Catalysis Today 145 (2009) 138–151

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

An examination of biorefining processes, catalysts and challenges

Daniel J. Hayes [a,b,*]

[a] Carbolea Biomass Research Group, Department of Chemical and Environmental Sciences, University of Limerick, Ireland
[b] Department of Agriculture Fisheries and Food, Dublin, Ireland

ARTICLE INFO

Article history:
Available online 25 June 2008

Keywords:
Biorefining
Cellulosic ethanol
Second generation biofuels
Enzymes
Thermochemical
Hydrolysis
Fischer-Tropsch

ABSTRACT

Biofuels offer the potential to substitute for a large proportion of fossil fuels, however it is considered that the utilisation of lignocellulosic biomass, via second-generation biorefining technologies, will be necessary for this to be achieved economically and sustainably. The lignocellulosic matrix is complex and recalcitrant to conversion but research in biorefining is advancing rapidly and commercial facilities are expected in the near-term. These facilities will either employ hydrolytic mechanisms to break apart the structural polysaccharides of the biomass, or thermochemical procedures to dehydrate and volatilise the feedstock. Catalysts serve vital roles in both approaches: acids and enzymes facilitate the hydrolysis of cellulose; while metal and biological catalysts can alter the volatilisation profiles of biomass or reform the gases that are liberated in the thermochemical process. Each potential biorefining technology currently has its own drawbacks and advantages and it is likely that a range of procedures will be needed in order to fully exploit the values of very diverse ranges of lignocellulosic feedstocks.

1. Introduction

The world is going through a crucial transitionary phase where circumstances dictate that economic activity and growth need to be decoupled from net energy expenditure. Fossil fuels currently serve the majority of our needs, both energetically and chemically [1]. However, their combustion is believed to be responsible for approximately three quarters of the anthropogenic emissions of CO_2 [2], a major greenhouse gas that contributes to global warming [3]. The possibility of reduced fossil fuel supplies in the future, either through geo-political conflicts, or through reaching a “Hubbert Peak” in their production, are also strong drivers for a search for alternatives. Electricity-producing renewable technologies, such as solar and wind, may satisfy our power needs but the short-term implementation of non-fossil-fuel-based chemicals and transport fuels will require the utilisation of biomass, particularly in view of the fact that hydrogen and fully electrified cars are unlikely to become viable on a mass scale for at least a decade [4]. Governments around the world have recognised this and have implemented minimum targets for the implementation of alternative fuels in the future, with the expectation that biofuels will play a major role in these targets. For example, the EU has indicative targets of a 5.75% (by energy content) substitution of fossil fuels by 2010 [5] and a mandatory target of 10% by 2020 while in the USA the Energy Independence and Security Act of 2007 mandates for 36 billion gallons of renewable fuels by 2022 [6].

2. First generation feedstocks

Currently all commercial production of biofuels comes from the conversion of sugar, starch or oil crops (termed first-generation feedstocks). Sugar (sucrose) and starch crops have been utilised for biofuel production due to the relative ease at which their constituent reducing sugar units can be separated in water (hydrolysed) and subsequently fermented. Sucrose, a disaccharide of α-D-glucopyranose and β-D-fructofuranose, freely hydrolyses in water [7]. Starch (Fig. 1) is a mixture of two polysaccharides: amylose and amylopectin. Amylose consists of repeating units of maltose, a disaccharide with α-$(1 \rightarrow 4)$-linked D-glucopyranose units. The axial nature of the glycosidic linkage limits the strength and abundance of intermolecular hydrogen bonds and thereby hydrolysis is facilitated. Amylopectin is the major constituent of most starches. It also contains glucose units linked via α-$(1 \rightarrow 4)$ bonds; however, there are also α-$(1 \rightarrow 6)$ branches that occur in plants every 24–30 glucose units [8]. These branches prevent the polymer from coiling into a helix so that no compact intermolecular alignment occurs. Hence, no significant hydrogen bonding can take place. Starches can be hydrolysed efficiently by the use of inexpensive enzymes, mainly alpha-amylase and gluco-amylase, and employing moderate reaction conditions [9].

---

[*] Tel.: +353 61 23 4381.
E-mail address: daniel.hayes@ul.ie.
URL: http://www.carbolea.ul.ie, http://www.biorefining.ie, http://www.baci.ie

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.04.017

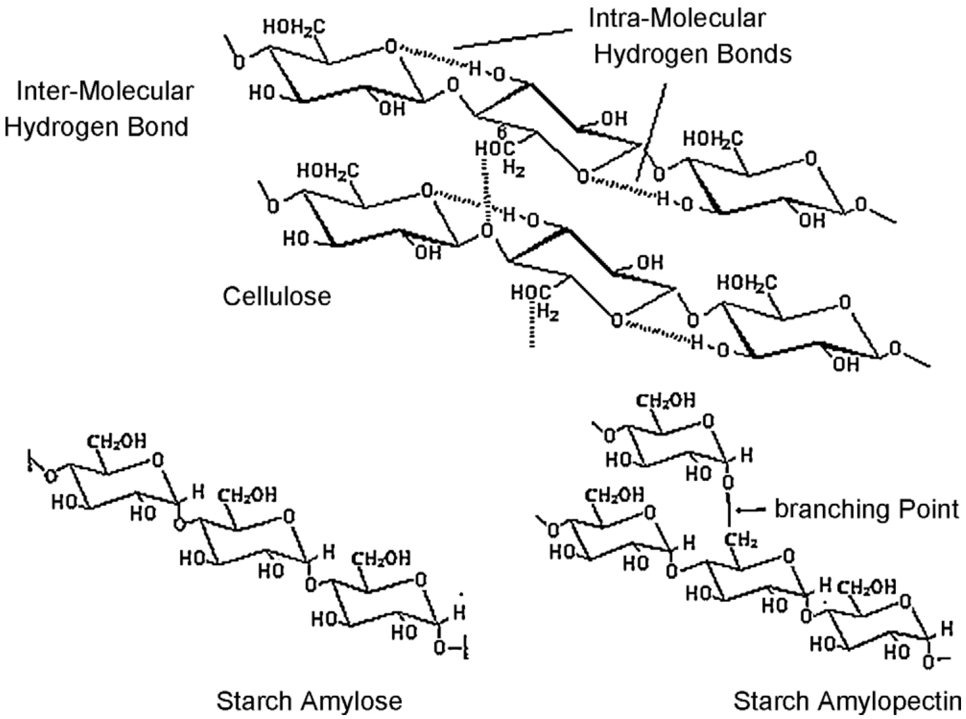

Fig. 1. Physical structure of cellulose and of starch amylose and amylopectin.

Despite their chemical advantages, there are drawbacks with first generation biofuels. Their costs can be high, particularly in Europe [10], and their net energy balance low [11]. The utilisation of high-quality arable land for their production has said to result in competition, between biofuel and food-requirements (the so-called fuel versus food issue), for this land and for the food/oil products that are produced. The recent rise in the price of various crops (such as wheat, maize and soya beans, which have dual roles as food and biofuel feedsocks), has been attributed, by some [12,13], to the greatly increased demand for biofuels in recent years by many developed nations. Furthermore, there are socio-economic concerns regarding the effects of these increased prices and reduced food production on the public health and economies of developing nations, particularly where these nations divert indigenous food production towards satisfying the biofuel needs of the western-world [14,15]. There are also concerns over the net benefits in terms of greenhouse gas production of many first generation feedstocks. For example, recent research has shown that the yield of the potent greenhouse gas, N_2O, from nitrogen applications in agro-biofuel production is 3–5 times greater than assumed in current life cycle analyses [16]. It is claimed that this could result in a net global warming of up to two times that which would have occurred if fossil-fuels had been used for transport instead [16]. It is possible that in the future excise relief given for biofuels may be proportionate to how sustainable the fuel is considered to be compared with the fossil-fuel equivalent [17,18].

3. Second generation biofuels and biorefining

Sucrose, lipids and starches are present in minor amounts only in most plants, and typically are not even the major components in most first-generation biofuel feedstocks. Most of the low-value, high-yielding biomass and wastes are termed lignocellulosic – which refers to their main constituent biopolymers of cellulose, hemicellulose and lignin. Cellulose is the most abundant biogenic polymer in the world with estimates of 3.24×1011 m^3 available globally [19] and an annual production of 100×10^9 tonnes [1]. Cellulose, like amylose, is a glucan whose D-anhydro-glucopyranose units are linked through $(1 \rightarrow 4)$-glycosidic bonds: however these links are of the β-configuration (Fig. 1). This allows intimate intermolecular associations, hydrogen bonding, and crystallinity. The end result is that cellulose is of the order of 100 times more difficult to hydrolyse than starch [20].

The term hemicellulose covers a variety of complex carbohydrate polymers that are mostly not extractable by hot water or chelating agents but, unlike cellulose, are extractable in aqueous alkali [21]. These constitute the cell wall polysaccharides of land plants that are not cellulose or pectins [22]. Hemicelluloses tend to be branched heteropolysaccharides that are mostly built up of the pentose D-xylose with smaller amounts of the pentose L-arabinose and the hexoses D-glucose, D-mannose and D-galactose, as well as some uronic acids and acetylated derivatives [7]. Hemicelluloses have typically a much lower degree of polymerisation than cellulose and are easier to hydrolyse. Lignin is a complex three-dimensional polymer of phenylpropane units that has a carbon content around 50% (greater than that of cellulose) [23].

The key to exploiting the chemical value of lignocellulosics is to depolymerise the lignocellulosic matrix in order to obtain smaller molecules that can be utilised, or further converted to platform chemicals and biofuels. The technologies for doing this can be termed second-generation (where biofuels are an end-product). They can also be termed biorefineries, an analogy to oil refineries since, like these, biorefineries obtain a variety of end products according to the chemical components of the starting materials. This definition of a biorefinery can also apply to biofuel facilities that process first-generation feedstocks [24,25] as well as existing pulp mills and various facilities in the food industry. For example, corn wet-mills can produce an array of products (such as sweetners, corn oils, animal feed, ethanol, and bio-plastics) and the quantities and variety of products can be manipulated according to the end needs of the market and producer. For example, the wet-mill plant of National Starch and Chemical in Indianapolis, USA, makes specialty starches, while their facility in Kansas focuses on adhesives [26]. This paper will only consider biorefineries that process lignocellulose, however, since these feedstocks (which include municipal wastes, straws, grasses, woods and energy crops such as Miscanthus) are much more abundant than first-generation biomass and, hence, are typically of a lower cost. Furthermore, lignocellulosic feedstocks can, to a large part, avoid many of the pitfalls associated with the use of food or oil crops for the synthesis of chemicals and fuels.

Firstly, the energy costs of the whole supply cycle of these feedstocks are generally significantly lower [11,27], for example a recent life cycle analysis found that ethanol produced from switchgrass contained 540% more energy than that required for its production [28]. Where pre-existing waste resources are used as feedstocks, the energy costs are likely to be even lower. An additional benefit, that is associated with lower energy costs, is that the life-cycle emissions of greenhouse gases are likely to be significantly lower with lignocellulosic feedstocks [29–31]. For example, the same study found that estimated average greenhouse gas emissions from cellulosic ethanol derived from switchgrass were 94% lower than those from gasoline [28], while Adler et al. [32] calculated that ethanol sourced from reed-canary grass could reduce greenhouse gas emissions, compared with the life cycle of gasoline, by approximately 85%, with corn-ethanol only providing a 40% reduction. Also, while the production of annual first-generation feedstocks, such as maize, can be associated with soil degradation and the loss of organic carbon from the soil [33], certain perennial energy crops, such as Miscanthus, avoid the need for frequent tillage while the extensive roots that they develop over their lifespan are said to result in an increase in soil organic carbon [34,35]. Considering this dynamic, Adler et al. [32] calculated that ethanol from switchgrass and hybrid poplars reduced greenhouse gas emissions (over petrol-derived transport fuels) by approximately 115%, while it has also been claimed that low-input high diversity mixtures of native grassland perennials can allow carbon-negative biofuels [36]. Refocusing biofuel production towards second-generation technologies can also address many of the food versus fuel and socio-economic concerns addressed earlier in this paper since there will be no direct competition for food crops, waste resources can be utilised (to the mutual benefit of developed and developing nations), and land that is unsuitable for the production of food can be utilised for lignocellulosic energy crops.

Table 1 lists the second generation biorefining companies that may have commercial facilities online within the next three years. The technologies and processes employed are also mentioned in Table 1, as are the pilot- or demonstration-scale facilities currently operated by these companies. There are numerous other companies and technologies that are currently operational on the pilot scale and these may also become commercial in the future.

