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HYDROXYMETHYLATION OF TECHNICAL LIGNINS FROM SOUTH-AMERICAN SOURCES WITH POTENTIAL USE IN PHENOLIC RESINS

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ABSTRACT

This work investigates the valorization of sodium lignosulfonate, kraft, and organosolv lignins from South America. A detailed characterization of the lignins and their chemical modification by hydroxymethylation, a reaction between lignin and formaldehyde, were performed. The characterization included measurements of moisture, ash, and carbohydrate contents, elemental and thermogravimetric analysis (TGA), and functional groups and molar mass distributions by Fourier transform infrared spectroscopy (FTIR) and size exclusion chromatography (SEC), respectively. Also, reactive aromatic hydrogens (—H_{Ar}) were quantified by the measurement of phenolic hydroxyl groups (P-

OH) content by UV-Vis spectroscopy. The different initial formaldehyde/lignin weight ratios (0.07, 1.47), temperatures (40 ºC, 50 ºC, 70 ºC) and pHs (9, 11); and the following of hydroxymethylation reactions by UV-Vis spectroscopy were investigated. All lignins resulted attractive for the use as replacement of phenol in phenolic resins but sodium lignosulfonate was the most appropriate due to its water solubility.

Keywords: TECHNICAL LIGNINS; CHARACTERIZATION; HYDROXYMETHYLATION; PHENOLIC RESINS.

INTRODUCTION

Nowadays, the use of biopolymers including polysaccharides such as cellulose, starch, chitin/chitosan, alginate as fillers, is attractive in the production of high-value-added and environmentally friendly composites and carbon materials. The incorporation of natural fibers (wood/non-wood) in polymer composite results in novel materials with a number of advantages such as lightweight, no/lower impact on the environment, reduced wear on processing equipment, low cost, biocompatibility, and biodegradability.[1] According to Xie et al.[2], cellulose nanocristals (CNCs) are attractive as reinforcing fillers but commercially available CNCs from cotton showed unimproved mechanical properties. On the other hand, the design and use of various functional biomaterials for drug loading and release in the development of electro-stimulated drug release devices have become in a promising trend using bacterial cellulose[3] or chitosan nanocapsules.[4] Green adsorbents based on cellulose or carbon nanocomposites are another promising area.[5-7] During the recent years, a noticeable growth in the demand of wearable bioelectronic devices, which can monitor motions, was registered. Various fields such as healthcare, robotic systems, prosthetics, visual realities, professional sports, and entertainments can be mentioned.[8-10]

Despite the abundant information about the use of natural fillers in polymers a limited research has been carried out on the preparation of lignin-based polymer composites.[1]

Lignins, cellulose, and hemicelluloses are renewable polymers and the main components of the cell wall of vascular plants. The structure of lignin is complex, amorphous, and is constituted by multi-phenolic rings.[11] Lignin isolation degrades its native structure producing technical lignins. Technical lignins are mainly obtained from wood sources by pulping industries that use sulfur-containing reagents. Kraft and sulfite processes generate most of the wood pulp for paper. Besides, promising sulfur-free processes such as bioethanol or the different organosolv processes, are currently being tested at laboratory or pilot scale.[12] Sulfur-free lignins are considered the most friendly and similar to native lignins.

The global annual production of chemical pulps worldwide is estimated at 150 million tons year[11],[12] from which 11% of pulp and 5% of paper are produced in South America.[13] Large investments in wood pulp capacity are expected to expand from 14 million tons to 36 million tons of pulp in South America in 2019.[14] The pulp industry in South America employs both hardwood and softwood as raw materials, but hardwoods such as eucalyptus are preferred in tropical and subtropical zones.[15] Chile and Brazil are the highest pulp producers. Also, Brazil is the first producer of sugarcane worldwide.[16]

The paper industry produces 50 million tons of technical lignins mainly from the kraft and sulfite processes. However, only about 2% (1.1 million tons) are commercially employed for low-value products such as binding or dispersing compounds, and the rest is used for the production of heat, steam, and power.[17,18] The preparation of novel materials from lignin/lignin-derived products can improve the economics of polymer composite materials as well as possibly address the problem of its waste disposal.[1] ~~The application of technical lignins in high-value-added products is limited due to their complex and non-uniform structure, their uncertain reactivity, and the presence of impurities.~~[9] The applications include the production of epoxy,[19, 20] polivinilalcohol,[21] polydimethylsiloxane,[22] polypropylene,[23] polyethylene,[24] controlled drug release,[25] ion removal,[26] hydrogels,[27] bitumen, refiner (carbon cracker), cement additives, biofuel, high-grade lignin, BTX (mixtures of benzene, toluene, and xylene), activated carbon, phenolic resins, carbon fibers, and vanillin.[28]

Lignin utilization as replacement of phenol in resol or novolac phenol-formaldehyde (PF) is an attractive alternative due to its high availability, abundance, less toxicity, and cost. Different composite materials based on resols PF adhesives using unmodified and chemically modified lignins have been obtained including strand boards, plywoods, and laminates. [29-38] It was reported that replacements greater than 50% of P by unmodified lignin produce a negative impact on the performance of wood composites.[33, 36, 37] However, a lignin obtained from corn stover by a dilute acid pretreatment and enzymatic hydrolysis (as byproduct of the cellulosic bioethanol production) was tested as total P replacement in plywood applications with a good mechanical performance.[31] Note that the lignin source and isolation method are not common.

P exhibits 3 reactive sites (aromatic hydrogens, —H_{Ar}) in the *ortho*- and *para*- positions, whereas the guaiacyl (G), the p-hydroxyphenyl (HH), and the syringyl (Sy) units of lignin have 1, 2, or no —H_{Ar}, respectively (Fig. 1). The HH units are practically negligible in wood lignins but are the principal component of non-wood lignins.[39]

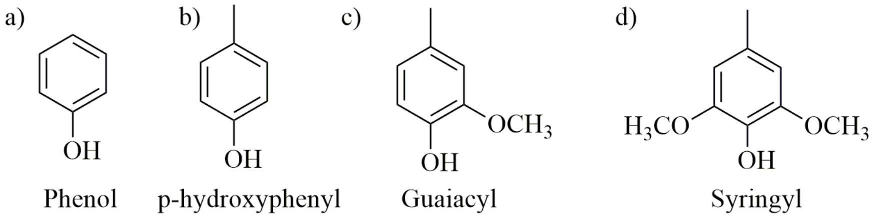


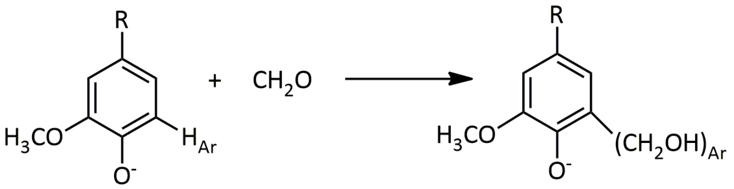
FIGURE 1 (a) Phenol (P); (b) Hydroxyphenyl (HH); (c) Guaiacyl (G); (d) Syringyl (Sy).

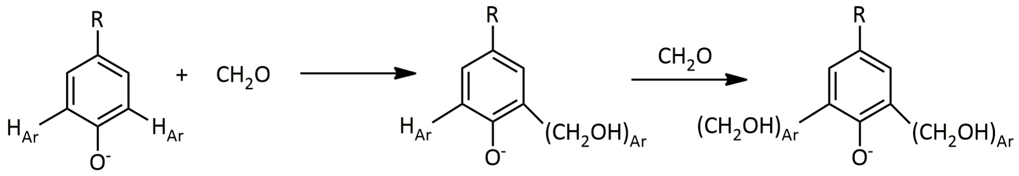
~~Several methods such as hydroxymethylation, phenolation, and demethylation, have been proposed and used to increase the reactivity of the technical lignins in phenolic resins synthesis.[31, 32] Phenolation is a chemical modification of lignin using phenol in acidic conditions. This chemical modification is the most often used in the synthesis of novolac PF resins and for lignosulfonate activation.[32] Hydroxymethylation consists in the reaction of lignin with formaldehyde (F) in alkaline conditions. Demethylation employs sulfured~~

~~reagents to increase the reactivity of lignin by forming catechol moieties in order to improve the quality of lignin-based PF adhesives. In order to produce resol PF resins, hydroxymethylation is the most used method.[33]~~

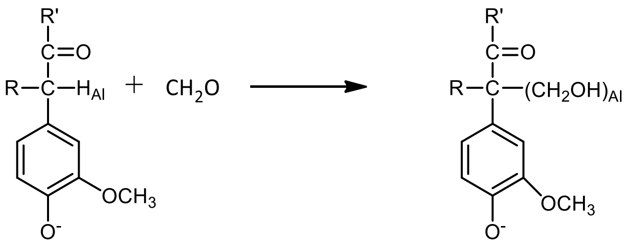
Several chemical methods such as demethylation, phenolation, and hydroxymethylation have been proposed and used in order to increase the reactivity of the technical lignins in phenolic resins synthesis.[40, 41] Demethylation is a direct method that increases the reactivity of lignin by forming catechol moieties. Also, an improvement of the quality of demethylated lignin-based PF adhesives was reported.[41] However, the method presents disadvantages related to the use of hazardous and expensive chemicals.[42] Phenolation employs P in acidic conditions and is the most often chemical modification used for lignosulfonate activation in the synthesis of novolac PF resins.[41] The mechanical performance of materials obtained by resins modified with phenolated lignins is better than that of materials obtained by using raw or hydroymethylated lignins.[42, 43] However, the subsequent hydroxymethylation of the phenolated lignin in the synthesis of the PF resin requires higher amounts of formaldehyde (F)[44] and the control of the reaction is difficult.[42] Hydroxymethylation of lignin consists in the reaction of lignin with F in alkaline condition, and offers the dual benefit of providing primary hydroxyl groups and electrophilic carbon atoms. Furthermore, hydroxymethylation is highly selective and produce easily maximum activation levels.[42, 45] Among its disadvantages, the content of methylol groups generated is relatively low and the effect of mechanical performance of materials obtained by hydroymethylated lignins is moderate. However, hydroxymethylation is the most used method in order to produce resol PF resins.[45]

Hydroxymethylation involves the Lederer Manasse reaction between F (CH_2O) and $—H_{Ar}$ of (G and HH) lignin units in alkaline conditions generating aromatic methylol groups $(—CH_2OH)_{Ar}$ as shown in Equations (1) and (2).


(1)


(2)

The mechanism of hydroxymethylation of lignin, similar to that of P, is very complex. Even though the hydroxymethylation reactions are irreversible, the ionic species are in equilibrium with their corresponding neutral species.[46, 47] Besides, F can be consumed through undesirable reactions that include generation of aliphatic methylol groups $(\text{—}CH_2OH)_{Al}$ from the aliphatic hydrogens in lignin $(\text{—}H_{Al})$ and the production of methanol and sodium formate by the Cannizzaro reaction at pH>10 as shown in Eq. 3 and Eq. 4, respectively.[48-50]


(3)

$$2CH_2O + NaOH \rightarrow CH_3OH + HCOONa \quad (4)$$

Note that only $(\text{—}CH_2OH)_{Ar}$ are able to generate methylene and ether bridges in cured phenolic materials (Eq. 1 and Eq. 2).

To follow the hydroxymethylation reaction enthalpy, hydroxyl, and total free formaldehyde (F_T) are determined by DSC, acetylation, and volumetric (hydroxylamine hydrochloride and sulfite) methods. [39, 45, 48, 50-54] Since F is consumed by the Lederer

Manasse reaction (Eq. 1 and Eq. 2) and also by undesirable reactions (Eqs. 3 and Eq. 4) a direct measurement of the reactive sites (—H_{Ar}) is needed to evaluate the lignin reactivity. In this context, the UV-Vis spectroscopy is a simple and fast technique to measure the phenolic structures.[53] Although UV-Vis spectroscopy is useful for the analysis of dry samples once hydroxymethylation reaction was completed,[55] and for the black liquor samples[54] no references about the use of UV-Vis spectroscopy to monitor hydroxymethylation along time were found.

Lignin reactivity towards F depends on the plant species, the isolation methods, and the reaction conditions (temperature, pH, and the F/lignin ratio). There are many reports on the hydroxymethylation of technical lignins obtained from different species and isolation methods, mostly involving alkali lignins form bamboo and wheat straw and sarkanda grass (non-wood fiber),[49, 55-58] kraft lignins from pine (softwood), [29, 48, 51, 52, 59] (ammonic, calcium, and sodium) lignosulfonates from spruce (softwood) and eucalyptus (hardwood), [39, 45] and several different organosolv lignins from *Picea abies* (softwood), eucalyptus and sugarcane bagasse (non-wood fiber), and pine.[30, 50, 60] Few works report the hydroxymethylation of hardwood lignins or the use of activated lignins from South America species as a potential replacement of P.[33, 35, 45, 50]

As far as the authors are aware, there is a lack of information about characterization and the hydroxymethylation of hardwood lignin and even more about South American species. This information is necessary to understand the relationship between the structure and properties of the composites materials. On the other hand, the study of different hydroxymethylation conditions is important to understand the reactivity of lignin towards F and a simple and fast technique is required to monitor hydroxymethylation reaction.

