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# Liquefaction of Kraft lignin using polyhydric alcohols and organic acids as catalysts for sustainable polyols production

Silvia Helena Fuentes da Silva, Itziar Egüés, Jalel Labidi*

Chemical and Environmental Engineering Department, University of the Basque Country – UPV/EHU, Plaza Europa 1 – 20018, Donostia-San Sebastián, Spain

* E-mail: jalel.labidi@ehu.es;

## Abstract

In this work, three different organic acid catalysts, (acetic acid, lactic acid and citric acid), are proposed as an alternative to common catalysts used in the liquefaction process of Kraft lignin. These organic acids can be easily obtained from renewable resources and their application as a catalyst could allow the development of more environmentally process in the production of biopolyols. The main objective of the present work was the study of the influence of these organic acids catalysts and their concentration (3%, 6% and 9%, w/w) on the yield and properties of the obtained liquefied products. The results demonstrated that the liquefaction yield of Kraft lignin has not been influenced by the type of the organic catalyst (85-88%). The highest hydroxyl number was obtained with lactic acid at 3% (660.08 mg KOH.g$^{-1}$), whereas acetic acid provided the lowest acid number (0.80 mg KOH.g$^{-1}$). The viscosity varied with catalysts (114.5 - 345.8-mPa.s) and the molecular weights of the liquefied products were in the range of 1459-1990 g.mol$^{-1}$, lower than Kraft lignin (3866 g.mol$^{-1}$). Moreover, volatile compounds showed traces of lignin derivatives and a few intermediate products from solvents. The low lignin signals observed by ATR-IR in the solid residue as well as the obtained liquefaction yields, suggested that most of the Kraft lignin has reacted during liquefaction process. The obtained results showed the potential value of these organic compounds to be used as renewable and more environmentally catalysts in the liquefaction of Kraft lignin.

**Keywords**: Kraft, lignin, liquefaction, organic acids, polyhydric alcohols, biopolyol

## 1. Introduction

In recent decades, the thermochemical conversion of lignocellulosic materials has been the subject of many research works as an alternative to obtaining fuels and chemicals from petrochemical resources. Thermochemical conversion includes gasification, catalytic liquefaction, and pyrolysis (Ong et al., 2018). Among them, catalytic liquefaction provides high conversion yields, low energy consumption and facilitates the application of mild conditions in the transformation process. Therefore, liquefaction of lignocellulosic biomass has converted in a relatively easy and inexpensive thermochemical process to convert biomass into high-value products.

The lignocellulosic materials are mainly constituted by cellulose, hemicellulose and lignin. Its renewable origin, availability and the biodegradability of its components make it a promising natural resource. Lignin is the only aromatic compound with phenolic properties widely available in nature. It is generated in millions of tons as a byproduct in pulping processes. Especially, lignosulfonate lignin is one of the most accessible lignin in the pulp and paper industry, where Kraft lignin accounts about 85% of the total lignin production in the world (Chen, 2015). This lignin together with hemicelluloses, which are present in black liquor, are combusted in a recovery boiler to provide heat to the pulp mill (Ong et al., 2018). However, this consists of a relatively low-value approach (Vale et al., 2019).Therefore, novel processing methods and product concepts are required to increase the use of Kraft lignin as a raw material for higher value materials production (Zhou, 2014). In this context, the valorization of this lignin and its transformation by catalytic liquefaction is of great interest to obtain important renewable and environmentally high added value products, such as biopolyols.

Currently, the commercially available polyols are made from petrochemical sources (Haro et al. 2016). However, the synthesis of biopolyols from renewable resources has increased considerably in the last years. This new trend could be considered as an excellent opportunity for the development of polyols derived from renewable resources and industrial waste byproducts, as Kraft lignin. In fact, lignin based polyols are valuable products that can be used in a broad range of applications, as the production of biodegradable plastics, polyurethane foams, renewable phenolic resins, adhesives, precursors for biomaterials, etc. In literature, biomass derived polyols have been successfully incorporated within polyesters (Kunaver et al., 2010) and polyurethane foams (Vale et al., 2019). Especially, the application of biopolyols in polyurethane application has been of highly interesting research, where they have gained increasing popularity in adhesives, sealants and insulating applications. In the bibliography, many authors demonstrated the potential use of Kraft lignin for the development of more environmentally phenol based resins and foams (Borges da Silva et al., 2009; Li et al., 2019).

In the liquefaction process, the raw material has been mixed with an appropriate solvent in the presence of a catalyst and it is heated to promote depolymerization by dehydration, dehydrogenation, deoxygenation and decarboxylation reactions. Hence, the raw material is broken into smaller fractions, which is transformed into a highly reactive, liquid, and viscous liquefied product rich in hydroxyl groups. Most of the common solvents used in the liquefaction process are simple alcohols such as methanol, ethanol, or less volatile polyhydric alcohols such as polyethylene glycol (PEG) and glycerol (G). In this process, the catalyst plays an important role in the reaction medium of liquefaction, since it allows the use of moderate temperatures and relatively small reaction times (Zhang et al., 2012b). In the acid catalyzed liquefaction process, the reaction temperature was around 110-180 °C, while in the base catalyzed process the temperatures are much higher, around 250 °C (Vale et al., 2019). The use of environmentally friendly technologies will be a key factor for the development of successful sustainable chemical processes in the production of biopolyols by liquefaction.

Sulfuric acid is widely used catalyst combined with polyhydric alcohols in the liquefaction of different wood species, enzymatic hydrolytic lignin and/or recycled newspaper (Budija et al., 2009; Jin et al., 2011; Jo et al., 2015; Kim et al., 2015; Lee and Lee, 2016; Shin et al., 2009; Xu et al., 2012; Zhang et al., 2012a). Preparation of polyols for rigid polyurethane foams was investigated via microwave-assisted liquefaction of lignin using 97 wt% sulfuric acid as catalyst (Xue et al. (2015). In addition, lignin liquefied product catalyzed by sulfuric acid to obtain a polyols with a high content of reactive hydroxyl groups was (Sequeiros et al., 2013). Other authors investigated the application of *p*-toluene sulfonic acid as a catalyst in the liquefaction of ground wood lignin (Jasiukaityte et al., 2010). This catalyst was also applied in the liquefaction of cork powder and eucalyptus bark (Vale et al., 2019). Liquefaction of woody biomass was performed using an acidic ionic liquid as a green catalyst alternative (Lu et al., 2015). On the other hand, most commonly used catalyst in the oxypropylation process was potassium hydroxide (KOH), also in the hydrothermal liquefaction process, where water is used as solvent (D`Souza et al., 2015; Mahmood et al., 2015a). Other authors (Long et al. 2016) studied the effects of hydrothermal liquefaction of the bagasse with different solid alkali catalyst ($MgMn_2$, $MgAlO_{2.5}$, $MgFeO_{2.5}$, $MgZrO_3$, $MgCrO_{2.5}$, $MgNiO_2$). Ross et al. (2010) studied KOH, $Na_2CO_3$ and some organic acids (acetic and formic acids) as catalysts for different microalgae hydrothermal liquefaction. In this work, the authors concluded that the yields were higher using organic acids than alkaline catalysts. In contrast, KOH, NaOH, $H_2SO_4$ and $CH_3COOH$ were used in the hydrothermal liquefaction of microalgae, the yield was better using KOH than other types of catalysts (Muppaneni et al., 2017).

