACs) are by far one of the most versatile support materials in catalysis. Not just in that their properties can be easily tailored on a purpose specific basis [133-136], but in the wide range of different parent materials from which they can be produced [137-140]. Virtually any high carbon content material can act as a parent

material making local production factors a major driving force in their wider use. Structurally ACs are generally amorphous, this like most characteristics of ACs is highly dependent on the parent material. ACs with controlled porosity are commonly produced from polymer resins or through soft templating routes (e.g. CMK-3), such ACs tent to be predominately mesoporous, especially when produced as supports for catalysis [140, 141]. These mesoporous ACs (meACs) can have acid sulphur sites introduced through several mechanisms, however the which predominates is sulphation in fuming sulphuric acid [142, 143]. Other mechanisms for the introduction acidic sulphur sites include grafting of alkyl thiols and the use of high sulphur content precursors [144]. Such ordered mesoporous carbons have also been prepared using SBA-15 as a hard template during the carbonisation process as shown in **Figure 18**.
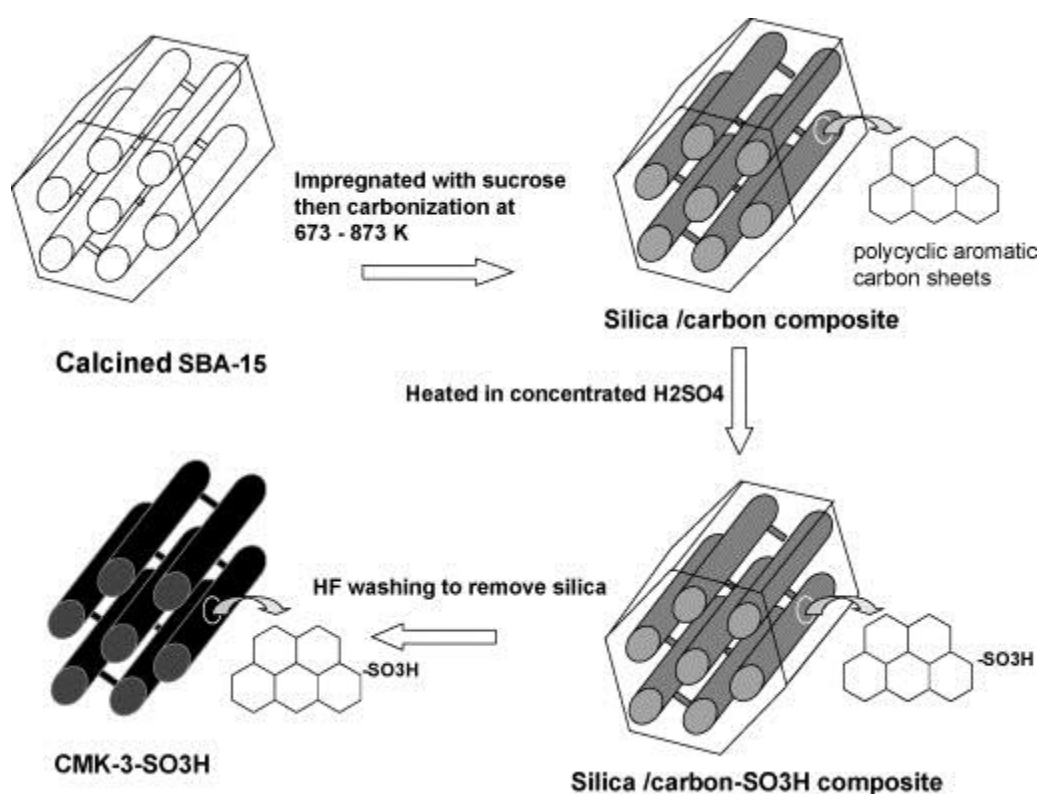
Figure 18. Synthesis of sulphonated, ordered mesoporous carbons for fatty acid esterification. Reprinted from reference [144], with permission from Elsevier.

Acid functionalised carbons have yet to attracted significant attention in the context of bio-oil esterification, however sulphated graphene prepared via hydrothermal sulfonation of reduced graphene oxide with fuming sulfuric acid has shown promise for acetic acid esterification with cyclohexanol (3:1 molar ratio) and 1-butanol (1:1 molar ratio) at 90-100 °C [145] (**Figure 19**). High alcohol cyclohexanol (79 %) and butanol (89 %) conversions were maintained over 5 recycles indicating excellent chemical stability, supported by thermal analysis which showed sulfonic acid decomposition occurred at higher temperatures than over ordered mesoporous carbons. The high activity of sulfonated graphene likely reflects the ready accessibility of acid sites across the two-dimensional nanosheets, since the sulfonic acid site loading was only 1.2 mmol.g^{-1}, identical to conventional sulfonated SBA-15 and far lower than less active Amberlyst-15 resins.

