

Assesment of technical lignins for uses in biofuels and biomaterials: Structure-related properties, proximate analysis and chemical modification



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ABSTRACT

The potential of organosolv and kraft eucalyptus and spruce lignin as feedstock for polymeric materials and biofuel applications was assessed. Proximate analysis was used to predict the heating values and char formation. Chemical modification, based on the esterification reaction with methacryloyl chloride, was applied to introduce vinyl groups into the lignin macromolecules for enhanced reactivity. Kraft eucalyptus and spruce lignins had a more condensed structure than organosolv lignins, which resulted in greater thermal stability for these lignins. For different species within the same process, the thermal parameters showed a correlation with certain structural and compositional parameters (ash and sugars content, molecular weight and degree of condensation). Organosolv spruce lignin produced the highest heating value of 24 MJ/Kg, which is suitable for biofuel applications. The content of phenolic OH groups was higher for kraft lignins and especially higher for softwood lignins, both organosolv and kraft. The degree of methacrylation, estimated from the content of vinyl groups per C9 lignin unit, was significantly greater for organosolv lignins than for kraft lignins despite the higher OH-groups content in the latter.

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1. Introduction

Increasing interest in the commercialization of various types of technical lignins is due, first, to their increasing availability, as result of the development of second generation biofuel technologies, and, second, to the emergence of new biorefineries that focus their production on bio-based platform chemicals and commodities from lignocellulosic feedstock (Ragauskas et al., 2014). Indeed, the manufacture of ethanol from biomass alone is expected to result in an annual generation of up to 66 million tonnes of lignin, an amount that is greater than the total quantity of lignin wastes currently produced by the pulp and paper industry and that substantially exceeds the current yield of biofuels (Langholtz et al., 2014). Traditionally, lignin has been obtained as a by-product of the pulp and paper industry. Approximately 45 and 2 million tonnes/year of

kraft lignin and liginosulfonates, respectively, are generated as a by-product of chemical pulp production (Hu, 2002; Song et al., 2011; Sahoo et al., 2011). Most of the lignin is used internally as a low-grade fuel for the pulping operation, while only 1–2% of the total amount of technical lignin is used in high-value applications. However, current cellulosic ethanol projects have demonstrated that 60% more lignin is generated through combustion than is needed to meet internal energy requirements (Sannigrahi and Ragauskas, 2011; Boerjan et al., 2003). As a result, there is a need to develop new processes for the recovery, upgrade and modification of lignin derived from both paper-making and novel biorefinery processes to produce lignin with chemical and physical properties suitable for high-value utilization.

Lignin, which is the second most abundant biopolymer after cellulose, is an important structural component of lignocellulosic biomass. The main functions of lignin in plants are to provide rigidity and physical strength to the plants, to transport water and nutrients internally, and to protect the plants from microorganisms and insects (Chung and Washburn, 2012; Mishra et al., 2007). Lignin in biomass has a complex heterogeneous structure which consists mainly of phenylpropane units that come from

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three aromatic alcohols: *p*-coumaryl, coniferyl and sinapyl alcohols. The phenolic substructures that originate from these monolignols are called *p*-hydroxyphenyl (H, from coumaryl alcohol), guaiacyl (G, from coniferyl alcohol) and syringyl (S, from sinapyl alcohol) (Laurichesse and Avérous, 2014). The chemical structure of lignin has distinctive characteristics, depending on the origin and growing conditions of the plant (Morandim-Giannetti et al., 2012; Notley and Norgren, 2010). In general, softwood lignins are composed mainly of G-units whereas hardwood lignins are based on guaiacyl (G) and syringyl (S) units present in different ratios (Derkacheva, 2013; Schorr et al., 2014). The most common linkages in the lignin molecule are the β -O-4 ether linkages, followed by other types of ether and C-C linkages such as α -O-4, β -5, 5-5, 4-O-5, β -1, and β - β (Sjöström, 1993). Although the lignin structure has been studied intensively for many years, it is not yet fully understood. Different kinds of linkages in lignin, and the diversity of their functional groups, such as methoxyl, phenolic and aliphatic hydroxyl groups, result in a complicated macromolecule (Crestini et al., 2011). Those functional groups have a great impact on the reactivity of lignin (Macfarlane et al., 2014). The extraction processes also have a great influence on the final structure and properties of lignin (Canetti and Bertini, 2007; Vishtal and Kraslawski, 2011). Kraft lignins usually contain sulfur in an amount of less than 1–2%. Moreover, it contains a high number of condensed structures (highly condensed G-units and some linkages related to condensed structures like β -5, 5-5', 4-O-5) and a high percentage of the phenolic hydroxyl group. Of the various technical lignins, organosolv lignins, such as those produced during bioethanol production, differ significantly from other technical lignins. Structurally, organosolv lignins have a higher relative amount of phenolic hydroxyl groups and a more oxidized structure, yet possess low Tg's and are easy to process thermally (Kubo and Kadla, 2004). As a result, organosolv lignins have advantages over other industrial lignins when considering composite-material applications.

Lignin is an excellent energy source/power source and is suitable in the production of electricity, fuel, steam and syngas (Laurichesse and Avérous, 2014; Macfarlane et al., 2014). When considering biomass thermal conversion for energy production, proximate analysis is one of the most important characterization methods. Lignin, like other biomass components, is composed of moisture, ash and organic matter (volatiles and fixed carbon). This makes it attractive as a solid biofuel for pyrolysis, gasification and combustion processes. The increasing price of fossil fuels, as well as growing environmental concerns, make the biomass an important renewable energy source (García-Maraver et al., 2015). Biomass presents distinct advantages when compared to traditional fossil fuels, namely: the reduction of greenhouse gas emissions, low NO_x and SO₂ emissions, its abundance and sustainability, and its economic competitiveness (García et al., 2014; Poddar et al., 2014; Shen et al., 2010). There are a limited number of studies available concerning assays of proximate analysis of lignin (Farag and Chaouki, 2015; Jin et al., 2013). Volatiles and fixed carbon content are two important parameters during thermal conversion of lignin (Moriani et al., 2014). Pyrolysis is inherently present in combustion and gasification processes and is one of the most applied techniques in thermal technology (Farag and Chaouki, 2015; Jin et al., 2013; Bridgwater, 2003) because it can directly generate solid (carbon), liquid and gaseous products (García et al., 2014; Farag and Chaouki, 2015). Moreover, it is important to note that the products and conversion yields depend mainly on the nature of the lignin, its composition and its functional groups, although processing conditions such as heating rate and temperature also have a strong influence (Shen et al., 2010; Ferdous et al., 2002). Lignins, in general, possess fewer volatiles and higher fixed carbon content than biomass (Shen et al., 2010; Won Kim, 2015). On the other hand, lignin also has a potential for use as a raw material in the