As it can be concluded that the most widely used catalyst in the liquefaction process are based mainly on strong inorganic acids, bases, and alkaline solid metals. In this area, the substitution of inorganic catalysts by renewable organic catalysts results very interesting from the environmental and economic point of view. In fact, the application of organic acids which can be obtained from inexpensive renewable resources as lignocellulosic materials, and their application as alternative catalysts could impulse more sustainable chemical biopolyols production. To the best of our knowledge, there is no information in the literature about lignin liquefaction process using alcohol solvents catalyzed with organic acids under mild reaction conditions.

In the present study, the main effort is focused on the application of renewable derived organic acids as catalysts in the liquefaction process. For that, the synthesis of liquefied Kraft lignin using polyhydric alcohols as solvents and three different renewable organic acids, such as acetic acid, lactic acid and citric acid were studied at mild conditions. Besides that, this work aims to impulse the valorization of industry byproducts as Kraft lignin, for valuable materials production.

This study presents the influence of the concentration and the type of organic catalysts on the yield and properties of the obtained liquefied products. The most important parameters as liquefaction yield, hydroxyl and acid number, pH, viscosity, molecular weight, as well as volatile compounds and structural changes of the liquefied products were discussed. The ATR-IR spectra of solid residues obtained after lignin liquefaction have also been reported.

## 2. Materials and Methods

### 2.1. Materials

Kraft lignin (KL) was precipitated using sulfuric acid (SA) from black liquor provided by CMPC-Cellulose Riograndense (Brazil). Sulfuric acid 96 wt. % technical grade, polyethylene glycol 400 pharma grade (PEG), glycerol 99% PS grade (G) and L(+)-lactic acid PA grade (LA) were supplied by Panreac. Acetic acid HPLC grade was supplied by Scharlau and citric acid analytical grade was provided by Fisher Chemicals.

### 2.2. Liquefaction process

The liquefaction procedure was described in Fig. 1. The liquefaction of Kraft lignin was performed using PEG and G as solvents in a ratio of PEG:G = 80:20 (w/w %), under reflux. Different organic catalysts, such as acetic acid, lactic acid or citric acid, at different concentration load of 3%, 6% or 9% (w/w) with respect to the solvents were used. The catalyst together with the solvents were charged into a glass flask, stirred and heated to 160 ºC. Then, Kraft lignin (15% (w/w %) respect to solvents) was added and the process was kept for 1 h. In the end, the reactor was immediately cooled in a water-ice bath. The obtained mixture was filtered while acetone was constantly added under vacuum. The aim was to facilitate the filtration process and to drag the liquefied product. The remained solid fraction was oven dried at 105 ºC for 24 h and weighted to determine the yield as shown in Eq. 1. Acetone was removed at 49 ºC by rotary evaporator under reduced pressure. All liquefaction experiments were performed in duplicate.

The yield of liquefaction reaction was calculated as follows:

$$Yield = (1 - m/m_0)*100 \qquad (1)$$

where: *Yield* = yield % of liquefied Kraft lignin (%); $m_0$ = amount of lignin used in liquefaction (g); *m* = solid residue of liquefaction (g).

**2.3. Characterization of the liquefied product**

The acid number (*An*) of the liquefied product was determined by titration method according to standard ASTM D974. For that, 1 g of liquefied product was dissolved in 50 mL solvent 1,4-dioxane/water (4:1, v:v ratio). The mixture was titrated with 0.1 M KOH solution in ethanol using a pH meter CRISON (BASIC 20). The required amount of KOH to neutralize one gram of sample was calculated as demonstrated in Eq.2.

$$An = ((C - B)*\mathrm{M}*56.1)/W \qquad (2)$$

where: *An* = acid number (mg KOH.g$^{-1}$); B = volume of the 0.1 M KOH solution in ethanol to titrate the blank sample (mL); C = volume of the 0.1 M KOH solution in ethanol to titrate the sample (mL); M = molarity of the 0.1 M KOH solution in ethanol; 56.1 = molecular weight of KOH; W = amount of sample (g).

The hydroxyl number (*OHn*) of liquefied product was determined according to standard ASTM D4274 (2005). 0.5-1.0 g sample was dissolved in 25 mL of phthalate reagent (115 g of phthalic anhydride dissolved in 700 mL of pyridine), under reflux for 1 h at 115 ºC. Then 50 mL of pyridine was added through the condenser. The mixture was titrated with 2 N sodium hydroxide solution (NaOH) using a pH meter. The hydroxyl number is defined as the amount of KOH in milligram equivalent to the OH content in 1 g of liquefied product (mg $KOH.g^{-1}$). Hydroxyl number was calculated using Eq.3.

$$OH_n = ((B-A)*M*56.1)/W + A_n \quad (3)$$

where: *OHn* = hydroxyl number (mg $KOH.g^{-1}$); A = volume of the 2 N NaOH solution to titrate the sample (mL); B = volume of the 2 N NaOH solution to titrate the blank (mL); M = molarity of 2 M NaOH solution; 56.1 = molecular weight of KOH; W = amount of sample (g); An = acid number $KOH.g^{-1}$.

The viscosity of the liquefied product was determined by a viscometer Fungilab (Alpha Series). Molecular weight distribution was analyzed by Gel Permeation Chromatography (GPC) using a JASCO instrument equipped with an interface (LC-NetII/ADC) and a refractive index detector (RI-2031 Plus). Two PolarGel-M columns (300x7.5 $mm^2$) and PolarGel-M guard (50x7.5 $mm^2$) were employed. The analyses were carried out at 40 ºC and a flow rate of 0.7 $mL.min^{-1}$ using N, N-dimethylformamide (DMF) as eluent. The calibration was made using polystyrene standards (Sigma Aldrich) ranging from 266 to 77.000 $g.mol^{-1}$. The liquefied product (0.025 g) was dissolved in a 5 mL of DMF solution.

The changes in the chemical structure of the lignin after liquefaction process, as well as the chemical characterization of the obtained residues was evaluated by Spectrum Two FT-IR Spectrometer (ATR-IR) with a L1050231 Universal Attenuated Total Reflectance accessory using a Perkin-Elmer instrument with the angle of incidence at 45º. Spectra were recorded over 20 scans with a velocity of 2 $mm.sec^{-1}$ and resolution of 4 $cm^{-1}$ in a wavelength range from 4000 to 400 $cm^{-1}$.

The volatile compounds of the liquefied product were analyzed by Gas Chromatography-Mass Spectrometry (GC-MS). The sample was dissolved in methanol (grade HPLC) and injected in a GC (7890A)-MS (5975C inert MSD with Triple-Axis Detector) Agilent equipped with a capillary column HP-5MS ((5%-Phenyl)-Methylpolysiloxane, 30 m x 0.25 mm), using helium as the carrier gas at a flow rate of 1 mL.min$^{-1}$. The temperature program started at 50 ºC, then the temperature is raised to 120 ºC at 10 C.min$^{-1}$, held 5 min, raised to 280 ºC at 10 C.min$^{-1}$, held 8 min, raised to 300 ºC at 10 C.min$^{-1}$ and held 2 min. Calibration was done (in the range 0-1000 ppm, with 10 different concentrations) using pure compounds (Sigma-Aldrich). Compounds were qualitatively identified by comparison of the retention time and mass spectra with available library data (Agilent Techno.). Quantitation was performed by internal calibration curve and the percentages of additional compounds were calculated by the area normalization method. The quantitative results of the compounds were expressed in ppm units.