4. Hydrolysis technologies

There are two major pathways by which biorefineries operate: through hydrolytic mechanisms that aim to liberate free monosaccharides from the lignocellulosic polysaccharides, and through thermochemical processes that degrade more extensively the components of both polysaccharides and lignin. The various technologies available for the hydrolytic or thermochemical processing of biomass, along with their products and possible pre-treatment steps, are illustrated in Fig. 2.

Cellulose is hydrolysed in pure water through attack by the electrophilic hydrogen atoms of the H_2O molecule on the glycosidic oxygen. This is a very slow reaction due to the recalcitrance of cellulose, but it can be speeded up using elevated temperatures and pressures, and catalysed by acids (concentrated or dilute) and highly selective enzymes such as cellulases.

4.1. Pre-treatment techniques

Biomass is more than just cellulose, however, and the process is complicated by the relative ease with which hemicellulose can be hydrolysed (at least through non-enzymatic means). A severe means of hydrolysis targeted for the liberation of glucose from cellulose may result in the sugars liberated from hemicellulose being degraded to derivatives of less value that may also inhibit fermentation [37].

Hydrolytic mechanisms are also influenced by the complex inter-associations between hemicellulose and cellulose and between these polysaccharides and lignin in the lignocellulosic matrix. In particular, the crystalline nature of much cellulose and the existence of a physical barrier of lignin surrounding the cellulose fibres are said to be major contributors to the recalcitrance of cellulose [7]. For this reason, most hydrolysis technologies employ pre-treatment processes that aim to break apart the matrix (and in particular the associations between lignin and cellulose), reduce cellulose crystallinty, and hydrolyse hemicelluloses, hence separating the hydrolysate from cellulose which can then undergo more severe/targeted treatment.

Pre-treatment is currently one of the most expensive stages in second-generation technologies with estimates of operating costs as a high as 30 c per gallon of ethanol [38], and with capital costs of $2.24 m per million gallon capacity [39] for the most cost-effective pre-treatment technology. Pre-treatment is, however, crucial for ensuring good ultimate yields of sugars from both polysaccharides. For example, yields from enzymatic hydrolysis without pre-treatment are usually less than 20% whereas with pre-treatment yields can rise to over 90% [40].

Table 1

The companies that are likely to have commercial scale (>10 ml output a year) biorefineries operational in the next three years

Company	Process	Main outputs	Current facility (April 2008)	Full scale	Output
Abengoa	Enzymatic hydrolysis	Ethanol	Demo plant—5 ml (2008)	2010	57 ml
Alico	Biocatalytic gasification	Ethanol	Pilot plant (2003)	2009	53 ml
BlueFire Ethanol	Concentrated acid hydrolysis	Ethanol	2 pilot plants, largest → 81,000 l/year	2010	72 ml
Choren	Gasification and FT synthesis	FT-Diesel	Pilot plant. Demo plant (15,000 tonnes output) expected 2008	2011	200,000 tonnes
Colusa	Solvent treatment and enzymatic hydrolysis	Ethanol	Pilot scale	2009	45 ml
Coskata	Plasma gasification and biocatalytic synthesis	Ethanol	Lab-scale. 150,000 l (late 2008)	2011	370 ml
Iogen	Steam explosion and enzymatic hydrolysis	Ethanol	Demo plant (2004): ~3 ml/year	2011	90 ml
Poet	Enzymatic hydrolysis	Ethanol	Pilot plant	2011	115 ml
Range Fuels	Gasification and mixed alcohol synthesis	Ethanol, methanol	Pilot plant	2008	38 ml
Royal Nedalco	Enzymatic hydrolysis	Ethanol	Lab-scale	2011	200 ml
Verenium	Enzymatic hydrolysis	Ethanol	3 pilot plants. Largest 1.3 ml (2007)	2011	110 ml

The commercial pyrolysis companies are not included since their current output is focussed on electricity.

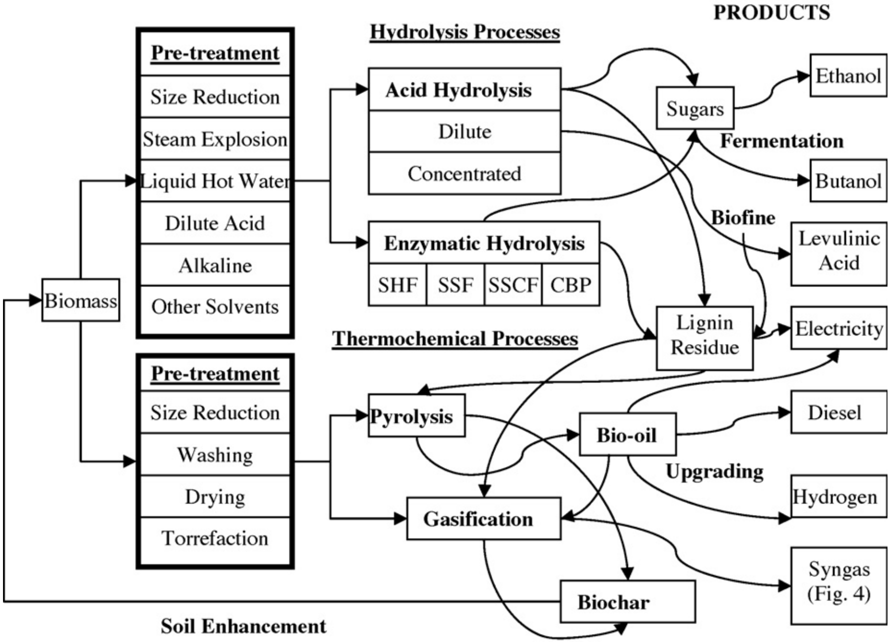

Fig. 2. The various pre-treatment and subsequent conversion technologies possible for the treatment of lignocellulosics. The production of a biochar through pyrolysis can offer a feedback mechanism to the cycle by increasing biomass yields when it is applied to land.

4.1.1. Physical pretreatments

4.1.1.1. Size-reduction. Small particle sizes, and hence greater surface areas, are necessary for many biorefining technologies, including many thermochemical processes, in order to facilitate an efficient and rapid reaction. There are various techniques used for the comminution of biomass, including dry, wet and vibratory ball milling [41,42] and compression milling [43]. However, where the smallest particle sizes are needed, as in some dilute acid pre-treatment processes and in entrained flow gasifiers, the energy costs required may account for up to a third of the total energy demand of the biorefinery [44].

4.1.1.2. Steam explosion. Steam explosion pre-treatment technologies have been an active area of research for the past two decades [45,46] and will be incorporated into many of the first commercial biorefineries that are based on the hydrolysis procedure. Iogen have developed their own steam pre-treatmernt process while Abengoa, China Alcohol Resources Corp., Celunol, and GreenField Ethanol have planned to utilise the technology developed by SunOpta. In that process, partially comminuted biomass is subjected to high pressure steam (at 210–290 °C) for several minutes before this steam is rapidly vented, resulting in an explosive decompression and flash cooling of the biomass. A feedstock that is much more amenable to enzymatic hydrolysis results and it is considered that this is possible due to the hydrolysis of hemicellulose (catalysed by acetic and other acids liberated from it by the steam, and also catalysed by the lowered pH of water seen at high temperatures [47]). The effectiveness of steam explosion is dependent on the biomass feedstock; for instance the process is less effective for softwoods than for hardwoods [40], probably due to the fact that softwoods have much less acetyl groups [22].

The process can take place uncatalysed (in which case the yield of xylose sugars is only 45–65% [48]), or catalysed with dilute sulphuric acid (where xylose yields can be over 70% [49]). Ammonia fibre explosion (AFEX) substitutes liquid ammonia for steam [50]. This does not result in an extensive solubilisation of lignin but it does disrupt lignin-hemicellulose bonds [51], depolymerises lignin [52], and results in a swelling and modification of the cellulose crystal structure form giving rise to change from cellulose I to cellulose III [38]. The result is a high sugar yield, and an excellent substrate for enzymatic hydrolysis [53]. While the more moderate conditions employed for AFEX decrease energy requirements, the expense of ammonia and the need to recycle it increase operating and capital costs [54]. Also, dealing with the oligosaccharides formed from hemicellulose is more complex than dealing with their component monosaccharides [55]. Carbon dioxide can also be used in a physical explosion process. It is more cost effective than steam or ammonia explosion, and it does not result in the fermentation inhibitors that can be arise in steam explosion [48]. However, the yields of glucose from the subsequent enzymatic hydrolysis are lower (approximately 75% [40]).

4.1.1.3. Liquid hot water. This pre-treatment process is still at the lab-scale but offers the potential for high xylose recovery from hemicellulose (88–98% [40]) and a reduction in cellulose recalcitrance to enzymatic hydrolysis [56], and with minimal/no comminution of the biomass necessary [57]. It involves superheated water (180–230 °C) that is kept in the liquid state through high pressures and put in contact with the biomass via various pathways [38]: co-current pre-treatments involve the biomass and water being held in a slurry which is warmed and then cooled; counter-current pretreatments move the biomass and water in opposite directions; and flow-through pre-treatments involve the water passing over the stationary biomass. Up to two thirds of the lignin and one quarter of the cellulose can also be dissolved, depending on the conditions employed and the feedstock used [38,58]. If the pH is maintained between 4 and 7, the degradation of monosaccharide sugars can be minimised [59].

4.1.2. Chemical pretreatments

4.1.2.1. Acid-catalysed pretreatment. Dilute acids (traditionally sulphuric, but nitric and hydrochloric acids have also been used), when employed in a pre-treatment stage, are principally concerned with the hydrolysis of hemicellulose and the subsequent removal of its component sugars and their degradation products. As with acid-catalysed cellulose hydrolysis, the main consideration with acid pre-treatment involves ensuring minimum degradation of the liberated monosaccharides (unless degradation products such as furfural are desired). Xylose yields of 75–90% are possible if this is done effectively [48]. Another issue with the use of acids is the buffering capacity of the feedstock. Ash tends to lower the acidity of the mixture—the catalytic hydrogen ion is a function of the concentration and amount of the applied acidic solution and the neutralizing power of the ash [60]. The effect of acid pretreatment on cellulose is also an important consideration. Some amorphous regions of the polymer can be hydrolysed [60] and this can result in a strong decrease in the degree of polymerisation (DP) of cellulose [61]. The term 'Level-Off Degree of Polymerisation' (LODP) is often used for the DP of the remaining crystallites of cellulose after this preliminary acid hydrolysis [62].

4.1.2.2. Alkaline catalysed pretreatment. Alkaline treatments are similar to those used in Kraft paper-pulping processes and, compared to acid pre-treatments, are more focused on the solubilisation and removal of lignin from the biomass rather than hydrolysis of hemicellulose which tends to remain insoluble [40]. However, acetyl and uronic acid groups are removed from hemicellulose, further improving the digestibility of the polysaccharides to enzymatic treatments [63]. Conditions are more mild than acid pre-treatments, with a corresponding increase in reaction times, which may be as long as several weeks where ambient conditions are used [59]. While sodium, calcium, and potassium hydroxide can be used, their high costs and poor recoveries (some of the alkali is converted to irrecoverable salts that may be incorporated into the biomass [45]) are distinct disadvantages and the use of lime, which is cheap and can be recovered from water as insoluble calcium carbonate by reaction with carbon dioxide [64], is favoured [38,59]. More complete removal of lignin can be facilitated by the addition of oxygen or air [65] to the biomass pile. Colusa, based in California, employs in their process a high-concentration of NaOH (∼50%) to dissolve the lignin from the biomass (which has already had its hemicelluloses hydrolysed via dilute acid pretreatment) over a period of approximately 2 h [66].

A more severe combination of oxygen and alkaline conditions occurs in the wet oxidation pre-treatment process. The biomass is treated, under alkaline conditions, with superheated water (185 °C+) that, as with LHW, is kept a liquid through elevated pressures. Oxygen is added and is said to facilitate the hydrolysis of most of the lignin and hemicellulose leaving a purified and less crystalline cellulose fraction that is highly amenable to enzymatic digestion [67] and with no effective ethanol-inhibitors formed [68]. The Dutch company Biogashol has developed a new process, called wet explosion, which integrates steam-explosion with this process by rapidly reducing the pressure after wet-oxidation [69].

