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Switchgrass as an energy crop for biofuel production: A review of its ligno-cellulosic chemical properties

Kasi David and Arthur J. Ragauskas *

BioEnergy Science Center, School of Chemistry and Biochemistry, Institute of Paper Science and Technology, Georgia Institute of Technology, Atlanta, Georgia 30332. E-mail: arthur.ragauskas@chemistry.gatech.edu; Tel: (+404) 894-9701

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Over the past two decades, the use of biomass as a resource for biofuels and bioenergy has garnered much interest. The reduction in green house gas emissions of renewable fuels as compared to conventional fossil fuels, coupled with the sustainability of these technological approaches, has fostered increased research into this field. Switchgrass is a perennial grass native to North America, and as a feedstock for biofuels it has garnered much interest because of its high productivity, adaptability and potential ease of integration into existing agricultural operations. In order to maximize the use of switchgrass as an energy crop, the chemical constituents as well as the chemical processes involved in its conversion to biofuels need to be understood. The goal of this paper is to review the published work on the chemistry of switchgrass as it pertains to biofuel production including elemental composition, chemical composition, biopolymer constituents and their structure. In addition, the impacts of these chemical constituents on the biological conversion to ethanol and pyrolysis oils are summarized.

Broader context

This review examines the use of switchgrass as a feedstock for biofuel production. Many studies have focused on the use of switchgrass since it is a highly adaptable and durable form of biomass. In terms of conversion technologies, switchgrass can be utilized both in the biological and thermal platforms, and has great potential based on a number of studies. Although some papers have dealt with the structure of switchgrass, there is a need to focus on the chemistry of switchgrass and how it affects conversion to biofuels.

This review will cover this topic and serve as a resource to add to the development of techniques to improve the chemical properties of switchgrass integral to the conversion process.

1. Introduction

The increase in global population and overall economic output has led to an increase in demand for transportation fuels over the past three decades, and fuel consumption is expected to increase approximately 60% in the next 20 years. In order to address this energy challenge, there has been an increase in research and development of biofuels.[1,2] Lignocellulosic biomass is a compelling candidate for alternative fuel production because it is readily available, avoids issues surrounding 'food or fuel' and has the potential of having a relatively small environmental impact.[3] The use of forage crops as a source of lignocellulosics for biofuel production has attracted renewed interest over the last few years.

One such crop which has proven to be advantageous is switchgrass (Panicum virgatum L.).[4] This ag-resource is a warm season perennial C_4 grass that is found broadly throughout North America. Switchgrass is highly adaptable and can grow in many different regions of the country including regions with less than ideal soil quality.[5] This plant is known to possess good tolerance to cold, disease and insects. As a biofuel resource, it is a productive crop with some studies showing yields of 15Mg ha^{-1} or more, and can be readily integrated into existing farming practices.[6] These benefits come about, in part, because it is inexpensive to seed and establishes itself fairly quickly. It can also be grown with conventional farming equipment and established harvesting processes.

Another advantage of using switchgrass is its environmental benefits as highlighted by Keshwani *et al.*[7] The use of switchgrass, relative to other annual row crops, leads to a 95% reduction in soil erosion and a 90% reduction in pesticide usage.[8,9] It has also been reported that switchgrass improves soil quality and carbon sequestration due to its extensive root system that increases carbon storage in the soil.[10] For example, Gebhart *et al.* showed that grasses such as switchgrass can store 1.1 Mg of carbon per hectare in the upper 1 m of soil each year. A study done by Ma *et al.* estimated that the top 15 cm of sandy loam showed a 116% increase in net carbon turnover over a two year period. Research has also shown that switchgrass was more effective at removing phosphorous and nitrogen from runoff compared to other cool season grasses.[11] These results demonstrate that switchgrass could be used to improve surface water quality.

In order to convert biomass to fuels, there are generally two basic methodologies that can be employed, these being a biological platform and thermo-chemical technologies.[12] The first approach involves converting biomass to ethanol or related liquid fuels by a saccharification and fermentation process. This involves deconstructing polysaccharides to monosaccharides followed by fermentation to 2nd or 3rd generation biofuels.[13] Following this approach, one of the most important considerations in overall biofuel production is the content of cellulose and hemicellulose in the cell walls of the biomass. It has been reported that in herbaceous energy crops, the total cell wall fraction is about 80% of the plant dry weight and is made up primarily of cellulose, hemicellulose and lignin.[14] Lignin is the third major component found in the cell walls of biomass, and is of higher energy. It has been reported that the energy content in lignin is 26.1GJ/Mg which is similar in value to coal.[14] Unlike cellulose and hemicellulose, lignin cannot be converted to ethanol using conventional fermentation technologies.[12] The value of the lignin in biomass can be captured through processes such as pyrolysis yielding a bio-oil. This process requires elevated temperatures in an oxygen free atmosphere for short times to volatilize low molecular weight compounds which are then condensed rapidly to a liquid bio-crude.[15–17]

Switchgrass contains a number of different inorganic elements which are not useful in the conversion of this bioresource to bio-fuels.[18] These elements must be treated as a side stream during the processing and conversion of biomass to bio-fuels, and in order to minimize and understand their effect, it is necessary to determine the amount of these species in the switchgrass samples. Thus it can be seen that the production of fuels from biomass is dependent on the content and structure of the structural components in the cell walls as well as the inorganic constituents. The objective of this work is to review the plant chemistry of switchgrass as it relates to its conversion to ethanol and/or bio-crude. In addition, the conversion chemistry for switchgrass will be discussed focusing on the pretreatment processes and pyrolysis to bio-oil.