## 3. Results and Discussion

The obtained yields of the liquefaction process with different catalysts are shown in Fig.2. In general, the liquefied products showed yields over than 86% with different organic acids. The liquefied product synthesized with 6% (w/w) lactic acid presented the highest yield, about 88.07% and the lowest with 3% (w/w) citric acid, about 85.68%. As shown, the different organic acids used in this work, do not have a significant influence on the yield. In comparison to the literature, where the yield of the liquefaction of Kraft lignin using other common catalysts (acid-based and metal oxide catalysts) was reported around 85.9-95.6% at high temperature (Jin et al., 2018; Wang et al., 2017) the obtained yields using renewable organic acids at mild conditions could be considered as acceptable values.

In Fig.3 the acid number (Fig.3a) and hydroxyl number (Fig.3b) of the liquefied products are reported. The OH groups could be derived from lignin fragmentation and the used solvents. The acid substances can be formed by lignin oxidized subunits, as p-hydroxybenzoate, syringic acid, 5-formyl vanillic acid, among others (El-barbary and Shukry, 2008; Martín-Sampedro et al., 2019). However, the excess of acid groups in the liquefied product can adversely affect its properties. In a polyurethane synthesis, undesirable carboxyl groups may consume isocyanates and catalyst resulting in an unstable reaction and poor properties end-product. In the present work (Fig.3a), the liquefied product obtained using acetic acid showed the lowest amount of acid groups (0.80 mg KOH.g$^{-1}$), followed by lactic acid and citric acid, respectively. It was evident that the presence of three carbonyl groups in the citric acid could contribute to obtaining higher values of *An* (10.70 mg/KOH.g$^{-1}$). In fact, with citric acid at 3% (w/w), the values of *An* were six times higher than those obtained with acetic acid and three times more than the obtained with lactic acid at the same concentration. In addition, the concentration also influences the formation of acid substances. In general, the acid substances increased with catalyst concentration. In this study, all acid values are in agreement with those reported in the literature (Kurimoto et al., 2000; Lee and Lee, 2016; Lou et al., 2013; Tohmura et al., 2005).

In the case of hydroxyl groups, the lowest value of *OHn* in all liquefied products was obtained with 6% (w/w) of catalyst. At 6% (w/w) of catalyst, the acid number increases while the hydroxyl groups are consumed and diminished. This could be due to the dominant reactions such as oxidation of lignin (El-barbary and Shukry, 2008; Yao et al., 1996) and esterification reactions that take place during the liquefaction process, corresponding to dehydration reactions between acidic substances and polyhydric alcohols producing ester and consuming the hydroxyl groups (El-barbary and Shukry, 2008). However, at higher concentration 9% (w/w) these reactions were less outstanding and the hydroxyl groups increased for all catalysts. Among the catalysts, the lactic acid provides the highest value at 3% (w/w) of concentration (660.08 mg KOH.g$^{-1}$). In the studies, hydroxyl values around ~645 to 661 mg KOH.g$^{-1}$ in the liquefaction products prepared by lignin liquefaction using glycerol and polyethylene glycol (Cinelly et al., 2013) ~263 mg KOH.g$^{-1}$ and 811 mg KOH.g$^{-1}$ using the same solvent with sulfuric acid as catalyst (Sequeiros et al., 2013) and ~863 mg KOH.g$^{-1}$ (Xue et al., 2015) were reported. As observed, the OH numbers of the samples reported in this study at the lowest catalyst load are in the same range reported in the literature. The obtained liquefied products in this study could be suitable for the preparation of polyurethane foams, where the required OH groups quantity for this application are in the range between 300 and 800 mg KOH.g$^{-1}$ (Cateto et al., 2009).

The pH, viscosity and molecular weight of the liquefied products synthesized with different organic acids are shown in Table 1. As mentioned, the type of catalyst did not influence strongly the pH of the liquefied products, which slightly varied from pH= 4.25 (L9) to pH= 5.68 (A3). However, the type of catalyst influenced the viscosity of the products. The highest and lowest viscosity were found using citric acid at 9% (C9 = 345.8 mPa.s) and at 3% (114.5 mPa.s), respectively. The lactic acid as liquefaction catalyst provided liquefied products with a more homogeneous viscosity, ranging from 148.8 mPa.s (L9) to 160.3 mPa.s (L3) and as also with acetic acid, whose viscosity varied between 118.0 (A3) and 156.8 (A6). Polyurethane films were obtained using liquefied wood with different viscosities, from 0.33 to 31.6 Pa.s (330 to 31,600 mPa.s, respectively)

(Kurimoto et al., 2000). Viscosities of polyols below 300 Pa.s were shown as adequate for polyurethane foams preparation (Cateto et al., 2009).

In Fig.4 the molecular weight distribution of the liquefied products is presented. It is possible to verify that all liquefied products have a similar molecular weight distribution, which is noticeably different from precipitated Kraft lignin. All GPC chromatograms showed a small shoulder ranging from 5127 to 8180 g.mol$^{-1}$ (21-24 min), a sharp peak range from 530 to 589 g.mol$^{-1}$ (25 min) and another peak varying from 155 to 165 g.mol$^{-1}$ (around 27.5 min) in all samples, in contrast to KL, which showed a very large molecular weight tail. As expected, all Mw were lower than precipitated Kraft lignin (3866 g.mol$^{-1}$), this indicated the effect of liquefaction process on the depolymerization of Kraft lignin. The lowest average molecular weight was verified at 3% (w/w) of concentration and the highest average molecular weight was determined at 9% (w/w) of citric acid.

The structural changes of the Kraft lignin and liquefied products were verified by ATR-IR spectra (Fig. 5). All liquefied products spectrums showed a similar profile. The broad band at 3400 cm$^{-1}$ corresponds to O-H stretching vibration of hydroxyl groups. The band at 2870 cm$^{-1}$ was attributed to vibrations of aliphatic C-H bonds of methylene mainly due to the solvents and methyl groups (Jin et al., 2011). The intensity of these bands were increased in liquefied products comparing with the Kraft lignin. This could be due to the fragmentation of lignin and the structure of the solvents (Jin et al., 2011). The absorption at 1709 cm$^{-1}$ was assigned to C=O stretching of carbonyl and carboxyl groups (Budija et al., 2009; Kobayashi et al., 2004). On the other hand, the decrease of the absorption peak of C–O in phenol hydroxyl groups (shifted at 1220 cm$^{-1}$), could indicated that the phenol hydroxyl of phenylpropane structure in lignin had participated in the liquefaction reaction (Jin et al., 2011). The bands presented in Kraft lignin at 1600 and 1510 cm$^{-1}$ were assigned to the skeletal vibrations of the benzene ring (Jin et al. 2011). On the other hand, the sharp band observed around ~1093 cm$^{-1}$ could be due to the C-O-C ether groups (Barnés et al., 2017). Their intensity suggest that the obtained liquefied products with organic acids may be a polyether (Gosz et al., 2018). The peak at 885 cm$^{-1}$ is ascribed to aromatic C-H out-of-plane deformation of the used lignin (Azadfar et al., 2015).

The ATR-IR spectra of solid residues obtained after lignin liquefaction is shown in Fig.6. As expected, the intensity in the hydroxyl region (~3294 cm$^{-1}$) was drastically reduced and the typically peaks corresponding to methylene and methyl groups (at 2870 cm$^{-1}$) disappeared. However, a strong peak at 1109 cm$^{-1}$ and another moderate peak at 613 cm$^{-1}$ were observed, which corresponds to polyethylene glycol. Besides that, traces of lignins can be seen due to weak bands observed at 1635–1592 cm$^{-1}$, 1457 cm$^{-1}$ and 1322 cm$^{-1}$ (Faix, 1991; Hussin et al., 2013). No appreciable difference was observed between the different residues, with neither the concentration nor the type of catalyst used. The low intensity of these peaks and the obtained yields in the liquefaction process suggest that most of the lignin reacted with solvents during liquefaction.