In this work, a comparative characterization and hydroxymethylation of three south-american technical hardwood and non-wood lignins were assessed as a possible valorization strategy for P replacement in resols. Gravimetric, spectroscopic, chromatographic and thermal techniques were employed for a detailed physicochemical characterization. Lignins were activated by hydroxymethylation using different initial F/lignin weight ratios at different pH and temperatures, taken into account the undesirable Cannizzaro reaction. Along the reactions, F_T was measured by a volumetric technique. Also, the UV-Vis spectroscopic method was evaluated to quantified —H_{Ar} without any sample pretreatment thorough the hydroxymethylation reactions.

EXPERIMENTAL WORK

Materials

Kraft lignin (KL) and sodium lignosulfonate (SL) from *Eucalyptus grandis* and *viminalis* mixtures were provided by Suzano (Brazil) and Vixilex (Brazil), respectively. Organosolv lignin (OL) from sugarcane bagasse was laboratory obtained using an ethanol-water catalyzed by sulfuric acid process as reported in a previous work.[61] The chemical reagents used in the characterization and hydroxymethylation of lignins were sodium hydroxide (Cicarelli), paraformaldehyde (Cicarelli), 0.1 and 1 N hydrochloric acid solution (Cicarelli), 0.1 N sodium sulfite, dioxane (Cicarelli), potassium bromide (Cicarelli), tetrahydrofuran (Cicarelli), sodium nitrate (Anedra), and 99%v/v sulfuric acid (Cicarelli). Buffer solutions at pH= 6 and pH=12 were prepared according to Zakis.[53]

The F solutions were obtained by depolymerization of paraformaldehyde. For this purpose, 30 g of paraformaldehyde were loaded in 250 mL of distilled water, and the depolymerization was carried out until completion, at 70 °C and pH= 10.0. The initial F concentrations were determined via the sulfite method and they all resulted 12 wt%.

Lignins Characterization

The moisture and ash contents were gravimetrically determined according to El Mansouri and Salvadó[62] and the carbohydrates content was determined by HPLC after hydrolysis of lignin samples.[62] For SL, the purity was calculated measured by UV-Vis spectroscopy as shown in Eq. 5:

$$\%Purity = \frac{A}{Abs} \times \frac{f}{Co} \qquad (5)$$

where Abs = 35 is the specific absorptivity of SL, f is the dilution factor (250) and Co is the initial concentration of lignosulfonate (g L^{-1}).

The composition of lignin was determined by elemental analysis, FTIR and UV-Vis spectroscopy.

An elemental CHNSO analyzer (SerieII, Perkin Elmer) was employed for the measurement of carbon (C), hydrogen (H), sulphur (S), and nitrogen (N) contents. Data were acquired using EA Data Manager 2400 software.

FTIR spectra of lignins were acquired on a Shimadzu Model 8201 Fourier transform spectrophotometer in the frequency region of 4000-400 cm^{-1}. KBr pellets were prepared with 2-3 wt% of dry sample. Spectra were analyzed by Hyper IR software. Bands were assigned according to Faix[63] and El Mansouri and Salvado.[63]

The P-OH content was determined by differential UV-Vis spectroscopy according to Reznikov-Goldschmid's method.[53] The presence of P-OH groups of four types is possible in lignins with structures I to IV as shown in Figure 2.[53, 62]

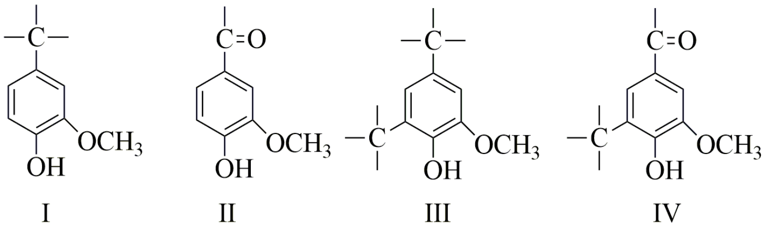


FIGURE 2. Phenolic structures (P-OH) determined by UV-Vis spectroscopy.[53]

The physicochemical characterization involved measurements of solubility, molecular weights and thermal behavior and stability.

The solubility of lignin was determined by dissolving 1 g of lignin in distilled water, tetrahydrofuran (THF) and 1N NaOH and 1N HCl solutions.

Molar mass distribution and averages were performed using a Waters® Model 1525 chromatograph fitted with an automatic injector (Waters 717plus). For water-insoluble lignins the chromatograph was fitted with a set of Waters® Styragel HR 4 E 7.6 × 300mm columns and a differential refractometer detector (Waters 2414). The carrier solvent was THF at 1 mL min^{-1} and the system was operated at 25 ºC. Dry samples were dissolved in 0.25 mL THF with a nominal concentration of 1 mg mL^{-1}. Injection volumes were 200 µL. Polystyrene standards were used for the calibration. For water-soluble lignins the chromatograph was fitted with a Waters 2414 refractive index detector and a set of 5 Waters Ultrahydrogel columns (pore sizes: 120, 250, 500, 1000 2000 Å) . A buffer solution at pH = 7.00 (0.1 M $NaNO_3$) was employed as mobile phase with a rate of 0.8 mL min^{-1} at 25 ºC. Injection volumes were 100 µL and polyethylene glycols were used as standards.

A 812e Mettler Toledo thermogravimetric balance was used in order to evaluate thermal behavior and the measurements were taken at nitrogen atmosphere at a scanning rate of 10 °C min $^{-1}$ from 30 to 900 °C. About 2-4 mg of lignins were used in all analyses.

Hydroxymethylation reactions

Nine hydroxymethylations were carried out by reaction between lignin and F in alkaline conditions (Exp.1-Exp.9). The recipes and operating conditions are presented in Table 1.

TABLE 1. Hydroxymethylation reactions: type of lignin, recipes, reaction conditions, and evolution of F_T and $\text{—}H_{Ar}$ (concentration in mol L^{-1})

	Exp. 1		Exp. 2		Exp. 3		Exp. 4		Exp. 5		Exp. 6		Exp. 7		Exp. 8		Exp. 9	
Type of Lignin (L):																		
	KL		OL		SL		SL		KL		OL		SL		SL		SL	
Recipe:																		
	$[F_T]^\circ=3.01$ $[-H_{Ar}]^\circ=0.04$ $[-H_2O]^\circ=45.4$ $[F_T]^\circ/[-H_{Ar}]^\circ=75$ $F_T^\circ/L^\circ=1.47$[a]		$[F_T]^\circ=3.00$ $[-H_{Ar}]^\circ=0.05$ $[H_2O]^\circ=46.3$ $[F_T]^\circ/[-[H_{Ar}]^\circ=60$ $F_T^\circ/L^\circ=1.47$[a]		$[F_T]^\circ=3.00$ $[-H_{Ar}]^\circ=0.05$ $[H_2O]^\circ=46.5$ $[F_T]^\circ/[-H_{Ar}]^\circ=60$ $F_T^\circ/L^\circ=1.47$[a]		$[F_T]^\circ=2.99$ $[-H_{Ar}]^\circ=0.05$ $[H_2O]^\circ=47.1$ $[F_T]^\circ/[-H_{Ar}]^\circ=60$ $F_T^\circ/L^\circ=1.47$[a]		$[F_T]^\circ=0.46$ $[-H_{Ar}]^\circ=0.17$ $[H_2O]^\circ=35.4$ $[F_T]^\circ/[H_{Ar}]^\circ=2.7$ $F_T^\circ/L^\circ=0.06$[a]		$[F_T]^\circ=0.46$ $[-H_{Ar}]^\circ=0.13$ $[H_2O]^\circ=35.5$ $[F_T]^\circ/[-H_{Ar}]^\circ=3.5$ $F_T^\circ/L^\circ=0.08$[a]		$[F_T]^\circ=0.46$ $[-H_{Ar}]^\circ=0.19$ $[H_2O]^\circ=36.4$ $[F_T]^\circ/[-H_{Ar}]^\circ=2.4$ $F_T^\circ/L^\circ=0.07$[a]		$[F_T]^\circ=0.42$ $[-H_{Ar}]^\circ=0.20$ $[H_2O]^\circ=33.7$ $[F_T]^\circ/[-H_{Ar}]^\circ=2.1$ $F_T^\circ/L^\circ=0.06$[a]		$[F_T]^\circ=0.43$ $[-H_{Ar}]^\circ=0.21$ $[H_2O]^\circ=35.4$ $[F_T]^\circ/[-H_{Ar}]^\circ=2.0$ $F_T^\circ/L^\circ=0.06$[a]	
Reaction conditions:																		
	T=50 °C pH=11±0.5		T=50 °C pH=11±0.5		T=50 °C pH=11±0.5		T=50 °C pH=9±0.5		T=50°C pH=11±0.5		T=50 °C pH=11±0.5		T=40 °C pH=9±0.5		T=50 °C pH=9±0.5		T=70 °C pH=9±0.5	
Measurements:																		
Time (min)	$[F_T]$	$[\text{—}H_{Ar}]$	$[F_T]$	$[\text{—}H_{Ar}]$	$[F_T]$	$[F_T]$	$[F_T]$	$[\text{—}H_{Ar}]$	$[F_T]$	$[\text{—}H_{Ar}]$	$[F_T]$	$[\text{—}H_{Ar}]$	$[F_T]$	$[\text{—}H_{Ar}]$	$[F_T]$	$[\text{—}H_{Ar}]$	$[F_T]$	$[\text{—}H_{Ar}]$
0[b]	2.87	0.04	2.71	—[c]	2.98	0.45	2.97	—[c]	0.46	—[c]	0.46	—[c]	0.45	0.21	0.41	0.18	0.42	0.21
15	2.83	—[c]	2.51	—[c]	2.91	—[c]	2.98	—[c]	0.44	0.08	0.39	0.13	—[c]	—[c]	—[c]	—[c]	—[c]	—[c]
30	2.70	—[c]	2.45	—[c]	2.82	0.42	2.96	—[c]	0.36	—[c]	0.32	—[c]	0.42	0.11	0.37	0.14	0.37	0.13
45	2.64	—[c]	2.41	—[c]	2.81	—[c]	2.99	—[c]	—[c]	—[c]	—[c]	—[c]	—[c]	—[c]	—[c]	—[c]	—[c]	—[c]
60	2.60	—[c]	2.43	—[c]	2.75	0.40	2.95	—[c]	0.35	0.07	0.27	0.17	0.40	0.10	0.35	0.11	0.29	0.12
90	2.53	—[c]	2.37	—[c]	2.7	—[c]	2.99	—[c]	0.35	—[c]	0.21	—[c]	—[c]	0.08	0.35	0.12	0.28	—[c]
120	2.55	0.04	2.40	—[c]	2.64	0.39	2.98	—[c]	0.34	—[c]	0.21	—[c]	0.39	0.09	0.34	0.11	0.31	0.05
150	2.60	—[c]	2.39	—[c]	2.70	0.38	2.97	—[c]	—[c]	—[c]	—[c]	—[c]	0.38	—[c]	0.33	0.13	0.25	0.06
180	2.55	—[c]	2.38	—[c]	2.63	0.36	2.98	—[c]	0.29	—[c]	0.18	—[c]	0.36	—[c]	0.33	—[c]	0.26	—[c]
240	2.49	0.04	2.36	—[c]	2.61	0.38	2.99	—[c]	0.29	0.10	0.17	0.3	0.38	0.07	0.31	0.12	0.24	0.07

[a]weight ratio (impure lignin), [b]zero time corresponds to the first measurement, and [c] not measured.

The effect of different variables (type of lignin, pH, F_Tº/ligninº, and temperature) were studied. In our previous work, a higher ratio (F_Tº/ligninº=1.47) was employed related to the industrial use of lignin for laminates,[33] then the Exp. 1-4 were performed using this ratio. The effect of the type of lignin at 50 ºC and F_Tº/ligninº=1.47 was evaluated in Exps 1-3 at pH=11 and in Exp. 4 at pH=9. Experiments for KL and OL at pH=9 could not be performed due to the incomplete dissolution of lignins at pH=9.

A lower F_Tº/ligninº weight ratio (0.07±0.01) was employed in Exp. 5 to 9. The lower value (lower than 1) was used due to the low reactivity of lignin.[49, 50] Exp. 5 and 6 were carried out at 50 ºC and pH=11 for the corresponding KL and OL, and different temperatures (40 ºC, 50 ºC, and 70 ºC) were adopted in Exp. 7 to 9 for SL at pH=9.

The reactions were carried out in a 250 mL 3-neck flask provided with a magnetic stirring, a sampler, and temperature control. The samples of SL were dissolved in water whereas water-insoluble lignins were dissolved in 3 wt% NaOH solution adjusting the pH and temperature according to the conditions of the experiments (Table 1). The reaction was started by loading the F solution at the same pH, and preheated at the same temperature.

Along the hydroxymethylations the following variables were measured: *i)* F_T by the volumetric method of hydroxylamine hydrochloride (ISO 11402:2004); and *ii)* —H_{Ar} by UV-Vis spectroscopy.

The UV-Vis spectroscopic[53] was adopted for the direct analyses of liquid samples avoiding long drying times and possible structural changes of lignins.