2. Types and yield of switchgrass

Over time, switchgrass evolved into different ecotypes with specific genetic and morphological characteristics that are suited to particular regions. These varying types are generally classified as lowland and upland varieties.[19] The lowland varieties are characterized by tall, thick stems and are generally found in heavier soils and wetter regions. The upland cultivars prefer drier soils and grow better in semi-arid regions. They are also shorter and thin-stemmed. Cassida *et al.* showed that genetically, the lowland varieties have the ability to produce more dry matter than the upland types.[20] The upland varieties of switchgrass include Trailblazer, Blackwell, Cave in Rock, Pathfinder and Caddo. Common lowland varieties are Alamo and Kanlow. A summary of the different attributes found in the various cultivars is presented in Table 1.[21] Yields of switchgrass in a study performed in Iowa showed that they varied from 6.9 to 13.1 Mg ha^{-1} with an average yield of 9 Mg ha^{-1} as summarized in Fig. 1.[22] Studies have shown that the lowland varieties of switchgrass produced the most biomass compared to the other cultivars.[22]

Table 1 Switchgrass cultivars and characteristics[21]

Variety	Characteristics
Cave-in-Rock	Tolerant to flooding, adapted to Midwest, released in 1973
Blackwell	Adapted to Kansas, Oklahoma, southern Nebraska, and northern Texas. Areas with 20 inches or more of annual precipitation, released in 1944
Trailblazer	Adapted to Midwest states and Central Great Plains, released in 1984

Pathfinder	Winter hardy, matures late, released in 1967
Caddo	Good recovery after mowing, Good forage yield under irrigation, released in 1955
Alamo	Heavy yields especially in south, released in 1978
Kanlow	Developed for soil conservation in poorly drained or flooded sites, released in 1963

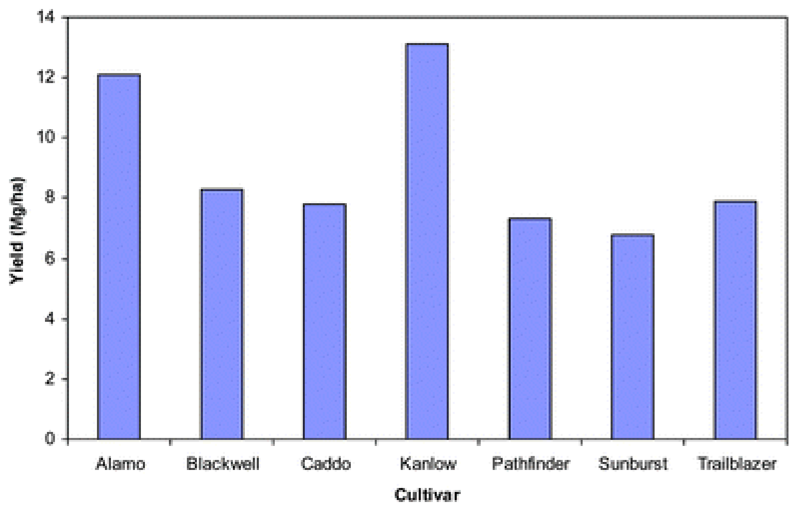

Fig. 1 Switchgrass yield of various cultivars grown in southern Iowa.[22]

3. Elemental analysis (C, H, N, O) and heating values

3.1 Elemental analysis

The elemental composition of biomass is a basic chemical property that is useful in determining the potential of a given bioresource for biofuels and biopower applications. These values are influenced by several considerations including extractives content, drying procedure and even the sampling size for switchgrass.[23] Literature C, H, N and O values for switchgrass are shown in Table 2.[5,24] The elemental analysis for switchgrass cultivars was found to be comparable to that of hybrid poplar, another potential biofuel feedstock.[23]

Table 2 Elemental (C,H,N,O) concentrations and heating values of switchgrass species

Variety	C (% mass)	H(% mass)	N(% mass)	O(% mass)	Heating Value (HHV) MJ kg^{-1}	Ref.
Cave-in-Rock	47.53	6.81	0.51	42.54	18.57	55
Cave-in-Rock	47.30	5.30	0.54	41.10		22
Cave-in-Rock[a] (<90 μm)	42.33	5.98	0.23	37.58		23
(>90 μm)	44.32	5.99	0.03	38.24		
Alamo	47.27	5.31	0.51	41.59	18.75	24
Alamo	48.00	5.40	0.42	41.70		22
Trailblazer	45.86	6.00	0.96			24
Blackwell	46.29	6.01	1.08			24
Kanlow	48.00	5.40	0.41	41.40		22
Kanlow stems	47.57	6.08				24
Kanlow leaves	47.10	6.02	1.16			24

[a] Study performed on switchgrass of two different sizes.

3.2 Heating values

It has been demonstrated that the ash and moisture content play a role in the suitability of a particular biomass species for energy conversion by thermo-chemical means.[14] The heating value of a particular feedstock is also important, and for some of the switchgrass cultivars these values are presented in Table 2. The values were obtained primarily from the NREL feedstock and composition database.[23] The reported values are comparable to that obtained from hybrid poplar which is around 19 MJ kg^{-1} and to other grasses such as reed canary grass which has been reported to have a value ∼18 MJ kg^{-1}.[22,25]

4. Ash content and inorganic element analysis

As was previously stated, the inorganic composition of switchgrass plays an important role in its conversion to biofuels both for thermo-chemical and biological conversion processes as it represents a process stream that will need to be properly disposed of and can impact process equipment. The elemental analyses of various cultivars of switchgrass found in the literature and averaged over different locations are summarized in Table 3.[26] It was shown that the dry biomass of switchgrass contained 3400 to 4200 mg kg^{-1} of P and 8100 to 10900 mg kg^{-1} of K.[26] In general, the results showed that the relative concentration of the elements in the switchgrass samples was Si≅K > P≅Ca > Cl > S > Al. The results also showed that Cave-in Rock, Blackwell and Kanlow generally contained the highest levels of minerals. In general, the ash contents found in literature varied between 4.5 and 6.4% and these values can be seen in Table 3.[22] This value is higher than the ash content of other potential energy crops such as hybrid poplar.

Table 3 Inorganic elemental concentration (mg kg^{-1}) of switchgrass cultivars[22,26,35]

Cultivar	Al	Cl	K	Si	P	S	Ca	Ash (%)
Alamo								5.2
Cave in Rock	74	1624	9148	8623	3577	820	3572	6.0
Blackwell	82	1514	9323	9904	3662	881	3792	6.2
Sunburst	73	1317	8112	9796	3367	896	3629	6.5
Trailblazer	75	1500	8674	9420	4176	920	3712	6.4
Kanlow	76	1596	10894	8767	3844	865	3512	5.4
Kanlow								5.0

5. Carbohydrates and lignin in switchgrass

The major structural components of biomass are cellulose, hemicellulose, and lignin. For ethanol production, cellulose and hemicellulose are converted to ethanol.[27] Although the lignin is not used for conversion to ethanol, it can be converted to other biofuels or used for biopower generation.[28,29] For both the fermentation and thermo-chemical pathway to biofuels, the proportion of these constituents in the cell wall is a significant consideration. Results for the amount of cellulose, hemicelluose and lignin in the varying switchgrass cultivars are presented in Table 4.[23] The results from Kanlow do indicate that there are differences in these components dependent on plant constituents (*i.e.*, leaves *vs.* stems).