Organic compounds of the liquefied products were characterized by GC-MS. The identified compounds (with more than 0.2% of the total area, defined as the area for each peak of the chromatogram related to the total area) are shown in Table 2. In Fig.7, the percentage area of each compounds is depicted. However, other compounds (~25) could not be determined because of their low percentage. As expected, the identified compounds were obtained mainly from solvents (polyethylene glycol and glycerol), while others corresponds to lignin-derived compounds such as alcohols, ethers, aldehydes, ketones, and phenolics groups (Table 2 and 3). The presence of some polyhydric alcohols and their derivatives such as glycerin, hexagol, 2-[2-[2-[2-[2-[2-(2-hydroxyethany)ethoxy] ethoxy] ethoxy] ethoxy] ethoxy] ethoxy]ethanol, and 2-[2-[2-[2-

[2-[2-[2-[2-(2 hydroxyethany)ethoxy]ethoxy] ethoxy] ethoxy] ethoxy]ethoxy] ethoxy]ethanol may indicate that polyhydric alcohols not only acts as a solvent but also can enhance the liquefaction of Kraft lignin with its intermediate products (Lu et al., 2015).

With the attempt to identify other compounds, the liquefied products were analyzed quantitatively (calculated by the area normalization method, ppm units) using GC-MS and the standards in the mass spectra database. Table 3 shows that beyond glycerin and acetosyringone mentioned above, other compounds derived from guaiacyl and syringyl units were found, such as acetovanillone, syringol, and syringaldehyde, respectively. The obtained low quantitative content of lignin derivatives (shown as very low chromatogram area in Fig. 5 and the results of the Table 3 indicates that most lignin were depolymerized and reacted with the solvents.

## 4. Conclusions

This study evaluated the potential of three different renewable organic acids as catalyst for the liquefaction process to develop more environmentally friendly process in the production of biopolyols. The present work reports the liquefaction of Kraft lignin catalyzed with acetic acid, lactic acid and citric acid under atmospheric pressure. The obtained yields were similar to related works, ranging between 85 and 88%. The liquefied products showed acid number less than 10.07 mg KOH.g$^{-1}$ and hydroxyl groups up to 660.08 mg KOH.g$^{-1}$. The molecular weight of the products was in the range of 1459-1990 g.mol$^{-1}$. The chemical structure and volatile compounds showed traces of lignin derivatives and a few intermediate products from solvents. The studied organic acids in the present work, showed their potential value to be used as catalysts in the liquefaction process, being renewable and environmentally friendly reagents.

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## References

1. ASTM D4274-05, 2005. Standard Test Method for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols. ASTM International, Pennsylvania, United States of America.
2. ASTM D974, 1964. Standard method of test for acidity of petroleum products. IP139/64.
3. Azadfar, M., Gao, A.H., Bule, M.V., Chen, S., 2015. Structural characterization of lignin: A potential source of antioxidants guaiacol and 4-vinylguaiacol. Int. J. Biol Macromol. 75, 58-66.
4. Barnés, M.C., Visser, M.M., Rossum, G., Kersten, S.R.A., Lange, GP., 2017. Liquefaction of wood and its model components. J. Anal. Appl. Pyrolysis, 125, 136-143.
5. Borges da Silva, E.A., Zabkova, M., Araújo, J.D., Cateto, C.A., Barreiro, M.F., Belgacem M.N., Rodrigues, A.E., 2009. An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin. Chem. Eng. Res. Des. 87, 1276-1292.

6. Budija, F., Tavzes, C., Zupancic-Kralj, L., Petric, M., 2009. Self-crosslinking and film formation ability of liquefied black poplar. Bioresour. Technol. 100(13), 3316-3323.
7. Cateto, C.A., Barreiro, M.F., Rodrigues, A.E., Belgacem, M.N., 2009. Optimization study of lignin oxypropylation in view of the preparation of polyurethane rigid foams. Ind. Eng. Chem. Res., 48, 2583-2589.
8. Chen, H., 2015. Lignocellulose biorefinery feedstock engineering, in: Chen, H. (Eds.), Lignocellulose Biorefinery Engineering Principles and Applications. Woodhead Publishing, UK, pp. 37-86.
9. Cheng, S., D'cruz, I., Wang, M., Leitch, M., Xu, C., 2010. Highly efficient liquefaction of woody biomass in hot-compressed alcohol- water co-solvents. Energy Fuels, 24(9), 4659-4667.
10. Cinelli, P., Anguillesi, I., Lazzeri, A., 2013. Green synthesis of flexible polyurethane foams from liquefied lignin. Eur. Polym. J. 49, 1174-1184.
11. D`Souza, J., George, B., Camargo, R., Yan, N., 2015. Synthesis and characterization of bio-polyols through the oxypropylation of bark and alkaline extracts of bark. Ind. Crops Prod. 76, 1-11.
12. El-barbary, M. H. and Shukry, N., 2008. Polydrydric alcohol liquefaction of some lignocellulosic agricultural residues. Ind. Crops Prod. 27(1), 33-38.
13. Faix, O., 1991. Classification of lignins from different botanical origins by FT-IR spectroscopy. Holzforschung, 45, 21-27.
14. Gosz, K., Kosmela, P., Hejna, A., Gajowiec, G., Piszczyk, L., 2018. Biopolyols obtained via microwave-assisted liquefaction of lignin: structure, rheological, physical and thermal properties. Wood Sci. Technol. 52, 599-617.

15. Haro, J.C., Rodríguez, J.F., Pérez, Á., Carmona, M. 2016. Incorporation of azide groups into bio-polyols. J. Clean Prod. 138, 77-82.

16. Hussin, M.H., Rahim, A.A., Ibrahim, M.N.M., Brosse, N., 2013. Physicochemical characterization of alkaline and ethanol organosolv lignins from oil palm (*Elaeis guineensis*) fronds as phenol substitutes for green material applications. Ind. Crops Prod. 49, 23-32.

17. Jasiukaityte, E., Kunaver, M., Crestini, C., 2010. Lignin behaviour during wood liquefaction—characterization by quantitative 31 p, 13 c NMR and size-exclusion chromatography. Catal. Today, 156(1), 23-30.

18. Jin, L., Li, W., Liu, Q., Wang, J., Zhu, Y., Xu, Z., Wei, X., Zhang, Q., 2018. Liquefaction of kraft lignin over the composite catalyst HTaMoO6 and Rh/C in dioxane-water system. Fuel Process. Technol. 178, 62-70.

19. Jin, Y., Ruan, X., Cheng, X., Lü, Q., 2011. Liquefaction of lignin by polyethyleneglycol and glycerol. Bioresour. Technol. 102(3), 3581-3583.

20. Jo, Y.J., Ly, H.V., Kim, J., Kim, S.-S., Lee, E., 2015. Preparation of biopolyol by liquefaction of palm kernel cake using peg# 400 blended glycerol. J. Ind. Eng. Chem., 29, 304-313.

21. Kim, K.H., Jo, Y.J., Lee, C.G., Lee, E., 2015. Solvothermal liquefaction of microalgal tetraselmis sp. biomass to prepare biopolyols by using peg# 400-blended glycerol. Algal Res.12, 539-544.