polymer industry. Several studies have shown that it is possible to incorporate lignin directly and without any modification into other commercial polymers, thereby introducing new or improved properties (Sahoo et al., 2011; Mishra et al., 2007; Morandim-Gandini, 2012; Pouteau et al., 2003, 2004; Alexy et al., 2000; Kaewtatip and Thongmee, 2013; Bhat et al., 2013). Also, lignin is used as the main component in the production of carbon fiber (Jin et al., 2013). The addition of lignin has an important influence on the thermal behavior of some polymers (Canetti and Bertini, 2007; Canetti et al., 2006; Bertini et al., 2012). Due to its structural features, lignin has a great potential for chemical modifications, which can result in improved reactivity and lead to value-added polymeric materials with specific properties (Dournel et al., 1988; Podkościelna et al., 2015). Usually, chemical modification is performed through the creation of new active sites or the functionalization of hydroxyl groups (Laurichesse and Avérous, 2014). The modifications are typically aimed at the derivatization of phenolic and aliphatic hydroxyl groups (OH phen and OH aliph) situated at the C- α and C- γ positions of the propane side chain in order to introduce more reactive functional groups into lignin molecules. The ratio of OH phen to OH aliph varies depending on the origin of the lignin (hardwood or softwood) and on the pulping process (e.g., kraft, alkali or organosolv pulping), and, thus, a detailed knowledge of the chemical structure of lignin is important. For that, NMR techniques like ³¹P and ¹³C are appropriate. The following types of chemical modification reactions involving hydroxyl groups of lignin have been proposed: etherification, esterification, reaction with isocyanates, silylation, phenolation, and oxidation/reduction (Laurichesse and Avérous, 2014). For the esterification reactions, three types of reagents can be used: acidic compounds, acid anhydrides and acid chlorides, with the latter two being more reactive. Considering the reaction parameters and reactant used, the esterification is the easiest type of lignin modification to perform. The chemical compounds used for esterification are often bi-functional, which results in lignin-based polyester networks. Another goal of lignin modification is the introduction of reactive groups into its macromolecular structure so as to enable it to crosslink with other polymeric systems—the phenomenon known as chemical activation (Naveau, 1975). This study focused on the comparative characterization of lignin samples from spruce (softwood) and eucalyptus (hardwood) woods extracted by two different methods, i.e., kraft and organosolv processes. Thorough structural and thermal characterization of four extracted lignin samples using FTIR, ³¹P NMR, ¹³C NMR, SEC, DSC and TGA methods, as well as proximate analysis, was performed, and the results thereof were used to discuss the potential use of the lignin samples in different applications, such as bioenergy and biomaterials. Methacrylic derivatives of technical lignins were obtained from the reaction with methacryloyl chloride and characterized by FTIR and ¹³C NMR. The results of the modification were discussed in relation to the structural differences of the lignin samples.

2. Materials and methods

2.1. Lignin isolation

Spruce (softwood) and eucalyptus (hardwood) were selected as raw materials for lignin extraction. Two different extractive methods were used to isolate lignin for each raw material, i.e., organosolv and kraft processes. For the organosolv extraction of spruce, a mixture of ethanol–water (50/50 w/w), with sulfuric acid (H₂SO₄) as a catalyst (1.2% w/w), was used (Pan et al., 2005). The treatment was carried out at 180 °C for 60 min in a 4 L pressure (20 Ba) stainless steel batch reactor with constant stirring (EL0723 Iberfluid) and with an electronic control unit for pressure and temperature

control. The solid to liquid ratio was 1:7 (w/w). Dissolved spruce organosolv (OS) lignin was isolated by precipitation with four volumes of cold water. The lignin was recovered by filtration and then dried at 50 °C. For organosolv extraction of eucalyptus wood, conditions reported by Dos Santos et al. (2014) were used. A mixture of ethanol water (60/40 w/w) was used without a catalyst. The treatment was carried out at 180 °C for 90 min in the same reactor. The solid to liquid ratio was 1:10 (w/w). Dissolved eucalyptus organosolv lignin (OE) was isolated by precipitation with water acidified by H₂SO₄ at a pH of around 2. The lignin was recovered by filtration and then dried at 50 °C. Eucalyptus kraft lignin (KE) was kindly provided by the Pulp and Paper Laboratory, Department of Forestry Engineering, Federal University of Viçosa, Brazil, and was used without any additional pretreatments. Softwood kraft lignin (KS) was Lignoboost lignin, Innventia AB, Stockholm, Sweden (Tomani, 2010).

2.2. Chemical composition of lignins

Acid-insoluble lignin (Klason lignin) was determined. Soluble lignin was determined with UV (band 205 nm). TGA was used to determine the ash content following the methodology described by Moriana et al. (2014). Carbohydrate contamination was measured by analyzing the hydrolyzate using High Performance Liquid Chromatography [Jasco LC Net II/ADC with a ROA Organic Acid (00H-0138-K0) column (Phenomenex) equipped with a refractive index detector (RI-2031Plus) and a photodiode array detector (MD-2018Plus)]. 0.005 M H₂SO₄ prepared with 100% deionized and degassed water was used as a mobile phase (0.35 ml/min flow, 40 °C, and injection volume 40 µl). High purity standards of D-(+)-glucose, D-(–)-xylose and D-(–)-arabinose (provided by Fluka, with 99% of purity) were used for calibration. Elemental analysis (C, H, N and S) was performed using 1–3 mg samples dried in a vacuum oven at 40 °C for 48 h, using a Flash EA 1112, Thermo Finnigan, USA elemental analyzer (external service provided by the Elemental Analysis Unit of the Santiago de Compostela University, USC, Santiago de Compostela, Spain).

2.3. Gel-permeation chromatography (GPC)

Molecular weight properties, such as the weight-average molecular weight (M_w), the number-average molecular weight (M_n) and the polydispersity index (PDI), of the lignin samples were determined by the GPC method according to Guerra et al. (2006). Samples were acetobrominated prior to analysis: a 5 mg sample was stirred for 2 h at room temperature in 1 ml of 9/1 (v/v) mixture of glacial acetic acid and neat acetyl bromide before surplus reagents were removed rapidly *in vacuo*. The residue was dissolved in 1 ml of HPLC grade tetrahydrofuran (THF), and the resulting solution filtered through a 5 µm syringe filter. GPC analysis was performed using a Waters instrument system (Waters Sverige AB, Sollentuna, Sweden) consisting of a 515HPLC-pump, 2707 autosampler and 2998 photodiode array detector (operated at 254 and 280 nm). HPLC-grade tetrahydrofuran, filtered through a 2 µm PTFE membrane filter and degassed, was used as a mobile phase using a flow of 0.3 ml/min. Separation was achieved on Waters Ultrastaygel HR4, HR2 and HR0.5 4.6 × 300 mm solvent efficient columns connected in series and operated at 35 °C. For analysis, a sample volume of 20 µl was injected using the partial loop needle overfill injection technique. Data was collected at both 254 and 280 nm to ensure minimal peak drift. Calibration was performed at 254 nm using polystyrene standards with nominal molecular weights ranging from 480 to 176 000 Da. Quantification was performed using the Waters Empower® 3 build 3471 software suite.

2.4. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was carried out on a PerkinElmer Spectrum 2000 FTIR with attenuated total reflectance (ATR) crystal accessory (Golden Gate). Spectra were obtained by taking the mean of 16 scans at 4 cm^{–1} resolution in the 4000–600 cm^{–1} interval. All spectra were smoothed and fitted to an automatic base line correction using OMNIC 7.0 software.

2.5. Phosphorus-31 nuclear magnetic resonance spectroscopy (³¹P NMR)

³¹P NMR analysis with 90° pulse angle, an inverse gated proton decoupling and a delay time of 10 seconds was used for the identification and quantification of hydroxyl and carboxyl groups. Prior to analysis, a 20 mg sample of the respective lignin fraction was functionalized using 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane in a 1/1.6 mixture (v/v) of CDCl₃ and pyridine for 2 h at room temperature (Granata and Argyropoulos, 1995).