Table 4 Cellulose, hemicellulose and lignin in switchgrass cultivars (% dry basis)

Cultivar	Cellulose	Hemicellulose	Lignin	Ref.
Alamo	33.48	26.10	17.35	24
Alamo	38.10	32.80		22
Blackwell	33.65	26.29	17.77	24
Blackwell	37.50	31.90		22
Cave-in-Rock	32.85	26.32	18.36	24
Cave-in-Rock	37.80	32.00		22

Kanlow	38.5	32.8		22
Kanlow –leaves	31.66	25.04	17.29	24
Kanlow- stems	37.01	26.31	18.11	24
Trailblazer	32.06	26.24	18.14	24
Trailblazer	36.8	32.5		22

5.1 Cellulose

Cellulose, which is the most abundant biopolymer, is a high molecular weight polymer composed of β-(1–4)-D-glucopyranose units.[30] Native cellulose (polymorph I) has garnered the most interest, and is further divided into two crystalline forms; namely I_α and I_β, with the latter being the thermodynamically stable version of cellulose I. The fraction of I_α and I_β in a given native cellulose sample has been shown to vary depending on the plant resource from which it is recovered. For example, the I_α phase is the dominant one in Valonia cellulose, while the I_β phase is the more prevalent form in cotton.[31] Cellulose tends to form a crystalline structure because of the presence of extensive hydrogen bonding and its linear structure. In addition to crystalline regions, there are also amorphous or disordered regions which exist in cellulose. Larsson *et al.* and others have shown the presence of another form called paracrystalline cellulose. This form of cellulose was described as containing less order and greater mobility than crystalline cellulose I_α and I_β phases.[32–34] In the literature, limited data can be found on the crystallinity of cellulose in the various switchgrass cultivars. A recent study done by Yang *et al.* using X-ray diffraction showed that in the leaves of switchgrass the crystallinity index was 68% compared to 61% in the stem.[35] Samuel *et al.* presented the structural characterization of Alamo switchgrass cellulose before and after dilute acid pretreatment using solid state NMR and line-fitting analysis. The results are presented in Table 5.[36] This data showed that the inaccessible fibril surface cellulose is the largest fraction seen in the switchgrass sample, followed by paracrystalline cellulose. A substantial proportion of inaccessible surface cellulose is important since the hydrolysis yield during the conversion to ethanol could be impacted as the enzyme system would have decreased access to the cellulose surface.

Table 5 Assignment and results from line fitting analysis of C4-region of CP/MAS ^{13}C-NMR spectra of switchgrass cellulose.[36]

	Relative proportion, %	
Assignment	Untreated	Pretreated
Cellulose I_α	2.3	3.6
Cellulose $I_{\alpha+\beta}$	8.8	10.1
Para-crystalline cellulose	27.3	32.7
Cellulose I_β	4.5	5.7
Accessible fibril surface	5.7	2.8
Inaccessible fibril surface	51.3	45.2

In terms of the conversion of cellulose to ethanol, the importance of cellulose crystallinity to the rate of enzymatic hydrolysis is an area that is still not settled in the literature. Some studies have shown an increase in the crystallinity index during hydrolysis. This suggests that there is preferential hydrolysis of the amorphous cellulose. Pu *et al.* showed a rapid initial phase for hydrolysis in which cellulose I_α, amorphous and para-crystalline cellulose were more readily hydrolyzed than the I_β cellulose. This was followed by a slower phase in which all the cellulose forms were equally susceptible to enzymatic hydrolysis.[37] On the other hand, studies by Buschle-Diller *et al.* and Mansfield *et al.* report no clear change in the crystallinity index after enzymatic hydrolysis.[38,39]

5.2 Hemicellulose

Hemicellulose is the second major carbohydrate component in switchgrass cell walls. On average, the switchgrass cultivars contain ~26% hemicellulose (Table 4). Hemicellulose is a combination of different monosaccharides including glucose, mannose, galactose, xylose, arabinose, and uronic acids.[28] The proportion of the polysaccharide sugars in individual switchgrass cultivars are summarized in Table 6.[24] From the results shown, xylose is the major hemicellulose sugar in switchgrass.[40–42] This was followed by arabinose (2.5 to 3.34%), galactose (0.61 to 2.12%), uronic acids (1.17 to 2.43%) and mannose (0.22 to 0.46%). Hu *et al.* also studied the composition of four populations of switchgrass looking at the differences in leaves, nodes and internodes. This data is presented in Table 7. They showed that the leaves contained the highest amount of arabinose and galactose on average.[43]

Table 6 Polysaccharide sugar content in switchgrass biomass (% mass)[a]

Cultivar	Glucan	Xylan	Galactan	Arabinan	Mannan	Uronic acids	Ref.
Alamo	30.97	20.42	0.92	2.75	0.29	1.17	24
Alamo	37.80	24.90	1.10	3.40	0.40		42
Alamo	45.60	26.10	1.10	3.10	0.50		54
Cave-in-Rock	32.81	21.15	1.16	2.99	0.30		24
Blackwell	33.08	20.93	1.04	3.01	0.27		24
Trailblazer	34.44	21.17	0.98	2.93	0.39		24
Kanlow	36.60	21.00	1.00	2.80	0.80		40
Kanlow – stems	36.90	23.42	0.61	2.50	0.22	1.56	24
Kanlow – leaves	33.81	20.09	2.12	3.34	0.46	2.43	24

[a] The calculation of the polymeric sugars content was done from the concentration of the corresponding monomeric sugars, using an anhydro correction of 0.88 for C-5 sugars and 0.90 for C-6 sugars following an NREL method (http://www.nrel.gov/biomass/pdfs/42618.pdf).