About 10-15 μl of the liquid reaction sample were dissolved in the corresponding 25 mL 0.2N NaOH and buffer solutions at pH=6 and pH 12. The absorbance of the alkaline solutions with respect to the neutral solution at 300 nm and 360 nm were measured. The absorbance spectra of a 12 wt% F and 1N NaOH solutions (Fig. 3) confirm the absence of the matrix absorption at P-OH range (300 and 360 nm).

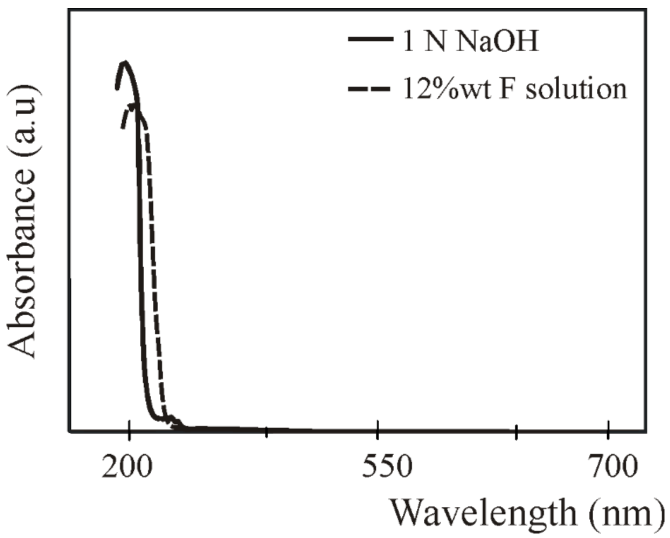


FIGURE 3. Absorption spectra of 1 N NaOH and 12%wt F solutions.

The following considerations were assumed: a) absorptivities of model compounds are the same as adopted by Reznikov-Goldshmid's method,[53] b) Lignin mass changes along hydroxymethylation are negligible (hydroxymethylated Lignin ≅ Lignin°), and c) $[-H_{Ar}] = [P\text{-}OH_{I+II}] = [G]$.

Cannizzaro reactions

Cannizzaro reactions recipes and conditions are presented in Table 2.

TABLE 2. Cannizzaro reactions: recipes, reaction conditions, and evolution of F_T (concentration in mol L^{-1})

	Exp. A	Exp. B	Exp. C
Recipe:			
	$[F_T]°=2.98$	$[F_T]°=0.46$	$[F_T]°=3.00$
	$[H_2O]°=35.4$	$[H_2O]°=45.5$	$[H_2O]°=50.6$
Reaction conditions:			
	T=50 °C	T=50 °C	T=50 °C
	pH=11±0.5	pH=11±0.5	pH=9±0.5
Measumerents:			
Time (min)	$[F_T]$	$[F_T]$	$[F_T]$
0	2.98	0.46	3.01
15	2.96	—[a]	2.99
30	2.92	0.41	3.01
45	2.89	—[a]	2.98
60	2.64	0.41	2.98
90	2.63	0.37	3.01
120	2.64	0.38	2.99
150	2.59	—[a]	3.01
180	2.59	0.38	3.01
240	2.41	0.38	2.98

[a] not measured.

Samples were taken for the measurement of F_T by the sulfite method (ISO 11402:2004). Also, the initial and final samples from the Exp. A were analyzed by ^{13}C NMR to confirm the production of methanol.

^{13}C NMR spectra were acquired on a 300 MHz spectrometer (^{1}H NMR, 300.14 MHz; ^{13}C NMR, 75.04 MHz) employing deuterated water as solvent.

RESULTS AND DISCUSSION

Lignin Characterization

Results of the moisture, ash, carbohydrates, purity, elemental composition, P-OH and different physicochemical properties of the studied lignins are presented in Table 3.

TABLE 3. Characterization of the studied technical lignins.

		SL	KL	OL
% Moisture		8.89	4.48	3.66
% Ash (dry basis)		23.45	21.67	0.05
% Carbohydrates (dry basis)		13.63	5.16	4.35
% Purity (dry basis)		62.92^a 62.28^b	73.17^a —	95.32^a —
Composition				
Elemental composition %	C	39.99	49.1	65.34
	H	5.34	3.7	7.99
	N	0.18	0.22	0.26
	S	4.14	1.90	0.72
% P-OH (dry basis)	I^*	1.37	2.39	0.61
	II^*	0.1	0.37	0.87
	III^*	0.03	0.9	2.79
	IV^*	0.53	0.03	0.18
	Total	2.03	3.69	4.46
	P-OH (I+II) (c)	1.47	2.76	1.48
	P-OH (III+IV) (d)	0.56	0.93	2.97
	(c)/(d) (wt%)	2.6	3.0	0.5
Physicochemical properties				
Solubility	THF	NO	YES	YES
	Water	YES	NO	NO
	NaOH 1 N	YES	YES	YES
	HCl 1 N	YES	NO	NO
$\bar{M}_w$ (g mol^{-1})		5259	2140	2122
$\bar{M}_n$ (g mol^{-1})		1520	1340	842
Dispersity ($\bar{M}_w/\bar{M}_n$)		3.45	1.59	2.12
Thermal stability (°C)		≈300	≈400	≈400

[a] obtained from: 100% -% carbohydrates-% ash (dry basis), [b] obtained by UV-Vis spectroscopy, [*]see Fig. 2

The purity of lignins decreased in the following order: OL> KL> SL. SL exhibited the highest degree of impurities due to its higher carbohydrate content. The ash content was similar for KL and SL. In contrast, negligible ash content was observed for OL. SL presented the highest moisture content in accordance with its higher S content due to the hygroscopicity of sulphonates groups. Nitrogen content was similar for all lignins.

The P-OH content decreased in the following order: OL> KL> SL. However, P-OH (I+II) units in KL were two folds higher than those of SL and OL.

Unlike KL and OL, SL is soluble in water and in acidic conditions and insoluble in THF. All lignins are soluble in alkaline conditions but the dissolution of OL was the lowest.

Functional groups

The FTIR spectra of the studied lignins are shown in Fig. 4.

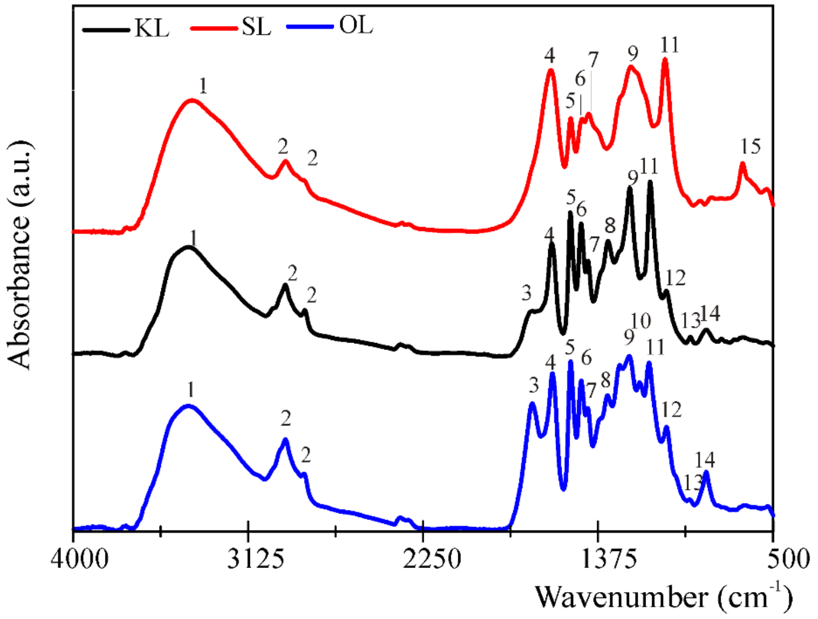


FIGURE 4. FTIR spectra from the studied technical lignins.

Bands at 3400 cm^{-1} (peak 1) and the region from 3000 and 2848 cm^{-1} (peaks 2) were attributed to OH groups and C—H stretch in the methyl and methylene groups, respectively. The carbonyl stretching vibrations at the region from 1738 and 1709 cm^{-1} (peak 3) were observed for OL and KL except for SL. Bands at 1539-1605 cm^{-1} (peak 4) and 1505-1515 cm^{-1} (peak 5) are pure bands corresponding to the aromatic skeleton. According to Faix[63] the intensity of peak 4 indicated a higher content of Sy groups in relation with G groups and peak 5 is associated with a higher content of G groups in relation with Sy groups. Thus, the intensity ratio of peaks 5/4 suggested the G/Sy ratio was higher for KL as compared with SL. Bands at 1460 cm^{-1} (peak 6), 1429 cm^{-1} (peak 7) and 1221 cm^{-1} (peak 9) were related to C—H deformation; aromatic skeleton vibration combined with C—H in-plane deformation; C—C, C—O, and C=O stretch, respectively. A band at 1325 cm^{-1} (peak 8) related to Sy units plus G condensed units were present in both the OL and the KL.

The signal at 1162 cm^{-1} (peak 10) characteristic of HH units was only present in OL. All lignins presented a band at 1120 cm^{-1} (peak 11) that correspond to aromatic C—H in-plane deformation, secondary alcohol, and C=O stretch. Bands at 1030 cm^{-1} (peak 12), at 930 cm^{-1} (peak 13) and at 829 cm^{-1} (peak 14) were observed for KL and OL. These bands are associated to aromatic C—H in plane, C—O deformation in primary alcohols, C=O stretch unconjugated, and C—H out of plane in position 2, 5 and 6 of G. SL exhibit a signal at 620 cm^{-1} (peak 15) corresponding to the sulfonate group.[62]

Molar mass distributions

The molar mass distributions (MMD) of lignins and the average molecular weights are presented in Fig. 5 and in Table 3 respectively.

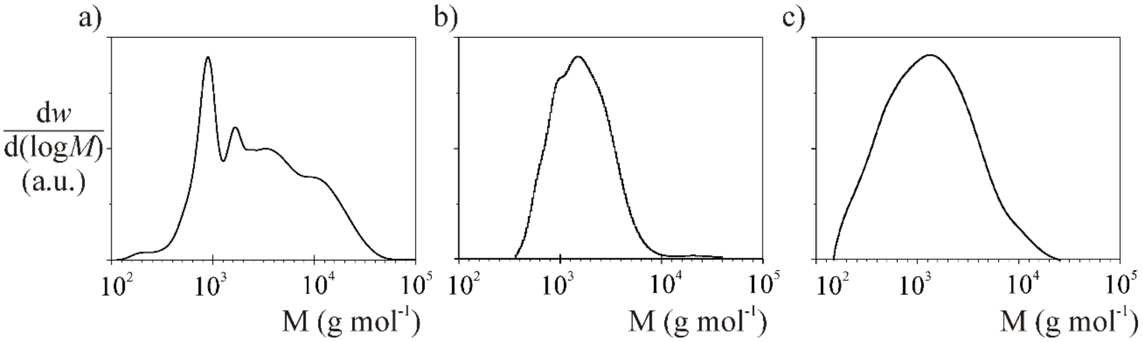


FIGURE 5. MMDs of technical lignins: a) SL; b) KL and c) OL.

OL exhibited the lowest average molar mass in weight ($\bar{M}_w$) and average molar mass in number ($\bar{M}_n$) whereas the average weights for KL are lower than those of SL. The $\bar{M}_n$ suggests that lignins have about 5-8 aromatic rings in their structure.

Thermogravimetric behavior and stability

The thermogravimetric analysis (TGA) and DTG curves from thermograms are shown in Fig. 6.

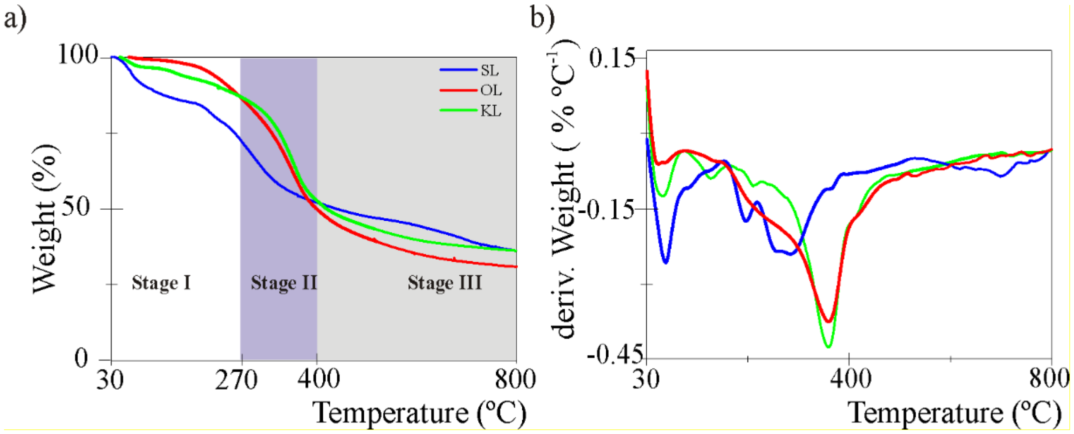


FIGURE 6. Thermogravimetric analysis: a) TGA, and b) DTG curves.

Three stages were identified with differences in stability, depending on the lignin type [Fig. 6.a)]. From 30 to 200 °C, OL exhibited the highest thermal stability due to its lowest moisture content. At 100 °C, SL (11%) weight loss was two folds higher than that of KL (3.5%), and this result is in accordance with the moisture content (Table 3). In the second stage (270-400 °C), KL showed the highest thermal stability. In the last stage, between 400-800 °C, SL showed the highest thermal stability. Char of SL, KL, and OL were 36.5%; 36%, and 30%, respectively. These results are consistent with the higher ash contents of SL and KL.