2.6. Carbon-13 nuclear magnetic resonance spectroscopy (¹³C NMR)

For ¹³C NMR analysis, 100 mg lignin was acetylated in 1 ml of anhydrous pyridine and 1 ml of acetic anhydride. After that, solution was poured into 20 ml of ethanol and the solvent was removed under reduced pressure (performed 3×). The same procedure was performed with toluene and chloroform until pyridine was completely gone. For the quantitative ¹³C NMR, the concentration of lignin was 20% in DMSO-_d₆ as solvent. A 90° pulse width, 1.4 s acquisition time and 1.7 s relaxation delay were used. Chromium (III) acetylacetonate (0.01 M) was added to the lignin solution to provide a complete relaxation of all nuclei. A total of 200,000 scans were collected.

2.7. Analytical pyrolysis

Py-GC/MS, was performed on lignin samples using a Frontier Lab (Japan) Micro Double-shot Pyrolyser Py-2020iD, with pyrolysis temperature of 500 °C and a heating rate of 600 °C/s. It was directly coupled with the Shimadzu GC/MS-QP 2010 apparatus (Japan) with capillary column RTX-1701 (Restec, USA), 60 m × 0.25 mm × 0.25 µm film, with injection temperature of 250 °C with EI of 70 eV, and MS scan range m/z 15–350 with gas helium at the flow rate of 1 ml/min and split ratio of 1:30. The sample size loaded was between 1.0–2.0 mg. The oven temperature program was 1 min isothermal at 60 °C, then heated 6 °C/min to 270 °C, and finally held at 270 °C for 10 min. The identification of the relevant peaks was performed on the basis of GC/MS chromatogram using Library MS NIST 147.LI13. The relative area of the peaks was calculated using the Shimadzu software and for some corrected or integrated manually where it was needed on the basis of the GC/MS data. The relevant peaks were averaged between the double samples.

2.8. Differential scanning calorimetric analysis (DSC)

The thermal behavior of the lignin samples was studied by differential scanning calorimetry (DSC) through a METTLER TOLEDO DSC 822e previously calibrated with indium standard. Samples of about 5–10 mg were sealed in standard aluminium pans previously pierced and tested under nitrogen atmosphere at a heating rate of 3 °C/min. The samples were first heated to 120 °C to eliminate interferences due to moisture and thermal history. Then the samples were cooled to 25 °C and reheated to 450 °C to determine their

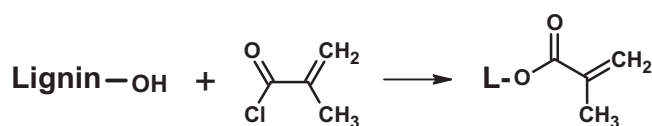


Fig. 1. Reaction schemes of the introduction of vinyl groups in lignin.

glass transition. Glass transition temperature (T_g) was recorded at the midpoint temperature of the heat capacity transition of the second heating run. The results for each sample were reported as the average of the two runs.

2.9. Thermogravimetric analysis (TGA)

Thermogravimetric analyses were carried out with TGA/SDTA 851 METTLER TOLEDO. In order to determine the thermal degradation behavior of lignins, 5–10 mg was tested under nitrogen atmosphere (50 ml/min) at a heating rate of 10 °C/min from 25 °C to 800 °C. On the other hand, both nitrogen and oxygen atmospheres were used to perform a proximate analysis of each lignin. This thermogravimetric method consisted of a heating ramp of 50 °C/min from 25 °C to 120 °C (3 min), followed by a new 100 °C/min heating ramp programmed to 950 °C. Finally, the samples were cooled to 450 °C and reheated to 800 °C under oxygen atmosphere (Moriana et al., 2014). The proximate analysis data (ash, volatile, organic matter and fixed carbon) were obtained through the direct measurement of weight changes in each experimental curve. The high heating value (MJ/Kg) was calculated according to equations found in literature (García et al., 2014; Cordero et al., 2011).

2.10. Modification of lignins with methacryloyl chloride

500 mg of dried lignin was dissolved in 10 ml of dioxane, and 0.75 ml of triethylamine was added. After 10 min at 14 °C, 0.85 ml of methacryloyl chloride in 1 ml dioxane was added dropwise over a 10 min period. The mixture was stirred for 50 min. 0.5% of hydroquinone was added as a polymerization inhibitor to avoid the polymerization of the vinyl groups. Then the solution was poured into 100 ml of cold water. The precipitate was recovered by centrifugation and washed with excess distilled water. The samples were then dried overnight in an oven vacuum at 40 °C. The recovered yields of lignin methacrylates were 118%, 131% and 165% for OE-MMA, OS-MMA and KS-MMA, respectively. However, the recovered amount of KE-MMA was lower than the starting amount of lignin. This difference was probably due to the high ash content, which was removed during the precipitation and washing steps. Structural characterization of methacrylic derivatives of lignin was performed using FTIR and ^{13}C NMR methods. Fig. 1. shows scheme of modification reaction of lignin polymer.

3. Results and discussion

3.1. Chemical composition and molecular weight

Results of the chemical composition analysis, together with molecular weight properties, are shown in Table 1. Carbon, hydrogen and oxygen are the main components of lignin. Both kraft lignins (KE and KS) presented the highest nitrogen and sulfur content, with values between 0.10–0.11% and 0.78–1.45%, respectively. Some amounts of nitrogen and sulfur in the lignin samples were also detected using the analytical pyrolysis method, Py-GC/MS (Tables 1 and 2 in SD), but only in the kraft lignin samples. In the literature, values for sulfur content of around 1–2% are usually reported for kraft lignins. These lignins can generate harmful emissions during thermal conversion. As observed by elemental

Table 1

Chemical composition and M_w , M_n , polydispersity index of isolated lignins.

	^a OE	^a KE	^a OS	^a KS
Klason Lignin (%)	83.7	58.6	94.3	88.5
Acid soluble lignin (%)	1.6	6.3	3.1	2.3
Ash (%)	3.6	22.4	3.2	2.5
Total Sugars (%)	2.9	2.2	0.5	1.0
C (%)	61.4	49.8	68.8	63.7
H (%)	6.0	5.0	6.3	6.1
N (%)	0.13	0.11	0.08	0.10
S (%)	0.06	0.78	0.20	1.45
M_n	1567	1059	1065	1540
M_w	5079	2653	3081	7195
PDI	3.24	2.51	2.89	4.67

^a OE: Organosolv Eucalyptus lignin, KE: Kraft Eucalyptus lignin, OS: Organosolv Spruce lignin, KS: Kraft Spruce lignin.

analysis, OS lignin also had a high sulfur content (0.19%). Py-GC/MS analysis, however, did not detect any S-containing compounds in the organosolv lignins. It is likely that some trace amount of acid used during the isolation of the lignin samples affected the results of the elemental analysis. As it has the highest carbon content (68.8%), OS seems to be the most suitable of all the investigated lignins for use as a biofuel. With respect to purity levels, the best result was obtained for OS, which showed a high value of Klason lignin (>90%). KS and OE also showed considerably high purity levels (>80%). The impurities in lignins are usually composed of residual carbohydrates and ashes. Based on the acid hydrolysis, all extracted lignins contained a small amount of sugars (0.5–3%) and ashes (2.5–3.6%). However, KE presented very low purity levels with a high amount of ash content (>20%). Data from the Py-GC/MS method, on the other hand, provided slightly higher numbers for carbohydrate-derived compounds in the lignin samples. For both kraft lignins, values were similar and corresponded to approximately 3% of all structures that were identified in the pyrolytic chromatogram. For organosolv lignin samples, the quantity of carbohydrate-derived compounds was higher, with OS lignin showing a three times higher content of carbohydrate-related structures than kraft lignins (Tables 1 and 2 in SD).

