

Lignin Liquefaction under Microwave Heating

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ABSTRACT: Organosolv lignin from olive tree pruning was subjected to liquefaction under microwave heating and modifying the experimental conditions (time, temperature, and concentration of catalyst) according to an experimental design. The organosolv lignin and obtained polyols were characterized using attenuated-total reflection infrared spectroscopy (ATR-IR), thermogravimetric analysis (TGA), gel permeation chromatography, and another parameter such as the hydroxyl number (I_{OH}). The ATR-IR and the TGA results showed that the solvents (polyethylene glycol #400 and glycerol) reacted with the lignin being present in the final product. The optimal polyol showed a liquefaction yield of 99.07% that was obtained in 5 min of reaction at 155°C with 1% of sulphuric acid. The liquefaction product showed a hydroxyl number of 811.8 mg KOH/g, suitable to be used as a precursor in polyurethane foam synthesis. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

KEYWORDS: biopolymers & renewable polymers; cellulose and other wood products; properties and characterization

Received 29 December 2012; accepted 20 May 2013; Published online

DOI: 10.1002/app.39577

INTRODUCTION

In a world that is based on the petroleum, lignocellulosic biomass (wood, agricultural, and forestry residues, etc.) represents a renewable source of various products and chemicals. The main constituents of lignocellulosic biomass (lignin, cellulose, and hemicelluloses) are fractionated in the so-called biorefineries. Cellulose and hemicelluloses are polysaccharides and structural components of the cell wall. Lignin has a complex aromatic structure and acts as cementing material that holds together the fibers and provides structural rigidity to the material.

Nowadays, lignin is a residue of paper industry that is burned for the production of energy. Nevertheless in the last few years the chemical modification of lignin for its use in the preparation of polyurethanes, acrylates, epoxies, polymer blends, and composites has received considerable attention.^{1–3}

Liquefaction is regarded as an efficient way to convert the biomass into polyols with high content of reactive hydroxyl groups. This process is usually carried out at high temperatures with the use of reagents and catalysts with sufficient reactivity toward biomass components. In most reported researches, liquefaction reagent such as phenol⁴ and various glycols^{5–7} are used in conjunction with strong acids as catalysts. The latter have been used as polyols in polyurethane foam preparation⁸ and as components of adhesives.^{9–11}

The liquefaction with organic solvents is usually carried out with conventional external heating systems such as water, oil, salt bath, fluidized sand bath, and electrical furnace.^{12–15} These heating systems are relatively slow and heat is not transfer efficiently due to the dependence on the conductivity. The use of microwave systems is emerging as an alternative heating mode allowing to achieve fast heating in the bulk material.¹⁶

In this work organosolv lignin from olive tree pruning was liquefied under microwave heating by using glycerol and polyethylene glycol (PEG) 400 as solvents and an acid catalyst (sulphuric acid) to produce polyols with high content of reactive hydroxyl groups that can be used as precursors in biomaterials.

Glycerol has three hydrophilic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. Its chemical structure and properties make of glycerol a quite suitable solvent for olive organosolv lignin liquefaction. The huge amount of glycerol as side product is produced from the transesterification of oil with methanol in the biodiesel production. Considering that glycerol is a commodity chemical widely used by pharmaceutical industry, the availability of glycerol has led to excessive supply and devaluation in the market price.^{17,18} Therefore, the use of glycerol as secondary reagent in organosolv lignin liquefaction would be opens the door for a new market of glycerol.

Based on the above, organosolv lignin from olive tree pruning was subjected to liquefaction using microwave heating and

modifying the experimental conditions according to an experimental design. This design was used to obtain the optimal experimental conditions to produce polyol with maximum liquefaction yield and good properties (OH number between 300 and 800 mg KOH/g and a viscosity below 300 Pa*s) which make the polyol suitable as a precursor in polyurethane foam synthesis¹⁹ and adhesive component. Organosolv lignin and the obtained polyol were characterized by some instrumental techniques such as attenuated-total reflection infrared (ATR-IR) spectroscopy, thermogravimetric analysis (TGA), and gel permeation chromatography (GPC).

EXPERIMENTAL

Raw Material and Lignin Extraction Process

The raw material was kindly supplied by an independent producer and originated from an olive tree (*Olea europea*) cultivated in Navarra belonging to the variety called Arróniz. It was locally collected and then dried at room temperature. The olive tree pruning was milled in a Retsch 2000 hammer mill to produce 4–6 cm chips free of small stones, dust, and soil. The raw material was characterized according to the standard methods²⁰ and bibliographic procedures. Ash content 1.4% ± 0.5 (TAPPI T211 om-93), ethanol-toluene extractives 12.2% ± 0.5 (TAPPI T 204 cm-97), acid insoluble lignin 24.4% ± 2.3 (TAPPI T22 om-98), holocellulose 51.8% ± 1.0,²¹ α-cellulose 29.3% ± 0.2,²² and hemicelluloses 22.4% ± 1.3.

