CHARACTERIZATION OF TOBACCO STALK BLEACHED PULP

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Tobacco stalks were treated by two pulping processes: acetone organosolv, using different catalysts (*e.g.* H_2SO_4, HCl, $FeCl_3$/HCl), and soda-anthraquinone (soda-AQ). Resulting pulps were bleached with sodium chlorite in acetic acid solution. Cross polarization/magic angle spinning solid state NMR (CPMAS-NMR) of bleached pulps (BPs) indicated the presence of characteristic peaks associated with the anhydroglucose repeating unit of cellulose. Both CPMAS-NMR and X-ray diffraction results showed that the crystallinity indices of celluloses from acetone organosolv BPs were higher than that of the cellulose from soda-AQ BP. Furthermore, bleached pulps were treated with phenyl isocyanate in order to yield cellulose tricarbanilates (CTC). Weight average (DP_w) and number average (DP_n) degree of polymerization of CTCs were determined by size exclusion chromatography. Both DP_w and DP_n values of CTC obtained from soda-AQ BP were higher than that of CTCs obtained from acetone organosolv BPs.

Keywords: cellulose, tobacco biomass, acid hydrolysis, CPMAS-NMR

INTRODUCTION

Tobacco stalk, along with sugarcane bagasse, corn stover and other annual crop wastes, is often mentioned as a significant biomass resource for the production of biofuels and chemicals.[1,2] Among agricultural waste materials, tobacco stalk represents a relatively small, but significant source of biomass. From 2011 to 2016, tobacco leaf production was between 2.7 and 4.0 million tons in the U.S., and, in 2016, total U.S. acreage devoted to tobacco production was of 130,259 hectares.[3] In 2014, about 6 percent of the raw tobacco global production was produced in the U.S.[4] Tobacco stalks make up a significant proportion of the total biomass production in the region where tobacco is grown. This especially refers to the large-leaf tobacco types, such as Virginia and Burley. Of the total yearly amount of tobacco stalks, a smaller part is usually plowed, while the remaining stalks are disposed as waste.[5] Agricultural extension agents recommend that tobacco stalk be destroyed at the end of the growing season to prevent the potential spread of disease.[6] It is reported that at 45% moisture content, about 6 tons of tobacco stalks are produced per hectare and year.[1] Thus, in the United States, a reasonable estimate of 0.4 million tons of dry tobacco stalk biomass, a material that would be otherwise destroyed, was available as a biomass feedstock in 2014. Globally, the estimated dry tobacco stalk available approaches 10.7 million tons, the majority being produced in China.[4] In general, agricultural waste represents a huge untapped resource for the production of liquid fuels or value-added chemical products.

The processing of annual biomass sources for fuels or chemicals can be accomplished in a number of ways, including direct conversion by pyrolysis[7-10] or stepwise conversion by chemical or mechanical means. The stepwise approach can include steam explosion, solvent extraction and chemical pulping. Chemical pulping methods include the sulfite, kraft,[11] organosolv[12] and soda-anthraquinone (soda-AQ)[13] processes. Soda and soda–AQ processes have been used to pulp non-wood raw materials[14-18] with good results. Some of the advantages they provide are as follows: (a) high throughput resulting from the use of relatively short pulping times, (b) good yields, (c) applicability to both wood and non-wood raw materials, (d) reusability of cooking liquors, and (e) more expeditious cooking. Soda-AQ pulping was selected for pulping tobacco biomass due to its environmental and economic advantages (such as no unpleasant smell generation – since no sulphur compounds are used, and an increase in the pulp production – as lower cooking time values are needed to obtain the same

pulp quality and high yield values), to make the implementation of this process possible in factories situated in the vicinity of agricultural areas, since it may be adapted for low productions and may be applied to any raw – wood or non-wood – material.[19]