From DTG curves [Fig 6 b)], the degradation processes were first due to the moisture of lignin at 100 ºC. The cleavage of C—C linkages[64] occurred at 295-300 ºC for SL and 376 ºC for KL and OL. In addition, a small degradation at 200 ºC was observed for KL, probably due to the cleavage of hydroxyl phenolic groups.

Cannizzaro and Hydroxymethylation reactions

The reactivity of lignin towards F is influenced by lignin purity, thermal stability, solubility and the presence of functional groups. As it was discussed in the previous sections, the main results of lignin characterization showed that OL is the purest and the most environmental friendly (due to the lowest ash, carbohydrates, and S contents); KL is the most reactive (because of its high amount of phenolic structures with free sites type guaiacyl); SL is the only lignin soluble in water at pH<11; and all lignins are thermally stable.

Cannizaro reactions

The ^{13}C NMR results for Exp. A are presented in Fig. 7. At the beginning of the reaction, the characteristic signals at 83.01 and 87.02 ppm corresponding to methylene glycol and poly(oxymethylene glycol) are observed [Fig. 7a)]. At the end of the reaction, the signals at 60.01 and 180.02 ppm corresponding to methanol and carbonyl of sodium formate confirm the Cannizzaro reaction [Fig 7 b)].

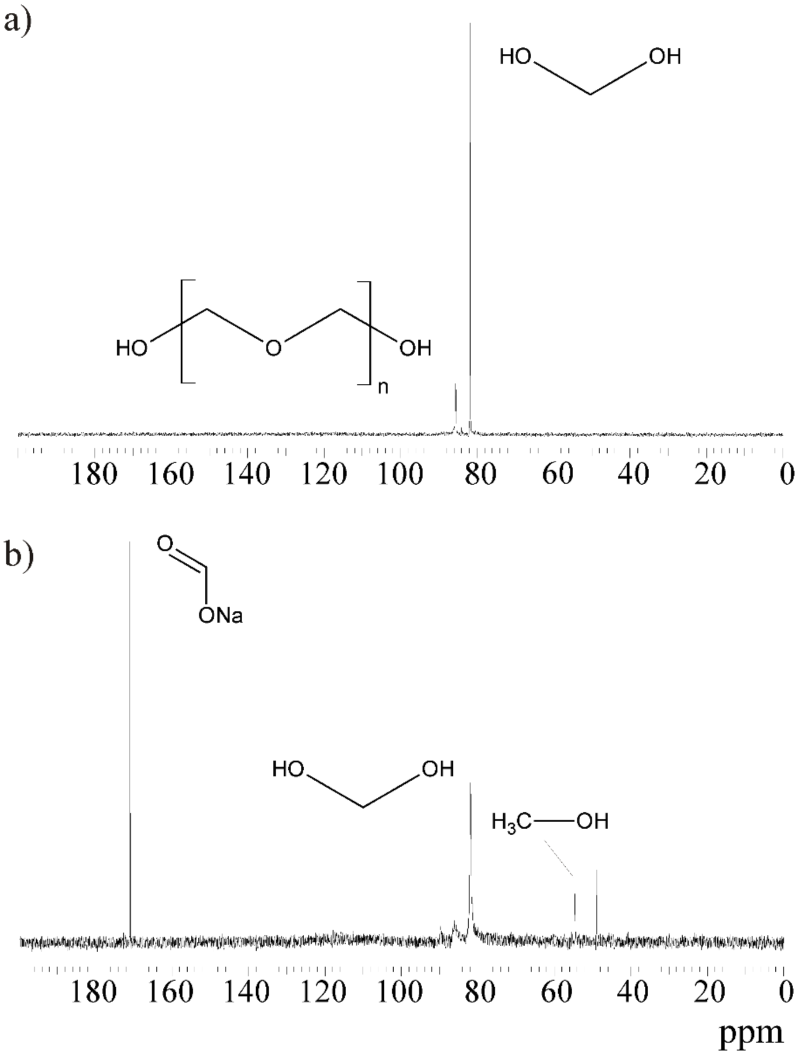


FIGURE 7. ^{13}C NMR of Exp. A for: a) *t*=0 min., and b) *t*=240 min.

Fig. 8 presents the evolution of F_T along time for Exps A to C. The final conversion of F was 19 and 17% for the corresponding Exps A and B and was negligible for Exp. C.

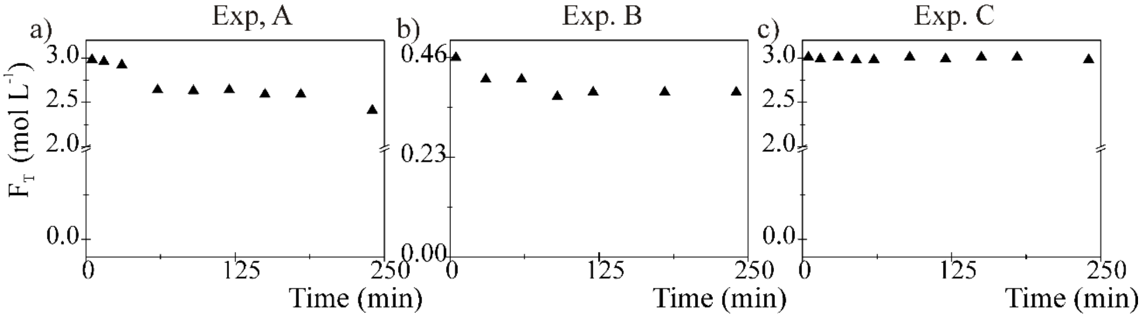


FIGURE 8. Time evolution of F_T for Cannizzaro reactions at 50 ºC: a) $[F_T]°$=2.98 mol/L and pH=11; b) $[F_T]°$=0.46 mol/L and pH= 11; and c) $[F_T]°$=3.00 mol/L and pH=9.

The optimal pH value for hydroxymethylation is 9 which ensures the ionization of the phenolic group in lignin macromolecule and negligible Cannizaro reaction.[49] However, according to the results obtained from the lignin characterization, KL and OL, which are the most reactive lignins, are soluble in strong alkaline conditions (pH>9). Under those conditions, the Cannizaro reaction is unavoidable.

Hydroxymethylation reactions of OL, KL and SL for F_T°/lignin° = 1.47

The time evolution of F_T and —H_{Ar} along the hydroxymethylation of lignin for F_T°/lignin° = 1.47 (Exps. 1 to 4) are shown in Fig. 9.

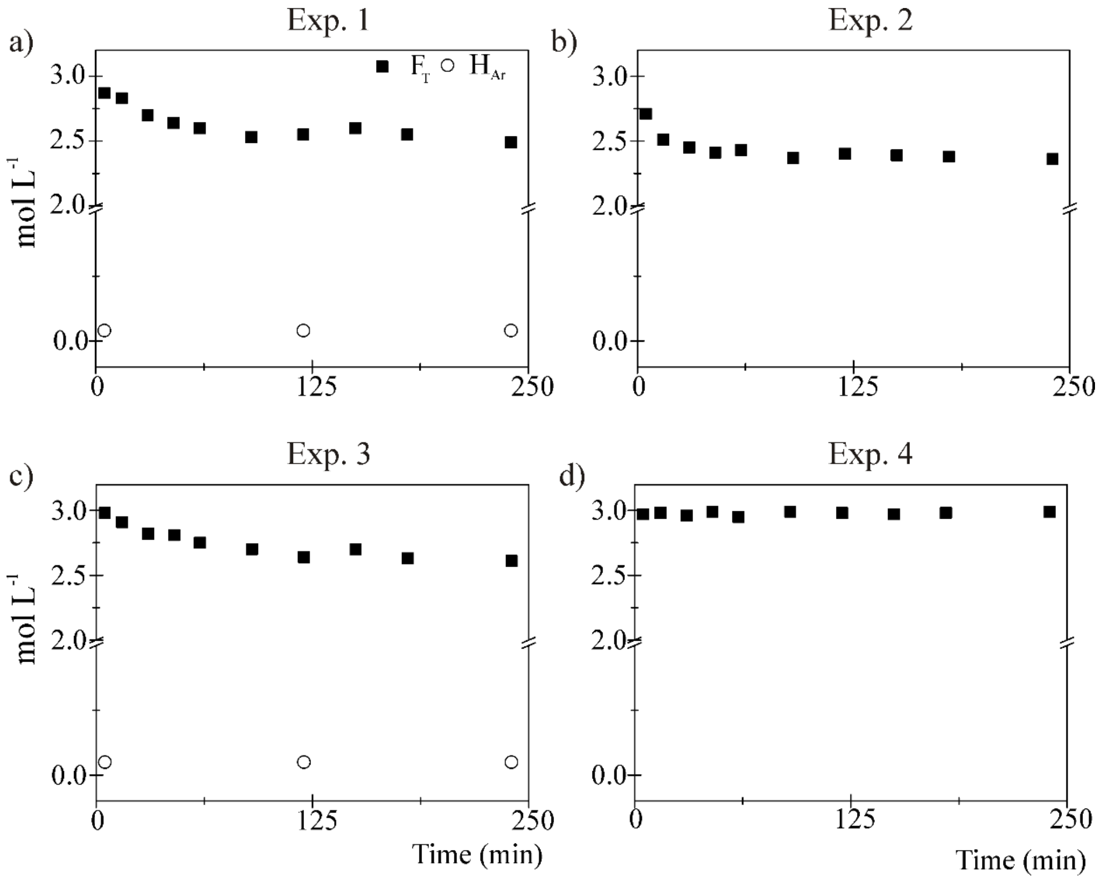


FIGURE 9. Time evolution of F_T and —H_{Ar} for F_T°/ lignin°=1.47 at T=50 ºC: a) KL at pH=11; b) OL at pH=11; c) SL at pH 11; d) SL at pH 9.

Although the final theoretical conversions of F_T (assuming total reaction and taking into account the purity of lignin) were 1.33%, 1.67%, 1.67%, and 1.67%, respectively; the experimental conversions were 17.27%, 21.59%, and 13% for KL [Fig. 9a)], OL [Fig. 9b)], and SL at pH = 11 [Fig. 9 c)], and 0% for SL at pH = 9 [Fig. 9 d)]. These results suggest a consumption of F by the undesirable reaction of Cannizzaro [Fig. 8 a)] for Exps. 1 to 3, and a low sensitivity of the volumetric test for Exp. 4. Similarly, the UV-Vis method was insensitive for the studied conditions. The use of high F_T/L^o is hindered due to the low content of P-OH groups. However, for the case of KL and OL, higher conversions were observed due to their lower impurity contents and higher OH_{I+II} concentration.

Hydroxymethylation reactions of OL and KL for F_T°/lignin° = 0.07±0.01.

Fig. 10 presents the time evolution of F_T and $—H_{Ar}$ along the hydroxymethylation for F_T°/Lignin°=0.07±0.01.

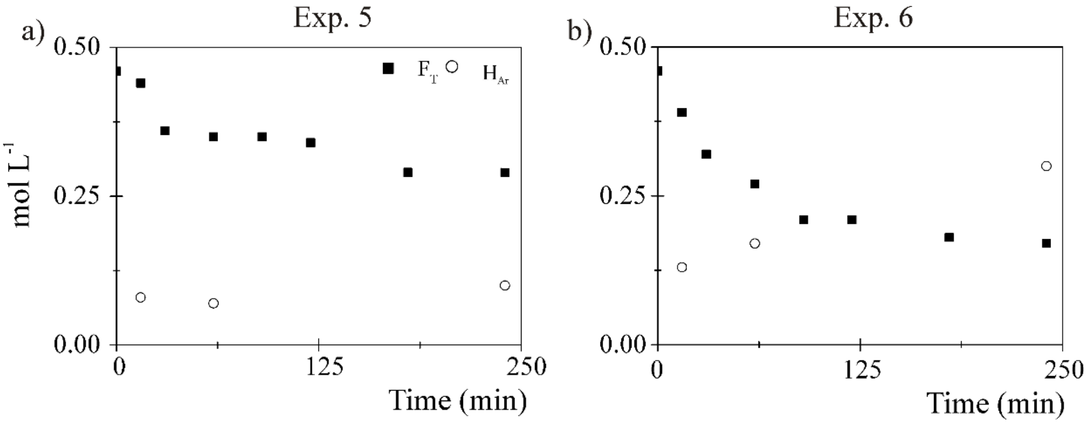


FIGURE 10. Time evolution of F_T and **—**H_{Ar} for F_T°/Lignin°=0.07±0.01 at T=50 ºC and pH=11 for: a) KL; and b) OL.

The final F_T of hydroxymethylation was corrected by the consumption of the Cannizzaro reaction and were 0.09 mol L^{-1} and 0.21 mol L^{-1} for Exp. 5 and Exp. 6, respectively. The F_T consumed in Exp. 5 was in accordance with the corresponding $—H_{Ar}$ of 0.07 mol L^{-1}. However,$—H_{Ar}$ showed a growth trend and was higher than the final F_T in Exp. 6. This result suggests hydroxymethylation of HH units to G units from OL.