22. Kobayashi, M. Asano, T., Kajiyama, M., Tomita, B., 2004. Analysis on residue formation during wood liquefaction with polyhydric alcohol. J. Wood Sci. 50, 407-414.

23. Kunaver, M., Jasiukaityte, E., Cuk, N., Guthrie, J.T., 2010. Liquefaction of wood, synthesis and characterization of liquefied wood polyester derivatives. J. Appl. Polym. Sci. 115, 1265-1271.
24. Kurimoto, Y., Takeda, M., Koizumi, A., Yamauchi, S., Doi, S., Tamura, Y., 2000. Mechanical properties of polyurethane films prepared from liquefied wood with polymeric MDI. Bioresour. Technol. 74, 151-157.
25. Lee, Y. and Lee, E.Y., 2016. Liquefaction of red pine wood, pinus densiflora, biomass using peg-400-blended crude glycerol for biopolyol and biopolyurethane production. J. Wood Chem. Technol. 36(5), 353-364.
26. Li, B., Yuan, Z., Schmidt, J., Xu, C., 2019. New Foaming Formulations for Production of Bio-Phenol Formaldehyde Foams using raw Kraft Lignin. Eur. Polym. J. 111, 1-10.
27. Long, J., Li, Y., Zhang, X., Tang, L., Song, C., Wang, F., 2016. Comparative investigation on hydrothermal and alkali catalytic liquefaction of bagasse: Process efficiency and product properties. Fuel, 186, 685-693.
28. Lou, X., Hu, S., Zhang, X., Li, Y., 2013. Thermochemical conversion of crude glycerol to biopolyols for the production of polyurethane foams. Bioresource technology, 139, 323-329.
29. Lu, Z., Fan, L., Wu, Z., Zhang, H., Liao, Y., Zheng, D., Wang, S., 2015. Efficient liquefaction of woody biomass in polyhydric alcohol with acidic ionic liquid as a green catalyst. Biomass and Bioenerg. 81, 154-161.
30. Mahmood, N., Yuan, Z., Schmidt, J., Xu, C.C., 2015a. Hydrolytic depolymerization of hydrolysis lignin: Effects of catalysts and solvents. Bioresour. Technol. 190, 416-419.

31. Mahmood, N., Yuan, Z., Schmidt, J., Xu, C.C., 2015b. Preparation of bio-based rigid polyurethane foam using hydrolytically depolymerized kraft lignin via direct replacement or oxypropylation. Eur Polym J. 68, 1-9.
32. Martín-Sampedro, R., Santos, J.I., Fillat, U., Wicklein, B., Eugenio, M.E., Ibarra, D., 2019. Characterization of lignin from Populus alba L. generated as by-products in different transformation processes: Kraft pulping, organosolv and acid hydrolysis. Int. J. Biol. Macromol. 126, 18-29.
33. Miyazawa, T., Fukushima, K., Ideguchi, Y., 1962. Molecular vibrations and structure of high polymers. III. Polarized infrared spectra, normal vibrations, and helical conformation of polyethylene glycol. J. Chem. Phys. 37(12), 2764-2776.
34. Muppaneni, T., Reddy, H.K., Selvaratnam, T., Dandamudi, K.P.R., Dungan, B., Nirmalakhandan, N., Schaub, T., Holguin, F.O., Voorhies, W., Lammers, P., Deng, S., 2017. Hydrothermal liquefaction of cyanidioschyzon merolae and the influence of catalysts on products. Bioresource Technol. 223, 91-97.
35. Ong, B.H.Y., Walmsley, T.G., Atkins, M.J., Walmsley, M.R.W, 2018. Hydrothermal liquefaction of Radiata Pine with Kraft black liquor for integrated biofuel production. J. Clean Prod. 199, 737-750.
36. Ross, A., Biller, P., Kubacki, M., Li, H., Lea-Langton, A., Jones, J., 2010. Hydrothermal processing of microalgae using alkali and organic acids. Fuel, 89(9), 2234-2243.
37. Sequeiros, A., Serrano, L., Briones, R., Labidi, J., 2013. Lignin liquefaction under microwave heating. J. Appl. Polym. Sci. 130, 3292-3298.
38. Shakooee, F., Yousefpour, M., Tajally, M., 2017. Synthesis and characterization of polymer/nanosilicagel nano-composite. Mech. Adv. Compos. Struct. 4, 1-8.

39. Shameli, K., Ahmad, M.B., Jazayeri, S.D., Sedaghat, S., Shabanzadeh, P., Jahangirian, H., Mahdavi, M., Abdollahi, Y., 2012. Synthesis and characterization of polyethylene glycol mediated silver nanoparticles by the green method. Int. J. Mol. Sci. 13, 6639-6650.
40. Shin, H.J., Kim, C.-J., Kim, S.B., 2009. Kinetic study of recycled newspaper liquefaction in polyol solvent. Biotechnol. Bioproc. E. 14(3), 349-353.
41. Tohmura, S., Li, G., Qin, T., 2005. Preparation and characterization of wood polyalcohol-based isocyanate adhesives. J. Appl. Polym. Sci. 98, 791-795.
42. Vale, M., Mateus, M.M., Galhano dos Santos, R., Nieto de Castro, C., de Schrijver, A., Bordado, J. C., Marques, A. C., 2019. Replacement of petroleum-derived diols by sustainable biopolyols in one component polyurethane foams. J. Clean Prod. 212, 1036-1043.
43. Wang, J., Li, W., Wang, H., Ma, Q., Li, S., Chang, H-m, Jameel, H., 2017. Liquefaction of kraft lignin by hydrocracking with simultaneous use of a novel dual acid-base catalyst and a hydrogenation catalyst. Bioresour. Technol. 243, 100-106.
44. Xu, J., Jiang, J., Hse, C., Shupe, T.F., 2012. Renewable chemical feedstocks from integrated liquefaction processing of lignocellulosic materials using microwave energy. Green Chem. 14(10), 2821-2830.
45. Xue, B.L, Wen, J.L, Sun. R.C., 2015. Producing lignin-based polyols through microwave-assisted liquefaction for rigid polyurethane foam production. Materials 8 (2), 586-599.
46. Yao, Y. Yoshioka, M. Shiraishi, N., 1996. Water-absorbing polyurethane foams from liquefied starch. J. Appl. Polym. Sci. 60, 1939-1949.

47. Zhang, H., Ding, F., Luo, C., Xiong, L., Chen, X., 2012a. Liquefaction and characterization of acid hydrolysis residue of corncob in polyhydric alcohols. Ind. Crop. Prod. 39, 47-51.
48. Zhang, H., Pang, H., Shi, J., Fu, T., Liao, B., 2012b. Investigation of liquefied wood residues based on cellulose, hemicellulose, and lignin. J. Appl. Polym. Sci. 123 (2), 850-856.
49. Zhou, X.F., 2014. Conversion of kraft lignin under hydrothermal conditions. Bioresour Technol. 170, 583-586.