The organosolv process, first reported by Kleinert in 1931,[20-22] includes the Alcell®[12,23] process and is used to extract lignin from lignocellulosic feedstocks with organic solvents or their aqueous solutions. Since the 1970s, organosolv processes have attracted much interest because the conventional pulping processes, kraft and sulfite processes, have some serious shortcomings, such as air and water pollution.[24] It has been known that organosolv pretreatment can occur in a large number of organic or aqueous–organic solvent systems with or without added catalysts in the temperature range of 100-250 °C.[25] The organosolv process has the following advantages: (a) reduction to small- and mid-scale production costs relative to kraft processes, and facilitation of the efficient recovery of solvents and by-products, (b) lower use of water, energy and chemicals, (c) less pollution and easier detoxification of bleaching effluents, (d) applicability to all types of wood and non-wood plants, (e) production of pulp with properties similar to those of kraft pulp, in addition to higher yields, lower lignin contents, higher brightness and easier bleaching and refining, (f) no need for additional investments if kraft pulping facilities are available, as the application of high-boiling solvents (glycols, ethanolamines) is sufficient to exploit them.[26]

Pulp from the organosolv process has received considerable attention as an attractive feedstock for cellulosic ethanol production.[24,27-29] Pan *et al*.[30] suggest that the crystallinity of organosolv cellulose increases as the pulping temperature is raised, since higher temperatures remove a greater proportion of the amorphous cellulose. Further, the organosolv process facilitates the isolation of lignin and hemicellulose fractions.[31] Because it is obtained with a less aggressive process, organosolv lignin differs from other lignin types provided by conventional chemical methods. Structurally, it contains more phenol hydroxyls and carbonyl groups, which lead to more oxidized forms. Also, organosolv lignin has a lower glass transition temperature (Tg) and is therefore easier to process thermally than kraft lignin.[32]

In the present study, we compared bleached pulps (BPs) obtained from Burley tobacco stalk by several variations of the organosolv method, which were all carried out under identical conditions, except the type of catalyst. We also investigated the BP obtained from Burley tobacco stalk by the soda-AQ process to compare it with that obtained by the organosolv processes. Characterization by CP/MAS ^{13}C solid-state NMR spectroscopy, X-ray powder diffraction and with regard to the degree of polymerization indicated that the tobacco stalk BPs presented structural characteristics similar to celluloses from other sources, as reported in the literature. In this context, tobacco stalk could be used as a future feedstock for obtaining cellulose.

EXPERIMENTAL

Materials

Tobacco stalks (Burley, Flue-cured and Oriental), tobacco whole plant (TWP), and no extract (NX) tobacco sheet were provided by R.J. Reynolds Tobacco Company, Winston-Salem, N.C. TWP and NX are the by-products of tobacco processing. The stalks, locally collected after tobacco-harvesting, were typically <5 cm diameter. They were milled in the laboratory using a Wiley Mill Model 4 to a particle size less than 6 mm, air-dried at room temperature to an equilibrium moisture content of about 10%. Burley tobacco stalks were selected for pulping and further homogenized using a Waring laboratory blender and used immediately. Sulfuric acid (98%) and sodium chlorite (80%) were supplied by Fisher Scientific. Anthraquinone (98%) and phenyl isocyanate (99%) were supplied by Acros Organics.

Chemical analysis

Oven-dried weights were determined by drying to constant weight at 105 °C in a convection oven. Samples were milled to pass through a 40 mesh screen before chemical analysis. Klason lignin (KL) content of biomasses and pulps was determined according to TAPPI standard method T-222. Ash content was determined according to TAPPI standard method T-211 om-93. Extractives of the biomasses were determined according to the procedure of TAPPI standard method T264 cm-97, using ethanol/benzene, ethanol and water as solvents consecutively. Holocellulose was determined according to the modified sodium chlorite method,[33] where 2 g of extractive-free biomass was treated with H_2O (65 mL) mixed with sodium chlorite (0.75 g) and acetic acid (0.5 mL) at 70 °C for 1 h.[34] The addition of sodium chlorite and acetic acid was repeated three more times until the sample became white and then the ash content of each recovered sample was determined. The final mass of the holocellulose present in the biomass was calculated by subtracting out the mass of ash present in the recovered sample from

the total mass of the recovered sample.