Hydroxymethylation reactions of SL for F_T°/lignin° = 0.07±0.01.

The time evolution of F_T and —H_{Ar} of Exps7-9 is shown in Fig. 11. From the results obtained in Exp. C (at pH= 9), a negligible consumption of F by the Cannizzaro reaction is expected.

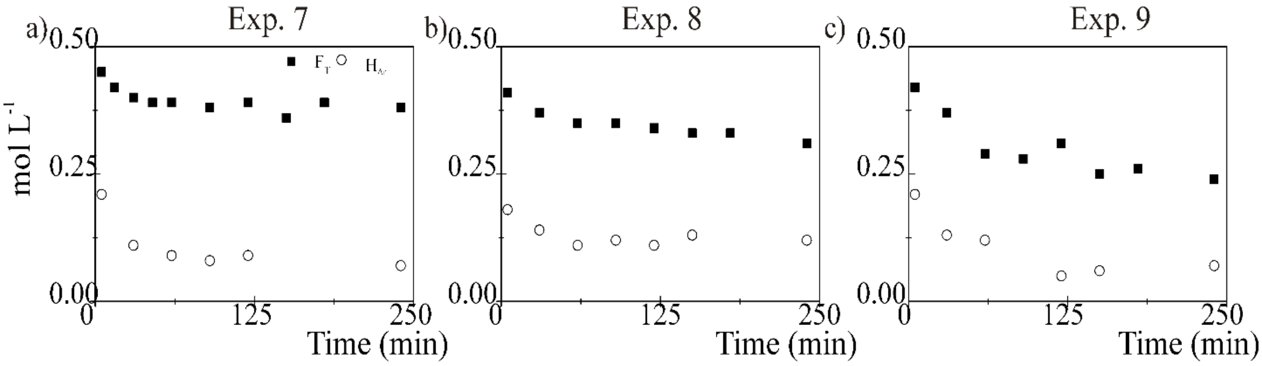


FIGURE 11. Time evolution of F_T and —H_{Ar} for SL. F_T°/lignin°=0.07±0.01 and pH=9: a) 40 ºC; b) 50 ºC; and c) 70 ºC.

For the studied conditions, the chemical equilibrium was reached at about 125 min. These equilibrium results are similar to that observed by Peng et al.[39] and Zhao et al.[29] that use lignosulfonates and kraft lignins, respectively. The consumptions of F_T at the end of the reaction (0.08, 0.11, and 0.19 mol L^{-1}) were similar to the corresponding —H_{Ar} (0.12, 0.08, and 0.14 mol L^{-1}). These results show that negligible Cannizaro is necessary to promote the Lederer-Manasse reaction. The higher hydroxymethylation conversion was reached at 70 ºC. Alonso et al.[45] observed that in absence of side reactions, higher temperatures promotes the reactivity of lignosulfonate towards F. In addition, Malutan et al.[49] and Căpraru et al.[55] observed good hydroxymethyl groups incorporation using temperatures higher than 70 ºC.

CONCLUSIONS

In this work, sodium lignosulfonate (SL) and kraft lignin (KL) from *Eucalyptus grandis* and *viminalis*; and organosolv lignin (OL) from sugarcane bagasse were physicochemically characterized and activated by hydroxymethylation.

The characterization of the studied lignins showed that: *i)* OL is the purest and the most environmental friendly (due to the lowest ash, sugars, and S contents); *ii)* KL is the most reactive (because of its high amount of phenolic structures with free sites type guaiacyl); *iii)* SL is the only lignin soluble in water at pH<11; *iv)* all lignins are thermally stable.

The UV-Vis spectroscopic method used in this work is a good tool to measure $–H_{Ar}$ from G units along the hydroxymethylation of hardwood lignins. The activation of lignin is affected by: *i)* type of lignin; *ii)* F_T°/Lignin°; *iii)* pH; and *iv)* T. With regard to pH, pH<11 ensure negligible consumption of F by the Cannizzaro reaction and is suitable for water-soluble SL. On the other hand, pH>11 is necessary for the water-insoluble OL and KL. With regard to T, hydroxymethylation conversion is higher at 70 ºC for SL.

Finally, the lignins studied in the present work could be adapted to the conditions of synthesis and processing to obtain high-value-added materials and can be used as a partial replacement of P. For this application, the results suggest the following: SL> KL> OL being SL the most appropriate for paper impregnation applications.

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FIGURE 1

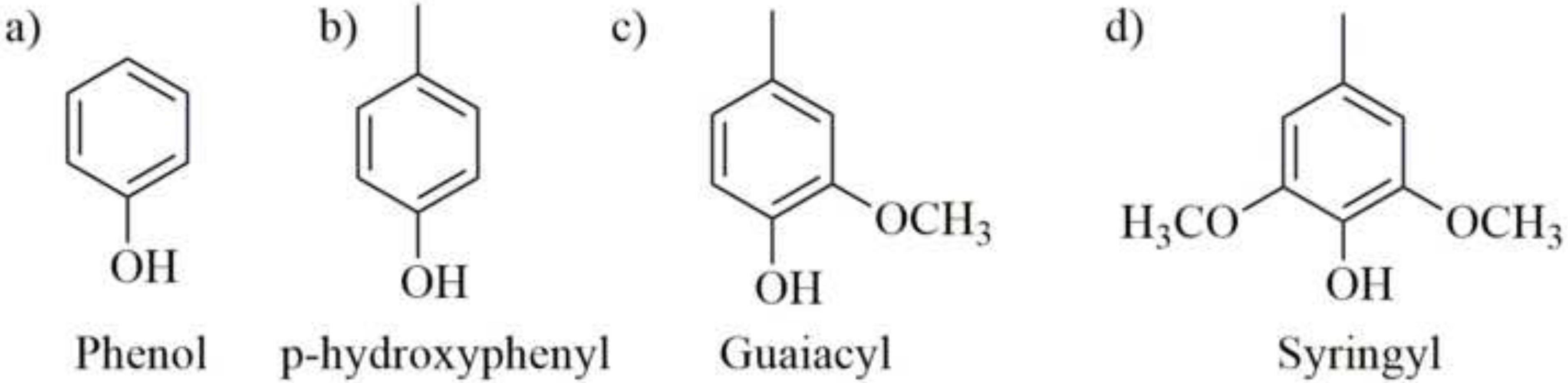
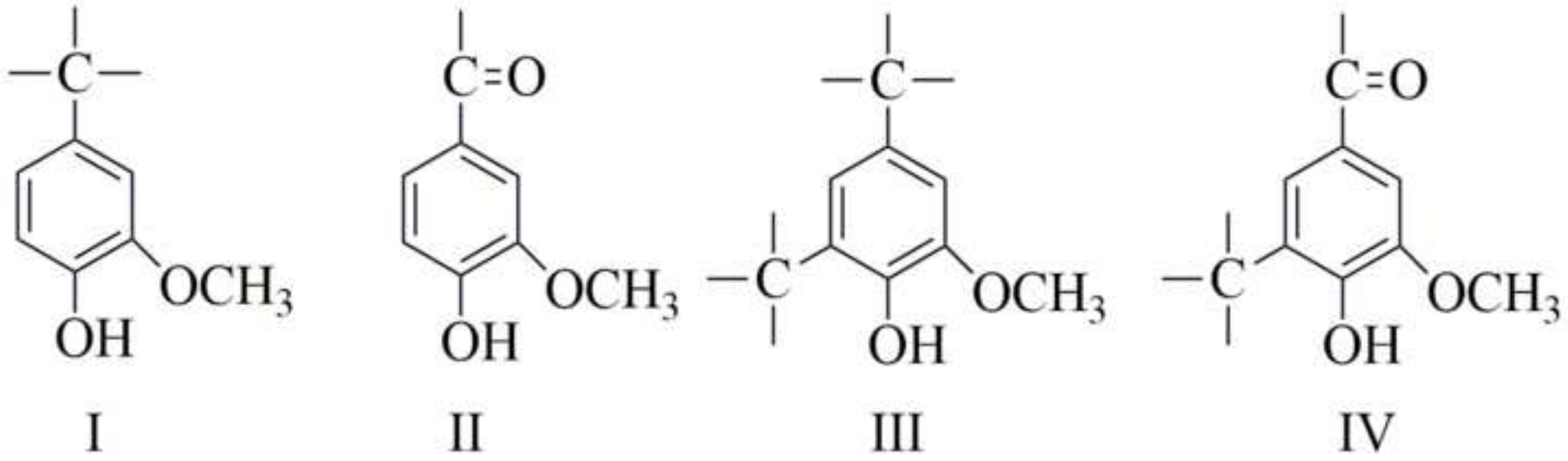
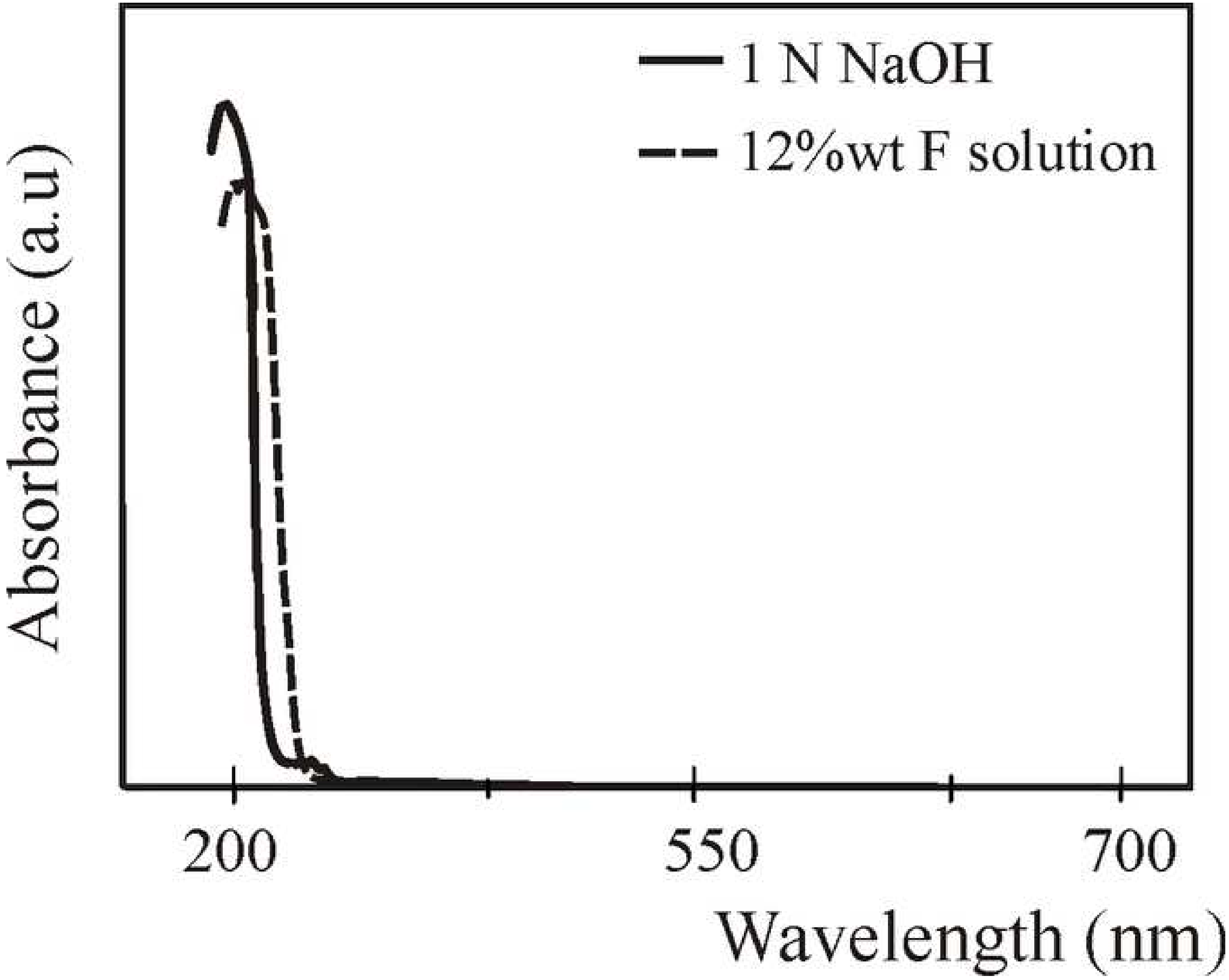
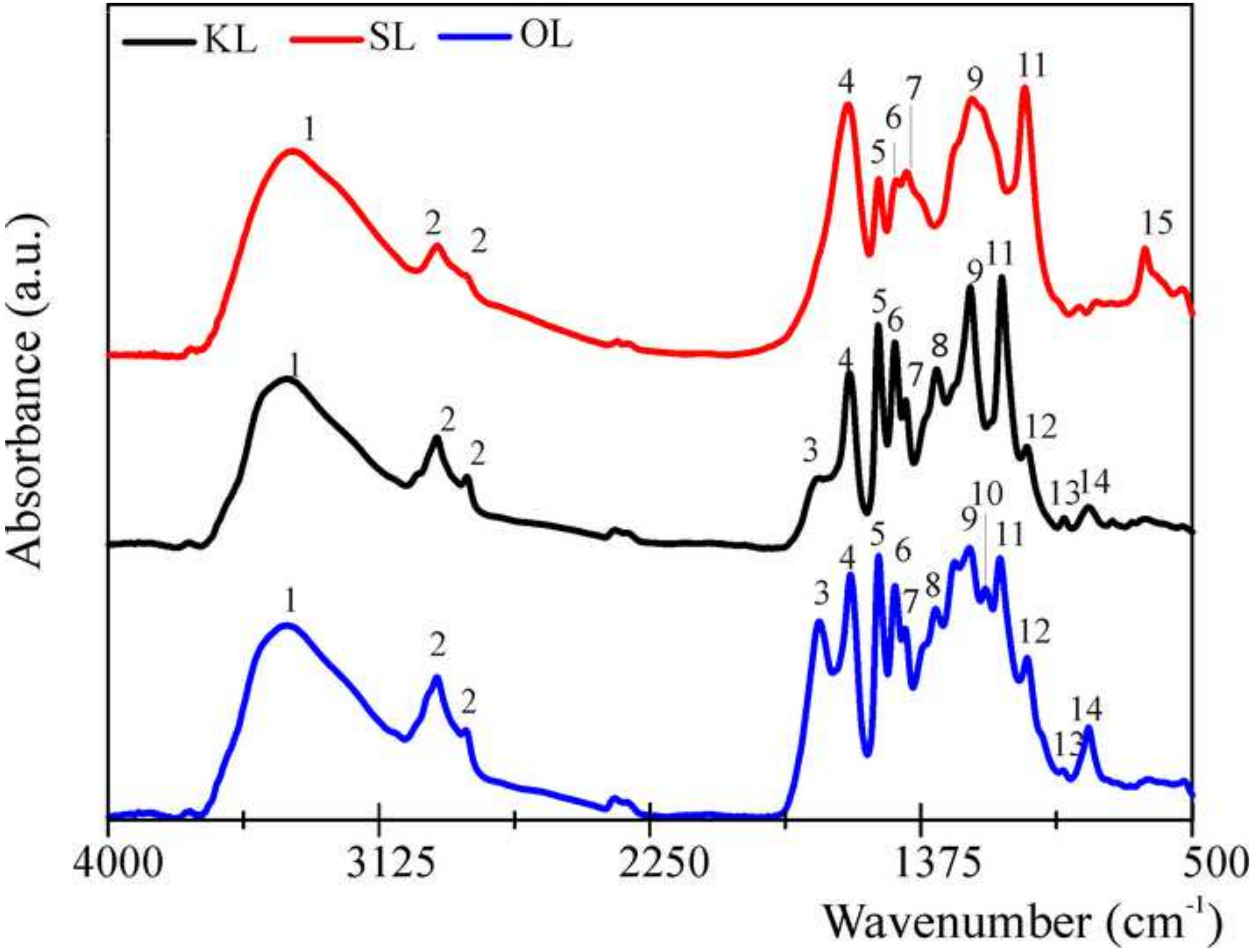