# List of tables

Table 1

| | A3 | A6 | A9 | L3 | L6 | L9 | C3 | C6 | C9 |
|---|---|---|---|---|---|---|---|---|---|
| pH | 5.68 | 5.42 | 4.96 | 4.99 | 4.82 | 4.25 | 5.02 | 4.65 | 4.49 |
| Viscosity (mPa.s) | 118.0 | 156.8 | 140.0 | 160.3 | 179.1 | 148.8 | 114.5 | 201.6 | 345.8 |
| Mw (g/mol) | 1570 | 1692 | 1592 | 1575 | 1705 | 1459 | 1561 | 1837 | 1990 |

Table 2

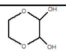
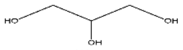
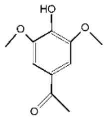
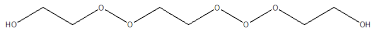
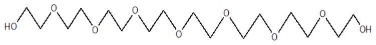
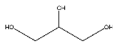
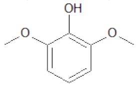
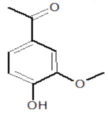
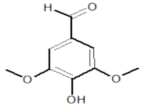
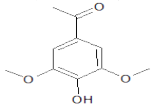
| Nº | Rt (min) | Name of compound | Structure |
|---|---|---|---|
| 1 | 3947 | *p*-Dioxane-2,3-diol |  |
| 2 | 6244 | Glycerin |  |
| 3 | 20487 | Acetosyringone |  |
| 4 | 24052 | Hexagol |  |
| 5 | 26562 | 2-[2-[2-[2-[2-[2-(2-hydroxyethany)ethoxy] ethoxy] ethoxy] ethoxy] ethoxy] ethoxy]ethanol |  |
| 6 | 28850 | 2-[2-[2-[2-[2-[2-[2-(2-hydroxyethany)ethoxy] ethoxy] ethoxy] ethoxy] ethoxy]ethoxy] ethoxy]ethanol |  |

Table 3

| | Glycerol<br>(6244) | Syringol<br>(13968) | Acetovanillone<br>(16895) | Syringaldehyde<br>(19582) | Acetosyringone<br>(20504) |
|---|---|---|---|---|---|
| |  |  |  |  |  |
| | ppm | | | | |
| A3 | 184.40 | 0.71 | 0.20 | 0.15 | 1.01 |
| A6 | 139.38 | 0.35 | 0.15 | | 0.85 |
| A9 | | 0.74 | 0.10 | | 1.05 |
| L3 | | 0.58 | 0.22 | | 1.11 |
| L6 | 139.94 | 0.62 | 0.15 | | 0.76 |
| L9 | 131.27 | 0.64 | 0.15 | | 0.92 |
| C3 | 148.63 | 0.54 | | | 0.82 |
| C6 | 114.19 | 0.53 | | | 0.76 |
| C9 | 93.87 | 0.52 | | | 0.68 |

# List of figures

Fig. 1. Procedure for Kraft lignin liquefaction.

Fig. 2. Effect of organic acids as catalyst on the yield of the liquefied Kraft lignin: A = acetic acid, L = lactic acid, C = citric acid, with 3%, 6% and 9 % (w/w) of concentration. The maximum standard deviation for yield was less than 5%.

Fig. 3. Effect of organic acid catalysts on a) the acid number (mg KOH.g$^{-1}$) and b) hydroxyl number (mg KOH.g$^{-1}$) of the liquefied Kraft lignin: A = acetic acid, L = lactic acid, C = citric acid, at 3%, 6% and 9% (w/w) of loading.

Fig. 4. Molecular weight distribution of liquefied products using organic acids as liquefaction catalyst: A = acetic acid, L = lactic acid, C = citric acid, each one with 3%, 6% and 9% (w/w) of concentration, and KL.

Fig. 5. ATR-IR spectra of liquefied Kraft lignin at 160 ºC and 60 min using different organic acids: A = acetic acid, L = lactic acid, C = citric acid with 3%, 6% and 9% (w/w) of concentration and KL.

Fig. 6. ATR-IR spectra of solid residues obtained after Kraft lignin liquefaction at 160 ºC and 60 min using different organic acids as catalyst: A = acetic acid, L = lactic acid, C = citric acid with 3%, 6% and 9% (w/w) of concentration.

Fig. 7. Area of volatile compounds (%) of liquefied products using organic acids as catalyst: A = acetic acid, L = lactic acid, C = citric acid with 3%, 6% and 9% (w/w).

Figure 1

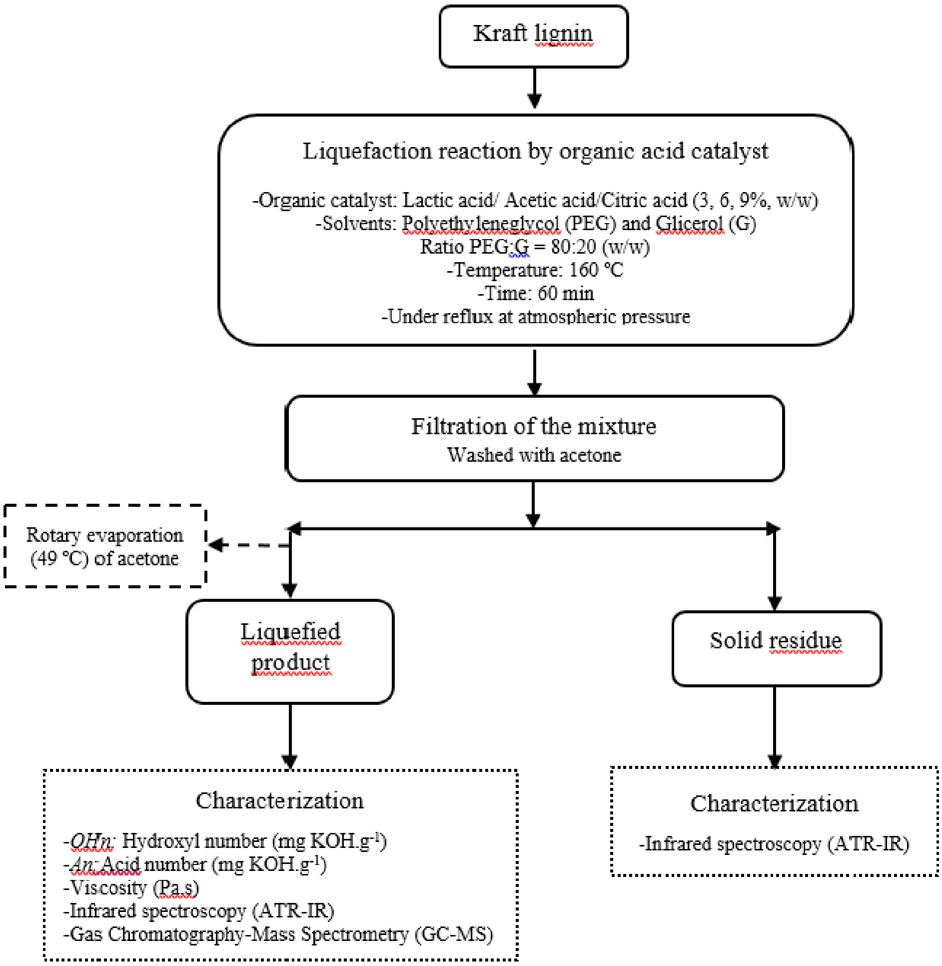

Kraft lignin
Liquefaction reaction by organic acid catalyst
-Organic catalyst: Lactic acid/ Acetic acid/Citric acid (3, 6, 9%, w/w)
-Solvents: Polyethyleneglycol (PEG) and Glicerol (G)
Ratio PEG:G = 80:20 (w/w)
-Temperature: 160 °C
-Time: 60 min
-Under reflux at atmospheric pressure
Filtration of the mixture
Washed with acetone
Rotary evaporation (49 °C) of acetone
Liquefied product
Solid residue
Characterization
-OHn: Hydroxyl number (mg KOH.g-1)
-An: Acid number (mg KOH.g-1)
-Viscosity (Pa.s)
-Infrared spectroscopy (ATR-IR)
-Gas Chromatography-Mass Spectrometry (GC-MS)
Characterization
-Infrared spectroscopy (ATR-IR)