Organosolv pulping

The experimental conditions for organosolv pulping were selected according to previous unpublished work. Tobacco stalk particles were cooked in aqueous acetone in a Parr reactor model 4662 (Parr Instrument Company). The 3.8 L stainless steel reactor was equipped with a 3 L glass liner. A 180 g (oven-dried weight) batch of chips was cooked at 160 °C. After cooking, the reactor was left to cool to room temperature. The pulp and liquor were then separated, using custom-made medium porosity glass fritted centrifuge cups. The ratio of liquor to chips was 10:1 v/w in all organosolv pulping experiments. The pulp was washed with acetone and the acetone wash was combined with the spent liquor. The pulp was then washed with water and the water-wash was discarded. Depending on the type of catalyst used, the pulps were described as organosolv pulp 1 (OSP1), organosolv pulp 2 (OSP2) and organosolv pulp 3 (OSP3) for H_2SO_4, HCl and $FeCl_3$/HCl, respectively. To precipitate the dissolved lignin, a modified procedure of Sannigrahi *et al.*[35] was applied. In this procedure, first the previously combined spent liquor and acetone washes were mixed with five volumes of water. Then, the lignin precipitate was isolated by centrifugation, followed by filtration and collected on a medium porosity glass frit. After washing thoroughly with water, the lignin precipitate was dried over P_2O_5 under vacuum. This lignin precipitate was described as acetone organosolv lignin (AOL).

Soda-AQ pulping

The experimental conditions for soda-AQ pulping were selected according to a previous study, which determined the optimum conditions for soda-AQ pulping of wheat straw.[36] In this study, the ratio of liquor to chips of 8:1 v/w was chosen instead of 10:1 v/w, in order to have sufficient white liquor to completely immerse the material because tobacco stalk is very bulky. Tobacco stalk particles were cooked in a Parr reactor model 4662 (Parr Instrument Company). The 3.8 L stainless steel reactor was equipped with a 3 L glass liner. A 180 g (oven-dried weight) batch of chips was cooked at 160 °C. After cooking, the reactor was left to cool to room temperature. The pulp and liquor were then separated using custom-made medium porosity glass fritted centrifuge cups. Then, the pulp was washed twice with water and the wash was combined with the spent liquor. The pulp was described as soda-AQ pulp (SAQP). Combined spent liquor and water washes were acidified with conc. HCl until pH~3 to precipitate the dissolved lignin. The lignin precipitate, henceforth described as soda-AQ lignin (SAQL), was collected on a medium porosity glass frit, washed thoroughly with water, and dried over P_2O_5 under vacuum.

Bleaching of organosolv and soda-AQ pulps

For bleaching, the pulp (80 g oven-dried weight) was suspended in a solution containing H_2O (2.6 L), sodium chlorite (30 g) and acetic acid (20 mL) at 70 °C for 1 h. The addition of sodium chlorite and acetic acid was repeated three times. The bleached pulp was collected on a Whatman No.1 filter paper, washed thoroughly with water, and dried at 50 °C in a convection oven.

Molecular weight distribution

To enhance the solubility and detection properties, phenyl isocyanate derivatives (cellulose tricarbanilate, CTC) of bleached pulp were prepared for the molecular weight determinations. CTC was prepared by the modified procedure of Wood *et al.*[37] BP samples were dried in a vacuum oven at 60 °C overnight before tricarbanylation. Then, BP (0.1 g) was mixed with anhydrous pyridine (25 mL) in a 50 mL round bottomed flask, which was then immersed in an oil bath at 80 °C. While the suspension was stirred, phenyl isocyanate (7 mL) was added for starting the modification. After 48 h, the formed clear yellow solution was removed from the oil bath and methanol (4 ml) was added to react with excess phenyl isocyanate. The reaction mixture was added dropwise into methanol (250 mL) under constant stirring in order to precipitate CTC. Centrifugation was used to separate the precipitated products. The clear supernatant was decanted and solids were filtered through a medium porosity glass frit and washed with methanol to remove the trace amount of residual pyridine and then air-dried.