Figure 19. Activity of SO_3H functionalised mesporous carbon and graphene in cyclohexanol esterification. Reproduced from reference [145] with permission from The Royal Society of Chemistry.
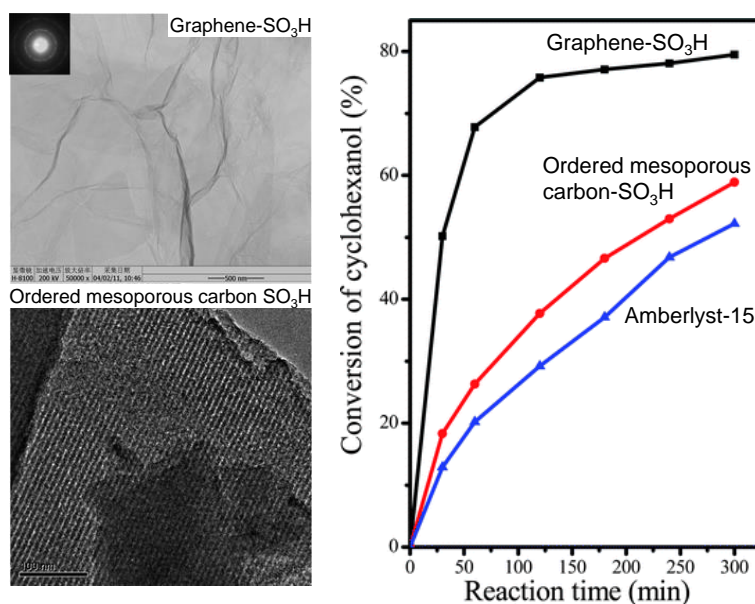
Sulfonated and carboxylated carbons derived from carbon xerogels (CXs) and nanotubes (CNTs) via sol-gel routes were employed by Rocha and co-workers for acetic acid esterification with ethanol (at a 1:10 acid:alcohol molar ratio) [146]. The two classes of carbon catalysts exhibited significantly different pore size distributions, with the CX materials possessing both micro- and mesopores, whereas the CNTs were purely microporous. Sulfonation was achieved via prolonged, high temperature treatment with concentrated H_2SO_4, resulting in S loadings ~1.80 mmol.g^{-1}, similar to those commonly reported for sulfonated silicas [90, 147, 148], whereas carboxylation was induced through nitric acid treatment of the parent carbons. The sulfated CX materials exhibited modest thermal stability, with sulphonic acid groups decomposing between 200-400 °C. Ethyl acetate production was approximately proportional to the sulphonic acid loading, as would be anticipated for a diffusion-free reaction occurring over isolated acid sites, proceeding with TOFs around 2 min^{-1} at 70 °C, comparable to values for single-walled carbon nanotubes under identical conditions [149], and for Nafion resin and sulfonated carbons synthesised via incomplete carbonisation of polycyclic aromatic hydrocarbons [150]. Unfortunately, recycle studies revealed a 40 % loss of sulfonic acid groups from the most active sulfonated CX material after three consecutive reactions, and concomitant fall in rates of ester formation, while the large excess of alcohol would be economically unfavourable for bio-oil upgrading.

2.6 PROCESS CONSIDERATIONS

The high water content in raw bio-oils has an undesirable impact on heating values, thus water removal from bio-oil is essential before using as a fuel. Furthermore, as organic acid esterification are equilibrium limited, removal of water is also critical to drive acid conversion in batch processes. While the use of molecular sieves to capture the water via reactive-adsorption has been proposed as a means to drive the reaction equilibrium for esterification [151], on-stream separation of water and/or ester via reactive distillation would lead to an improved efficiency. Reduced hydrogen bonding in the ester-containing mixtures also means removal of water is more facile from than

from the original acidic oil, allowing reactions to be conducted in which water is continuously separated by distillation [152]. In this instance to prevent excessive evaporation of the added alcohol, butanol was chosen as it has a higher boiling point than water and can also be source sustainably.