a)
OH
Phenol
b)
OH
p-hydroxyphenyl
c)
OCH3
OH
Guaiacyl
d)
H3CO
OCH3
OH
Syringyl

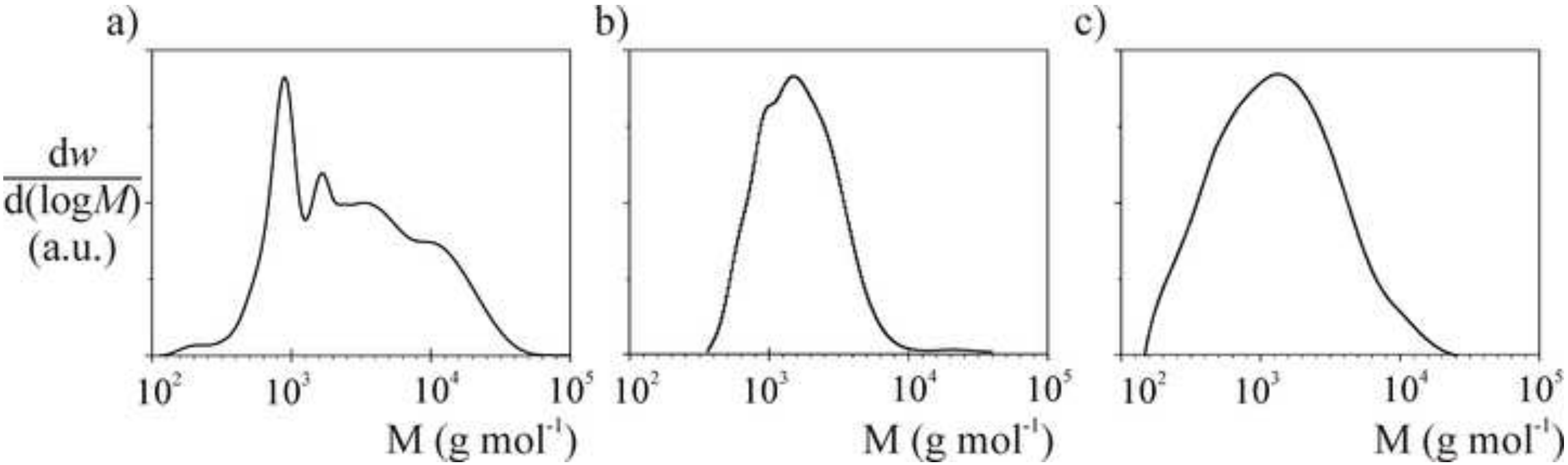
FIGURE 2



I II III IV


1 N NaOH
12%wt F solution
Absorbance (a.u)
200
550
700
Wavelength (nm)


KL
SL
OL
Absorbance (a.u.)
Wavenumber (cm^{-1})
4000
3125
2250
1375
500
1
2
2
3
4
5
6
7
8
9
10
11
12
13
14
15


a)
b)
c)
dw / d(logM) (a.u.)
10^2
10^3
10^4
10^5
M (g mol^-1)

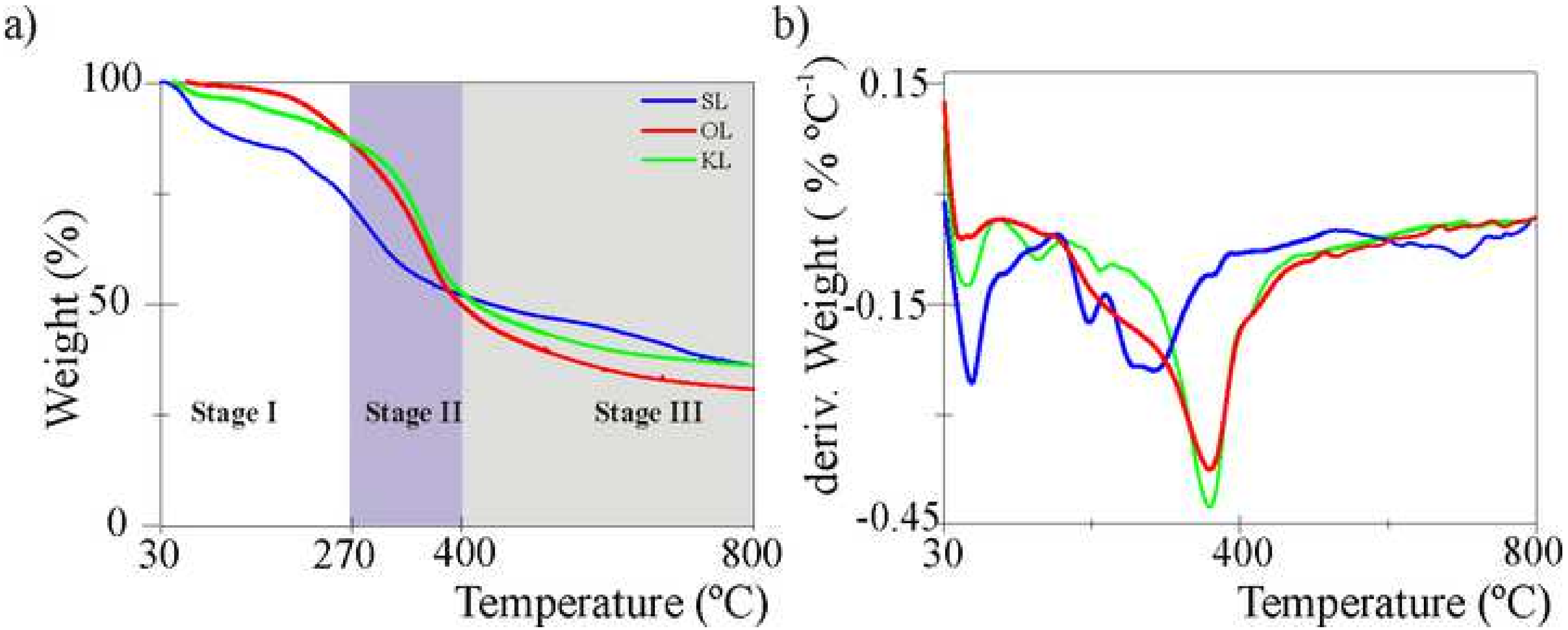
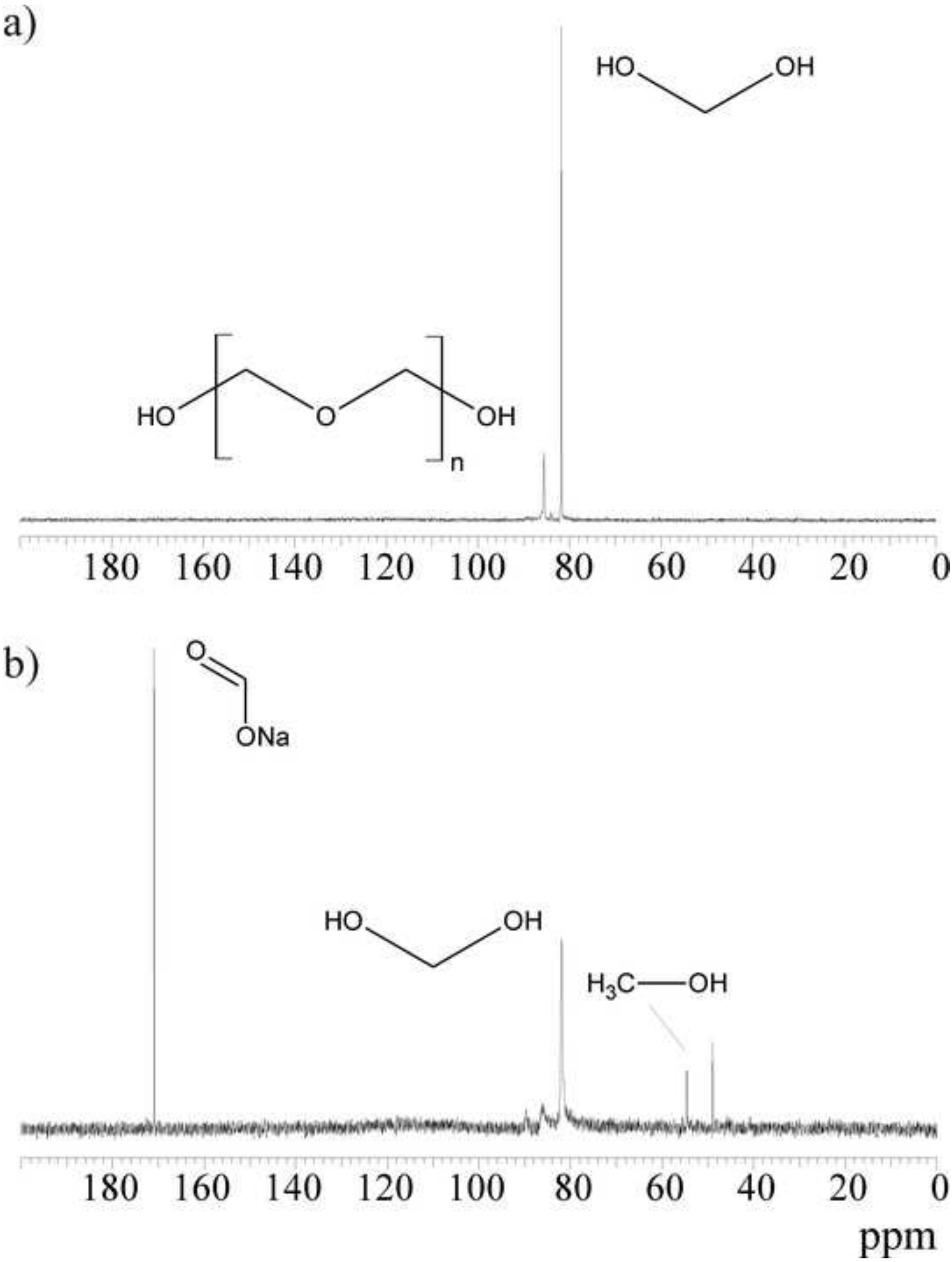
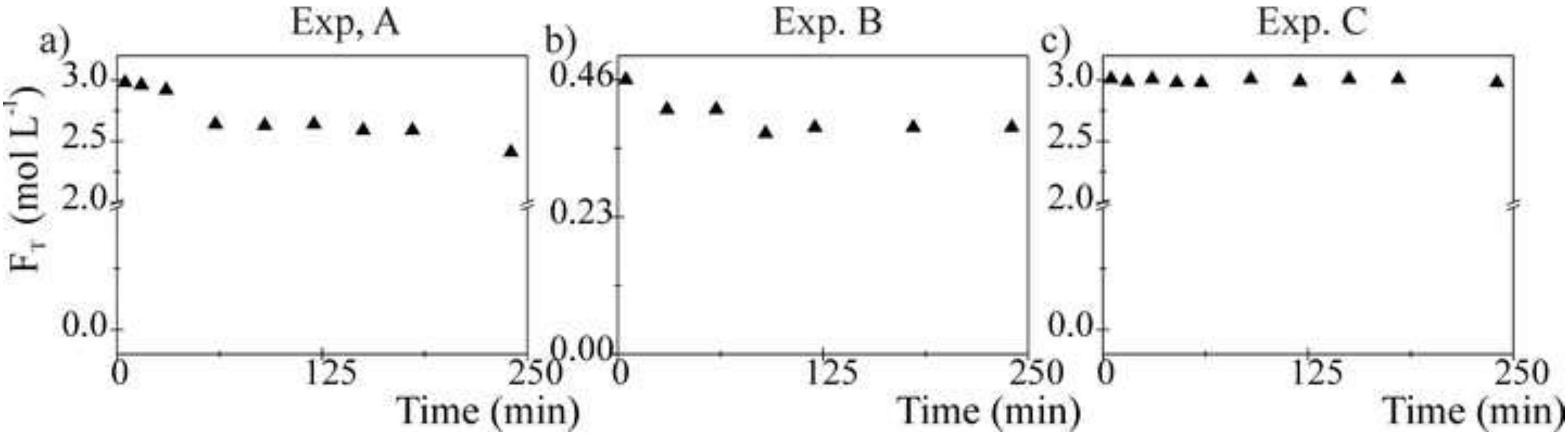