Table 7 Chemical compositions of three morphological portions for four populations of switchgrass[43]

Sample name[a]	Arabinose[b]	Galactose[b]	Glucose[b]	Xylose[b]
Alamo (S)	2.1	0.6	43.7	22.8
Kanlow (S)	2.3	0.6	43.7	24.2
GA 993 (S)	2.2	0.7	46.1	24.5
GA 992 (S)	2.3	0.7	43.8	24.6
Alamo (N)	3.2	0.9	35.7	23.7
Kanlow (N)	3.5	1.0	35.6	24.4
GA 993 (N)	3.3	0.9	40.1	26.8
GA 992 (N)	3.5	0.9	37.9	26.0
Alamo (L)	4.6	1.5	37.2	23.2
Kanlow (L)	3.8	1.5	35.2	22.6
GA 993 (L)	4.4	1.6	34.3	20.8
GA 992 (L)	4.6	1.6	35.8	22.4

[a] S: internodes portion; N: nodes portion; L: leaves portion. [b] Based on O.D. weight of switchgrass.

5.3 Soluble carbohydrates

Other than the structural cell wall carbohydrates, switchgrass also contains other carbohydrates such as sucrose, fructose, glucose and starch. Compared to cellulose and hemicellulose, these sugars make up a much smaller amount of the carbohydrate content of switchgrass. Among these soluble carbohydrates, sucrose has been shown to be the most prevalent. Johnson *et al.* studied the composition of Sunburst switchgrass using hot ethanol to extract the soluble sugars and amyloglucosidase to remove the starch. They found that in the stems, there was about three times more sucrose than starch (2.86% to 0.88%).[44] In the leaves, the amount of sucrose increased to seven times as much as the amount of starch

(2.87% to 0.41%). The fructose content was 0.06% in the leaves and 0.75% in the stems, while the glucose content was 0.25% in the leaves and 1.43% in the stems. In a study conducted by Dien *et al.* on Cave-in-Rock switchgrass, where ethanol was also used to extract the sugars, the concentrations of sucrose (2.7%) was the highest followed by glucose (0.6%), fructose (0.6%) and starch (0.5%).[28] These non-cell wall carbohydrates can also serve as a source of fermentable sugars for ethanol production, and should be considered in the overall conversion of switchgrass to biofuels.

5.4 Lignin structure

Lignin is the third main component of switchgrass cell walls. It is an amorphous polyphenolic cross-linked biopolymer, and is generally associated with the cellulose and hemicellulose in the cell walls. It acts as a primary binder for cellulosic fibers and also provides a defense against microbial and fungal attack of the cellulose fibers.[1] Lignin is a branched polyphenolic macromolecule consisting of hydroxyl- and methoxy-substituted phenylpropane units based on p-coumaryl, coniferyl and sinapyl structures (see Fig. 2).

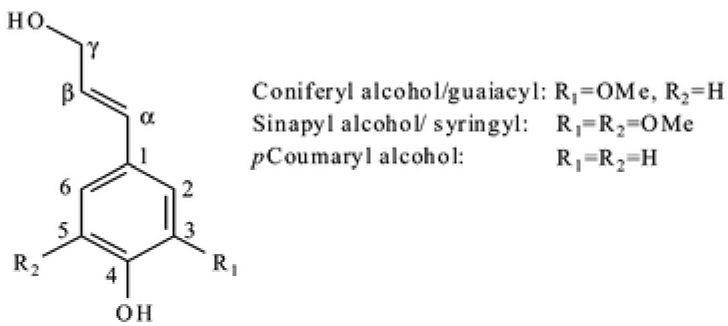

Fig. 2 Three monolignol structures found in lignin.

During biosynthesis, these monolignol units undergo a radical polymerization to dimers, then oligomerized, and eventually polymerized. Higuchi *et al.* found that grass lignins are made up of syringyl, guaiacyl, and p-hydroxy phenyl units together with a large amount of p-coumaric and ferulic acid ester.[45] This is different from softwood lignins which contain mostly guaiacyl units, and hardwood lignins which are primarily a copolymer of guaiacyl and syringyl units. There are various ways to isolate lignin from biomass, but ball milled biomass is considered to yield a fairly representative lignin. In order to study the structure of lignin, NMR spectroscopy has proven to be a valuable tool.[46]

As reported by Hu *et al.*, the S/G ratio varied significantly among node, internode and leaf portions of select switchgrass with the internode portion having an average S/G ratio of 0.68 whereas the leaves had an S/G ratio of 0.46.[43] The S/G ratio for the internodes was very close to the reported S/G ratio (*i.e.* 0.7) for miscanthus lignin.[47] It is well known that the greater the lignin S/G ratio in wood, the more efficient kraft pulping occurs.[48] With respect to the conversion of biomass to fuels, studies have shown that the levels and structure of lignin present in the biomass is proportional to enzymatic hydrolysis after acid pretreatment and that lignin modification can decrease the recalcitrance of select bioresources.[49,50] A publication by Davison *et al.* reported that for Populus, both the lignin content and the S/G ratio contribute to the release of xylose from acid pretreatment.[51] Likewise, Corredor *et al.* have reported that forage sorghums with a low S/G value were more readily enzymatically hydrolyzed after an acidic pretreatment.[52] The relationship of lignin structure to the efficiency of pretreatment remains under active study, as highlighted by a recent paper by Balan.[53] They concluded that for AFEX treatment of corn stover and poplar, the pretreatment severity and enzymatic hydrolysis efficiency are influenced to a large extent by lignin carbohydrate complexes and arabinoxylan cross-linkages.

Samuel *et al.* performed studies on lignin from ball milled Alamo switchgrass, using ^{13}C NMR.[54] The results confirmed the presence of p-hydroxyl phenyl units (H), guaiacyl units (G) and syringyl units (S). The S:G:H ratio was found to be 41 : 51 : 8 and some of the detected structures in the ball milled switchgrass lignin are illustrated in Fig. 3.[54] It was also reported that the major lignin interunit in this ball milled switchgrass sample was the β-O-4 linkage with minor amounts of phenylcoumaran, resinol and spirodienone units. These results are presented in Table 8.[54]