The lignin molecular weight average can be quite different depending on the feedstock and extraction process used (Manjarrez Narváez, 2011). The GPC curves of the investigated samples are shown in Fig. 2. As a result of different isolation conditions for each sample, no correlation could be made between the origin, isolation process and molecular weight characteristics of lignin. Typically, for organosolv lignins, lower molecular weights are reported with M_w values of around 2000 Da for hardwood lignins and around 3000 Da for softwood lignins (Pan et al., 2005; Sevastyanova et al., 2010; Vishtal and Kraslawski, 2011). In this study, however, OE presented a higher molecular weight than OS. Also, the molecular weights of both organosolv lignins were higher than those for the

Table 2

Contents of functional groups (mmol/g) determined by ^{31}P NMR.

Functional groups (mmol/g)	OE	KE	OS	KS
Aliphatic OH	1.58	1.24	0.75	1.75
Phenolic OH	2.12	2.73	2.99	4.04
S ^a OH	0.69	1.16	ND	ND
G ^a OH	0.80	0.76	1.79	2.56
Condensed G ^b	0.63	0.78	1.20	1.48
β-5	0.49	0.46	0.38	0.66
5-5'	0.36	0.34	0.59	0.91
4-O-5	0.66	1.13	0.35	0.47
Total OH	3.70	3.94	3.74	5.79
COOH	0.11	0.88	0.23	0.40

^a G: guaiacyl, S: syringyl.

^b Area between 144 and 140.5 ppm minus area of Syringyl phenolic (Berlin and Balakshin, 2014).

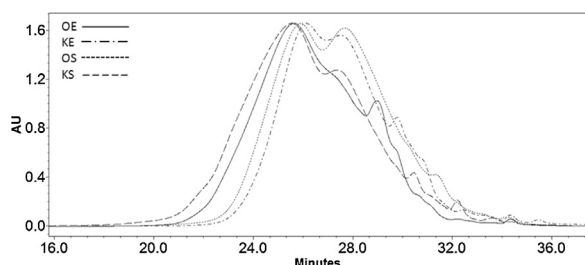


Fig. 2. GPC (molecular weight distribution) curves for lignin samples. GPC measurements were performed using acetobrominated samples.

kraft eucalyptus lignins. The molecular weight of lignin depends on the type of specie and, to an even larger extent, on the isolation process and the specific process conditions. The origin of the lignin samples investigated in the current study, as well as the isolation procedures, were different, which resulted in significant variations in the molecular weights. The highest average molecular weight value was observed in KS lignin, while KE had the lowest M_w . GPC curves show that KE and OS lignins both had lower molecular weights and lower polydispersity, but also a different elution profile of bimodal character with two distinct peaks. GPC curves for KS and OE lignin samples, on the other hand, had a major peak at higher molecular weight and a number of minor peaks at lower molecular weight. Such inhomogeneous composition resulted in higher polydispersity for KS and OE lignin samples. In general, all of the studied lignins presented high polydispersity, similar to results previously obtained by Baumberger et al. (2007).

3.2. Structural analysis

FTIR spectra of original extracted lignin are shown in Fig. 3. All lignin samples showed a wide absorption band at 3400 cm^{-1} , which indicated the presence of O–H stretching vibrations in aromatic and aliphatic O–H groups (Faix, 1991). Bands around 2930 and 2840 cm^{-1} can be assigned to C–H stretching in $-\text{CH}_2-$ and $-\text{CH}_3$ groups (Cachet et al., 2014). All lignin samples presented a peak at 1740 cm^{-1} , corresponding to stretching of carbonyl groups ($\text{C}=\text{O}$) in an ester or carboxylic acid group (Manjarrez Nevárez et al., 2011), with the intensities highest for the kraft lignin samples (KS and KE). On the other hand, the small band at 1710 cm^{-1} indicated the presence of non-conjugated carboxylic acids in the lignins (Cachet et al., 2014). A certain number of carboxylic groups

were also quantified using the ^{31}P NMR method (Table 2), with the highest quantities being observed for the kraft lignins (KS and KE). Signals between 1400 and 1700 cm^{-1} were attributed to the aromatic skeletal vibrations. The peaks at 1595 and 1510 cm^{-1} were due to $\text{C}=\text{C}$ of aromatic skeletal vibrations. The bands found at 1460 and 1420 cm^{-1} were attributed to the C–H deformation in $-\text{CH}_2-$ and $-\text{CH}_3$ groups and C–H aromatic ring vibrations, respectively. The band at 1365 cm^{-1} corresponded to aliphatic C–H stretching in $-\text{CH}_3$ groups. The band at 1325 cm^{-1} can be attributed to the presence of syringyl units (C–O stretch), but it could only be found in eucalyptus lignins. However, the peak at 1265 cm^{-1} assigned to guaiacyl (C–O stretch) ring appeared in all samples, although it had greater intensity in spruce lignin samples. Some characteristic bands associated with syringyl and guaiacyl units in lignin were detected at 1220 , 1110 and 1030 cm^{-1} , corresponding to C–C, C–O and C=O stretching (G), aromatic C–H in-plane deformation (S) and aromatic C–H in-plane deformation ($\text{G} > \text{S}$) (García et al., 2012; Sun et al., 2012; Mansouri and Salvado, 2006). In addition, it could be observed that the band at 1110 cm^{-1} was very intense in eucalyptus lignins, but practically negligible in spruce lignins. However, the band at 1025 cm^{-1} that corresponds to G units was similar in all lignin samples. Meanwhile, the signal of aromatic C–H out-of-plane deformation in G and S units appeared at around 840 – 820 cm^{-1} .

The functional groups of the lignin, such as hydroxyl and carboxylic groups, can easily be quantified by ^{31}P NMR (Granata and Argyropoulos, 1995), thereby providing the total content of potential active sites in the lignin polymer structures. For the elaboration of new materials, knowledge of the chemical structure of lignin is very important. Identifying the different functional groups in lignin, such as aliphatic and phenolic hydroxyl groups, is essential for the chemical modification of lignin. For studied lignin samples, aliphatic and total phenolic hydroxyl group signals appeared at 149 – 146 ppm and 144 – 137.5 ppm , respectively (Table 2). The peaks at 139.5 and 142.5 were assigned to guaiacyl and syringyl units, respectively. Condensed guaiacyl OH groups were found at 144 – 141 ppm and, at 135 ppm , the signal was assigned to carboxyl groups (Joffres et al., 2014; Hult et al., 2013). C_5 substituted condensed phenolic OH (β -5, 5-5', 4-O-5 linkages) were integrated into the region between 144.7 – 142.8 , 141.7 – 140.2 and 142.8 – 141.7 , respectively (Farag et al., 2014). In both eucalyptus lignins (OE and KE), spectra appeared at 142.5 ppm , which corresponded to syringyl units that were not visible in spruce lignins. It has been shown previously that lignin isolated from industrial liquors have large amounts of condensed structures that formed in the final stage of the pulping process (Chung and Washburn, 2012; Laurichesse and Avérous, 2014; Doherty et al., 2011; Doherty and Mousavioun, 2011; Berlin and Balakshin, 2014). The presence of condensed structures in the studied samples is also shown in Table 2. The quantity of condensed structures was higher in spruce lignins, with more condensed structures observed for kraft than for organosolv lignins. Regarding the analyzed linkages related to condensed structures, a higher content of β -5 and 5-5' in both softwood lignins was detected. While β -5 linkages can be present in native lignins, the formation of 5-5' linkages takes place during the pulping stage, especially for softwood lignins that consist mostly of guaiacyl-type units with a vacant C_5 position in the aromatic ring. These results correspond to the general percentages of linkages present in different types of wood, as reported by other authors (Sjöström, 1993). In softwood lignins, it is usual to find a higher content of β -5 and 5-5', which contributes to the higher degree of condensation in the lignin molecule (Holtman et al., 2006). The content of phenolic OH-groups was also higher for kraft lignins than for organosolv lignins. The kraft process generates lignins with a high content of phenolic hydroxyl groups due to the cleavage of α -aryl and β -aryl ether linkages of lignin (Chung and Washburn,