Samples were dissolved in THF (~1 $mg \cdot mL^{-1}$) and filtered through a 0.2 um filter prior to analysis. Size Exclusion Chromatography (SEC) was carried out at 35 °C in THF (HPLC grade) at 1 $mL \cdot min^{-1}$ on a Waters 717 Autosampler, equipped with 3 in-line PLgel 5 um MIXED-C columns, a Waters 2414 differential refractive index detector. The reported molecular weights of CTCs are relative to polystyrene standards. The degree of polymerization of cellulose was obtained from the molecular weight of CTC divided by the molecular mass of the repeating unit of CTC (monomer molecular weight of 519 $g \cdot mol^{-1}$).

X-ray diffraction

X-ray diffraction (XRD) measurements were performed on a Bruker D8 Discover XRD system, using CuKα (λ = 0.154 nm) radiation generated at 40 kV and 40 mA. BP samples were spread onto a SiO_2 substrate, which had dimensions of 30×30×2.5 mm (zero diffraction plate for XRD). Scans were obtained from 5° to 50° 2Θ in

0.01° steps for 0.1 s per step. Separation of the diffraction profile of the sample into the amorphous halo and the crystalline reflection profiles was done using a curve fitting program, Fityx, assuming Gaussian functions for each peak. The maximum of the amorphous peak was considered to coincide with the minimum of the diffraction profile of the sample observed between the (101) and (200) peaks (Fig. 1). The crystallinity index (CrI^{XRD}) was calculated from the diffraction profiles using the integral scattering intensities of crystalline (I_c) and amorphous (I_a) regions:[38]

$$CrI^{XRD} = \frac{I_c}{I_c + I_a} \times 100 \quad (1)$$

Cross polarization/magic angle spinning (CP/MAS) solid-state NMR spectroscopy

CP/MAS solid state ^{13}C NMR spectra of BP samples were collected at 7.05 T in a Bruker Avance II 300 MHz spectrometer, operating at Larmor frequencies of 75.47 MHz for ^{13}C and 300.13 MHz for ^{1}H nuclei. Samples were packed into a zirconia rotor sealed with Kel-F^{TM} caps and spun at 6000 Hz. 2048 scans were averaged using a 1 ms contact time and a pulse repetition rate of 2.0 s. The crystallinity index (CrI^{NMR}) was determined from the relationship between the integration areas of the ordered ($A_{86–92\ ppm}$) and amorphous ($A_{79–86\ ppm}$) C-4 signals in cellulose:[38,39]

$$CrI^{NMR} = \frac{A_{86-92}}{A_{79-86} + A_{86-92}} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Chemical composition

The holocellulose, Klason lignin, extractives and ash content of tobacco biomass samples were determined by TAPPI methods and the results are illustrated in Table 1. Among different types, tobacco stalk biomasses have higher holocellulose and Klason lignin content than non-stalk biomasses (TWP and NX). In contrast, non-stalk biomass samples have higher ash contents. Lower holocellulose and higher ash-contents for non-stalk tobacco biomass types tested in this study make them unfavorable for pulping processes. Across species, Burley and Flue-cured stalks contain higher holocellulose content than Oriental stalk. Burley and Oriental stalks had similar lignin content, whereas Flue-cured stalks had the highest lignin content among the three species. Overall, Klason lignin content of tobacco stalks is lower than that of woody biomass.[29] The results obtained here are comparable to the values reported for Klason lignin content of tobacco stalks determined by Agrupis *et al.*[1] Based on the chemical composition results of tobacco biomass, Burley tobacco stalks were chosen for further pulping experiments because they had the lowest ash content and relatively high holocellulose content.

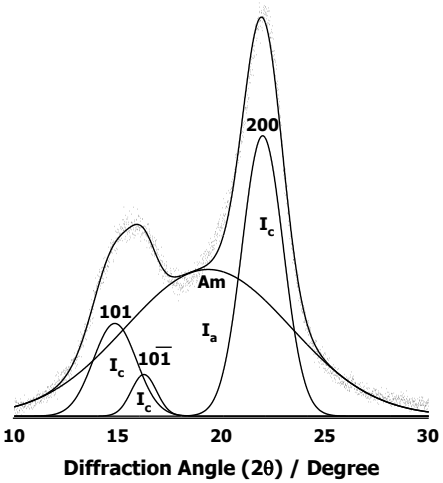

Figure 1: X-ray diffractogram of soda-AQ pulp showing fitted crystalline regions and the amorphous halo