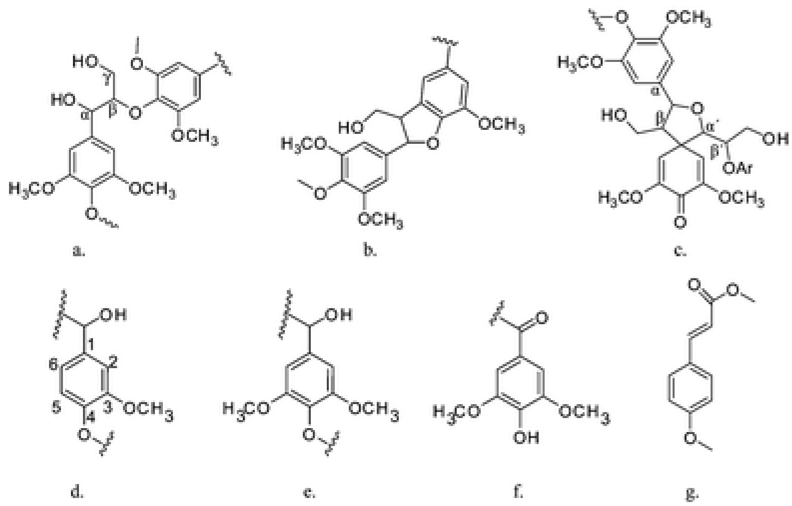

Fig. 3 Select structures found in ball milled switchgrass lignin a) β-O-4 ether linkage; b) β-5/α-O-4 phenylcoumaran; c) spirodienone; d) guaiacyl unit; e) syringyl unit; f) oxidized syringyl with C_α=O; g) cinnamate.

Table 8 Signal assignment and contents for the quantitative ^{13}C NMR spectra of ball milled switchgrass lignins from Alamo and Kanlow[a]

	Amount/Ar			
Assignments	Alamo[54]	GA992[55]	GA993[55]	Kanlow[55]
C=O in spirodienone unit	0.02			
C=O in aliphatic COOR	0.22	0.37	0.40	0.39
C=O in conjugated COOR	0.17	0.19	0.20	0.20
C_4 in H unit	0.07	0.05	0.07	0.07
C_3/C_4 in G units, C_3/C_5 in S units, C_α in cinnamate	1.71			
C_1 in G, S and H units, C_4 in S, $C_{2/6}$ in H	2.17			
C_6 in G units	0.44	0.47	0.46	0.43
C_5 in G, $C_{3/5}$ in H, C_β in cinnamate	0.85	0.80	0.83	0.75
C_2 in G units.	0.44	0.40	0.44	0.40
C_2/C_6 in S units	0.70	0.60	0.59	0.64
C_β in β-O-4, C_α in β-5 and β-β	0.74			
C_γ in β-5 and β-O-4 with C_α=O in G& S units	0.35			
C_γ in β-O-4 without C_α=O	0.39	0.43	0.45	0.39
Methoxyl	0.99	0.97	0.98	0.91
C_β in β-β and C_β in β-5 structures	0.10	0.14	0.14	0.13

[a] Syringyl unit (S), Guaiacyl unit (G), p-hydroxyphenyl (H).

Yan *et al.* also performed ^{13}C NMR on ball milled switchgrass lignin of samples from GA992 (an intercross between Alamo and Kanlow), GA993 (an experimental population derived from Alamo by recurrent selection) and Kanlow.[55] The results from this work suggested that p-coumarate and ferulate (∼ 0.20 units per aromatic ring) were linked to the switchgrass lignin and most of the p-coumarate was non-etherified and esterified to the lignin. This result corroborates work seen in the literature, in which these compounds act as cross linkers between lignin and the cell wall carbohydrates.[56] It was found that the S:G:H ratio was 33 : 40 : 27 for Kanlow, 31 : 42 : 26 for GA992 and 31 : 45 : 24 for GA993. Compared to Alamo switchgrass, the data showed similar levels of the various species present in lignin from ball milled Kanlow, such as the methoxyl, and C_γ in β-O-4 units. The main difference occurred in the levels of unconjugated COOR groups, in which the amount in Kanlow was approximately 80% higher than that found in Alamo. These results from this study are summarized in Table 8.[54,55]

In addition to ^{13}C NMR, Samuel *et al.* used ^{31}P NMR to quantify the hydroxyl containing functional groups present in the milled switchgrass lignin after phosphitylation with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane.[57] An example of the derivatization reaction is illustrated in Fig. 4.

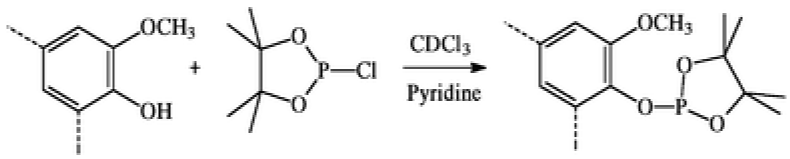

Fig. 4 Derivatization of hydroxyl structures using 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP).

The results from ^{31}P NMR allow researchers to gain insight into the content of aliphatic hydroxyl groups, condensed and noncondensed phenolics and carboxylic groups present in lignin (see Fig. 5).[54] This study showed that the guaiacyl phenolic content in the switchgrass was about 2.5 times that of the C-5 condensed phenolic content.

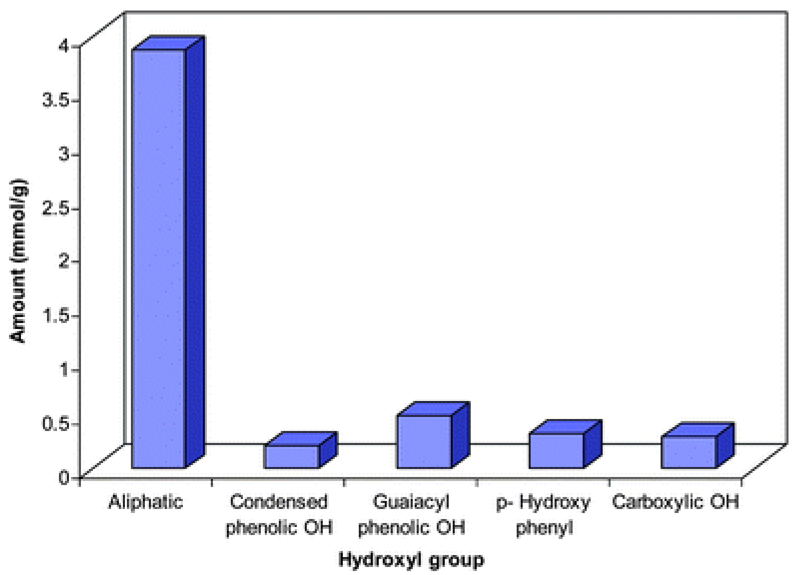

Fig. 5 Hydroxyl group contents in ball milled Alamo switchgrass lignin calculated from quantitative ^{31}P NMR spectra (mmol/g).[49]