Olive tree pruning was treated by the organosolv fractionation process. Organosolv treatment consisted in the fractionation of olive tree pruning with an ethanol/water mixture (70:30, v/v) with a solid/liquid ratio of 1 : 6, in a 4 L pressurized reactor (180°C, 90 min) under constant stirring. This reaction conditions were selected in the basis of the previous experiences for ensuring high quality lignin. After the reaction time, the solid fraction was separated from the liquid by filtration and washed to remove residual liquor.

The main physico-chemical properties of obtained liquid fraction were determined according to standard methods: pH = 4.53 was measured with a digital CRISON GLP 22 pH-meter. Density (0.9 g/mL) was determined measuring the weight of the black liquor in a known volume previously weighed and moisture free. Total dissolved solids (7.39%) were measured after keeping a weighed sample at 100°C until constant weight. Inorganic matter (0.04%) was determined after combustion of the sample at 525°C (TAPPI T211 om-93). Organic matter (7.35%) was defined as the difference between total dissolved solids and inorganic matter. Lignin content of liquor (2.91%) was determined by weighting the mass of precipitated lignin from the liquid fraction. Lignin was isolated from organosolv liquor by precipitation by adding two volumes of acidified water²³ after that the solid was centrifuged and oven dried at 50°C.

Liquefaction Under Microwave Heating

In the liquefaction reaction, PEG with an average molecular weight (M_w) of 400 and glycerol (G) were used as solvents and sulphuric acid 98 % (AS) as the catalyst. All used chemicals were reagent grade supplied by Panreac Company. PEG # 400 was chosen among other average molecular weight PEG because

liquefaction efficiency reached the highest of 97% and was more beneficial for the process.²⁴

A mixture of PEG #400 and glycerol (80/20 w/w) was used as solvent in the liquefaction process with different temperatures, times, and catalyst concentrations. The liquefaction reactions were carried out in CEM Microwave Discover System Model. The microwave system was a temperature-controlled instrument with an internal temperature sensor.

Microwave power was applied in order to heat the reaction mixture until reaching the desired temperature, residence time, and cooling time was defined using the microwave system software. There was constant stirring during the time of the microwave activation. A typical workout procedure for the experiments was as follows: organosolv lignin, solvent ratio was 15/85 w/v which contained a percentage of sulphuric acid as a catalyst; they were loaded into the reaction vessel. After the liquefaction time, the pressurized vessel was immersed in cold water and could safely be opened after 15 min.

After cooling the liquefaction product was diluted with dioxane/water (80/20 v/v) and filtered to remove remaining solids which were dried to constant mass. The liquefaction yield (η) was calculated as the weight percent based on the starting sample material by the eq. (1):

$$\eta = \left[1 - \frac{M}{M_0} \right] \times 100 \quad (1)$$

where M_0 is the mass of initial organosolv lignin and M is the mass of the residue insoluble in dioxane/water obtained after the liquefaction process.

Experimental Design

The applied model uses a series of points (experiments) around central one and several additional points to estimate the first and second order interaction terms of a polynomial. The design meets the general requirement that it allowed all parameters in the mathematical model to be estimated with a relatively small number of experiments.²⁵

Experimental data were fitted to the following second order polynomial model:

$$Y = a_0 + \sum_{i=1}^n b_i X_{ni} + \sum_{i=1}^n c_i X_{ni}^2 + \sum_{i=1; j=1}^n d_{ij} X_{ni} X_{nj} \quad (i < j) \quad (2)$$

where

$$X_n = 2 \frac{X - X}{X_{\max} - X_{\min}} \quad (3)$$

Y is the dependent variables (liquefaction yield and OH number), X_n are the independent variables (X_T temperature, X_t time, and X_C catalyst concentration) normalized from -1 to $+1$ and a_0 , b_i , c_i , and d_{ij} are constants. X is the experimental value of the variable concerned; X is the middle point of the variation range value for the variable in question; and X_{\max} and X_{\min} are the maximum and minimum values of such a variable.

The X_n were normalized in order to facilitate direct comparison of the coefficients and visualization of the effects of the individual independent variables on the response variable.

Experimental results were subjected to regression analysis using the STATGRAPHIC software. The normalized values of independent variables, for the 27 experiments of the experimental design plus two repetitions of the central experiment to measure the method error, are shown in Table 1.