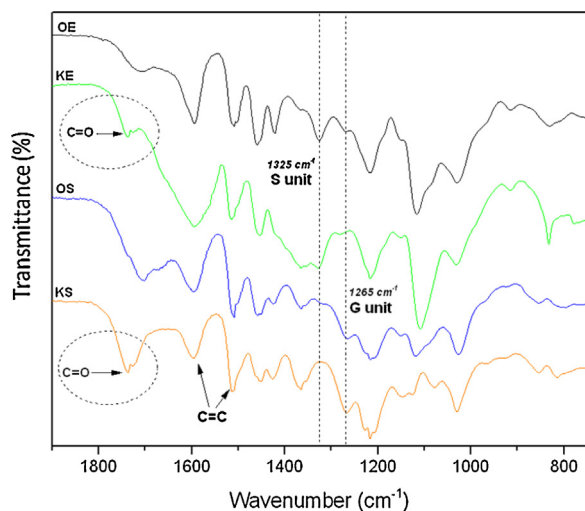


Fig. 3. FTIR spectra of isolated lignins.

Table 3
¹³C NMR of the acetylated lignin samples.

Assignment	(ppm)	Functional group per C9			
		OE	KE	OS	KS
Aromatic C-O	160–140	1.84	2.04	1.74	1.62
Aromatic C-C	140–123	2.16	2.12	2.41	2.79
Aromatic C-H	123–100	2.00	1.84	1.88	1.60
Aliphatic C-O	90–58	2.14	1.24	1.31	0.32
Methoxyl OCH ₃	57–54	1.19	1.14	0.70	0.85
CH ₃ acetyl	20	1.25	0.84	0.93	1.31
Primary OAc γ	170	0.33	0.23	0.15	0.3
Secondary OAc α	169.4	0.33	0.18	0.02	0.7
Phenolic OAc	168.1	0.46	0.50	0.63	0.77
S/G ^{a,c}		1.5	1.6	nd	nd
Degree of condensation ^b	123–100	1.00	1.16	1.12	1.40

^a Based on the assumption that softwood lignin is made up of only G units and hardwood – of S and G units.

^b Calculated from 3.00–I_{123–106} (Holtman et al., 2006).

^c S (104 ppm) and G (111 ppm).

2012). Spruce lignin had a higher content of phenolic OH groups than the eucalyptus lignin samples, with an especially high value for KS lignin (Chung and Washburn, 2012; Berlin and Balakshin, 2014). The total number of OH-groups, as a result, was also higher for KS lignin, with a value of 5.79 mmol/g. The lower content of phenolic OH in eucalyptus could be associated with those units present in hardwoods that are preferentially linked through phenolic hydroxyls to form ether bonds such as β-O-4 and 4-O-5 (Schoor et al., 2014). The ³¹P NMR analysis showed that eucalyptus lignins have a higher content of 4-O-5 bonds, especially KE lignin (see Table 2). As found by other authors and demonstrated in our work also organosolv pulping generated lignins with low amounts of carboxylic groups (Monteil-Rivera et al., 2013).

Quantitative ¹³C NMR is another analytical method that can provide useful information on the structure of lignin. ¹³C NMR analysis of acetylated lignin samples were carried out in order to determine, for each lignin sample, the distribution of functional groups per one C₉ unit. The assignment of signals was based on information found in literature regarding other acetylated lignin samples (Holtman et al., 2006; Wen et al., 2013; Fernandez-Costas et al., 2014; Capanema et al., 2004; Weon Choi and Faix, 2011). All integrations were performed assuming the integration of the aromatic region (160–100 ppm) as 6 carbon atoms. The obtained results are set out in Table 3. The content of phenolic and aliphatic hydroxyls groups determined after acetylation of the lignin samples showed the same trend as that evidenced by ³¹P NMR. Each eucalyptus lignin had a different proportion of guaiacyl and syringyl units, while no syringyl units were detected in spruce lignins. The S/G ratios for both eucalyptus lignins were quite similar, 1.5 for OE and 1.6 for KE. These numbers are slightly lower than those typically reported for various eucalyptus lignins, with values which are in the range of 1.8–2.7 (Balakshin et al., 2015). As shown in Table 2 in SD, the data from Py-GC/MS also indicates similar numbers (2.03 and 2.09 for OE and KE, respectively), although higher than those provided by ¹³C NMR for organosolv and kraft eucalyptus lignins. It is important to know the G and S content in lignins, as these units play a vital role during the processing of lignins for use in the polymer industry (Crestini et al., 2011). Lignins with high guaiacyl content present a more condensable structure. However, for chemical modification, the lignin reactivity basically depends on the S/G ratio or the existence of uncondensed phenolic OH groups (Derkacheva, 2013). Low S/G ratio is more favorable for the chemical modifications. The reason for this is that the guaiacyl units are more reactive than syringyl units, as S units have the C₃ and C₅ substituted while G units have the C₅ position free.

The oxygenated aromatic C-O (140–160 ppm) and condensed aromatic regions C-C (123–140 ppm) have some degree of overlap,

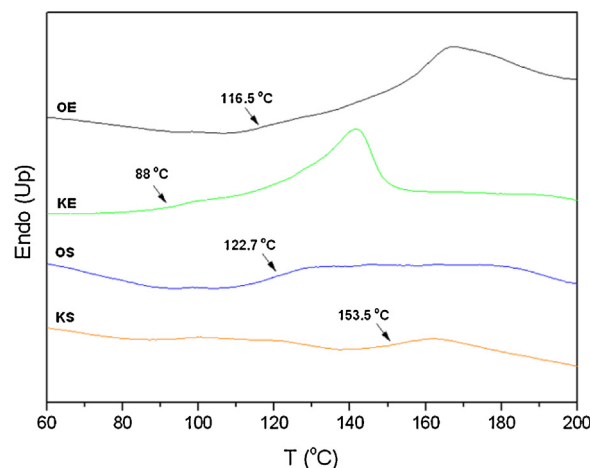


Fig. 4. DSC of different lignin samples.

which makes the calculation of the degree of condensation less precise (Holtman and Kadla, 2004). The protonated aromatic region, on the other hand, does not suffer from overlap and, as a result, the degree of condensation can easily be estimated. Three minus the value of integration for this region will yield an estimate of the degree of condensation based on the assumption that completely uncondensed lignin will have protons at the C₂, C₅ and C₆ positions (Holtman et al., 2006). So, the content of aromatic C-H in the lignins could be closely related to the degree of condensation (DC). Due to the conditions during the isolation process, kraft lignins showed a higher degree of condensation than organosolv lignins. Moreover, softwood lignins presented a higher DC than hardwood lignins due to their structural features as being based almost entirely on guaiacyl units.