This lignin was also analyzed using size exclusion chromatography. In order to do this analysis, the ball milled switchgrass lignin was acetylated using acetic anhydride in pyridine to facilitate dissolution in a non self-associating solvent. The number-average molecular weight was found to be 2.94×10^3 g/mol, while the weight-average molecular weight of the lignin was 5.00×10^3 g/mol. These values were less than those obtained from milled wood lignin from a hardwood Buddleja davidii, another potential bioresource, which had a Mw of 1.68×10^4 g/mol and a M_n of 7.26×10^3 g/mol.[58]

6. Conversion processes

The biological approach to biofuels utilizing lignocellulosic feedstocks is currently more challenging than the utilization of corn starch, where starch is readily enzymatically hydrolyzed to glucose.[9,59] In order to enhance the access to carbohydrates of nonfood biomass for biological conversion, a variety of pretreatment technologies have been developed to reduce the recalcitrance of biomass. The methods presented in the literature include chemical pretreatments with acids and alkali, and biological pretreatments with micro-organisms to selectively degrade hemicellulose or lignin.[60] The pretreatment technologies of switchgrass, and the subsequent hydrolysis and fermentation were reviewed by Keshwani *et al.*[7] As noted in this review, Kurakake *et al.* used an ammonia water pretreatment in which the sample was mixed with ammonia water (25–28%) and autoclaved at 120 °C for 20 min.[61] Alizadeh *et al.* used an ammonia fiber explosion pretreatment (AFEX), which yielded a 93% glucan conversion, and a 70% xylan conversion.[62] A summary of pretreatment conditions found in the literature for switchgrass can be found in Table 9.[61–65] Samuel *et al.* looked at the effect of dilute acid pretreatment on the lignin chemistry for Alamo switchgrass. They found that the main effect of the pretreatment was cleavage of the β-O-4 ether bond resulting in a 36% reduction in this inter-lignin linkage. In addition, the S/G value decreased from 0.80 to 0.53. Utilizing ^{31}P NMR analysis of the phosphitylated lignin, a 75% increase in C5-condensed phenolics was detected for the post pretreated lignin. This lignin also exhibited a reduced molecular weight and slight increase in the polydispersity index (*i.e.*, 1.77 *vs*. 1.70 for the starting lignin).[54] In a study on pretreatment of cellulose, Samuel *et al.* found that after pretreatment the relative proportion of para-crystalline and crystalline cellulose increased 20% and 24% respectively, while that of the fibril surface cellulose decreased by approximately 16%.[36]

Table 9 Summary of pretreatment methods and conditions for switchgrass

Pretreatment	Conditions	Yield	Ref.
Ammonia water	120 °C, 20min, 25–28% ammonia		61
AFEX	100 °C, 5 min, 1 : 1 NH_3:dry matter, 80% moisture (dry weight basis)	93% glucan conversion to glucose, 70% xylan conversion of resulting biomass	62
	90 °C, 30 min, 1 : 1 NH_3:dry matter, 15% moisture (air dried)	80% conversion to reducing sugars	63
Dilute acid	140 °C, 1h, 0.45–0.50% v/v dilute sulfuric acid	70% cellulose conversion of resulting biomass	64
Lime	120 °C, 2h, 0.1g $(CaOH)_2$/g dry biomass, 9ml H_2O/g dry biomass	85% conversion of switchgrass to reducing sugars	65

Recent studies have highlighted the potential of using pyrolysis to convert switchgrass to bio-crude. Boateng *et al.* reported pyrolysis oil yields greater than 60% using a bench scale fluidized bed pyrolysis unit. The reaction was run at 480 °C for a period of about 30 min.[66] Another study by Boateng examined the influence of maturity level of the switchgrass samples on the pyrolysis products. This study used a flash pyrolysis unit and temperatures ranging from 600 to 1050 °C, and showed average bio-oil yields from 58.56% to 76.57% after 20s in the pyrolyzer.[6] The results showed that the maturity of switchgrass plays an important role in the pyrolysis products. For example, they found that it may be beneficial to use more mature switchgrass samples together with temperatures lower than 900 °C in order to maximize the yield of condensable gases.

He *et al.* studied the effect of pyrolysis conditions such as moisture content and temperature on the yield and physio-chemical properties of switchgrass bio-oils.[67] The study found that changes in those two parameters caused large variations in the properties of the bio-oil obtained. Comparing the bio-oil yields, they found that pyrolysis using a moisture content of 10% and 450 °C, or a moisture content of 15% and 550 °C, produced bio-oils with the best properties including the highest heating value of 19.6 MJ/kg (10% moisture and 450 °C) and the lowest solids content of 1.23% (15% moisture and 550 °C). Mullen *et al.* looked at the differences in bio-oils obtained from various feedstocks and found that the levoglucosan levels in switchgrass bio-oils were 12 times higher than that of alfalfa stems.[68] The study also found that switchgrass bio-oils had less aromatic hydrocarbons and nitrogen containing compounds than the alfalfa stem bio-oils. Fahmi *et al.* looked at the influence that alkali metals had on the pyrolysis of switchgrass. They found that a strong catalytic effect, especially with potassium, was seen in both pyrolysis and combustion of the switchgrass. They showed that the presence of the metals reduced the degradation temperatures and lowered yield. They also found that the char yield in pyrolysis increases as the alkali metal content of the switchgrass increases.[18] A summary of the conditions, yield and elemental composition where available, of these pyrolysis studies is shown in Table 10.[4,6,66–69] The results showed that the bio-crude yield varied from 43% to 77% for the switchgrass samples studied.

Table 10 Summary of pyrolysis methods, yields and conditions for switchgrass

Conditions	Reactor type	Bio-oil Composition %				Yield %	Ref.
		C	H	N	O		
480 °C, ~0.1s residence time	Fluidized bed	52.97	6.43	0.38	39.13	43	4
600 °C to 1050 °C, 20 s	Flash Pyrolyzer					58.6 to 76.6	6
480 °C, 30 min	Fluidized Bed					60.7	66
450 °C to 550 °C, 5–15% moisture content	Fluidized bed						67
500 °C	Fluidized bed					60	68
500 °C, <0.4s	Fluidized Bed	55.80	6.90	0.79	36.3	62.4[a]	69

[a] Data averaged over two runs.