4.1.2.3. Other solvents. Hydrogen peroxide, ozone, glycerol, dioxane and phenol are some other solvents that have facilitated the de-crystallisation and depolymerisation of cellulose [70]. Examples of solvents employed in pre-commercial technologies include ethanol (by Lignol [71] and Flambeau River Biorefinery [72]) and acetone (employed in the Acid Catalysed Organosolv Saccharification (ACOS) process of Paszner Technologies [73]).

Some of the traditional solvents for the dissolution of cellulose, hemicellulose and/or lignin can be toxic, however, and may require the use of relatively harsh conditions [74,75]. In recent years there has been a growing interest in the use of the more environmentally benign Ionic Liquids (ILs) as solvents for lignocellulose [74,76,77]. These are salts, typically composed of large organic cations and small inorganic anions, that exist as liquids at relatively low temperatures, often at room temperature [75]. Their solvent properties can be varied by adjusting the anion and the alkyl constituents of the cation [77]. Attractive properties include chemical and thermal stability, non-flammability, low vapour pressures and a tendency to remain liquid through a wide range of temperatures [74]. The solubility of cellulose has been demonstrated in some hydrophyllic ILs, such as 1-butyl-3-methylimidazolium chloride (BMIMCl) and 1-allyl-3-methylimidazolium chloride (AMIMCl) [75,78], with dissolution accelerated under microwave heating [75] and sonication [77]. The mechanism of dissolution is said to involve the chloride ions in the IL breaking the hydrogen bonding of cellulose, while longer alkyl chains of the cation reduce dissolution efficacy [77]. The use of ILs has also been demonstrated on lignocellulosic feedstocks such as wood [79] and straw [80]. The whole lignocellulosic matrix is dissolved, disrupting the complex associations between the cellulose, hemicellulose and lignin. A relatively pure cellulose can then be precipitated by the addition of water, ethanol or acetone [75] while the lignin and other components remain dissolved [74]. This regenerated cellulose can have a similar degree of polymerisation as before IL treatment, however the degree of crystallinity can be manipulated during regeneration. This means the use of ILs can be an effective means of pre-treatment, producing a cellulose that is more amenable to hydrolysis [81]. Results have shown this cellulose enables a higher eventual yield of reducing sugars than other pre-treatment methods, such as steam explosion, allow [76]. Some enzymes, such as cellulases [35], can retain their activities in ILs [82] with improved enzyme compatibility being associated with a reduced hydrogen bonding affinity of the IL anion [77]. Since an increase in this affinity favours the dissolution of cellulose, there can be a trade-off between dissolution and enzyme activity [77]. Therefore, where ILs are to be used as a pre-treatment in enzymatic hydrolysis processes, it may be necessary to recover the regenerated cellulose [81] or to develop ILs, such as 1-ethyl-3-methylimidazolium diethylphosphate, that are compatible with both cellulose solubility and cellulase activity [83]. ILs may also have utility in the synthesis of important carbohydrate degradation products, such as hydroxymethyl furfural [77] and, hence, offer the potential to increase yields and reduce energy costs of technologies such as the Biofine process [84] that target these. Research is also ongoing into the extraction of non-cellulosic products, such as oil from pine needles [74], with ILs and into the synthesis of tunable cellulose composites and derivatives, such as cellulose acetate [85], with ILs under much milder conditions than traditional methods [75]. It is generally considered [76,77], however, that further research is needed to improve the economics of ILs before they can be used at an industrial scale since they are currently expensive and commercial IL recovery methods have not been fully developed. Also, techniques need to be developed to recover hemicellulose and lignin from solution after the extraction of cellulose. Despite these current limitations, IL's could have a great potential in future lignocellulosic biorefining processes and advances such as the potential synthesis of ILs from carbohydrates [86] may play a role in reducing their costs.

4.2. Hydrolysis techniques

Assuming a pre-treatment step that hydrolyses the hemicelluloses has already taken place, most current technologies either use acids or enzymes to catalyse the subsequent degradation of cellulose. The acid hydrolysis of lignocellulosic materials was commercialised in the late 19th century [40] and several dilute-acid facilities existed in the USA, Germany, Japan, and Russia by World War 1 while concentrated acid hydrolysis facilities were being built between 1937 and the late 1960s [87]. However, these were uneconomic where fossil fuels were available and none exist for the commercial production of ethanol fuel today. It is hoped that modern technologies, using either acids or enzymes, can reinvigorate the industry.

4.2.1. Dilute acid hydrolysis

Typically, most of these technologies employ a dilute acid pretreatment step under moderate temperature conditions (140–160 °C) to release the pentoses. In the second stage the temperatures are raised to 200–240 °C to facilitate the hydrolysis of cellulose and recovery of six carbon sugars. Modern experimental yields for this two-stage acid process (3 min per stage) are 89% for mannose, 82% for galactose, but only 50% for glucose with a glucose to ethanol conversion that is 90% of the theoretical maximum [88]. Indeed, it is considered that this glucose yield is close to the theoretical limit possible with plug-flow reactors [89]. It is probably the crystallinity of cellulose that limits yields, given that the rate of hydrolysis of amorphous cellulose is significantly greater than that of crystalline cellulose (Bungay, 1981). Hence, conditions for the hydrolysis of crystalline cellulose may degrade the sugars obtained from amorphous regions into products such as hydroxymethyl furfural and levulinic acid. The National Renewable Energy Laboratory (NREL) estimated that a counter-current hydrolysis, where a steam pre-treatment is employed, may allow an increase in glucose yields to 84%, and an increase in fermentation yield of ethanol to 95%, [90]. Other alternatives involve the use of sulphur dioxide rather than sulphuric acid.

4.2.2. The Biofine process

The Biofine process [84,91,92] is unique among all the near-commercial biorefining technologies employing hydrolytic mechanisms in that it does not require any biotic activity for the conversion of biomass to the final saleable product. It uses dilute sulphuric acid in a two-reactor system engineered to obtain high yields of the platform chemicals levulinic acid (with hydroxymethylfurfural as a key intermediate) and furfural (Fig. 3) from the degradation of the hexoses and pentoses liberated from the structural polysaccharides of lignocellulosic biomass [84]. The advantage of the technology over previous attempts to obtain LA is that the yields are 70–80% [91,92] of the theoretical maximum of 71.6% by mass of cellulose [93]. This translates to the conversion of approximately 50% of the mass of 6-carbon sugars to LA, with 20% being converted to formic acid and 30% being incorporated in the residual "char" material which also contains all of the Klason lignin and the 50%, by mass, of pentoses that do not convert to furfural. Previously developed technologies that attempted to produce LA from lignocellulosics had high costs due to low LA yields (around 3% by mass) and significant tar formation due to the complexity of the glucose to LA pathway [84,94,95]. The Biofine yield data result from trials at two pilot plants in the US where various feedstocks, including agricultural residues, paper sludges, and the organic fraction of municipal waste, have been processed [96], as well as by a 50 tonne per day commercial facility that is being commissioned in Caserta, Italy and will process waste paper, municipal wastes and agricultural residues.

LA is a useful platform chemical [97,98]. Its value comes from its particular chemistry—it has two highly reactive functional groups that allow a great number of synthetic transformations; LA can react as both a carboxylic acid and a ketone. The carbon atom of the carbonyl group is usually more susceptible to nucleophilic attack than that of the carboxyl group. Due to the spatial relationship of the carboxylic and ketone groups, many of the reactions proceed, with cyclisation, to form heterocyclic type molecules. It is this mechanism that is used to produce methyltetrahydrofuran (MTHF—Fig. 3) from LA [1]. Work at the Pacific Northwest Laboratory (PNL) in the US [99] allowed MTHF to be produced in high yields (63 kg [71 l] MTHF from every 100 kg of LA) via catalysed hydrogenation of LA to γ-valerolactone (GVL) which, upon further hydrogenation, yields 1,4-pentanediol and finally MTHF. The catalyst is bifunctional. The first functionality involves hydrogenation and the second, ring-opening. Highest yields were achieved when a bimetallic catalyst with a weight ratio of Pd (5%)/Re (5%) supported on a carbon carrier material was used. The first reaction is catalysed by palladium, and the second by rhenium. In the process, LA is pumped into a tube where it is warmed to about 40 °C, then mixed with hydrogen. Both compounds are then pumped through a reactor filled with the catalyst, where conditions of 240 °C and 100 atmospheres pressure create MTHF [99]. The procedure requires three moles of hydrogen per mole of LA. MTHF has shown promise as a petroleum additive where volumes of up to 30% can be added with no adverse effects on performance, or engine modifications needed [100]. The ability of MTHF to significantly reduces the vapour pressure of ethanol when co-blended in gasoline led to the development of "P-Series" fuels where MTHF acts as co-solvent for ethyl alcohol (high-octane) in "pentanes-plus" hydrocarbons obtained from natural gas [101].

Ethyl levulinate (EL) can be produced by esterifying LA with fuel-grade ethanol. Biofine and Texaco developed EL as an oxygenated diesel additive. The 21:79 formulation consists of 20% ethyl levulinate, 1% co-additive and 79% diesel, and can be used in regular diesel engines. LA esters are similar to the biodiesel fatty acid methyl esters (FAME) but they do not have their principal drawbacks (cold flow properties and gum formation [102]). The addition of ethyl or methyl levulinate to FAME may be expected to alleviate both these problems.

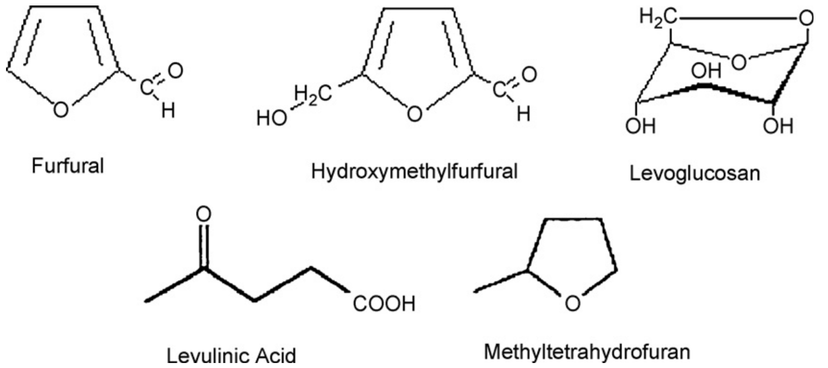

Fig. 3. Chemical structures for some of the products from the Biofine process and pyrolysis.

Formic acid has many existing uses in agriculture, clothing, and industry. The catalyst preparation sector represents a very large potential future market for formic acid. Formic acid is also used in the regeneration of catalyst metals poisoned with sulphur. Additionally, esters of formic acid (e.g. methyl and ethyl formate) may have value as fuel components and as platform chemicals.

Furfural can be sold as a solvent or used in the production of furfuryl alcohol, tetrahydrofuran (THF) and LA [95]. THF is produced by decarbonylation of furfural to furan followed by catalytic hydrogenation [103].

The residual char from the Biofine process has use as combustion or pyrolysis/gasification feedstock, and it is expected that a facility processing 300 dry tonnes of feedstock per day will have an energy surplus allowing extra revenue from the sale of electricity [84]. Economic forecasts predict that a facility processing 1000 dry tonnes of wood per day could produce 133,000 tonnes of EL a year (assuming an input of 35,000 tonnes of ethanol) at a production cost of $291/tonne, equivalent to $12/GJ [84].

4.2.3. Concentrated acid hydrolysis

This process involves an acid (dilute or concentrated) pre-treatment to liberate the hemicellulosic sugars while the subsequent stage requires the biomass to be dried followed by the addition of concentrated sulphuric acid (70–90%) [90]. The concentrated acid converts the cellulose to a completely amorphous state. Once decrystallised, it forms a homogeneous gelatin with the acid. The cellulose is extremely susceptible to hydrolysis at this point. Thus, dilution with water at modest temperatures provides complete and rapid hydrolysis to glucose, with little degradation [61], particularly when compared with dilute acid treatments [88,104]. Indeed, the degradation is so low that the use of concentrated sulphuric acid is an accepted test method for quantifying the monosaccharide content of the polysaccharides of biomass as well as for the Klason lignin content [19,105,106]. A variety of feedstocks processed in bench-scale studies averaged over 95% conversion of xylan to xylose and over 87% conversion of cellulose to glucose [107].

The procedure takes approximately 10–12 h and the concentrated acid conditions allow a greater variety of feedstocks, such as municipal wastes, than other techniques. The major problem with this process, apparent since its inception, is the need to minimise the cost involved in purchasing concentrated acid, by recovering it via effective separation from the sugars. While acid recovery rates have risen from 80% to 97% in the last 50 years, via continuous ion exchange separation techniques [40], the capital and operational costs involved are still higher than for dilute acid methods [108].