a)
100
50
0
30
270
400
800
Weight (%)
Temperature (°C)
Stage I
Stage II
Stage III
SL
OL
KL
b)
0.15
-0.15
-0.45
30
400
800
deriv. Weight (% °C⁻¹)
Temperature (°C)

FIGURE 7


a)
HO
OH
HO
O
OH
n
180
160
140
120
100
80
60
40
20
0
b)
O
ONa
HO
OH
H3C
OH
180
160
140
120
100
80
60
40
20
0
ppm


a)
Exp, A
b)
Exp. B
c)
Exp. C
F_T (mol L^{-1})
3.0
2.5
2.0
0.0
0.46
0.23
0.00
0
125
250
Time (min)

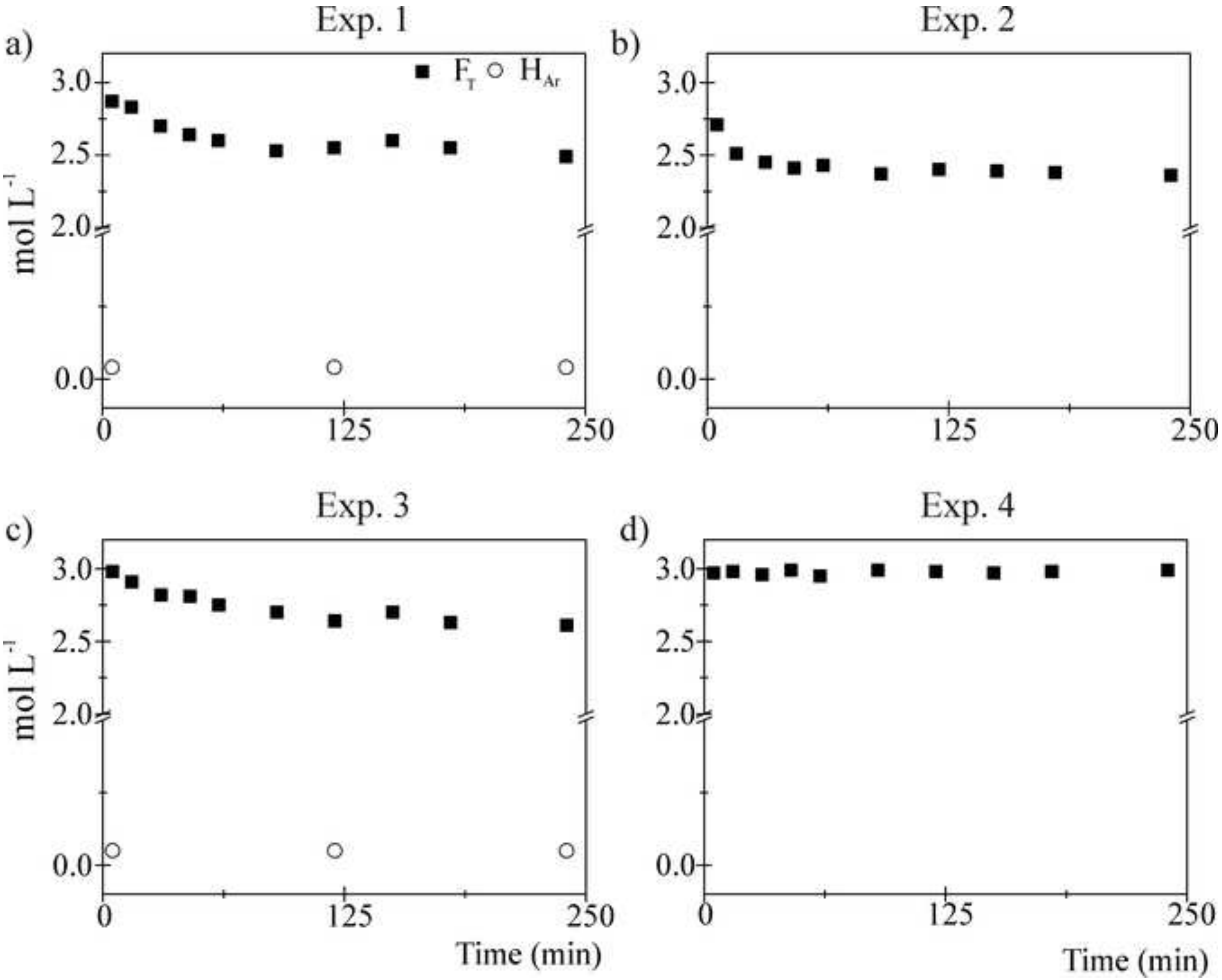

Exp. 1
a)
■ F_T ○ H_{Ar}
3.0
2.5
2.0
0.0
mol L⁻¹
0
125
250
Exp. 2
b)
3.0
2.5
2.0
0.0
0
125
250
Exp. 3
c)
3.0
2.5
2.0
0.0
mol L⁻¹
0
125
250
Time (min)
Exp. 4
d)
3.0
2.5
2.0
0.0
0
125
250
Time (min)

FIGURE 10

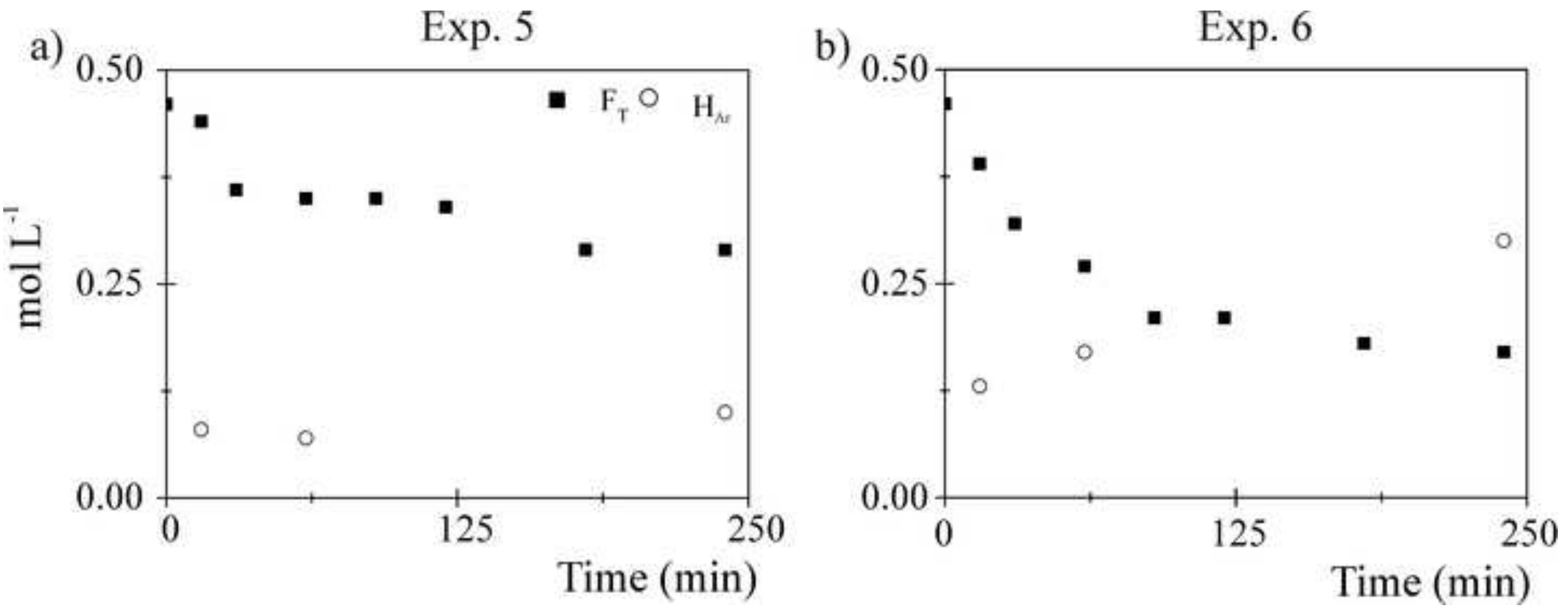

a)
Exp. 5
0.50
0.25
0.00
mol L^{-1}
0
125
250
Time (min)
■ F_T
○ H_{Ar}
b)
Exp. 6
0.50
0.25
0.00
0
125
250
Time (min)

FIGURE 11

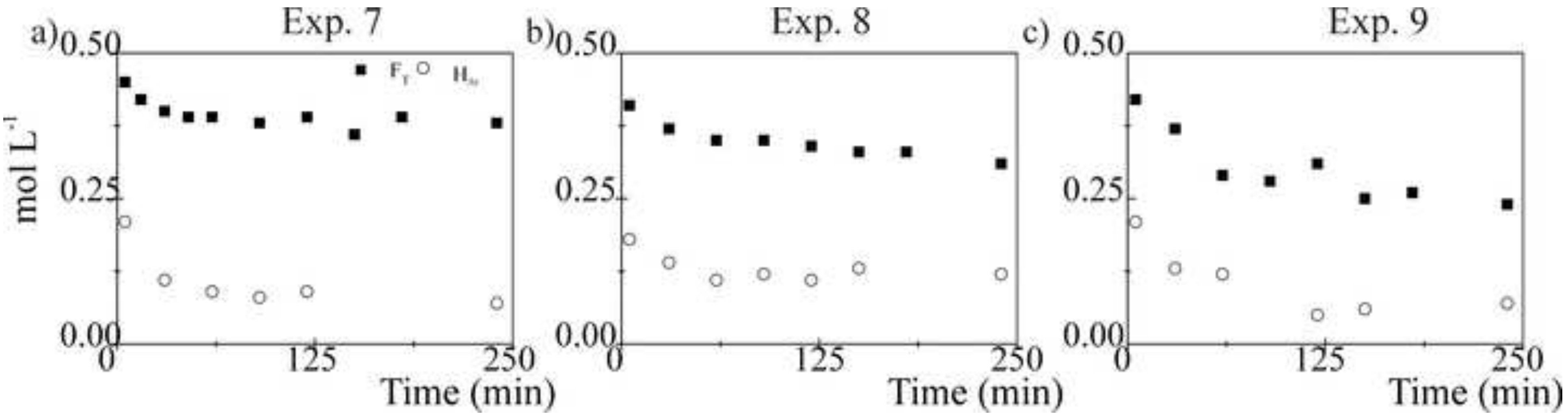


Table 1. Hydroxymethylation reactions: type of lignin, recipes, reaction conditions, and evolution of F_T and $—H_{Ar}$ (concentration in mol L^{-1})