6. Conclusions

Switchgrass has been shown to be a very promising energy crop resource for biofuels. The high yields and ability to use existing technology to grow and harvest switchgrass make it a good candidate among biomass species for the conversion to ethanol using the saccharification and fermentation process, and also for thermo-chemical conversion to pyrolysis oils. Studies have shown that the maturity of the switchgrass plays a role in the quality of the biofuel, both ethanol and pyrolytic oils, and this is something that must be considered. The composition of the switchgrass also changes during storage, and must be taken into account when producing switchgrass based biofuels.

It should be noted that some of these results are from samples obtained from a particular location at a particular time in the year. Thus it is important to continue the research into these processes using samples from multiple locations and over a number of years to get a truly representative set of data. The resistance of switchgrass and other herbaceous crops to release their sugars, a characteristic described as recalcitrance, has been well documented. More research into the ultrastructure of these cell wall components in the various cultivars will help increase the future yield of ethanol from these plants. The effect of varying pyrolysis parameters has also been studied, but more work specific to switchgrass should be conducted.

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References

1 D. Mohan, C. U. Pittman and P. H. Steele, *Energy Fuels*, 2006, **20**, 848–889 [Links].

2 H. B. Goyal, D. Seal and R. C. Saxena, *Renew Sustain Energy Rev.*, 2008, **12**, 504–517 [Links].

3 L. Ingram, D. Mohan, M. Bricka, P. Steele, D. Strobel, D. Crocker, B. Mitchell, J. Mohammad, K. Cantrell and C. U. Pittman Jr, *Energy Fuels*, 2008, **22**, 614–625 [Links].

4 C. A. Mullen, G. D. Strahan and A. A. Boateng, *Energy Fuels*, 2009, **23**, 2707–2718 [Links].

5 M. A. Sanderson, P. R. Adler, A. A. Boateng, M. D. Casler and G. Sarath, *Can. J. Plant. Sci.*, 2006, **86**, 1315–1325.

6 A. A. Boateng, K. B. Hicks and K. P. Vogel, *J. Anal. Appl. Pyrolysis*, 2006, **75**, 55–64 [Links].

7 D. R. Keshwani and J. J. Cheng, *Bioresour. Technol.*, 2009, **100**, 1515–1523 [Links].

8 Z. Ma, C. W. Wood and D. I. Bransby, *Biomass Bioenergy*, 2000, **18**(6), 93–104 [Links].

9 W. G. Hohenstein and L. L. Wright, *Biomass Bioenergy*, 1994, **6**(3), 161–173 [Links].

10 D. I. Bransby, S. B. McLaughlin and D. J. Parrish, *Biomass Bioenergy*, 1998, **14**(4), 379–384 [Links].

11 K. H. Lee, T. M. Isenhart, R. C. Schultz and S. K. Mickelson, *Agrofor. Syst.*, 1998, **44**(2–3), 121–132 [Links].

12 G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044–4098 [Links].

13 K. A. Gray, L. S. Zhao and M. Emptage, *Bioethanol. Curr. Opin. Chem. Biol.*, 2006, **10**(2), 141–146.

14 S. B. McLaughlin, R. Samson, D. Bransby and A. Wiselogel, Bioenergy '96- The Seventh National Bioenergy Conference, 1996.

15 A. J. Demirbas, *J. Anal. Appl. Pyrolysis*, 2005, **73**, 39–43 [Links].

16 O. Paris, C. Zollfrank and G. A. Zickler, *Carbon*, 2005, **43**(1), 53–66 [Links].

17 A. V. Bridgewater, *Chem. Eng. J.*, 2003, **91**, 87–102 [Links].

18 R. Fahmi, A. V. Bridgewater, L. I. Darvell, J. M. Jones, N. Yates, S. Thain and I. S. Donnison, *Fuel*, 2007, **86**, 1560–1569 [Links].

19 L. E. Gunter, G. A. Tuskan and S. D. Wullschleger, *Crop Sci.*, 1996, **36**(4), 1017–1022.

20 K. A. Cassida, J. P. Muir, M. A. Hussey, J. C. Read, B. C. Venuto and W. R. Ocumpaugh, *Crop Sci.*, 2005, **45**, 682–692 [Links].

21 L. Rinehart, 2006, www.attra.ncat.org/attra-pub/switchgrass.html.

22 R. Lemus, E. C. Brummer, K. J. Moore, N. E. Molstad, C. L. Burras and M. F. Barker, *Biomass Bioenergy*, 2002, **23**, 433–442 [Links].

23 T. G. Bridgeman, L. I. Darvell, J. M. Jones, P. T. Williams, R. Fahmi, A. V. Bridgewater, T. Barraclough, I. Shield, N. Yates, S. C. Thain and I. S. Donnison, *Fuel*, 2007, **86**, 60–72 [Links].

24 NREL Biomass Feedstock Composition and Properties Database, 2004, http://www1.eere.energy.gov/biomass/feedstock_databases.html.

25 B. S. Dien, H. G. Jung, K. P. Vogel, M. D. Casler, J. F. S. Lamb, L. Iten, R. B. Mitchell and G. Sarath, *Biomass Bioenergy*, 2006, **30**, 880–891 [Links].

26 H. M. El-Nashaar, G. M. Banowetz, S. M. Griffith, M. D. Casler and K. P. Vogel, *Bioresour. Technol.*, 2009, **100**, 1809–1814 [Links].

27 D. Pimentel and T. W. Patzek, *Nat. Resour. Res.*, 2005, **14**(1), 65–76.

28 R. W. Thring, S. P. R. Katikaneni and N. N. Bakhshi, *Fuel Process. Technol.*, 2000, **62**, 17–30 [Links].

29 A. Oasmaa, R. Alen and D. Meier, *Bioresour. Technol.*, 1993, **45**, 189–194 [Links].

30 M. M. de Souza Lima and R. Borsali, *Macromol. Rapid Commun.*, 2004, **25**, 771–787 [Links].

31 M. A. S. Azizi Samir, F. Alloin and Alain Dufresne, *Biomacromolecules*, 2005, **6**, 612–626 [Links].

32 P. T. Larsson, U. Westermark and T. Iversen, *Carbohydr. Res.*, 1995, **278**(2), 339–343 [Links].

33 T. Larsson, E. L. Hult, K. Wickholm, E. Pettersson and T. Iversen, *Solid State Nucl. Magn. Reson.*, 1999, **15**, 31–40 [Links].