BlueFire Ethanol received a grant of $40 m from the US Department of Energy to build a commercial facility in California that will process MSW via their Arkenol concentrated acid process [109] that has been tested at two pilot facilities. It is claimed that it will produce 72 ml of ethanol per year from 700 tonnes per day of waste (255,000 tonnes per year) at a cost of less than $1 per gallon (US). However, it is not clear if such a low price is the result of significant gate fees. Such fees are considered vital for the MSW to ethanol concentrated acid hydrolysis facility planned by Masada OxyNol for Middleton, New York [110].

4.3. Enzymatic hydrolysis

Most enzymatic hydrolysis technologies first employ any of the pre-treatment methods mentioned above for the hydrolysis of hemicellulose and to make a more digestible cellulose (although there has been some research on enzymatic hydrolysis of hemicellulases without prior pre-treatments [111]). Cellulase enzymes are then used to selectively hydrolyse the cellulose to glucose. This occurs under much milder process conditions (30–70 °C) than with dilute acid hydrolysis; hence the potential for sugar degradation is significantly decreased [112]. Indeed, it is considered that enzymatic hydrolysis may ultimately offer the highest potential yield of glucose from cellulose [113]. The cellulases can be obtained from a variety of micro-organisms, including bacteria and fungi. However, aerobic fungi typically give higher growth rates and are the focus of most research [49].

A cellulase is actually a mixture of many different enzymes each of which has a specific role in the hydrolysis of cellulose. For instance, endo-1,4-β-D-glucanases act internally within a cellulose chain at amorphous cellulose regions to cleave glyocisidc bonds, reducing the degree of polymerisation, while cellobiohydrolases degrade the cellulose chain from either the reducing or non-reducing ends and can cleave glycosidic bonds within crystalline cellulose regions releasing cellobiose [114]. Current technologies (including those of Iogen and Genencor) produce enzymes in a separate tank to that for hydrolysis. Glucose is a poor carbon source for enzyme productivity since it favours the production of cellular mass. Inducers of cellulase include cellobiose, lactose, and sophorose [37]. A cellulase production run lasts approximately one week after which the spent cell mass is disposed of [37].

There are a variety of factors that affect both the yield of sugars and the rate of hydrolysis. Regarding the biomass: cellulose crystallinity [63] and degree of polymerisation [115], hemicellulose acetyl content [116], and increased particle size [117] all hinder enzymatic hydrolysis. These are all considerations when selecting an appropriate pre-treatment technique [37,118]. The lignin polymer is also a hindrance to hydrolysis, not only because of its absolute content [114], but also because of its particular composition [119] and its associations with polysaccharides [120]. Iogen claims that the efficiency of cellulose hydrolysis is dependant on the arabino-xylan content of the feedstock and that feedstocks, such as softwoods, with low levels demand unacceptably high levels of enzymes [37]. Enzymes are also somewhat sensitive to contaminants such as silica [37]. Thus, the range of feedstocks that are considered suitable for enzymatic treatment have been somewhat limited to date.

The products of cellulose hydrolysis, such as glucose and cellobiose, can also be inhibiting to cellulase activity. Hence these need to be removed by some means or an oversupply of enzymes will be necessary. A high substrate concentration may increase rates and yields. However, if the ratio of substrate to cellulase is too high inhibition may occur [40]. Hydrolysis can also be facilitated through the addition of surfactants, other enzymes (e.g. pectinase), and by using a mixture of enzymes from other organisms [40].

5. Fermentation of sugars

There are numerous technologies proposed for the enzymatic hydrolysis of biomass. The most basic of these involves the enzymatic hydrolysis of cellulose followed by fermentation of the liberated hexoses. Pentose fermentation can occur after the distillation of the resulting beer, or with a separate stream taken from the hydrolysate of the pre-treatment process. This process is termed Separate Hydrolysis and Fermentation (SHF). The more advanced enzymatic hydrolysis technologies combine the processes of hydrolysis and fermentation; hence it is necessary to examine the issues relating to the fermentation of sugars liberated from lignocellulosic biomass.

While aerobic mechanisms allow rapid growth for microorganisms via the conversion of sugars to water and carbon dioxide, anaerobic conditions can favour the production of ethanol in high yields. Historically, the yeast *Saccharomyces cerevisie* has been used for the fermentation of ethanol from glucose with carbon dioxide as the inevitable by-product. In an ideal situation, where the micro-organism worked at 100% efficiency and required none of the sugar for the growth of its own cell mass, the weight of ethanol would be 51.11% of that of glucose (according to the molar ratios and masses of glucose and the products). Hence, at least 48.89% of the sugar mass from glucose will be converted to CO_2 which has little or no value.

Xylose fermentation can occur via several pathways, according to the conditions and specific biotic activity, with practical mass yields of ethanol ranging between 20 and 50% [121,122]. However *S. cerevisa* can not ferment pentoses, hence much research over the last few decades has been concerned with finding or engineering microorganisms that can efficiently ferment hexose and pentose sugars with no overpowering selectivity for either. Bacteria, such as *Zymomonas mobilis* and *E. coli*, have attracted particular interest, given their rapid fermentation, which can be minutes compared to hours for yeasts [40]. Several companies have been involved in engineering efficient hexose-fermenting microorganisms so that they can also ferment arabinose and xylose. For example, NREL has incorporated the pentose metabolism genes of *E. coli* into *Z. mobilis* [123], and this microorganism will be utilised in the BlueFire Ethanol process. BioGasol will use a *Saccharomyces* yeast that has had the xylose-fermentation pathway gene from the *Piromyces* fungus incorporated [124].

There are other problems seen in the fermentation of lignocellulosic hydrolysates beyond the diversity of sugars; these include the presence of sugar degradation products from pre-treatment and hydrolysis (if hydrolysis is non-enzymatic). These products include furfural from pentoses and hydroxymethylfurfural and levulinic acid from hexoses. These can be present in significant quantities [60]. These by-products can also be inhibiting to enzymatic hydrolysis. Technologies to remove these inhibitors can be expensive and are not wholly efficient. Research is ongoing to develop hardier microorganisms that are less sensitive to the presence of inhibitors, so minimising the need for extensive detoxification of the hydrolysate. For example the Research Institute of Innovative Technology for the Earth (RITE) in Japan claims, in conjunction with Honda, to have developed a micro-organism that is more resistant to inhibitors, allowing high ethanol yields and aims to test the technology in a pilot plant in 2008. Research is also ongoing to find or engineer micro-organisms that can tolerate higher ethanol concentrations given that the maximum level currently tolerated is about 10% at 30 °C and less at higher temperatures [40]. A higher ethanol concentration will reduce the costs associated with its recovery.

It is important to note that there any many other possible fermentation products besides ethanol, provided different metabolic pathways are employed. These include lactic acids and acetic acid [117]. Butanol is another potential fermentation product that is the focus of much research since it has several superior properties over ethanol. For instance, it is less corrosive, has a similar energy content to petrol, is more compatible with existing fuel-infrastructure and can be blended to higher extents in conventional engines. The necessary research to make bio-butanol economical is centred on the fermentation pathway [125], since conventional hydrolysis mechanisms can be employed to get the liberated sugars. The ABE processes [126] produce acetone, butanol, and ethanol, but the micro-organisms can deliver only a very low butanol concentration and the energetic and economic costs associated with separation are currently too high [126]. Several companies, including LS9 and Synthetic Genomics, are investigating the bio-production of petrol-/diesel-like fuels from free sugars (and, ultimately, virgin biomass) via complex pathways that synthesise hydrocarbons of a longer carbon-chain length than the original carbohydrate [127].

Some of the derivatives of the lignocellulosic components of biomass also have value as platform chemicals for the synthesis of products for numerous sectors, such as the pharmaceutical industry, whose current needs can only be satisfied via the catalytic and physical conversion of fossil-fuel feedstocks. Indeed, biomass-derived chemicals may have advantages in the synthesis of many products, especially those that are oxygenated. Adding oxygen to hydrocarbons is not easy and often involves the use of toxic reagents such as chromium, resulting in significant waste disposal problems [128]. Conversely, biomass, particularly the carbohydrate fraction, is highly oxygenated. Studies in the US [97] and Europe [98] identified a number of important biomass-derived platform chemicals (12 in the US study and 21 in the EU study). Some of the chemicals that were identified in both studies include levulinic acid and succinic acid.

5.1. *Combined enzymatic hydrolysis and fermentation*

Some of the hurdles seen in enzymatic hydrolysis technologies can be decreased, along with the capital and energy costs, by a reduction in the number of steps and reactors involved. A progression from SHF is the Simultaneous Saccharification and Fermentation (SSF) process. In this, following a pre-treatment to liberate the hemicellulosic sugars, the hydrolysis of cellulose and the fermentation of the liberated sugars occurs in the same reactor [44]. Since the sugars are fermented on release, the inhibitory effects on enzymatic hydrolysis that are seen with increased glucose concentrations are reduced [129]. An increased supply of cellulases will increase the rate of reaction and reduce fermentation costs, although, given that the cost of cellulases are still relatively high, there are economic limits on their concentration [40]. A variant on SSF is Simulatneous Saccharification and Co-Fermentation (SSCF), where the hexoses and pentoses are fermented together (in the same reactor that is used for cellulose hydrolysis). SSF/SSCF have yet to be implemented commercially because the optimal conditions required for hydrolysis are different from those for fermentation and improved micro-organisms, such as thermophiles for the (co)fermentation of sugars (as being engineered by Agrol Biotechnologies for utilisation in Colusa's planned biorefineries) are necessary. Hence yields are currently highest where separate reactors are employed.

SSF and SSCF still require the yeast to be produced in a separate reactor as is the case in most current pilot biorefining schemes where approximately 9% of the carbohydrate released from hydrolysis is used to grow the cellular mass of yeast [44]. In contrast, Consolidated BioProcessing (CBP), which is considered to have the potential to offer the lowest costs for biofuels and chemicals [113], involves all activities taking place in the same reactor, ideally with one micro-organism. An appropriate micro-organism for this is the holy grail of enzymatic research [130], and there are several companies active in this area. SunEthanol Inc. claim that their Q Microbe represents a viable micro-organism for a CBP facility; however, its application has yet to be demonstrated on the pilot scale [131].

6. Thermochemical technologies

Historically, the main means of gaining value from low value lignocellulosic materials has been to combust these for heat and/or electricity generation. This process typically operates at low efficiencies with biomass feedstocks and cannot compete economically with power production from fossil fuels or efficient renewables such as wind. Modern technologies, however, exist to produce more valuable gas, liquid and solid products from the thermal treatment of biomass. This paper will only consider technologies where high-value end-products, other than electricity, are the result. Hence, if chemical and/or biofuel synthesis is the target, the types of feasible technologies can be categorised according to two groups: indirect liquefaction and direct liquefaction.

6.1. Direct liquefaction—pyrolysis

A direct liquefaction process results in the production of a bio-oil from the condensable volatile components of biomass. Typically, conditions of pyrolysis are employed in order to achieve this. Pyrolysis can be considered to be the thermal treatment of a material in the absence of oxygen that can also result in the evolution of non-condensable gases and a residual solid component that does not decompose under the conditions employed [132]. Over time, refinements have allowed process conditions and the feedstock to be manipulated in order to achieve high yields of bio-oil, gases, or biochar, depending on the particular end product desired [117]. Under flash (or fast) pyrolysis, the feedstock is ground to very fine particles, in order to facilitate rapid heat transfer, and moderate temperatures of 450–700 °C are employed for a very short residences time (in the order of seconds). The gases evolved are rapidly quenched in order to prevent their depolymerisation to non-condensable gases. The end result is a high yield of bio-oil, which may be up to 70% by mass of the feedstock, depending on the starting material. This bio-oil is a complex mixture of water, carboxylic acids and lignin- and carbohydrate-derived products [133] that can deteriorate rapidly over time, with polymerisation reactions forming additional water and causing phase separations [134]. Dynamotive, a company that has commercial facilities producing electricity via the combustion of bio-oil, claim that the bio-oil produced from sugarcane baggasse processed in their flash pyrolysis reactor contained an array of products [135] including water (20.8%), levoglucosan (3.0%), hydroxyacetaldehyde (10.2%), acetic acid (6.6%), and formaldehyde (3.4%). Ensyn is another company with several commercial-scale bio-oil to energy facilities [136].