Table 1
Chemical composition of tobacco biomass

Biomass type	Holocellulose (wt%)	Klason lignin (wt%)	Ethanol-benzene extracts (wt%)	Hot water extracts (wt%)	Ash content (wt%)
Burley	68.6±1.6	14.8±0.5	4.2±0.2	7.6±0.4	0.4±0.1
Flue-cured	69.5±2.1	18.7±0.9	4.9±0.6	6.8±0.9	0.9±0.2
Oriental	64.2±2.8	14.2±0.5	10.2±0.5	9.0±0.6	2.1±0.4
TWP	51.4±2.6	8.6±0.8	8.7±1.0	12.6±0.6	6.5±0.8
NX	60.1±1.9	10.8±1.1	4.0±0.4	4.3±0.5	8.9±0.6

Table 2
Yields of organosolv and soda-AQ pulping of tobacco burley stalk

Sample	Pulping conditions[a]						Pulp yield (wt%)	KL in pulp (wt%)	Isolated lignin yield (wt%)
	Catalysis	A	C	T	AC	t			
OSP1	H_2SO_4	1.0	60	160	—	120	64.9±2.0	18.7±0.4	4.8±0.3
OSP2	HCl	0.4	60	160	—	120	68.0±1.5	17.9±0.5	4.0±0.4
OSP3	$FeCl_3$/HCl	2.0	60	160	—	120	55.5±1.7	16.5±0.7	8.1±0.5
SAQP	AQ	0.1	—	160	16.0	60	60.2±1.2	19.7±0.5	8.0±0.4

[a]A, amount of catalyst (wt% of oven-dried wood); T, cooking temperature (°C); t, time (min) at cooking temperature; C, concentration of acetone with respect to H_2O, (%, v/v); AC, alkaline charge of the pulp (%, w/w, oven-dried wood)

Table 3
Bleached pulp yields of different organosolv and soda-AQ pulps

Sample	Bleaching yield (wt%)	Overall bleached pulp yield (wt%)	CI^{XRD}	CI^{NMR}	DP_n	DP_w	MWD
OSP1	70.4	45.7	42.4±0.9	37.6±0.4	244±29	1722±14	7.07
OSP2	69.8	47.5	42.0±0.6	37.0±0.4	273±3	1664±10	6.09
OSP3	78.5	43.6	43.9±0.5	38.9±0.5	261±42	1820±9	6.97
SAQP	66.0	39.7	39.9±0.2	35.8±0.4	324±2	1904±19	5.87
WCF	—	—	53.9 ±0.7	50.8±0.6	1158±92	3044±27	2.64

[a] MWD: DP_w/DP_n

Pulping conditions, pulp and isolated lignin yield, and KL in pulp are listed in Table 2. Here, the pulp yield and the isolated lignin yield represent the yield of pulp and the yield of recovered lignin, respectively. KL in pulp represents the Klason lignin still left in the residue after pulping of the biomass. The lowest pulp yield is observed for organosolv pulping catalyzed with $FeCl_3$/HCl (OSP3). OSP3 also has the lowest KL in pulp and the highest isolated lignin yield. Based on the Klason lignin analysis of the isolated lignins from different pulping techniques, organosolv pulping experiments (OSP1, OSP2 and OSP3) yielded lignins that have the same amount of Klason lignin (~96 wt%), and soda-AQ pulp (SAQP) yielded a poor quality lignin, which has a lower Klason lignin content (~35 wt%).

Table 3 shows the weight-average (DP_w) and number-average (DP_n) degrees of polymerization of the cellulose in BP samples. For comparison with cellulose from other sources, Table 3 also lists DP_w and DP_n of cellulose from Whatman cellulose filters (WCF) Grade 1. The samples OSP1, OSP2, OSP3, and SAQP have DP_n values of 244, 273, 261 and 324 anhydroglucose units (AGU), respectively. The DP_w values fall within the range of reported DP_w values (500-2,100) for celluloses obtained from bleached pulp.[40] Both DP_n and DP_w for SAQP were the highest among the values obtained for the pulping conditions tested. This result is expected as alkaline peeling occurs at chain ends, one monomer at a time,[41] whereas random cleavage occurs in acid hydrolysis, which reduces the molecular weight significantly. Acidic pretreatments also result in a lower degree of polymerization for celluloses obtained from mountain pine beetle-killed lodgepole pine.[42]