Hydroxyl Number

The hydroxyl numbers²⁶ of the liquefied organosolv lignin were determined as follows: 0.5–1.0 g of sample was dissolved in 25 mL of a phthalation reagent and heated at 115°C, for 1 h under reflux. This was followed by an addition of 50 mL of pyridine through the condenser. The mixture was backtitrated with 0.5 M sodium hydroxide solution. The indicator was 1% phenolphthalein solution in pyridine. The phthalation reagent consisted of 115 g of phthalic anhydride dissolved in 700 mL of pyridine.

The hydroxyl number, defined as mg KOH/g of sample, was calculated as follows:

$$\text{Hydroxyl number} = \frac{(B-A) \cdot M \cdot 56.1}{w} + \text{acid number} \quad (4)$$

Here, A is the volume of the 0.5 M sodium hydroxide solution required for the titration of sample (mL). B is the volume of the sodium hydroxide solution required for the titration of the blank solution (mL). M is the molarity of the sodium hydroxide solution and w is the amount of the sample (g) to be analyzed.

If the sample is acidic, the acid uses the phthalation reagent during the analysis and the hydroxyl number must be corrected

Table 1. Experimental Conditions Applied to the Organosolv Lignin

| Experiment | X_T^a | X_t^b | X_C^c | Experiment | X_T^a | X_t^b | X_C^c |
|------------|---------|---------|---------|------------|---------|---------|---------|
| 1 | -1 | -1 | -1 | 16 | +1 | +1 | +1 |
| 2 | +1 | 0 | +1 | 17 | -1 | -1 | 0 |
| 3 | 0 | -1 | 0 | 18 | +1 | +1 | 0 |
| 4 | -1 | +1 | -1 | 19 | -1 | -1 | +1 |
| 5 | -1 | +1 | 0 | 20 | +1 | 0 | 0 |
| 6 | 0 | 0 | +1 | 21 | 0 | +1 | -1 |
| 7 | +1 | 0 | -1 | 22 | +1 | -1 | +1 |
| 8 | +1 | -1 | 0 | 23 | -1 | 0 | +1 |
| 9 | +1 | -1 | -1 | 24 | 0 | -1 | -1 |
| 10 | 0 | -1 | +1 | 25 | +1 | +1 | -1 |
| 11 | -1 | 0 | 0 | 26 | 0 | +1 | 0 |
| 12 | 0 | 0 | -1 | 27 | 0 | 0 | 0 |
| 13 | -1 | 0 | -1 | 28 | 0 | 0 | 0 |
| 14 | -1 | +1 | +1 | 29 | 0 | 0 | 0 |
| 15 | 0 | +1 | +1 | | | | |

^a X_T : normalized temperature

^b X_t : normalized time

^c X_C : normalized concentration of sulphuric acid.

Ranges: temperature 130–155–180°C, time 5–10–15 min; concentration of sulphuric acid 1–2–3%.

accordingly. The acid number was determined as follows. Total of 0.4 g of sample was weight into a 400 mL Erlenmeyer flask and dissolved in 50 mL of the solvent mixture. The solvent mixture consisted of dioxane and water (4:1 v/v). 0.5 mL of phenolphthalein indicator solution (1 % in ethanol) was added and titrated with 0.1M KOH solution in ethanol, to the equivalent point. The acid number (mg KOH/g of sample) was calculated using the eq. (5):

$$\text{Acid number} = \frac{(C-B) \cdot M \cdot 56.1}{w} \quad (5)$$

Here, C is the titration volume of the potassium hydroxide solution (mL). B is the titration volume of blank solution (mL). M is the molarity of the potassium hydroxide solution, and w is the amount of the sample (g) being analyzed.

Lignin and the Optimized Polyols Characterization

Attenuated-Total Reflection Infrared (ATR-IR) Spectroscopy.

Organosolv lignin and obtained polyols were characterized by ATR-IR spectroscopy by direct transmittance in a single-reflection ATR system (ATR top plate fixed to an optical beam condensing unit with ZnSe lens) with a MKII Golden Gate SPE-CAC instrument. Each spectrum was recorded over 20 scans in the range from 4000 to 800 cm^{-1} , with a resolution of 2 cm^{-1} .

Thermogravimetric Analysis (TGA). Thermal degradation of the samples was studied via a thermogravimetric analysis (TGA), which was carried out in a TGA/SDTA RSI analyzer of Mettler Toledo. The samples of ~5 mg were heated of 25°C up to 800°C at rate 10°C/min, using a constant nitrogen flow as inert atmosphere during the experiment.