Figure 2

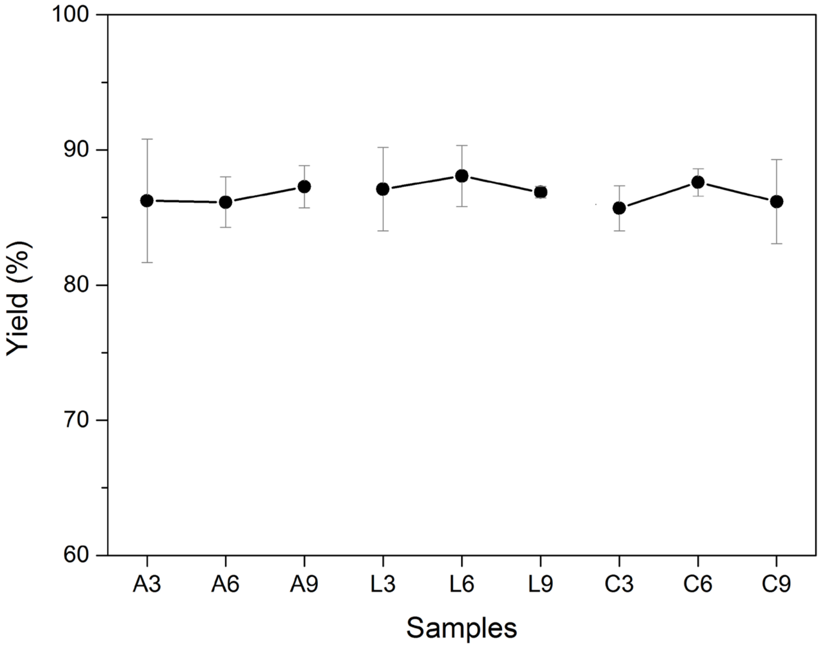


Figure 3

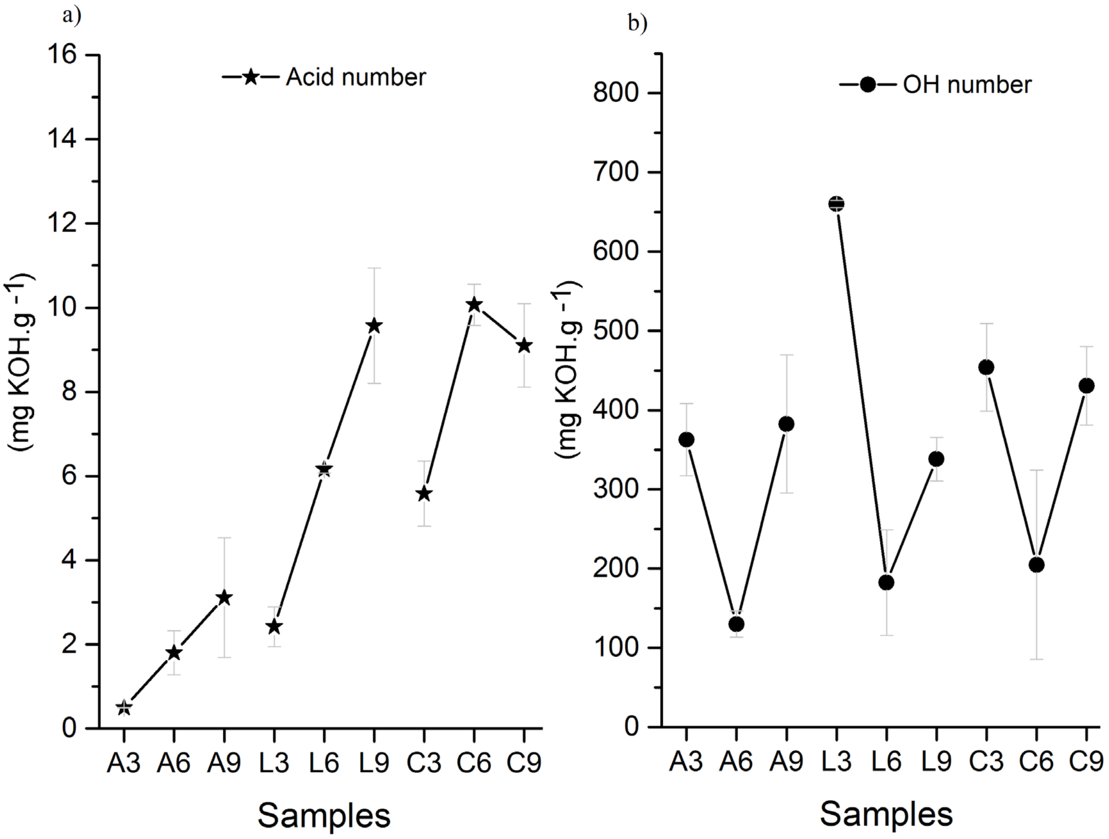
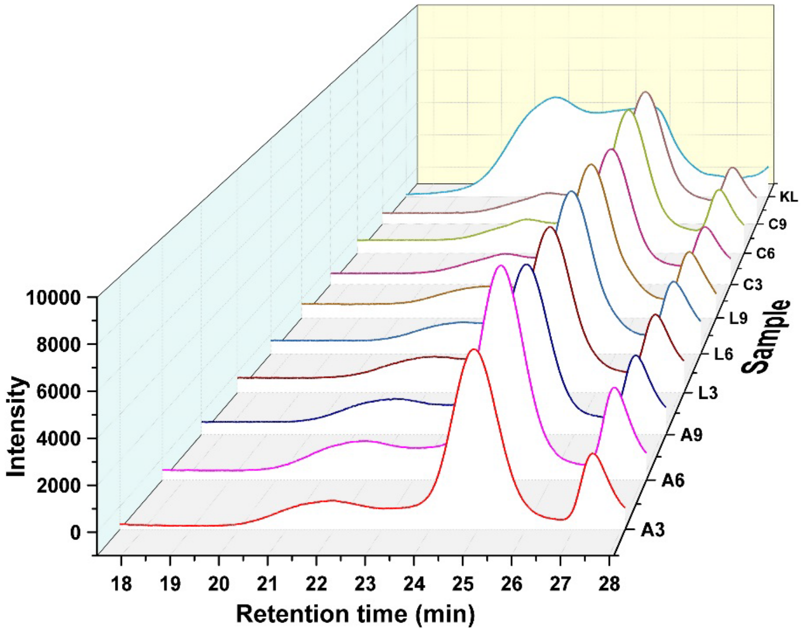

a)
Acid number
(mg KOH.g $^{-1}$)
0
2
4
6
8
10
12
14
16
A3
A6
A9
L3
L6
L9
C3
C6
C9
Samples
b)
OH number
(mg KOH.g $^{-1}$)
0
100
200
300
400
500
600
700
800
A3
A6
A9
L3
L6
L9
C3
C6
C9
Samples

Figure 4



Intensity
10000
8000
6000
4000
2000
0
18
19
20
21
22
23
24
25
26
27
28
Retention time (min)
Sample
A3
A6
A9
L3
L6
L9
C3
C6
C9
KL