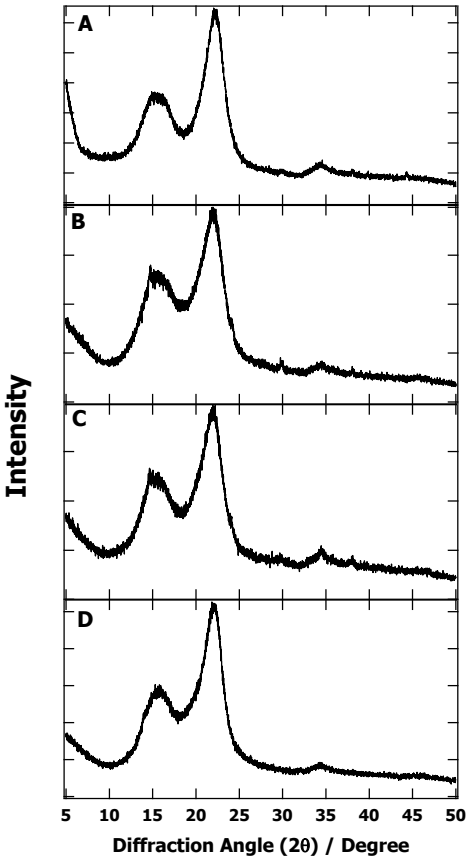

Figure 2: X-ray diffractogram of BP obtained from (A) OSP1, (B) OSP2, (C) OSP3, and (D) SAQP

X-ray diffraction

Figure 2 shows the XRD of BPs obtained from Burley tobacco stalk by organosolv pulping with different catalysts and soda-AQ pulping. As shown in Figure 2, all the samples have a typical crystal lattice for cellulose I[43] and exhibit similar diffraction patterns. The calculated crystallinity index values of the different BP samples were obtained by the application of Eq. 1. These are given in Table 3. SAQP has the lowest CI^{XRD} among the BPs tested. Because the organosolv pulping processes use acid as catalyst, the amorphous cellulose content in the cellulose microfibrils is attacked preferentially and leaves the crystalline fraction relatively untouched. The result is an increase in the crystallinity index. Among the BPs obtained by the different organosolv pulping processes tested, CI^{XRD}(OSP3) > CI^{XRD}(OSP1) > CI^{XRD}(OSP2). Even though the range of crystallinities for the materials is very narrow, the crystallinity index values for the BPs obtained from organosolv pulping experiments follow an opposite trend to that of the overall bleached pulp yield. As the overall bleached pulp yield decreases, the crystallinity index value increases. This result is mostly caused by the residual hemicelluloses left in the BP samples. As the overall bleached pulp yield decreases, the BP samples have lower residual hemicellulose and higher cellulose content, and as a result they have higher crystallinity index values.

CP/MAS ^{13}C solid-state NMR spectroscopy

Figure 3 shows the CP/MAS ^{13}C solid-state NMR spectra of the BPs obtained from Burley tobacco stalk by organosolv pulping with different catalysts and by the soda-AQ pulping process. Sharp signals are assigned to the cellulose and hemicelluloses present in the BPs. In accordance with the literature, the signals between 72 and 75 ppm are assigned to the C-2, C-3 and C-5 of AGU in cellulose, and the signal at 105 ppm is assigned to the C-1 of cellulose. The signals at 89 and 65 ppm are assigned to the more ordered C-4 and C-6 of cellulose, respectively, whereas the signals at 84 and 62 ppm are assigned to the less ordered C-4 and C-6 of cellulose. Moreover, in Figure 3A-C, the signals of methyl (22 ppm) and carboxylic carbons (173 ppm) derived from acetyl groups attached to hemicelluloses can be identified.[44] The absence of signature hemicellulose peaks (22 ppm and 173 ppm) in the BPs obtained from SAQP (Fig. 3D) indicates that the soda-AQ pulp process is more

effective for the removal of hemicelluloses from the matrix.