Where lower temperatures (300–550 °C) are employed and the biomass is less finely comminuted, residence times tend to be longer and a higher yield of biochar results at the expense of significant bio-oil formation [137]. These temperatures facilitate the depolymerisation of polysaccharides along with their slow dehydration to unsaturated species that can further react, via an array of potential pathways, to unsaturated polymers and char [117]. Conversely, the higher temperatures of fast pyrolysis result in the depolymerised polysaccharides being made volatile and forming complex tars and oils. When the conditions are so severe (over 700 °C) that these tars are extensively broken to non-condensable gases, a potential fuel gas, containing hydrogen and methane as well as carbon oxides, is produced. As with gasification technologies, this gas has potential as a feedstock for chemical synthesis via various catalytic pathways.

Research has focussed on understanding how the lignocellulosic components of biomass behave under pyrolysis conditions [138–140] in order to engineer specific conditions that may allow a more targeted end product to result. For instance, studies have considered how to obtain the platform chemical levoglucosan (LG—Fig. 3), an anhydroglucose derived from cellulose, in high yields [141,142]. A detailed consideration of the feedstock of interest is also often necessary when predicting how it will perform under pyrolysis, and what end products will result. For example, ash tends to promote char formation during pyrolysis [143] and the bio-oils that are generated from high-ash feedstocks may contain high levels of chlorine and alkali metals such as potassium that may be damaging to turbines if the oil is to be utilised for power production [144].

Catalysts have roles in many areas of pyrolysis. For example, zinc chloride allows the process to take place at lower temperatures [7] and iron 3+ introduced to wood has been shown [145] to increase the yield of LG and levoglucosenone. Levoglucosenone (another anhydrosaccharide obtained from cellulose) is, like LG, optically active and, hence, also has utility in the chemical and pharmaceutical industry [146]. Al-MCM-41 type mesoporous catalysts with a Si/Al ratio of 20 have been tested at various pore sizes and have resulted in the elimination of levoglucosan from pyrolysis gas and a preference for acetic acid, furfural and furans from cellulose [147]. Acidically catalysed pyrolysis has been shown to result in the production of levoglucosene which also has applications in the pharmaceutical industry [142].

As an alternative to the use of catalysts during pyrolysis, the bio-oil may be upgraded after it is produced (possibly utilising the hydrogen produced from other biomass technologies). There are many possible catalytic mechanisms for this [148]. For instance, it has been found that the upgrading of bio-oils with silicate was inefficient compared with acidic zeolite catalysts (e.g. HZSM-5, H-mordenite H-Y, silicalite and silica-alumina) and that an increase in pore size resulted in a higher production of a char by-product [149,150]. Ultimately, it is hoped that an oil can be produced that can be suitable as a transport fuel or is compatible with existing petrochemical processing facilities [151]. A production of a bio-oil that is a viable substrate for biochemical processing is another option. This can occur via acid hydrolysis of the levoglucosan to glucose [152], but there also microorganisms that can directly ferment levoglucosan [153].

As well as catalysts, solvents are of use in pyrolysis; for example, sulfolane has been shown to inhibit the polymerisation reactions that may decrease yields of anhydromonosaccharides such as LG [154]. Sulfolane has also been shown to allow the complete pyrolysis of cellulose to soluble products with no char formation [155].

However, the char itself is of value, both as a fuel due to its high energy content ($\sim$30 GJ/t [117]) and as a soil amender due to the porosity properties conferred by particular pore-sizes, and the ultrastructure that result from the pyrolysis process [156]. This structure is said to afford protection to the arbuscular mycorrhizal fungae (AMF) that live symbiotically with plant roots and, in doing so, affect significant increases in plant growth and tolerance to stress [157,158]. Interest in biochar was spurred by the observations of the terra preta (or Amazonian Dark Earth, or ADE) soils of the Amazon Region which have dramatically increased productivity over the adjacent unamended soils [159]. The ADE were formed in pre-Columbian times, several thousand years ago, by the local Indian tribes who covered their refuse in soil and slowly burnt it (a crude form of slow pyrolysis). Slow pyrolysis therefore offers a great potential both in agriculture and as a carbon sequestration tool since much of the char is recalcitrant to decomposition, hence a significant amount of the carbon added to soil is effectively locked away [160]. Chars also reduce emissions of N_2O from the soil and help to trap nitrates and dissolved organics from drainage waters [160]. The process is of particular relevance to the residual components of hydrolysis biorefining technologies given that these will be lacking in polysaccharides and will predominately be composed of the lignin polymer and its alteration products. These will give poor yields of bio-oil in a fast pyrolysis system but could represent an excellent feedstock for biochar production.

6.2. Indirect liquefaction—gasification

In these technologies the desired end product is synthesised by the catalytic or biological reforming of the gases produced from the thermal treatment of biomass. A clean gas devoid of the complex carbohydrate/lignin thermal degradation products seen with pyrolysis technologies is key; hence most indirect liquefaction technologies employ the gasification route. Gasification occurs best under higher temperatures (>1000 °C) and in less oxygen restricted conditions than pyrolysis. Since the formation of the gas from gasification is endothermic, the necessary temperature is attained via the oxygen burning of approximately 25% of the feedstock [117]. Where air is used to supply the oxygen the resulting gas is termed a producer gas. The use of air is only a viable option for gasification technologies where electricity production is the target. The catalytic processes required for the synthesis of biofuels and chemicals require a much cleaner gas. Hence, oxygen or steam are used and the resulting gas is termed a synthesis gas (or syngas). The general formula for the oxygen-fuelled gasification of carbohydrates is included below:

$$C_6H_{12}O_6 + \tfrac{3}{2}O_2 \rightarrow 6CO + 3H_2 + 3H_2O$$

Many of the potential products that can be synthesized from these gases are represented in Fig. 4, along with the catalysts used. Their synthesis depends on the ratio of carbon monoxide to hydrogen in the syngas. The amount of hydrogen (and hence carbon dioxide) produced can be increased via the water gas shift reaction (at conditions of approximately 300 °C and 15–25 bar [49]) which involves mixing steam with the syngas, since insufficient water vapour is usually released from the biomass.

Providing the syngas can be cleaned and contaminants such as tars and inorganic components effectively removed, the catalytic mechanisms for subsequent chemical synthesis from biomass-derived syngas should be the same as those employed on a large scale for the syngas produced from fossil fuels. The production of biomethanol from syngas (ideal H_2:CO ratio of 3:1 [162]), via copper/zinc based catalysts at conditions of 220–300 °C and 50–100 bar [49], is probably the easiest route and several Swedish companies are considering commercial systems that can upgrade the black liquor from pulp and paper mills [163]. However, methanol is no longer considered suitable as a major transport fuel but can be converted to viable transport fuels and platform chemicals, using the Methanol to Gasoline (MTG) process [164].

There are several companies considering commercialising the production of ethanol from syngas. One route involves the production of a mixture of alcohols, including ethanol, butanol, and methanol using either a modified copper methanol catalyst or a molybdenum sulfide catalyst with a modification of the catalyst or of the conditions influencing the composition of the product stream [165]. A research project aims to have a pilot plant utilising this technology operational by 2012 and is targeting the production of ethanol, at a cost of $1.01 per US gallon, via the conversion of forest residues [165]. This project uses a moly-sulfide-based (MoS2) catalyst system, promoted with cobalt and alkali metal salts, because of its ability to produce linear alcohols (as opposed to branched), and its potential for higher ethanol selectivity [165]. It considers that, by the end of 2012, the current problems associated with the catalysts, which include poor selectivity and stability, will be overcome. Range Fuels are said [17] to be preparing a biomass to syngas to ethanol facility that they claim will produce 38 ml of ethanol and about 8 ml of methanol per year. The company also says that the process [166] can work efficiently at high moisture contents (40–50%), and that massive economies of scale are not required. Clean Energy Technologies claim to be developing a pilot/demonstration syngas to ethanol unit based on the CET process which is a modification of a process developed by Pearson Technologies [167].

For about 20 years there has been research into the biocatalytic synthesis of chemicals, including ethanol, from syngas [168]. Autotrophs use C1 compounds, such as CO, CO_2 and methanol, for their carbon source and hydrogen as their energy source while unicarbonotrophs use C1 compounds alone for both these purposes [169]. These microorganisms also utilise metals such as cobalt and nickel (which are contained in their enzymes) for the conversion of C1 compounds into value added products such as ethanol, but they are less sensitive to many of the gas contaminants, such a sulphur, that poison metal-based catalysts [170]. Also, the adjustment of the H_2:CO ratio via the water gas shift reaction is not necessary where biological catalysts are employed and synthesis conditions can be much milder [169].

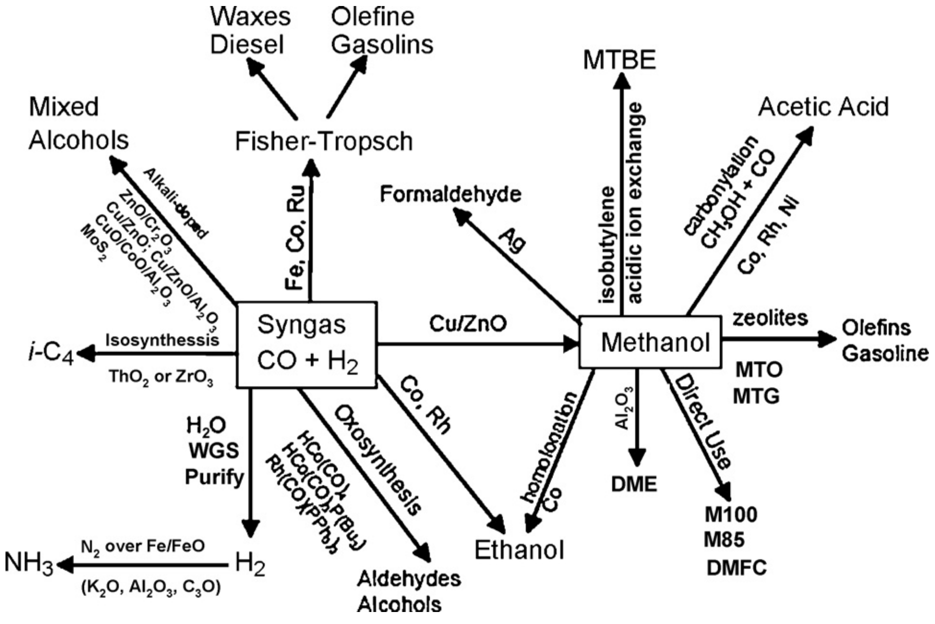

Fig. 4. The potential chemicals from syngas and some of the catalysts involved. From [161].

Alico Inc. aim to use *Clostridium ljungdahlii* to produce ethanol from syngas in their planned commercial biorefinery [171]. The proposed plant will produce 53 ml of ethanol a year and 6.55 MW of electric power, as well as hydrogen and ammonia, from 770 tonnes of agricultural wastes per day [172]. The company has received a grant of $33 m from the US Department of Energy towards the cost of constructing this biorefinery [172].

The Fischer-Tropsch (FT) synthesis of a mixed range of linear hydrocarbons from syngas is a complex, highly exothermic, process that may require that many of the products are recycled in order to achieve satisfactory yields. It has been used, for about 50 years, in South Africa where the technology was developed in order to synthesise chemicals and fuels from coal when oil supply was limited [173,174]. A H_2:CO ratio of 2:1 is best for FT and process temperatures and catalysts (iron or cobalt) can be manipulated according to the particular hydrocarbons desired [174]. The products of this process are not yet comparable to diesel fuels and are typically waxes that can be hydrocracked to produce a diesel that is suitable as a transport fuel (although it does suffer from a reduced lubricity and density) as well as naptha and kerosene as co-products [175].

Various components in biomass feedstocks cause problems in the gasification and catalytic synthesis stages. Firstly, it is generally required for the biomass to be relatively dry [176], otherwise some of the syngas will need to be utilised for drying purposes. Costs rise rapidly once moisture contents rise above 50%; hence such feedstocks are not currently considered suitable for the gasification platform [165]. Regarding catalysts, methanol synthesis catalysts can be poisoned by sulphur compounds, and Fischer-Tropsch catalysts are highly sensitive, particularly to tars, carbon dioxide, halides and alkalis [49]. Catalysts can also be deactivated by ash [177]. Indeed, the amount and composition of ash is also a very important consideration in gasification schemes. A study estimated that, for mixed alcohol synthesis from forest residues, the minimum selling price for ethanol rises by approximately 50% (from $1.01 to $1.50 a gallon) when the ash content is increased from 1 to 15% [165]. Issues relating to ash slagging and sintering in the reactor are particularly problematic with the gasification of some feedstocks. Fluidised bed gasifiers, by operating at less than 1000 °C, reduce this problem, but such conditions produce more tars and methane in the syngas. It is considered that such reactors will be inappropriate at the scales needed for the economical synthesis of many chemicals [49]. Instead it is likely that entrained flow gasifiers will be necessary for the economies of scale needed for competitive biofuel production [176]. These operate at higher temperatures but are engineered to minimise slagging. However, they require the biomass particles to be very fine which may incur a significant energy expense [178].