Figure 5

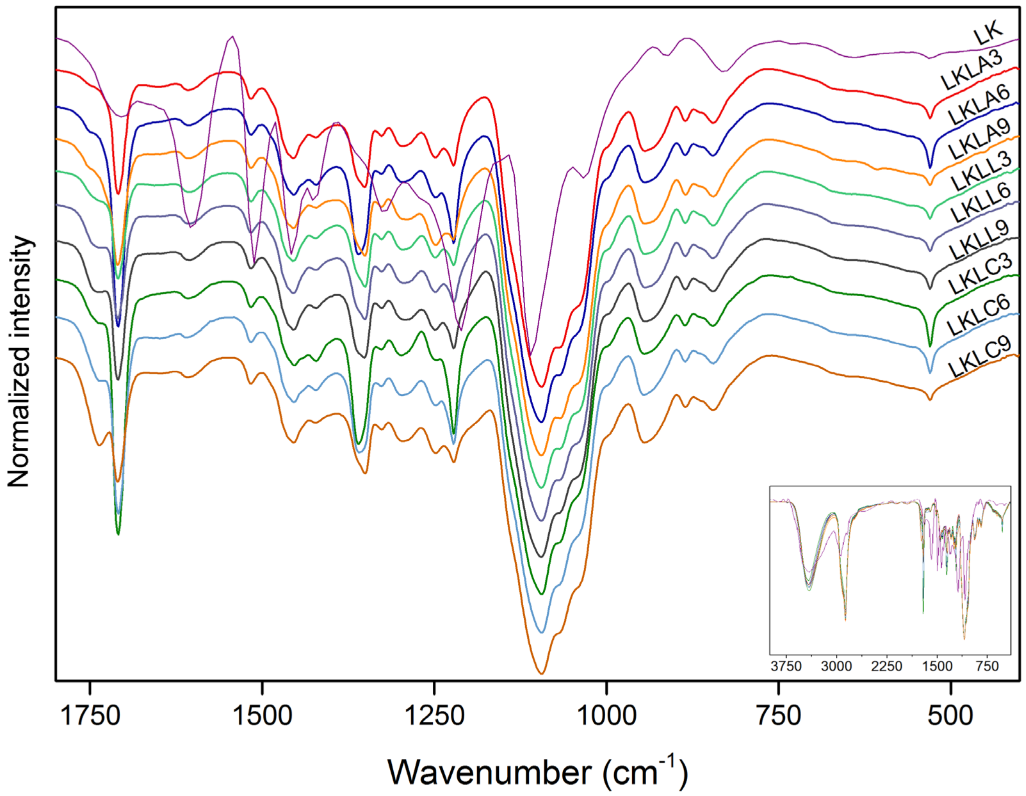

LK
LKLA3
LKLA6
LKLA9
LKLL3
LKLL6
LKLL9
LKLC3
LKLC6
LKLC9
Normalized intensity
1750
1500
1250
1000
750
500
Wavenumber (cm$^{-1}$)
3750
3000
2250
1500
750

Figure 6

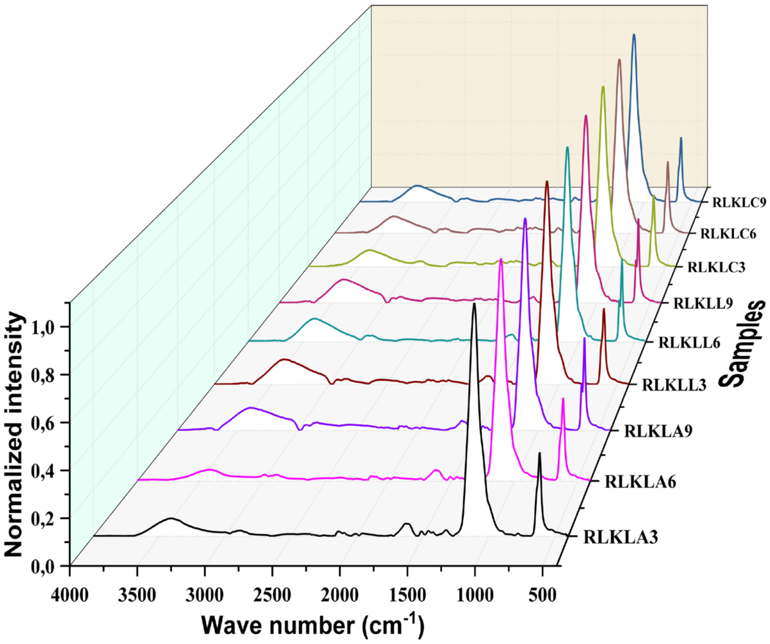
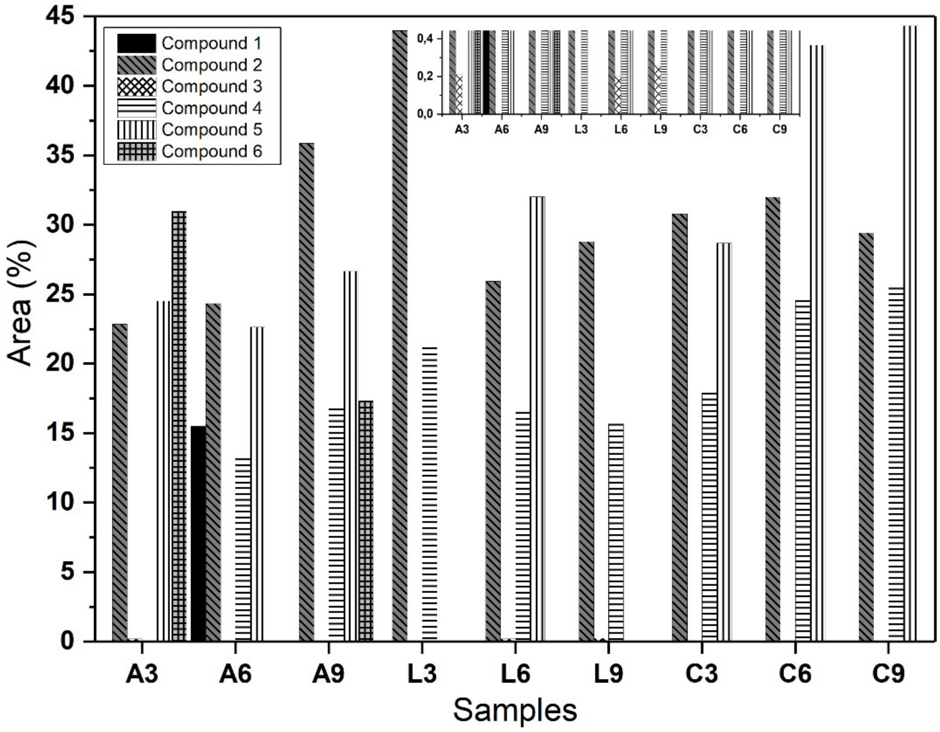

Normalized intensity
1,0
0,8
0,6
0,4
0,2
0,0
4000
3500
3000
2500
2000
1500
1000
500
Wave number (cm$^{-1}$)
Samples
RLKLC9
RLKLC6
RLKLC3
RLKLL9
RLKLL6
RLKLL3
RLKLA9
RLKLA6
RLKLA3

Figure 7


Compound 1
Compound 2
Compound 3
Compound 4
Compound 5
Compound 6
Area (%)
Samples
0
5
10
15
20
25
30
35
40
45
A3
A6
A9
L3
L6
L9
C3
C6
C9
0,0
0,2
0,4