The calculated crystallinity indices of the different BP samples were calculated using Eq. 2. These are given in Table 3. The CI^{NMR} values correlate well with CI^{XRD} values as they both show the same order of the crystallinity for different pulping methods used. However, the CI^{NMR} values are consistently lower than the CI^{XRD} values. The reason for the systematic difference in the two methods of crystallinity determination is probably related to the partial overlap of relevant signals both in NMR and by X-ray diffraction. Park *et al.*[45] also observed that CI values obtained by the XRD peak deconvolution method were higher than CI values obtained by the NMR peak separation method for commercial cellulose samples.

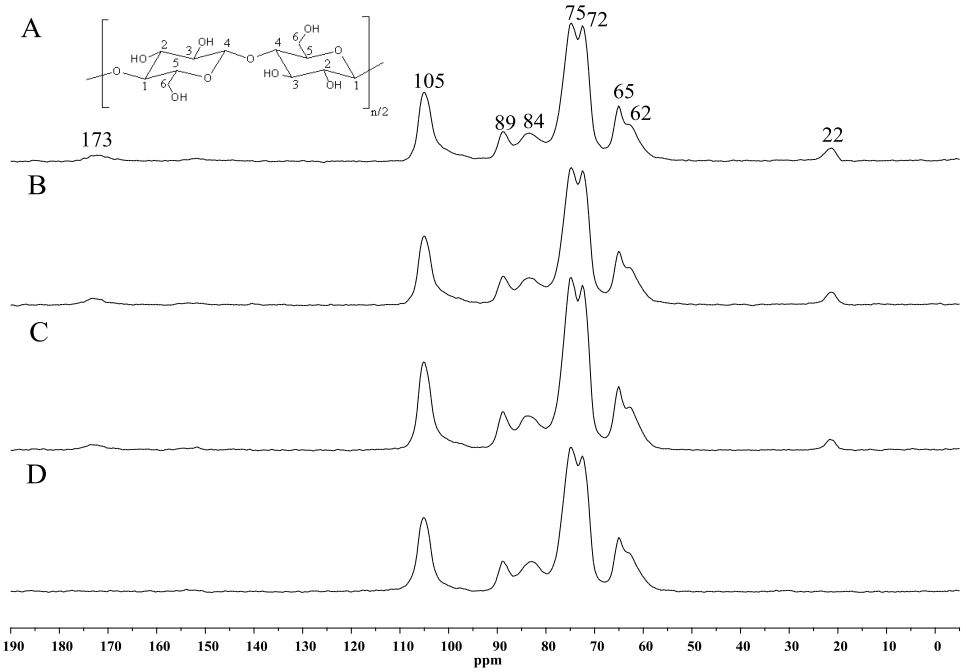

Figure 3: CP/MAS 13C solid-state NMR of BPs obtained from (A) OSP1, (B) OSP2, (C) OSP3 and (D) SAQP