	Exp. 1		Exp. 2		Exp. 3		Exp. 4		Exp. 5		Exp. 6		Exp. 7		Exp. 8		Exp. 9	
Type of Lignin (L):	KL		OL		SL		SL		KL		OL		SL		SL		SL	
Recipe:	$[F_T]^\circ=3.01$ $[-H_{Ar}]^\circ=0.04$ $[-H_2O]^\circ=45.4$ $[F_T]^\circ/[-H_{Ar}]^\circ=75$ $F_T^\circ/L^\circ=1.47$[a]		$[F_T]^\circ=3.00$ $[-H_{Ar}]^\circ=0.05$ $[H_2O]^\circ=46.3$ $[F_T]^\circ/[-[H_{Ar}]^\circ=60$ $F_T^\circ/L^\circ=1.47$[a]		$[F_T]^\circ=3.00$ $[-H_{Ar}]^\circ=0.05$ $[H_2O]^\circ=46.5$ $[F_T]^\circ/[-H_{Ar}]^\circ=60$ $F_T^\circ/L^\circ=1.47$[a]		$[F_T]^\circ=2.99$ $[-H_{Ar}]^\circ=0.05$ $[H_2O]^\circ=47.1$ $[F_T]^\circ/[-H_{Ar}]^\circ=60$ $F_T^\circ/L^\circ=1.47$[a]		$[F_T]^\circ=0.46$ $[-H_{Ar}]^\circ=0.17$ $[H_2O]^\circ=35.4$ $[F_T]^\circ/[H_{Ar}]^\circ=2.7$ $F_T^\circ/L^\circ=0.06$[a]		$[F_T]^\circ=0.46$ $[-H_{Ar}]^\circ=0.13$ $[H_2O]^\circ=35.5$ $[F_T]^\circ/[-H_{Ar}]^\circ=3.5$ $F_T^\circ/L^\circ=0.08$[a]		$[F_T]^\circ=0.46$ $[-H_{Ar}]^\circ=0.19$ $[H_2O]^\circ=36.4$ $[F_T]^\circ/[-H_{Ar}]^\circ=2.4$ $F_T^\circ/L^\circ=0.07$[a]		$[F_T]^\circ=0.42$ $[-H_{Ar}]^\circ=0.20$ $[H_2O]^\circ=33.7$ $[F_T]^\circ/[-H_{Ar}]^\circ=2.1$ $F_T^\circ/L^\circ=0.06$[a]		$[F_T]^\circ=0.43$ $[-H_{Ar}]^\circ=0.21$ $[H_2O]^\circ=35.4$ $[F_T]^\circ/[-H_{Ar}]^\circ=2.0$ $F_T^\circ/L^\circ=0.06$[a]	
Reaction conditions:	T=50 °C pH=11±0.5		T=50 °C pH=11±0.5		T=50 °C pH=11±0.5		T=50 °C pH=9±0.5		T=50°C pH=11±0.5		T=50 °C pH=11±0.5		T=40 °C pH=9±0.5		T=50 °C pH=9±0.5		T=70 °C pH=9±0.5	
Measurements:																		
Time (min)	$[F_T]$	$[—H_{Ar}]$	$[F_T]$	$[—H_{Ar}]$	$[F_T]$	$[F_T]$	$[F_T]$	$[—H_{Ar}]$	$[F_T]$	$[—H_{Ar}]$	$[F_T]$	$[—H_{Ar}]$	$[F_T]$	$[—H_{Ar}]$	$[F_T]$	$[—H_{Ar}]$	$[F_T]$	$[—H_{Ar}]$
0[b]	2.87	0.04	2.71	—[c]	2.98	0.45	2.97	—[c]	0.46	—[c]	0.46	—[c]	0.45	0.21	0.41	0.18	0.42	0.21
15	2.83	—[c]	2.51	—[c]	2.91	—[c]	2.98	—[c]	0.44	0.08	0.39	0.13	—[c]	—[c]	—[c]	—[c]	—[c]	—[c]
30	2.70	—[c]	2.45	—[c]	2.82	0.42	2.96	—[c]	0.36	—[c]	0.32	—[c]	0.42	0.11	0.37	0.14	0.37	0.13
45	2.64	—[c]	2.41	—[c]	2.81	—[c]	2.99	—[c]	—[c]	—[c]	—[c]	—[c]	—[c]	—[c]	—[c]	—[c]	—[c]	—[c]
60	2.60	—[c]	2.43	—[c]	2.75	0.40	2.95	—[c]	0.35	0.07	0.27	0.17	0.40	0.10	0.35	0.11	0.29	0.12
90	2.53	—[c]	2.37	—[c]	2.7	—[c]	2.99	—[c]	0.35	—[c]	0.21	—[c]	—[c]	0.08	0.35	0.12	0.28	—[c]
120	2.55	0.04	2.40	—[c]	2.64	0.39	2.98	—[c]	0.34	—[c]	0.21	—[c]	0.39	0.09	0.34	0.11	0.31	0.05
150	2.60	—[c]	2.39	—[c]	2.70	0.38	2.97	—[c]	—[c]	—[c]	—[c]	—[c]	0.38	—[c]	0.33	0.13	0.25	0.06
180	2.55	—[c]	2.38	—[c]	2.63	0.36	2.98	—[c]	0.29	—[c]	0.18	—[c]	0.36	—[c]	0.33	—[c]	0.26	—[c]
240	2.49	0.04	2.36	—[c]	2.61	0.38	2.99	—[c]	0.29	0.10	0.17	0.3	0.38	0.07	0.31	0.12	0.24	0.07

[a] weight ratio (impure lignin), [b] zero time corresponds to the first measurement, and [c] not measured

Table 2. Cannizzaro reactions: recipes, reaction conditions, and evolution of F_T (concentration in mol L^{-1})

	Exp. A	Exp. B	Exp. C
Recipe:			
	$[F_T]°=2.98$ $[H_2O]°=35.4$	$[F_T]°=0.46$ $[H_2O]°=45.5$	$[F_T]°=3.00$ $[H_2O]°=50.6$
Reaction conditions:			
	T=50 °C pH=11±0.5	T=50 °C pH=11±0.5	T=50 °C pH=9±0.5
Measumerents:			
Time (min)	$[F_T]$	$[F_T]$	$[F_T]$
0	2.98	0.46	3.01
15	2.96	—[a]	2.99
30	2.92	0.41	3.01
45	2.89	—[a]	2.98
60	2.64	0.41	2.98
90	2.63	0.37	3.01
120	2.64	0.38	2.99
150	2.59	—[a]	3.01
180	2.59	0.38	3.01
240	2.41	0.38	2.98

[a] not measured.

Table 3. Characterization of the studied technical lignins.

		SL	KL	OL
% Moisture		8.89	4.48	3.66
% Ash (dry basis)		23.45	21.67	0.05
% Carbohydrates (dry basis)		13.63	5.16	4.35
% Purity (dry basis)		62.92[a] 62.28[b]	73.17[a] —	95.32[a] —
Composition				
Elemental composition %	C	39.99	49.1	65.34
	H	5.34	3.7	7.99
	N	0.18	0.22	0.26
	S	4.14	1.90	0.72
% phenolic hydroxyls (dry basis)	I	1.37	2.39	0.61
	II	0.1	0.37	0.87
	III	0.03	0.9	2.79
	IV	0.53	0.03	0.18
	Total	2.03	3.69	4.46
	P-OH (I+II) (c)	1.47	2.76	1.48
	P-OH (III+IV) (d)	0.56	0.93	2.97
	(c)/(d) (wt%)	2.6	3.0	0.5
Physicochemical properties				
Solubility	THF	NO	YES	YES
	Water	YES	NO	NO
	NaOH 1 N	YES	YES	YES
	HCl 1 N	YES	NO	NO
$\bar{M}_w$ (g mol^{-1})		5259	2140	2122
$\bar{M}_n$ (g mol^{-1})		1520	1340	842
Dispersity ($\bar{M}_w/\bar{M}_n$)		3.45	1.59	2.12
Degradation temperature (°C)		≈300	≈400	≈400

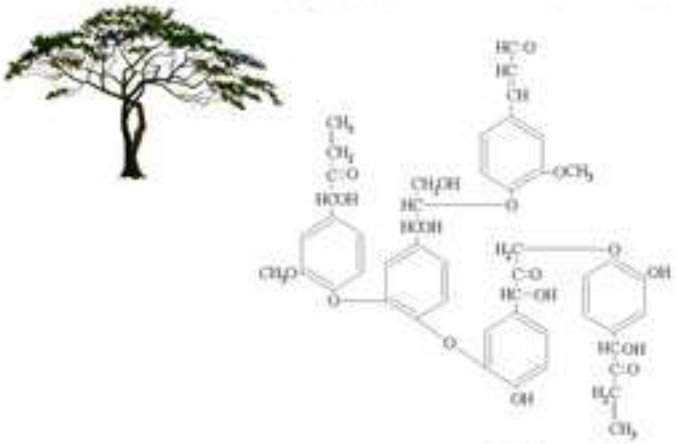
[a] obtained from: 100% -% carbohydrates-% ash (dry basis), [b] obtained by UV-Vis spectroscopy

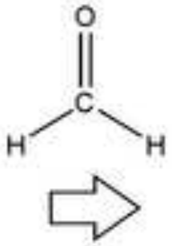
Graphical Abstract

Technical Lignins

Hydroxymethylation

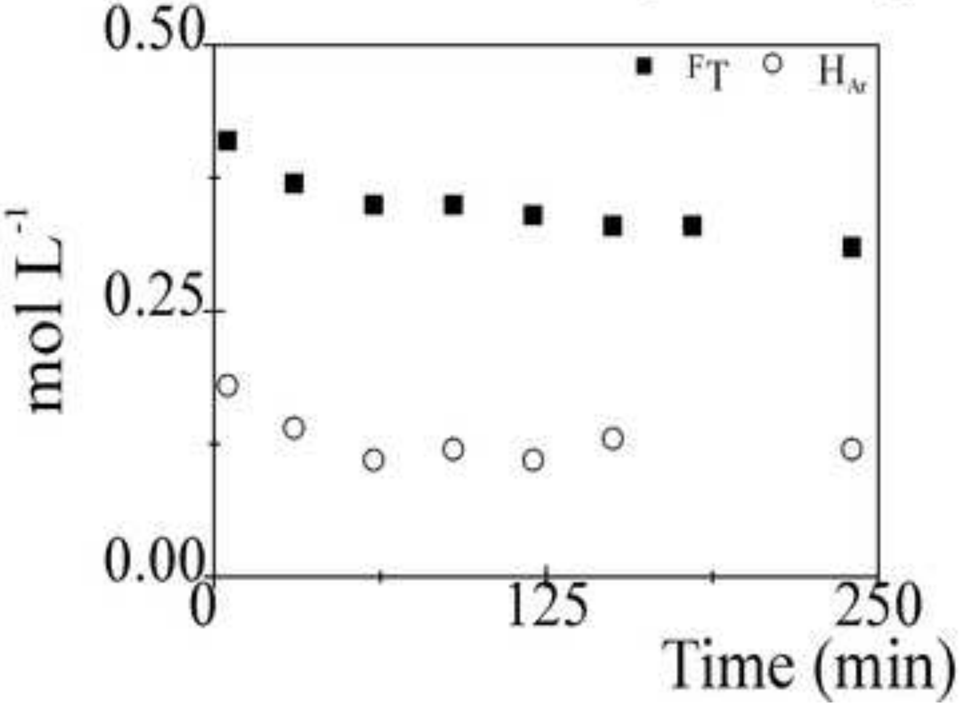
South America





F/L
T
pH

Evolution of F_T and H_{Ar}



Feb 14th, 2019

Subramanian Iyer

Executive Editor

Journal of Applied Polymer science

Thank you for your mail regarding our manuscript “Hydroxymethylation of Technical Lignins from South-American Sources with Potential Use in Phenolic Resins” by M.E. Taverna, F.E. Felissia, M.C. Area, D.A. Estenoz, V.V. Nicolau that was submitted for publication to *Journal of Applied Polymer Science.*

The manuscript now includes all of the last reviewer suggestions.

Hoping that you will now find this final version acceptable for publication, please receive my kind regards,

Prof. Dra. Verónica Nicolau
GPol- UTN Facultad Regional San Francisco

Reviewer #1: The paper still needs major revision before recommendation can be made:

We thank for the comments. We think that the new version of the manuscript has certainly improved with respect to its original.

1. For the claim "Several methods such as hydroxymethylation, phenolation, and demethylation, have been proposed and used to increase the reactivity of the technical lignins" The author should compare the strengths and weaknesses of each method.

As the reviewer requested, the paragraph 7 of *Introduction* Section (previous version) was rewritten in order to compare the strengths and weaknesses of modification methods.

2. The papers with the lignin and cellulose as fillers for making composites and carbon materials need be introduced, cited and properly compared. These should include Fabrication of pH-electroactive Bacterial Cellulose/Polyaniline Hydrogel for the Development of a Controlled Drug Release System, ES Mater. Manuf., 2018, 1, 41-49, www.doi.org/10.30919/esmm5f120; Cellulose Nanocrystals (CNCs) Applications: A Review, Eng. Sci., 2018, 2, 4-16, www.doi.org/10.30919/es.1803302; , J. Colloid Interf. Sci., 2019, 536, 245-251; Induestral & Engingeering Chemistry Research, 2018, 57(1), 231−241; Electrochim. Acta, 2019, 296, 907-915; Biosensors and Bioelectronics, 2019, 123, 167-177; Polymer, 2018, 158, 223-230; J. Colloid Interf. Sci., 2019, 539, 332-341; J. Mater. Chem. C, 2018, 6, 8812 - 8822.

As the reviewer requested, some comments about the use of lignin and biopolymers including cellulose as fillers for making composites and carbon materials was introduced in Paragraph 1 of *Introduction* Section.

3. FIGURE 3. Absorption spectrums of: a) 1 N NaOH solution and b) 12 wt% F solution needs be combined together.

As the reviewer suggested, results related to absorption spectra of NaOH and F solutions were combined in a Figure 3.

4. FIGURE 6. Thermogravimetric analysis: a) TGA, and b) DTG curves, the unit is wrongly provided

As the reviewer noted, the unit was wrong, but it has been corrected.

Please note that the number of references and the citation along the manuscript were modified in the new version of the article following the reviewer's suggestion.