The formation of tars, and measures to deal with their removal are big considerations in biomass gasification schemes. Catalysts have a vital role in the reforming of these tars and non-metallic calcined dolomites and nickel based catalysts have been the focus of much research. However, both have problems, and further research is needed [49]. It is generally considered that fundamental advances in state of the art catalyst preparations will be needed in order to make large-scale biomass to liquid facilities practical. The fossil-fuel to liquid facilities that currently exist are very large; for example, a (natural) gas to liquids facility recently built in Qatar produces about 34,000 barrels of FT products a day [179]. Such economies of scale are necessary for many gasification technologies, particularly those employing the Fischer-Tropsch mechanism [180]. It is estimated that a minimum gasifier rating of 500 MW will be necessary in order for FT biomass to liquids to be viable [39]. Clearly, a massive quantity of biomass would be required for such a facility, and it may be necessary to source material from long distances, increasing transport costs.

Several approaches have been considered to overcome the hindrances associated with biomass gasification. One option is to convert the biomass to a more appropriate state for gasification and/or transport. The production, via pyrolysis, of a bio-oil, or a bio-oil and char slurry, has been studied as one means of achieving this and Dynamotive claim to have tested syngas produced from such a slurry [181,182]. The bio-oil/slurry should be more suitable for utilisation in an entrained flow gasifier, and its greater density (than the original biomass material) will increase the potential radius (since transport costs will be lowered) within which biomass can be sourced for a large scale gasification facility. Hence, a network of smaller flash pyrolysis facilities could “upgrade” the biomass to a bio-oil which is then delivered to a central facility [181]. Torrefaction is an alternative to bio-oil production. In this, slow pyrolysis conditions at low temperatures (250–300 °C) facilitate biomass grinding at reduced energy costs, and allows biomass to be utilised effectively in an entrained flow gasifier [183]. The Choren process [176] consists of a slow-pyrolysis stage which produces a gas which goes to a gasifer and to a char that is ground down and injected in the lower part of the gasification chamber, facilitating a reaction with the hot gases. The syngas then feeds a Fischer-Tropsch chamber, based on a Shell Gas to Liquids process [175], for the synthesis of a diesel-type fuel, termed SunDiesel. A pilot plant has demonstrated the Choren technology and a 15,000 tonne capacity demonstration plant, that will process 75,000 tonnes of biomass per year, is being commissioned [49]. Choren have claimed that commercial facilities will have an output of 200,000 tonnes per year, and current estimates are that the cost of diesel production will be in the order of 70 euro cents per litre [17].

7. Discussion

There are numerous possible pathways for producing chemicals and fuels from lignocellulosic materials. Each has its own particular strengths and weaknesses. The most extensively demonstrated technologies involve the acid hydrolysis of biomass to a sugar platform that can then be fermented. However, it is likely that the margin for significant improvement and costs reductions for these may be limited. By contrast, it appears that the enzymatic hydrolysis route offers much greater scope for advancement in the future. The National Renewable Energy Laboratory in the US has estimated that future cost reductions could be four times greater for the enzyme process than for the concentrated acid process, and three times greater than for the dilute acid process [184]. Indeed, since that report was written, the US Department of Energy has funded research, at both Genencor International and Novozymes Biotech, to produce cost effective enzymes with the goal of achieving a tenfold cost reduction and bringing down the cost of enzymes to an estimated $0.50 per gallon of ethanol [185]. Both companies achieved similar results and exceeded the Department’s expectations by achieving a 30-fold drop in the cost of enzymes for hydrolysis; to approximately $0.1–0.2 per gallon of ethanol [186]. There is still scope for further reduction in these costs as well as in the energy and capital costs of such facilities through the development of more efficient processes such as consolidated bio-processing. Indeed, it has been estimated that a mature CBP facility that sources biomass for $40 per dry tonne, could produce ethanol for 63 cents per gallon [187].

A wide variety of products are possible from the sugar platform, but it would appear that most commercial activity is currently focusing on ethanol, despite its drawbacks as a fuel. While the activities of companies such as BP, in their research of butanol, and

LS9, in their pursuit of hydrocarbon analogues via novel fermentation pathways, are encouraging, they would seem to be prospects more for the mid to long term. In contrast, the Biofine technology is currently operational and the levulinic acid product has many high value applications. Biofine also offers the only current means for producing diesel additives via the hydrolysis platform. The lack of any biotic activity in the process is also attractive given the variety of problems currently seen with the enzymatic hydrolysis of the complex lignocellulosic matrix and with the fermentation of, the often very heterogeneous, hydrolysates. Sugar fermentation platforms can only get a maximum of 51% ethanol by mass from the feedstock; however, the Biofine process can achieve, from cellulose, a 50% yield of LA plus a 20% yield of formic acid. Hence the yield of potential saleable products is significantly greater.

This is also an advantage in thermochemical technologies, particularly those employing the gasification route, where ultimate yields are more dependent on the carbon content of the feedstock than on the amount of carbohydrates. Hence, these offer the potential of chemical/biofuel synthesis from the lignin polymer which is typically a residue when polysaccharides hydrolysis is targeted. An increase in theoretical yields of saleable products could therefore be a result. Indeed, one mixed-alcohols synthesis company is claiming that it can achieve net yields of over 530 l of ethanol per dry tonne of biomass [188]. Two of the six companies that received grants from the US Department of Energy for the establishment of commercial biorefineries plan to use the themochemical platform. One of these (Alico Inc) will employ the biological fermentation of ethanol from syngas while the other (Range Fuels) will employ mixed-alcohols synthesis through the use of metal catalysts. If these catalysts can be shown to be economical and reliable and their previous obstacles overcome, then this route may offer the best near-term potential for biofuel synthesis. If not, then proven techniques exist for the synthesis of diesel type fuels from syngas via the FT process. The hurdle with this approach involves the significant production of tars from biomass feedstocks, when compared with syngas produced from fossil fuels, and how these can be effectively reformed by catalysts.

Pyrolysis technologies (such as those of Dynamotive and Ensyn) are the only processes currently being demonstrated on a commercial scale, but the bio-oils currently produced represent low value end-products. Such facilities do not require the economies of scale of hydrolysis and gasification technologies, however, and they could offer value for local communities that wish to strive towards energetic and chemical self sufficiency with limited lignocellulosic resources. This will be particularly true if catalytic processes to refine or engineer the bio-oil to platform chemicals and transport fuels can be implemented on the small-scale. Pyrolysis can also offer a positive feedback mechanism to the supply cycle of biorefining schemes. This can occur through the utilisation of residues from hydrolysis technologies in order to produce a biochar that can then be used to enhance the growth of biomass destined for the hydrolysis-platform biorefinery (Fig. 2).

In summary, it is not currently possible to choose which biomass conversion mechanism is likely to be most cost competitive when commercial operations come online, nor to select which mechanism will ultimately supply the most biofuels or biochemicals. Indeed, it is unlikely that there will be one “winner”. Instead, different technologies may be most appropriate for different feedstocks. For example, the high ash contents of many straws [189] are likely to prohibit their utilisation in gasification schemes, yet these are the feedstocks of most interest currently for enzymatic hydrolysis technologies (such as Iogen and Colusa). Neither enzymatic nor gasification technologies are likely to be suitable for unsorted municipal solid waste due to its high heterogeneity. Instead this feedstock is currently more suited for slow-pyrolysis or acid-hydrolysis technologies (such as those of BlueFire Ethanol and Biofine, both of which have had successful tests on MSW [96,190]). Also, feedstocks with a moisture content of over 50% will exhibit unfavourable energy balances when utilised in concentrated acid hydrolysis [90], most gasification [165], and some pyrolysis [135] schemes, but are suitable for dilute acid and enzymatic hydrolysis platforms. There are numerous other examples of where the competitive advantage between technologies changes according to the specifics of conditions and feedstock; hence, in order to fully determine the most appropriate biorefining scheme, a detailed holistic examination is needed for each lignocellulosic material specific to the location in which it will be treated.

References

[1] J.J. Bozell, Chemicals and Materials from Renewable Resources, American Chemical Society, Washington DC, 2001.
[2] IPCC, Climate Change 2001: The Scientific Basis, Cambridge University Press, Cambridge, UK, 2001.
[3] V. Ramaswamy, O. Boucher, J. Haigh, D. Hauglustaine, J. Haywood, G. Myhre, T. Nakajima, G.Y. Shi, S. Solomon, in: J.T. Houghton, D.J. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell, C.A. Johnson (Eds.), Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the third assessment report of the Intergovernmental Panel on Climate Change (IPCC), Cambridge University Press, 2001, p. 349.
[4] B.D. Solomon, A. Banerjee, Energy Policy 34 (2006) 781.
[5] EC, Official J. Eur. Union 123 (2003) 42.
[6] US Congress, Energy Independence and Security Act of 2007, 2007, p. 1491.
[7] H.R. Bungay, Energy, the Biomass Options, John Wiley and Sons, New York, NY, 1981.
[8] E. Sjostrom, Wood Chemistry: Fundamentals and Applications, Academic Press, Inc., London, UK, 1981.
[9] A. McAloon, F. Taylor, W. Yee, K. Ibsen, R. Wooley, Determining the Cost of Producing Ethanol from Corn Starch and Lignocellulosic Feedstocks, NREL/TP-580-28893, NREL, Golden, CO, 2000.
[10] C. Hamelinck, R. van den Broek, B. Rice, A. Gilbert, M. Ragwitz, F. Toro, Liquid Biofuels Strategy Study for Ireland, Sustainable Energy Ireland, 2004.
[11] J. Hill, E. Nelson, D. Tilman, S. Polasky, D. Tiffany, Proc. Natl. Acad. Sci. 103 (2006) 11206.
[12] The Economist, The End of Cheap Food, The Economist, 2007.
[13] House of Commons, Are Biofuels Sustainable? First Report of Session 2007–2008, 2008.
[14] G. Ferrett, Biofuels ‘Crime Against Humanity’, vol. 27-10-07, BBC Online, 2007.
[15] J. Diouf, Biofuels Should Benefit the Poor, Not the Rich, Financial Times, London, 2007.
[16] P.J. Crutzen, A.N. Mosier, K.A. Smith, W. Winiwarter, Atmos. Chem. Phys. Discuss. 7 (2007) 11191.
[17] Earth News, Will Sleepy GA. Town Lead Cellulosic Revolution?, 2007.
[18] B.T. Turner, R.J. Plevin, M. O’Hare, A.E. Farrell, Creating Markets for Green Biofuels: Measuring and Improving Environmental Performance, Institute of Transportation Studies, UC Berkeley Transportation Sustainability Research Center, Berkeley, California, 2007.
[19] L.T. Fan, M.M. Gharpuray, Y.-H. Lee, Cellulose Hydrolysis, Springer-Verlag, Berlin, 1987.
[20] D.L. Klass, Biomass as a Nonfossil Fuel Source, American Chemical Society, 1981.
[21] B.A. Dehority, Fed. Proc. 32 (1973) 1819.
[22] J.P. Casey, Pulp and Paper: Chemistry and Chemical Technology, John Wiley and Sons, New York, NY, 1980.
[23] J.C. Roberts, The Chemistry of Paper, Royal Society of Chemistry, Cambridge, UK, 1996.
[24] K.S. Tyson, Fuel Process. Technol. 86 (2005) 1127.
[25] D.L. Johnson, in: B. Kamm, P.R. Gruber, M. Kamm (Eds.), Biorefineries—Industrial Processes and Products, Status Quo and Future Directions, vol. 1, Wiley, Weinheim, Germany, 2006.
[26] Corn Refiners Association, 2001 Corn Annual, Washington, D.C., 2001.
[27] P. Venturi, G. Venturi, Biomass Bioenergy 25 (2003) 235.
[28] M.R. Schmer, K.P. Vogel, R.B. Mitchell, R.K. Perrin, PNAS 105 (2008) 464.
[29] A.E. Farrell, R.J. Plevin, B.T. Turner, A.D. Jones, M. O’Hare, D.M. Kammen, Science 311 (2006) 506.
[30] L.R. Lynd, J.H. Cushman, R.J. Nichols, C.E. Wyman, Science 251 (1991) 1318.
[31] Worldwatch Institute, Biofuels for Transportation—Prepared for the German Federal Ministry of Food, Agriculture and Consumer Protection, Worldwatch Institute, Washington, DC, 2006.
[32] P.R. Adler, G.S.J.D. Grosso, W.J. Parton, Ecol. Appl., 17 (2007) 675.
[33] M. Wang, M. Wu, H. Huo, Environ. Res. Lett., Online (2007).
[34] E.M. Hansen, B.T. Christensen, L.S. Jensen, K. Kristensenc, Biomass Bioenergy 26 (2004) 97.