The use of reactive distillation as a means of effecting ester separation during esterification reaction has been explored for a number of industrial scale processes [153-155] for commodity chemical production. The application of such processes to bio-oil esterification has begun to receive some interest in the context of bio-oil pre-treatment using Amberlyst ion-exchange resins as benchmark esterification catalysts [145, 156, 157], enabling the continuous production of esters from bio-oil [26]. In this instance reactive distillation allows for an increase in acid conversion due to continuous removal of products, and reduction in energy costs as separation and reaction are performed in the same unit.
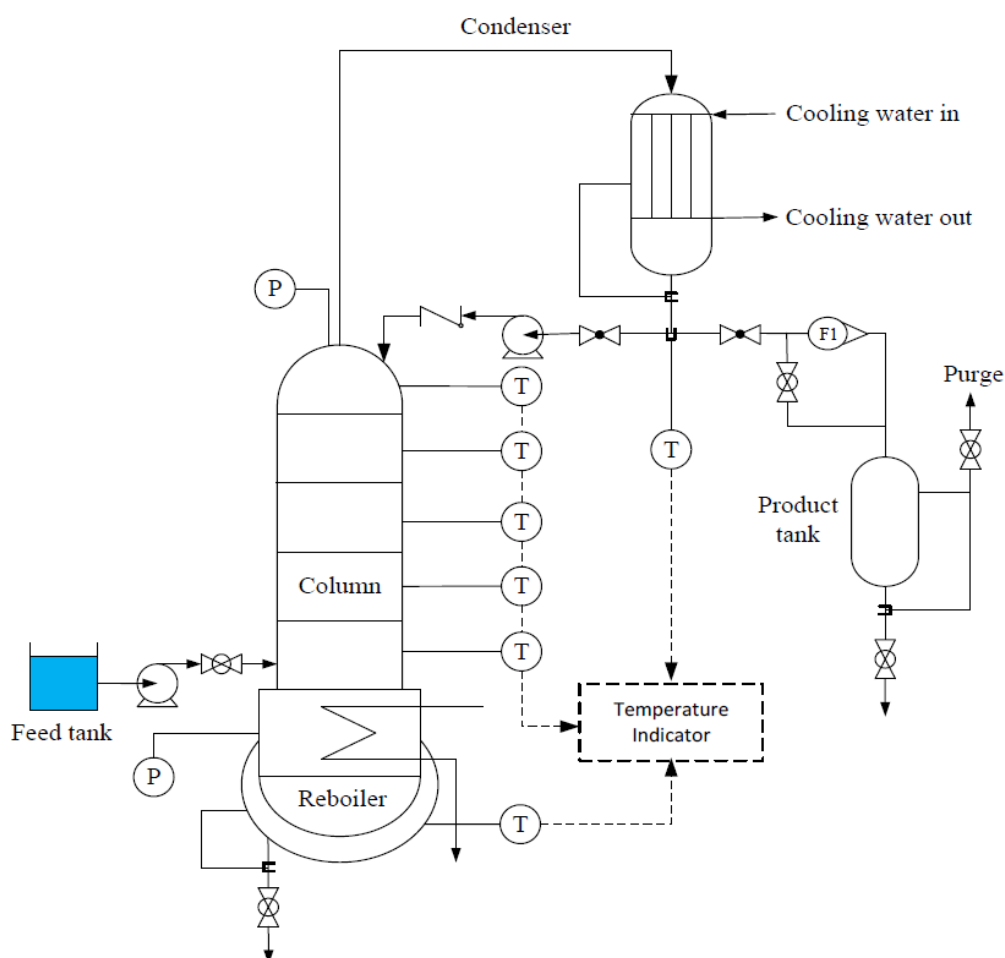
Figure 20. Schematic showing reactive distillation configuration. Reprinted from reference [158], with permission from Elsevier.

The application of reactive distillation to the esterification of bio-oil with ethanol has been explored using sulphated ZrO_2, TiO_2 and SnO_2 catalysts [31], in which SO_4^{2-}/ZrO_2 catalyst found to exhibit the highest catalytic activity. Ethyl formate and ethyl acetate have boiling points lower than their corresponding acids, (54.3 and 77.1°C c.f. 100.8 and 118 °C respectively) making reactive distillation and interesting method to allow on-stream separation of reactively formed esters from bio-oil. Reaction temperatures of 320–328 K were found to give good

acid conversion, with light oil components containing the ester removed ~328 K. The resulting esterified bio-oils were found to have reduced dynamic viscosity and enhanced fluidity, which was maintained after aging for 3 months under ambient conditions confirming the success of this approach.

2.7 CONCLUDING REMARKS

Catalytic esterification has a key role to play in the pre-treatment of acidic fast pyrolysis bio-oils in order to improve the oil stability and reduce its corrosiveness prior to additional thermochemical upgrading. In light of the high water content of conventional fast pyrolysis oils, new heterogeneous, solid acid catalysts are required for esterification which exhibit good hydrothermal stability and possessing hydrophobic surfaces designed to displace water from the active site and hence shift the reaction equilibrium to permit full conversion. Tandem design of catalysts and process will be important, as careful selection of the alcohol should facilitate reactive catalytic distillation to remove both water and ester on-stream, and thereby improve the fuel properties while simultaneously adding value to the process through the by-production of commodity chemicals which may find application as solvents and monomers.

Future developments and improvements are also likely to arise related to the pyrolysis process itself, with growing interest in fractional pyrolysis, which through careful control over the condensation of pyrolysis products enables better separation of the volatile acidic components from the less polar hydrocarbon fraction [159, 160]. Such approaches could conceivably permit in situ thermal separation of the different pyrolysis products arising from lignin, cellulose and hemicellulose, delivering oils of much reduced acidity and water content. However, this methodology would also lower the overall yield of liquid fuels, with predominantly lignin-derived components taken forward for upgrading to fuel. Esterification of acids contained within the polar, cellulosic-derived liquid phase could form an underpinning technology for the co-production of chemicals and fuels in such bio-refineries [161, 162].

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