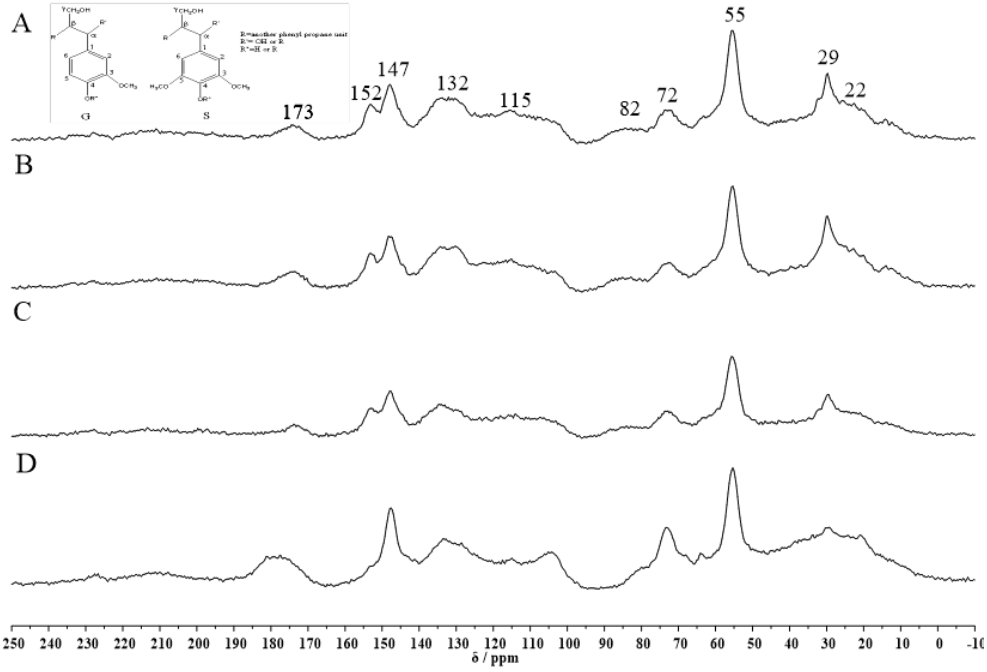

Figure 4: CP/MAS ^{13}C solid-state NMR of lignins obtained from (A) OSP1, (B) OSP2, (C) OSP3 and (D) SAQP

Figure 4 shows the CP/MAS ^{13}C solid-state NMR spectra of the lignin fractions obtained from Burley tobacco stalk by organosolv pulping with different catalysts and soda-AQ pulping. Resonances are assigned to CH_3 in acetyl groups of hemicellulose (22 ppm), methoxy groups in lignin (55 ppm), unsubstituted olefinic or aromatic carbon atoms (110-127 ppm), quaternary olefinic or aromatic carbon atoms (127-143 ppm), olefinic or aromatic carbon atoms with OH or OR substituents (143-167 ppm), esters and carboxylic acids (169-195 ppm), including acetyl groups in hemicellulose at 173 ppm.[46] More specifically, the peak at 152 ppm is assigned to the aromatic carbon-3 (S3e) and carbon-5 (S5e) of the syringyl unit, and aromatic carbon-4 (G4e) of the guaiacyl unit with etherified carbon-4. The peak at 147 ppm is assigned to the aromatic carbon-3 (S3f) and carbon-5 (S5f) of the syringyl unit, and aromatic carbon-3 (G3f) of the guaiacyl unit with free phenolic carbon-4. The broad peak between 133-136 ppm is assigned to the aromatic carbon-1 (S1e) and carbon-4 (S4e) of the syringyl unit, aromatic carbon-1 (G1e) of the guaiacyl unit with etherified carbon-4, and the aromatic carbon-1 (S1f) and carbon-4 (S4f) of the syringyl unit, aromatic carbon-1 (G1f) of the guaiacyl unit with free phenolic carbon-4. The broad peak between 112-120 ppm is assigned to the aromatic carbon-2 (G2), carbon-5 (G5), and carbon-6 (G6) of the guaiacyl unit.[44] The resonances at 82 and 72 ppm are typical of alcoholic carbons, and may be assigned to hydroxylated C-α and C-β in α-O-4/ β-O-4 linkages in guaiacyl and syringyl units, respectively. The peak at 29 ppm may be attributed to carbons in lignin lateral chains.[47] It is interesting to note that SAQL does not show the peak at 152 ppm, which corresponds to the aromatic carbon-3 (S3e) and carbon-5 (S5e) of the syringyl unit, and aromatic carbon-4 (G4e) of the guaiacyl unit with etherified carbon-4.

CONCLUSION

Tobacco stalk is an attractive annual biomass feedstock for the production of cellulosic pulp and lignin. The cellulose and lignin obtained by organosolv and soda-AQ pulping of tobacco stalk is comparable to those available from other annual biomass sources, such as corn stover and sugarcane bagasse. Soda-AQ pulping of tobacco stalk yields a pulp containing more cellulose, compared to the organosolv methods tested here. The organosolv methods show some residual hemicellulose in the BP fraction. On the other hand, the lignin recovered by the organosolv methods has above 95% Klason lignin, whereas the isolated lignin fraction obtained by soda-AQ pulping typically contains less than 50% Klason lignin. The solid-state NMR spectra of the lignins separated by both methods also revealed the presence of signals associated with the lignin structure.

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