34 B. Xiao, X. F. Sun and R. C. Sun, *Polym. Degrad. Stab.*, 2001.

35 N. Reddy and Y. Yang, *Biotechnol. Bioeng.*, 2007, **97**(5), 1021–1027 [Links].

36 R. Samuel, Y. Pu, M. Foston and A. J. Ragauskas, *Biofuels*, 2010, **1**, 85–90.

37 Y. Pu, C. Ziemer and A. J. Ragauskas, *Carbohydr. Res.*, 2006, **341**, 591–597 [Links].

38 G. Buschle-Diller, C. Fanter and F. Loth, *Text. Res. J.*, 1999, **69**, 244–251 [Links].

39 S. D. Mansfield, E. deJong, R. S. Stephens and J. N. Saddler, *J. Biotechnol.*, 1997, **57**, 205–216 [Links].

40 L. Suryawati, M. R. Wilkins, D. Bellmer, R. L. Huhnke, N. O. Maness and I. M. Banat, *Biotechnol. Bioeng.*, 2008, **101**(5), 894–902 [Links].

41 J. J. Fenske, A. Hashimoto and M. H. Penner, *Appl. Biochem. Biotechnol.*, 1998, **73**, 145–157 [Links].

42 A. E. Wiselogel, F. A. Agblevor, D. K. Johnson, S. Deutch, J. A. Fennell and M. A. Sanderson, *Bioresour. Technol.*, 1996, **56**(1), 103–109 [Links].

43 Z. Hu, R. Sykes, M. F. Davis, E. C. Brummer and A. J. Ragauskas, *Bioresour. Technol.*, 2010, **101**(9), 3253–3257 [Links].

44 J. M. F. Johnson, N. W. Barbour and S. L. Weyers, *Soil. Sci. Soc. Am. J.*, 2007, **71**(1), 155–162 [Links].

45 T. Higuchi, Y. Ito and I. Kawamura, *Phytochemistry*, 1967, **6**, 875–881 [Links].

46 Y. Pu, S. Anderson, L. Lucia and A. J. Ragauskas, *Journal of Pulp and Paper Science*, 2003, **12**, 401–406.

47 J. J. Villaverde, J. B. Li, M. Ek, P. Ligero and A. de Vega, *J. Agric. Food Chem.*, 2009, **57**(14), 6262–6270 [Links].

48 A. D. Magaton, J. L. Colodette, A. D. G. Gouvea, J. L. Gomide, M. C. D. Muguet and C. Pedrazzi, *Tappi*, 2009, **8** (8), 32–39.

49 F. Chen and R. Dixon, *Nat. Biotechnol.*, 2007, **25**(7), 759–761 [Links].

50 R. Kumar and C. E. Wyman, *Biotechnol. Prog.*, 2009, **25**(3), 807–819 [Links].

51 B. H. Davison, S. R. Drescher, G. A. Tuskan, M. F. Davis and N. P. Nghiem, *Appl. Biochem. Biotechnol.*, 2006, **130**(1–3), 427–435 [Links].

52 D. Y. Corredor, J. M. Salazar, K. L. Hohn, S. Bean, B. Bean and D. Wang, *Appl. Biochem. Biotechnol.*, 2009, **158** (1), 164–179 [Links].

53 V. Balan, L. D. C. Sousa, S. P. S. Chundawat, D. Marshall, L. N. Sharma, C. K. Chambliss and B. E. Dale, *Biotechnol. Prog.*, 2009, **25**(2), 365–375 [Links].

54 R. Samuel, Y. Pu, B. Raman and A. J. Ragauskas, *Appl. Biochem. Biotechnol.*, 2009 In Press.

55 J. Yan, Z. Hu, Y. Pu, E. C. Brummer and A. J. Ragauskas, *Biomass Bioenergy*, 2010, **34**(1), 48–53 [Links].

56 R. Hatfield, J. Ralph and J. H. Grabber, *Planta*, 2008, **228**, 919–928 [Links].

57 M. Zawadzki and A. J. Ragauskas, *Holzforschung*, 2001, **55**, 283–285 [Links].

58 B. B. Hallac, P. Sannigrahi, Y. Pu, M. Ray, R. J. Murphy and A. J. Ragauskas, *J. Agric. Food Chem.*, 2009, **57**, 1275–1281 [Links].

59 R. J. Bothast and M. A. Schlicher, *Appl. Microbiol. Biotechnol.*, 2005, **67**, 19–25 [Links].

60 N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Y. Lee, M. Holtzapple and M. Ladisch, *Bioresour. Technol.*, 2005, **96**, 673–686 [Links].

61 M. Kurakake, W. Kiska, K. Ouchi and T. Komani, *Appl. Biochem. Biotechnol.*, 2001, **90**, 251–259 [Links].

62 H. Alizadeh, F. Teymouri, T. I. Gilbert and B. E. Dale, *Appl. Biochem. Biotechnol.*, 2005, **121**, 1133–1141 [Links].

63 B. E. Dale, C. K. Leong, T. K. Pham, V. M. Esquivel, I. Rios and V. M. Latimer, *Bioresour. Technol.*, 1996, **56**, 111–116 [Links].

64 C. E. Wyman, D. D. Spindler and K. Grohmann, *Biomass Bioenergy*, 1992, **3**(5), 301–307 [Links].

65 V. S. Chang, B. Burr and M. T. Holtzapple, *Appl. Biochem. Biotechnol.*, 1997, **63**, 3–19 [Links].

66 A. A. Boateng, D. E. Daugaard, N. M. Goldberg and K. B. Hicks, *Ind. Eng. Chem. Res.*, 2007, **46**, 1891–1897 [Links].

67 R. He, X. P. Ye, B. C. English and J. A. Satrio, *Bioresour. Technol.*, 2009, **100**, 5305–5311 [Links].

68 C. A. Mullen and A. A. Boateng, *Energy Fuels*, 2008, **22**, 2104–2109 [Links].

69 F. A. Agblevor, S. Besler and A. E. Wiselogel, *Energy Fuels*, 1995, **9**, 635–640 [Links].