[35] P. Grogan, R. Matthew, Review of the Potential for Soil Carbon Sequestration under Bioenergy Crops in the U.K., MAFF Report on Contract NF0418, Institute of Water and Environment, Cranfield University, Silsoe, 2001.

[36] D. Tilman, J. Hill, C. Lehman, Science 314 (2006) 1598.

[37] J.S. Tolan, in: B. Kamm, V.R. Gruber, M. Kamm (Eds.), Biorefineries: Industrial Processes and Products, vol. 1, Wiley, Weinheim, Germany, 2005, p. 193.

[38] N.S. Mosier, C. Wyman, B. Dale, R. Elander, Y.Y. Lee, M. Holtzapple, M. Ladisch, Bioresour. Technol. 96 (2005) 673.

[39] W. Smith, Mapping the Development of UK Biorefinery Complexes, Tamutech Consultancy, 2007.

[40] C.N. Hamelinck, G. van Hooijdonk, A. Faaij, Biomass Bioenergy 28 (2005) 384.

[41] M.A. Millett, M.J. Effland, D.P. Caulfield, Adv. Chem. Ser. 181 (1979) 71.

[42] D.B. Rivers, G.H. Emert, Biotechnol. Lett. 9 (1987) 365.

[43] T. Tassinari, C. Macy, L. Spano, Biotechnol. Bioeng. Symp. 24 (1982) 1495.

[44] R. Wooley, M. Ruth, J. Sheehan, K. Ibsen, Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-current Dilute acid Prehydrolysis and Enzymatic Hydrolysis Current and Futuristic Scenarios, National Renewable Energy LaboratoryTech. Rpt., NREL/TP-580-26157, US Dept. of Energy, 1999.

[45] T.-A. Hsu, in: C.E. Wyman (Ed.), Handbook on Bioethanol Production and Utilization, Applied Energy Technology Series, Taylor & Francis, Washington DC, 1996.

[46] B. Toussaint, G. Excoffier, M.R. Vignon, Anim. Feed Sci. Technol. 32 (1991) 235.

[47] J.R. Weil, M. Brewer, R. Hendrickson, A. Sarikaya, M.R. Ladisch, Biochem. Biotechnol. 70–72 (1998) 99.

[48] Y. Sun, J. Cheng, Bioresour. Technol. 83 (2002) 1.

[49] W. Smith, Literature Review: State of the Art in Biorefinery Development, Tamutech Consultancy, 2007.

[50] F. Teymouri, L. Laureano-Perez, H. Alizadeh, B.E. Dale, Bioresour. Technol. 96 (2005) 2014.

[51] L.E. Gollapalli, B.E. Dale, D.M. Rivers, Appl. Biochem. Biotechnol. 98–100 (2002) 23.

[52] A.T. Martinez, A.E. Gonzalez, M. Valmaseda, B.E. Dale, M.J. Lambregts, J.F. Haw, Holzforschung 45 (1991) 49.

[53] M. Moniruzzaman, B.E. Dale, R.B. Hespell, R.J. Bothast, Appl. Biochem. Biotechnol. 67 (1997) 113.

[54] M.T. Holtzapple, J.E. Lundeen, R. Sturgis, J.E. Lewis, B.E. Dale, Appl. Biochem. Biotechnol. 34 (1992) 5.

[55] B. Sulbaran-de-Ferrer, M. Aristiguieta, B.E. Dale, A. Ferrer, G. Ojedade-Rodriguez, Appl. Biochem. Biotechnol. 105 (2003) 155.

[56] N.S. Mosier, R. Hendrickson, D.R.G. Welch, B.S. Dien, R. Bothast, M.R. Ladisch, 225th American Chemical Society Meeting, New Orleans, 26 March 2003, 2003.

[57] J.R. Weil, A. Sarikaya, S.-L. Rau, J. Goetz, C.M. Ladisch, M. Brewer, R. Hendrickson, M.R. Ladisch, Appl. Biochem. Biotechnol. 68 (1997) 21.

[58] W.S.-L. Mok, M.J. Antal Jr., in: A.V. Bridgewater (Ed.), Advances in Thermochemical Biomass Conversion, vol. 2, Blackie Academic & Professional Publishers, New York, 1994, p. 1572.

[59] C.E. Wyman, B.E. Dale, R.T. Elander, M. Holtzapple, M.R. Ladisch, Y.Y. Lee, Bioresour. Technol. 96 (2005) 1959.

[60] J.I. Zerbe, A.J. Baker, in: D.L. Klass (Ed.), Energy from Biomass and Wastes X, Institute of Gas Technology, Chicago, 1987, p. 927.

[61] R.J. Dinus, Genetic Modification of Short Rotation Poplar Biomass Feedstock for Efficient Conversion to Ethanol, Bioenergy Feedstock Development Program, Environmental Sciences Division, Oak Ridge National Laboratory ORNL/Sub/99-4500007253/1, 2000.

[62] H.A. Krässig, Cellulose: Structure, Accessibility and Reactivity, Gordon and Breach, Yverdon, 1993.

[63] V.S. Chang, M.T. Holtzapple, Appl. Biochem. Biotech. 84–86 (2000) 5.

[64] V.S. Chang, M. Nagwani, M.T. Holtzapple, Appl. Biochem. Biotechnol. 74 (1998) 135.

[65] V.S. Chang, M. Nagwani, C.H. Kim, M.T. Holtzapple, Appl. Biochem. Biotechnol. 94 (2001) 1.

[66] J.W. Lucas, F.E. Martin, Process for Production of Lignin Fuel, Ethyl Alcohol, Cellulose, Silica/silicates, and Cellulose Derivatives from Plant Biomass, vol. 5,735,916, USA, 1998.

[67] A.S. Schmidt, A.B. Thomsen, Bioresour. Technol. 64 (1998) 139.

[68] H. Klinke, A. Thomsen, B. Ahring, Appl. Microbiol. Biotechnol. 57 (2001) 631.

[69] Biogasol, Biogasol Process Technology, 2007.

[70] T.M. Wood, J.N. Saddler, in: W.A. Wood, S.T. Kellogg (Eds.), Methods in Enzymology, vol. 160, 1988, p. 3.

[71] C. Arato, Biorefining: Back to the Future, Innovation, 2002,, p. 12.

[72] T. Retsina, V. Pylkkanen, TAPPI Web Exclusives (2007).

[73] L. Paszner, ACOS Biomass Ethanol Refinery, in: Meeting the Challenge of Oil Dependence, Paszner Technologies, Surrey, Canada, 2005.

[74] D.A. Fort, R.C. Remsing, R.P. Swatloski, P. Movna, G. Movna, R.D. Rogers, Green Chem. 9 (2007) 63.

[75] S. Zhu, Y. Wu, Q. Chen, Z. Yu, C. Wang, S. Jin, Y. Ding, G. Wu, Green Chem. 8 (2006) 325.

[76] S. Zhu, J. Chem. Technol. Biotechnol., Online (2008).

[77] S. Murugesan, R.J. Linhardt, Curr. Org. Synth. 2 (2005) 437.

[78] H. Zhang, J. Wu, J. Zhang, J. He, Macromolecules 38 (2005) 8272.

[79] I. Kilpeläinen, H. Xie, A. King, M. Granstrom, S. Heikkinen, D.S. Argyropoulos, J. Agric. Food Chem. 55 (2007) 9142.

[80] Y. Liu, H. Chen, Chin. Sci. Bull., 51 (2006) 2432.

[81] A.P. Dadi, S. Varanasi, C.A. Schall, Biotechnol. Bioeng. 95 (2006) 904.

[82] S. Park, R.J. Kazlauskas, Curr. Opin. Biotechnol. 14 (2003) 432.

[83] N. Kamiya, Y. Matsushita, M. Hanaki, K. Nakashima, M. Narita, M. Goto, H. Takahashi, Biotechnol. Lett., Online (2008).

[84] D.J. Hayes, S.W. Fitzpatrick, M.H.B. Hayes, J.R.H. Ross, in: B. Kamm, P.R. Gruber, M. Kamm (Eds.), Biorefineries: Industrial Processes and Products, vol. 1, Wiley, Weinheim, Germany, 2005, p. 139.

[85] M.B. Turner, S.K. Spear, J.D. Holbrey, R.D. Rogers, Biomacromolecules 5 (2004) 1379.

[86] S.T. Handy, M. Okello, G. Dickinson, Org. Lett. 5 (2003) 2513.

[87] H.F.J. Wenzl, The Chemical Technology of Wood, Academic Press, New York, 1970, p. 157.

[88] Q. Nguyen, Milestone Completion Report: Evaluation of a Two-Stage Dilute Sulfuric Acid Hydrolysis Process, Internal Report, National Renewable Energy Laboratory, Golden, Colorado, 1998.

[89] A.H. Brennan, W. Hougland, D.J. Schell, Biotechnol. Bioeng. Symp. 17 (1986) 53.

[90] J. DiPardo, Outlook for Biomass Ethanol Production and Demand, vol. 2000, Energy Information Administration, 2000.

[91] S.W. Fitzpatrick, Lignocellulose Degradation to Furfural and Levulinic Acid: U.S. Patent 4,897,497 (1990).

[92] S.W. Fitzpatrick, Production of Levulinic Acid from Carbohydrate-Containing Materials: U.S. Patent 5,608,105 (1997).

[93] R.H. Leonard, Ind. Eng. Chem. 48 (1956) 1331.

[94] J. Horvat, B. Klaic, B. Metelko, V. Sunjic, Tetrahedron 26 (1985) 2111.

[95] B.V. Timokhin, V.A. Baransky, G.D. Eliseeva, Russ. Chem. Rev. 68 (1999) 73.

[96] BioMetics Inc., Municipal Solid Waste Conversion Project, Final Report, Contract No: 4204-ERTER-ER-96., Biometics Inc., Boston, MA, 1996.

[97] A. Aden, J.J. Bozell, J. Holladay, J. White, A. Manheim, Top Value Added Chemicals From Biomass Joint NREL/PNNL report, August 2004, National Renewable Energy Laboratory/Pacific Northwest National Laboratory, 2004.

[98] M. Patel, M. Crank, V. Dornburg, B. Hermann, L. Roes, B. Husing, L. Overbeek, F. Terragni, E. Recchia, Medium and Long Term Opportunities and Risks of the Biotechnological Production of Bulk Chemicals from Renewable Resources, Utrecht University, Utrecht, Netherlands, 2006.

[99] D.C. Elliott, U.S. Patent 5,883,266 (1999).

[100] J.J. Thomas, Biomass Energy Dev. [Proc South Biomass Energy Res. Conf.], 1986.

[101] S.V. Lucas, D.A. Loehr, M.E. Meyer, J.J. Thomas, Soc. Auto. Eng. Fuels and Lubricants Sect. Mtg., Philadelphia, PA, 1993.

[102] C. Huang, D. Wilson, Presented at the 91st AOCS Annual Mtg., April 26th, 2000.

[103] J. Gravitis, N. Vedernikov, J. Zandersons, A. Kokorevics, in: J.J. Bozell (Ed.), Chemicals and Materials from Renewable Resources, American Chemical Society, Washington DC, 2001, p. 110.

[104] I.S. Goldstein, J.M. Easter, TAPPI J. 75 (1992) 135.

[105] O. Theander, E. Westerlund, in: H.G. Jung, D.R. Buxton, R.D. Hatfield, J. Ralph (Eds.), Forage Cell Wall Structure and Digestibility, ASA-CSSA-SSSA, Madison, WI, 1993, p. 83.

[106] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, D. Crocker, Determination of Structural Carbohydrates and Lignin in Biomass, National Renewable Energy Laboratory, 2006.