In addition, OE and KE both had a higher content of methoxyl groups than softwood lignins due to the presence of syringyl units in their structures. Aromatic C-O content could be related to the ether bonds, so the lower content of aromatic C-O in softwood lignins may have been due to the lower content of ether bonds in their structures.

3.3. Thermal properties and proximate analysis

The DSC curves of all lignins are reported in Fig. 4. The glass transition temperature (*T_g*) is important to know when considering the use of lignins in polymer applications, but it is often difficult to determine. This difficulty is attributable to the heterogeneity of the lignin chemistry, as well as the broad molecular weight distributions caused by isolation procedures. Generally, *T_g* depends on the molecular weight of the polymer and, for non-derivatized lignins, have been found at temperatures between 90 and 180 °C (Crestini et al., 2011; Cachet et al., 2014; Sevastyanova et al., 2014). Moreover, the glass transition temperature of lignins is influenced by the degree of condensation (number of C-C linkages), as well as the content of both phenolic hydroxyl and methoxyl groups (syringyl content) (Cachet et al., 2014; Doherty et al., 2011; Cazacu et al., 2013). Eucalyptus lignins presented lower *T_g* than spruce lignins, despite, for example, the higher molecular weight for organosolv eucalyptus than for spruce lignin (see Table 1). In general, hardwood lignins usually present lower *T_g* than softwood lignins, regardless of the extraction process used (Doherty et al., 2011). This may be because softwoods usually have a more condensed structure and higher phenolic hydroxyls group content than hardwoods, which restricts the mobility of the molecule by strong intermolecular hydrogen bonding interactions (Chung et al., 2013). In the present study, as seen in Table 2, spruce lignins (OS and KS)

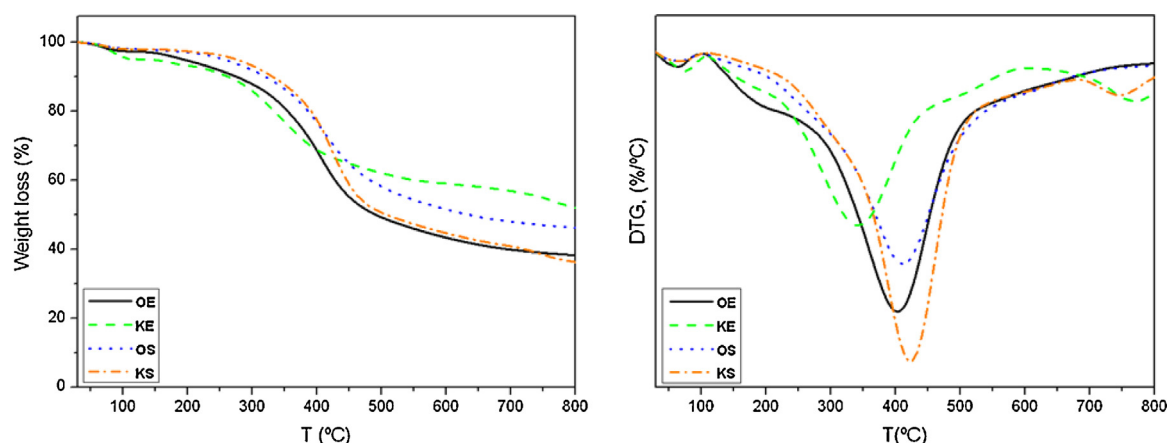


Fig. 5. TG and DTG curves of extracted lignins.

exhibited a higher content of condensed guaiacyl and phenolic OH groups than eucalyptus lignins (OE and KE). Also, as seen from the ^{13}C NMR results, the degree of condensation of spruce lignins is higher than that for eucalyptus lignins, which resulted in their high T_g . Within the same species, on the other hand, T_g values correlated with molecular weights: OE presented higher T_g than KE, and KS presented higher T_g than OS (see data for M_w in Table 1).

Thermal degradation in polymers is another important parameter to know for thermal processing and to establish service life conditions. The lignin molecule has great potential for use as biomaterial. It can be used as a macromonomer or simply as filler in other natural and synthetic polymers (Doherty et al., 2011). The thermal properties of lignin, therefore, are important when considering the impact of lignin addition to the polymeric system. In general, high molecular weight, high purity and high thermal stability are required properties in the polymer field. The thermogravimetric (TG) and first derivative (DTG) curves obtained for extracted lignins under nitrogen atmosphere are presented in Fig. 5. All lignin samples exhibited various distinct weight loss stages. The first small weight loss (2–5%) below 100 °C was assigned to the gradual evaporation of moisture. Some lignins exhibited other small degradation steps at around 150 °C, probably due to the presence of solvent or sulfate groups that occur during the extraction processes (Hu et al., 2013). The main weight loss stage in all lignins occurs in the temperature range between 300 and 600 °C (Hatakeyama and Hatakeyama, 2010), and is centered around 337–390 °C. The main stage is associated with the fragmentation of inter-units linkage (Bertini et al., 2012), such as cleavage of typical ether linkages among the aromatic units. After that, cracking of aliphatic side-chains and cleavage of functional groups occurs (Laurichesse and Avérous, 2014; Monteil-Rivera et al., 2013; Zhao et al., 2014). The thermal stability of the samples was assessed at the onset temperature (determined as 5% weight loss based on a dry basis) of the main stage, and these parameters, together with the weight loss and maximum degradation temperature, are summarized in Table 4. The isolated lignins from eucalyptus (OE and KE) presented lower thermal stability than spruce lignins (OS and KS). In general,

it is common that hardwood lignins present lower thermal stability than softwood lignins (Zhao et al., 2014). The thermal stability of lignins depends, on the one hand, on the structure (functional groups and linkages), and, on the other hand, on their molecular weight and, therefore, on the origin and the applied extraction processes that determine the chemical composition of each sample. The thermal stability of the samples showed a good correlation with the degree of condensation, with the highest values being those for the spruce lignins. As result, the KS exhibited the higher thermal resistivity. In addition, the spruce samples also showed higher T_{\max} than the eucalyptus samples when subjected to the same extractive process. These results corresponded with those obtained by DSC and NMR techniques. Spruce lignins showed higher onset degradation temperatures and higher T_g than eucalyptus lignins, particularly KS, which also presented the highest content of OH groups and highest DC. However, considering the influence of the isolation process on the same species, the T_{\max} did not show the same trend as the thermal stability, and higher values were exhibited for the OE than for the KE, as was evidenced in the M_w and T_g . This indicates a lower thermal decomposition rate, and the broader thermal decomposition region may be due not only to the higher M_w but also to the presence of more sugars and higher PDI.

Proximate analysis was used to obtain information about moisture, ash content, volatile matter and fixed carbon in the samples. The TGA is an appropriate technique for carrying out this assay (Moriani et al., 2014). The results of proximate analysis and HHV (MJ/Kg) are shown in Table 5 and have been calculated for dry lignin. The moisture content in all samples was 2–5%, which is similar to results for other lignins, but less than found in the literature for woods, annual plants and agricultural residues (García et al., 2014; Poddar et al., 2014; Shen et al., 2010; Moriani et al., 2014). Thermal conversion processes require low moisture levels because moisture greatly affects fuel combustion behavior, plant design and transport costs (Shen et al., 2010). The ash content also has a significant influence on the thermal conversion of lignin. This inorganic waste can affect transportation and processing costs, and may generate harmful emissions and slag deposits that create greater thermal resistance to heat transfer and lead to corrosion (García et al., 2014; Poddar et al., 2014). In general, all lignins presented a normal value for ash content of 2–4%, when compared to other lignins and some species of wood and plants (Shen et al., 2010; Womn Kim, 2015; Gillespie et al., 2013), but KE showed an ash content that was too high (23%) due to the high content of salts formed during the extraction and precipitation processes. In the present study, OE and KS presented normal values for volatiles of around 63% and for fixed carbon of 33%, while OS lignin showed lower values for volatile matter and a high fixed carbon content. KE displayed very low val-

Table 4
Thermogravimetric parameters of different lignin samples.

Samples	[25–100] °C		[200–600] °C		Residue at 800 °C	
	wt (%)	T_{\max} (°C)	$T_{5\%db}$ (°C)	wt (%)	T_{\max} (°C)	Weight (%)
OE	3.6	53.4	208.8	49.2	366.4	38.8
KE	6.5	61.6	239.5	33.5	338.9	46.9
OS	2.2	49.7	243.2	43.8	382.2	46.9
KS	2.7	55.3	262.0	52.8	390.7	38.8

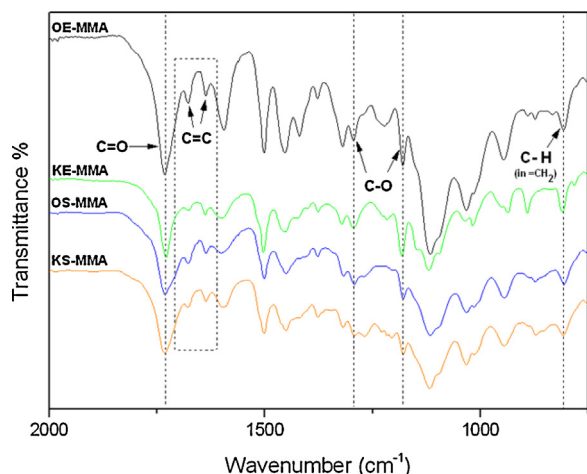


Fig. 6. FTIR spectra of modified lignins with methacryloyl chloride.

ues for volatiles and for carbon content, due to the high content of impurities in the studied lignin sample (Farag and Chaouki, 2015; Jin et al., 2013). The heating values obtained varied between 18 and 24 MJ/Kg and were similar to those calculated by other authors (Jin et al., 2013). These values are, in general, higher than those for the lignocellulosic biomass, which confirms lignin's potential as an energy source (García et al., 2014; Jin et al., 2013; Saldarriaga et al., 2015). It also indicates that volatiles and carbon content may have an important influence on the HHV. Lignins with higher volatiles and fixed carbon content are the most appropriate for pyrolysis and combustion processes due to their high HHV. On the other hand, KE lignin presented the lowest HHV due to its low content of fixed carbon and volatiles and high ash content. For this reason, KE lignin is not suitable for these applications. In addition, this lignin could cause serious problems in boilers, as well as harmful emissions. Additional purification steps are necessary. Regarding the other lignins, although both sulfur and ash contents are above those recommended by European standards for pellets elaboration (ISO 17225-2, 2014), they are not so high when compared with the other studied raw materials (Shen et al., 2010).

3.4. Preparation of methacrylic derivatives of lignin

FTIR spectroscopy confirmed the successful esterification reaction of the lignin samples with methacryloyl chloride (Fig. 6). After chemical modification, new strong signals at 1175 cm^{-1} and 1740 cm^{-1} , attributed to the C=O stretching vibrations in the ester or carboxyl acid groups, were observed. The intensity of the other lignin-related signals in the $1000\text{--}1300\text{ cm}^{-1}$ and $1400\text{--}1700\text{ cm}^{-1}$ regions, however, were significantly reduced. The new signal at $1680\text{--}1640\text{ cm}^{-1}$, corresponding to C=C bonds, indicated the presence of methacrylate units in all of the lignin samples (Naveau, 1975). Ester C-O-C stretching vibrations in acrylates resulted in doublets at 1180 and 1290 cm^{-1} . An increased intensity of the signal at 940 cm^{-1} , attributed to out-of-plane deformation vibrations

of C-H, also indicated the presence of $=\text{CH}_2$ groups in the modified lignin molecule.

Carbon NMR spectra were analyzed to provide additional support for the conclusion that the formation of lignin ester resulted from the modification of the lignin samples. From the ^{13}C NMR spectra of the modified lignins in Fig. 7, we can observe the signals from the $-\text{CH}_3$ group at 18 ppm, the C=O signal at 166 ppm and the double bond signals at 128 and 135 ppm (Lawrence, 1985). All of these signals indicated a successful derivatization of the lignin structures with the methacryloyl chloride reagent in accordance with NMR signal simulation (see Fig. 1 in SD). If one assumes that the reaction of methacryloyl chloride went different, due to the polymerization of the methacrylic groups and the resultant formation of poly-methacrylate homopolymer, different NMR signals should be expected (Fig. 1b in SD). In such a case, we would expect the CH_3 signal that appeared at 28 ppm and the C=O signal that appeared at 182 ppm. The double bond signals at 128 and 135 ppm, however, should not be present in the NMR spectra at all. Rather, we should find saturated CH_2 signals at 34 and 57 ppm, but these are not found in Fig. 7. Therefore, the NMR spectra strongly supported the successful derivatization of the lignin with methacryloyl chloride.

In order to understand the differences in the behaviour of various lignin samples during the esterification reaction, the ^{13}C NMR method was also applied to quantify the contents of the vinyl groups (C=C) in the modified lignins (Fig. 7). The content of C=C groups was estimated based on the quantification of the methyl groups, assuming that their contents were the same as those for the vinyl groups. Fig. 8 shows the contents of C=C groups per C9. The calculations for the content of $-\text{CH}_3$ groups in the lignin samples were performed based on the methoxy group's contents using the values obtained for the original lignins. By using this approach, however, any traces of the reagent (methacryloyl chloride) may have affected the calculations. The carbohydrate structures present in the lignin samples could also have reacted with the methacryloyl chloride, contributing to the $-\text{CH}_3$ signal in the NMR spectra. Both organosolv lignins (OE and OS) had quite similar contents of C=C groups, the number of which exceeded the total number of available Ph-OH group per one C9-unit, as shown by the ^{13}C NMR analysis of the original lignins (Table 3). This indicates that the methacryloyl chloride reacted with both phenolic and aliphatic OH-groups and that the obtained numbers represent an upper limit of saturation (as compared to the total number of aliphatic and phenolic functional groups, as shown in Table 3). For organosolv spruce (OS) lignin, the number of introduced vinyl groups (Fig. 8) seems to be higher than the number of possible active sites (see the total number for primary, secondary and phenolic OH groups in Table 3). OS lignin samples seem to contain a higher amount of residual methacryloyl chloride, as was indicated using the analytical pyrolysis method, Py-GC/MS (see Table 1 in SD). Based on the data from Py-GC/MS, both organosolv lignins, and especially OS, had a higher content of carbohydrate structures (Tables 1 and 2 in SD). This could have affected the ^{13}C NMR data and have contributed to the high number of introduced vinyl groups. Although both kraft lignins had quite high contents of hydroxyl groups, as shown by ^{31}P NMR, the contents of introduced vinyl groups as a result of the modifi-

Table 5
Proximate analysis (% dry basis).