[107] J.D. Broder, J.W. Barrier, Paper 88-6007: Producing ethanol and coproducts from multiple feedstocks, Am. Soc. Agric. Eng., 1988.

[108] A. Graf, T. Koehler, Oregon Cellulose-Ethanol Study, Oregon Office of Energy, Salem, Oregon, USA, 2000.

[109] W.A. Farone, J.E. Cuzens, Method of Producing Sugars Using Strong Acid Hydrolysis of Cellulosic and Hemicellulosic Materials, US, 1996.

[110] Record Online, Masada Timeline, 2002.

[111] S.W. Kang, Y.S. Park, J.S. Lee, S.I. Hong, S.W. Kim, Bioresour. Technol. 91 (2004) 153.

[112] Cooper, Chem. Eng. 106 (1999) 35.

[113] L.R. Lynd, R.T. Elander, C.E. Wyman, Appl. Biochem. Biotechnol. 57/58 (1996) 741.

[114] S.A. Teter, F. Xu, G.E. Nedwin, J.R. Cherry, in: B. Kamm, V.R. Gruber, M. Kamm (Eds.), Biorefineries: Industrial Processes and Products, vol. 1, Wiley, Weinheim, Germany, 2005, p. 357.

[115] Y.-H.P. Zhang, L.R. Lynd, Biotechnol. Bioeng. 88 (2004) 798.

[116] X. Pan, N. Gilkes, J.N. Saddler, Holzforschung 60 (2006) 398.

[117] J.-P. Lange, Biofuels Bioproducts Biorefining 1 (2007) 39.

[118] D. Gregg, J.N. Saddler, Biomass Bioenergy 9 (1995) 287.

[119] H. Palonen, Role of Lignin in the Enzymatic Hydrolysis of Lignocellulose, Vol. Doctor of Technology, Helsinki University of Technology, Espoo, Finland, 2004.

[120] H.G. Jung, D.A. Deetz, in: H.G. Jung, D.R. Buxton, R.D. Hatfield, J. Ralph (Eds.), Forage Cell Wall Structure and Digestibility, ASA-CSSA-SSSA, Madison, WI, 1993, p. 315.

[121] J.D. Murphy, K. McCarthy, Appl. Energy 82 (2005) 148.

[122] R. Shleser, Ethanol Production in Hawaii: Processes, Feedstocks, and Current Economic Feasibility of Fuel-grade Ethanol Production in Hawaii, State of Hawaii, Department of Business, Economic Development & Tourism, 1994.

[123] M. Zhang, Y.-C. Chou, S.K. Picataggio, M. Finkelstein, Single Zymomonas Mobilis Strain for Xylose and Arabinose Fermentation, vol. 5,843,760, USA, 1998.

[124] M. Kuyper, M.M.P. Hartog, M.J. Toirkens, M.J.H. Almering, A.A. Winkler, J.P. van Dijken, J.T. Pronk, FEMS Yeast Res. 5 (2005) 399.

[125] K.D. Jitesh, V.G. Pangarkar, K. Niranjan, Bioseparation 9 (2000) 145.

[126] D.T. Jones, D.R. Woods, Microbiol. Rev. 50 (1986) 484.

[127] A. Patrinos, Scientific Challenges for Energy Research, OECD, 2006.

[128] A.H. Haines, Methods for the Oxidation of Organic Compounds, Acadmeic Press, New York, 1988.

[129] L.R. Lynd, Annual Rev. Energy Environ. 21 (1996) 403.

[130] L.R. Lynd, P.J. Weimer, W.H. van Zyl, I.S. Pretorius, Microbiol. Mol. Biol. Rev. 66 (2002) 506.
[131] SunEthanol, 2007.
[132] R.C. Brown, D. Radlein, J. Piskorz, in: J.J. Bozell (Ed.), Chemicals and Materials from Renewable Resources, American Chemical Society, Washington DC, 2001 .
[133] D.R. Huffman, A.J. Vogiatzis, A.V. Bridgwater, in: A.V. Bridgwater (Ed.), Advances in Thermochemical Biomass Conversion, vol. 2, Blackie, London, 1994, p. 1095.
[134] P. James, P.E. Diebold, in: A.V. Bridgewater (Ed.), Fast Pyrolysis of Biomass—A Handbook, vol. 2, CPL Press, Newbury, UK, 2002, p. 243.
[135] Dynamotive Energy Systems Corporation, Presented at the 2001 Sugar Conference, Trinidad and Tobago, April, 2001.
[136] Ensyn, Bio-Oil Combustion Due Diligence: The Conversion of Wood and Other Biomass to Bio-Oil, Ensyn, Wilmington, Delaware, 2001.
[137] D. Day, R.J. Evans, J.W. Lee, D. Reicosky, Energy 30 (2005) 2558.
[138] A. Demirbas, Energy Convers. Manage. 41 (2000) 633.
[139] T. Fisher, M. Hajaligol, B. Waymack, D. Kellogg, J. Anal. Appl. Pyrolysis 62 (2002) 331.
[140] H. Yang, R. Yan, H. Chen, C. Zheng, D. Ho Lee, T. Liang, Energy Fuels 20 (2006) 388.
[141] G.-J. Kwon, D.-Y. Kim, S. Kimura, S. Kuga, J. Anal. Appl. Pyrolysis (2007), doi:10.1016/j.jaap.2006.12.012.
[142] G. Dobele, T. Dizhbite, G. Rossinskaja, G. Telysheva, D. Meier, S. Radtke, O. Faix, J. Anal. Appl. Pyrolysis 68–69 (2003) 197.
[143] F.A. Agblevor, S. Besler, R.J. Evans, Specialists Workshop, Biomass Pyrolysis Oil Propoerties and Combustion, Estes Park, CO, 1994.
[144] A.E. Wiselogel, F.A. Agblevor, D.K. Johnson, S. Deutch, J.A. Fennell, M.A. Sanderson, Bioresour. Technol. 56 (1996) 103.
[145] G. Dobele, G. Rossinskaja, T. Dizhbite, T. Telysheva, D. Meier, O. Faix, J. Anal. Appl. Pyrolysis 74 (2005) 401.
[146] Z.J. Witczak, Levoglucosenone and Levoglucosans, ATL Press, Mount Prospect, 1994.
[147] J. Adam, M. Blazso, E. Meszaros, M. Stocker, M.H. Nilsen, A. Bouzga, J.E. Hustad, M. Grønli, G. Øye, Fuel 84 (2005) 1494.
[148] S. Czernik, R. Maggi, G.V.C. Peacocke, in: A.V. Bridgwater (Ed.), Fast Pyrolysis of Biomass-A Handbook, vol. 2, CPL Press, Newbury, UK, 2002, p. 141.
[149] J.D. Adjaye, N.N. Bakhshi, Fuel Process. Technol. 45 (1995) 161.
[150] J.D. Adjaye, N.N. Bakhshi, Fuel Process. Technol. 45 (1995) 185.
[151] A. Gutierrez, M.E. Domine, Y. Solantausta, Co-processing of upgraded bio-liquids in standard refinery units—fundamentals, in: 15th European Biomass Conference & Exhibition, Berlin, 2007.
[152] Z. Yu, H. Zhang, Biores. Technol. 93 (2004) 199.
[153] X.L. Zhuang, H.X. Zhang, J.Z. Yang, H.Y. Qi, Bioresour. Technol. 79 (2001) 63.
[154] H. Kawamoto, W. Hatanaka, S. Saka, J. Anal. Appl. Pyrolysis 70 (2003) 303.
[155] H. Kawamoto, S. Saka, J. Anal. Appl. Pyrolysis 76 (2006) 280.
[156] E. Cetin, R. Gupta, B. Moghtaderi, Fuel 84 (2005) 1328.
[157] E. Marris, Nature (London) 442 (2006) 624.
[158] M.H.B. Hayes, Nature (London) 442 (2006) 144.
[159] W.I. Woods, B. Glaser, in: B. Glaser, W.I. Woods (Eds.), Amazonian Dark Earths: Explorations in Space and Time, Springer-Verlag, Berlin, 2004, p. 1.
[160] M. Fowles, Biomass Bioenergy 31 (2007) 426.
[161] R.P. Overend, Stanford University: Global Climate and Energy Project (GCEP), 2004.
[162] M.G. Poirier, A. Ahmed, J.L. Grandmaison, S.C.F. Kaliaguine, Ind. Eng. Chem. Res. (1987) 1738.
[163] T. Ekbom, M. Lindblom, N. Berglin, P. Ahlvik, Cost Competetive, Efifcient Biomethanol Production from Biomass via Black Liquor Gasification, Nykomb Synergetics AB, Stokholm, Sweden, 2003.
[164] M. Stöcker, Microporous Mesoporous Mater. 29 (1999) 3.
[165] S. Phillips, A. Aden, J. Jechura, D. Dayton, T. Eggeman, Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass, Technical Report NREL/TP-510-41168, National Renewable Energy Laboratory, Golden, Colorado, 2007.
[166] R.E. Klepper, Method and Apparatus for Producing Synthesis Gas from Carbonaceous Materials, Vol. 6,863,878 B2, USA, 2002.
[167] NREl, Gridley Ethanol Demonstration Project Utilizing Biomass Gasification technology: Pilot Plant Gasifier and Syngas Conversion Testing, National Renewable Energy Laboratory, Golden, Colorado, 2005.
[168] J.G. Zeikus, R. Kerby, J.A. Krzycki, Science 227 (1985) 1167.
[169] R.C. Brown, in: B. Kamm, V.R. Gruber, M. Kamm (Eds.), Biorefineries—Industrial Processes and Products, vol. 1, Wiley, Weinheim, Germany, 2005, p. 227.
[170] A.J. Grethlein, M.K. Jain, Trends Biotechnol. 10 (1993) 418.
[171] R. Kotrba, Sunshine Summit: A Review of Florida's Farm-to-Fuel Conference, Ethanol Producer Magazine, BBI International Media, Grand Forks, ND, USA, 2007.
[172] Green Car Congress, DOE Awards Up to $385 Million to Six Cellulosic Ethanol Plants; Total Investment to Exceed $1.2 Billion, 2007.
[173] H. Schulz, Appl. Catal. A: Gen. 186 (1999) 3.
[174] M.E. Dry, Catal. Today 71 (2002) 227.
[175] S.T. Sie, M.M.G. Senden, H.M.H. van Wechem, Catal. Today 8 (1991) 371.
[176] M. Rudloff, Automobile & Environment at Belgrade EAEC Congress, 2005.
[177] S. Ahlgren, A. Baky, A. Bernesson, Å. Nordberg, O. Norén, P.-A. Hansson, Biosyst. Eng. 99 (2008) 145.
[178] R. Wooley, M. Ruth, D. Glassner, J. Sheehan, Biotechnol. Progr. 15 (1999) 794.
[179] Qatar Petroleum, Oryx GTL Inauguration—A Key Step in Qatar's Bid to Become the GTL Capital of the World, Qatar Petroleum, 2006.
[180] A.V. Bridgewater, The Future for Biomass Pyrolysis and Gasification: Status, Opportunities and Policies for Europe-Contract No: 4.1030/S/01-009/2001, Altener, 2002.
[181] Nexant Ltd, The Feasibility of Second Generation Biodiesel Production in the UK, Nexant Chem Systems, London, 2007.
[182] E. Henrich, Second Generation Automotive Biofuel Conference, Stockholm, Sweden, 2005.
[183] P.C.A. Bergman, A.R. Boersma, J.H.A. Kiel, 2nd World Conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection 10 May 2004, Rome, Italy, 2004.
[184] NREL, Bioethanol Multi-Year Technical Plan, Preliminary Draft, National Renewable Energy Laboratory, Golden, CO, 1999.
[185] R. Katzen, D.J. Schell, in: B. Kamm, M. Kamm, P.R. Gruber (Eds.), Biorefineries—Industrial Processes and Products, Wiley, Weinheim, Germany, 2005.
[186] D. Greer, BioCycle 46 (2005) 61.
[187] L.R. Lynd, W.H. van Zyl, J.E. McBride, M. Laser, Curr. Opin. Biotechnol. 16 (2005) 577.
[188] R. Shleser, Ethanol Workshop, Feb 9, 2006.
[189] Clean Washington Center, Wheat Straw as a Paper Fiber Source, The Clean Washington Center—A Division of the Pacific Northwest Economic Region (PNWER), Seattle, Washington, 1997.
[190] Booz-Allen & Hamilton Inc., Arkenol Technology Valuation, Booz-Allen & Hamilton Inc., McLean, Virginia, 1996.