Sample	Ash%	Volatiles%	Fixed carbon%	Organic matter%	HHV (MJ/Kg)	
					(Garcia et al., 2014)	(Cordero et al., 2011)
OE	3.6 ± 1.9	63.4 ± 1.7	32.9 ± 0.0	96.3 ± 1.9	22.7	22.5
KE	22.4 ± 0.3	49.1 ± 0.0	27.2 ± 0.0	76.3 ± 0.1	18.3	18.0
OS	3.2 ± 0.3	55.0 ± 0.2	41.7 ± 0.0	96.7 ± 0.3	24.0	24.2
KS	2.5 ± 0.0	63.9 ± 2.0	33.5 ± 2.5	97.4 ± 0.0	23.0	22.8

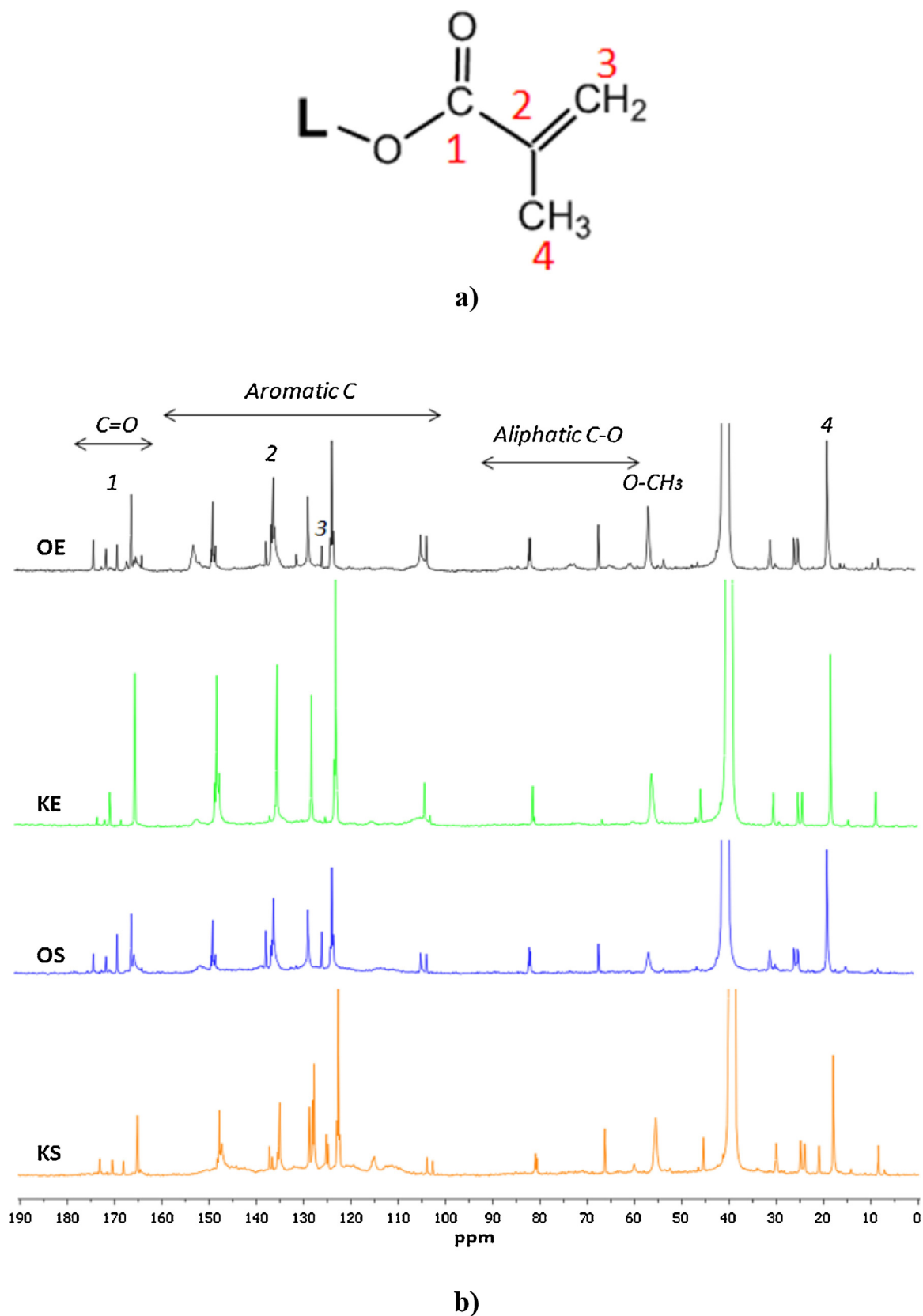


Fig. 7. Schematic representation of methacrylic derivative of lignin (a) and ^{13}C NMR spectra of modified lignins (b).

cation are lower than those for the organosolv lignins (0.51–0.72 groups per C9 unit as compared to 1.10–1.11, respectively), with the lowest number for spruce kraft lignin having the highest total OH-

groups content. Both kraft lignins, and especially softwood kraft lignin, on the other hand, had a very high degree of condensation, which suggests that the reaction of the methacryloyl chloride with

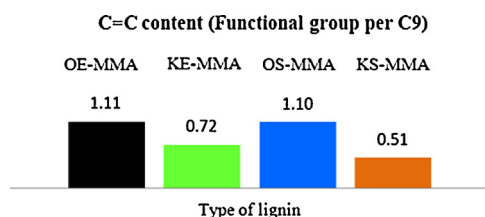


Fig. 8. C=C content per C9 in different modified lignins.

OH groups of lignin could be suppressed due to steric hindrance and strong hydrogen bonds (Evtugin and Gandini, 1996; Duval and Lawoko, 2014). In order to describe the mechanism of the reaction in greater detail, further studies are required, including those with lignin model compounds.

4. Conclusions

- Spruce lignins (OS and KS) had more condensed structures than eucalyptus lignins (OE and KE), as was shown by the NMR method. As a result, the thermal stability, determined as 5% of mass loss, was higher for spruce lignin.
- Higher molecular weight generally resulted in higher T_g values for lignin samples of the same origin.
- Lignin samples of high purity demonstrated appropriate HHV at 22–24 MJ/Kg, as determined by proximate analysis, irrespective of their origin and the isolation process. KE lignin, which had a high ash content, would require additional purification so as to increase its HHV prior to use in biofuel applications.
- The total content of OH groups was generally high for all lignins, making them suitable raw materials for chemical modification. The content of phenolic OH groups was higher for kraft lignins and especially higher for softwood lignins, both organosolv and kraft. Spruce kraft lignin had a 30% higher content of total OH groups as compared to the other samples.
- Methacrylic derivatives of various industrial lignins were successfully prepared through reaction of the lignins with methacryloyl chloride. The degree of methacrylation, estimated from the content of vinyl groups per C9 lignin unit, was significantly greater for organosolv lignins than for kraft lignins despite the higher OH-groups content in the latter. This was related to the elevated degree of condensation of kraft lignin that may have affected its reactivity during the esterification reaction.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.indcrop.2015.12.048>.

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