Gel Permeation Chromatography (GPC). GPC was used to determine organosolv lignin average molecular weight (M_w). Lignin samples were examined using Jasco system equipped with an interface (CLC-NETII/ACD) and a reflexion detector (RI-2031Plus). Two columns were used, one of them PolarGel (300 × 7.5 mm) and the other one PolarGel-M (50 × 7.5 mm). Dimethylformamid with 1 % of lithium bromide was used as an eluent of the samples as well as the mobile phase. The calibration was made by the use of polystyrene standards.

RESULTS AND DISCUSSION

Organosolv olive tree pruning lignin presented the following composition: acid insoluble lignin 80.3% ± 2.6, acid soluble lignin 3.1% ± 0.2, and total sugars 0.7% (glucose 0.2% ± 0.03 and xylose 0.5% ± 0.01). This lignin presented an average molecular weight of 4252 g/mol with polydispersity of 4.7 (M_w/M_n). The relatively high polydispersity was connected to the possibility of forming C–C bonds between the units; this type of bonds is related to the structures involving C5 in the aromatic ring, guaiacyl-type unit. Guaiacyl-type units are able to form this kind of bonds, so raw materials with high content of guaiacyl-type units are expected to show high fractions of high molecular weight.

Liquefaction Experimental Design

Two dependent variables were considered to follow the liquefaction process, liquefaction yield (%) and OH number (I_{OH})

mgKOH/g). Three independent variables were varied during the liquefaction process under microwave heating: temperature (T) (130, 155, and 180°C), time (t) (5, 10, 15 min) and concentration of sulphuric acid as catalyst (C) (1, 2, and 3%). Temperature and catalyst concentration was established empirically on the bases of previous studies of liquefaction, and time was established given the fact that microwave chemistry is claimed to need shorter times than conventional reactions. All the experiments were carried out with a solvent ratio of 15/85 w/v in base of previous liquefaction works.^{15,18} The results of 29 experiments are shown in Table II.

Applying the software STATGRAPHICS Centurion to the data in the Table II, the following equations that predict the behaviour of the dependant variables were obtained:

$$I_{OH} = 411.158 - 16.6056X_C + 0.462107X_T - 0.478329X_t + 0.410008X_C^2 - 0.637006X_T^2 - 0.321671X_t^2 + 0.15X_CX_T - 0.383333X_CX_t + 0.0151735X_TX_t \quad (6)$$

$$\text{Yield} = 97.9513 - 0.055556X_C + 0.462107X_T - 0.478329X_t + 0.410008X_C^2 - 0.637006X_T^2 - 0.321671X_t^2 + 0.15X_CX_T - 0.383333X_CX_t + 0.0151735X_TX_t \quad (7)$$

Tables III shows the statistical values (Snedecor's F , R^2 , and R^2 -adjusted) for the different terms in the eqs. (6) and (7).

The dependant variable of the hydroxyl number was not taken into account for the experimental design for presenting bad regression values; it was adequate for the OH number to be between 300 and 800 mgKOH/g in view to future applications.

The Figure 1 shows the influence of the time, temperature and the concentration of catalyst on the yield of the liquefaction

Table II. Yield and the Hydroxyl Number of the Experiments of the Experimental Design

| Experiment | Yield (%) | IOH (mg KOH/g) | Experiment | Yield (%) | IOH (mg KOH/g) |
|------------|-----------|----------------|------------|-----------|----------------|
| 1 | 96.7 | 264.2 | 16 | 98.3 | 380.4 |
| 2 | 97.1 | 443.8 | 17 | 96.8 | 749.6 |
| 3 | 97.2 | 351.3 | 18 | 96.8 | 757.5 |
| 4 | 98.0 | 415.9 | 19 | 96.7 | 700.6 |
| 5 | 96.0 | 432.2 | 20 | 96.6 | 273.4 |
| 6 | 99.7 | 667.2 | 21 | 97.1 | 318.3 |
| 7 | 99.9 | 464.4 | 22 | 98.8 | 737.4 |
| 8 | 99.9 | 278.6 | 23 | 97.4 | 493.5 |
| 9 | 97.3 | 746.7 | 24 | 99.1 | 811.8 |
| 10 | 99.3 | 261.3 | 25 | 97.8 | 502.8 |
| 11 | 98.8 | 263.7 | 26 | 97.3 | 457.9 |
| 12 | 97.2 | 441.9 | 27 | 97.6 | 610.8 |
| 13 | 96.9 | 507.5 | 28 | 96.7 | 612.5 |
| 14 | 94.9 | 314.8 | 29 | 95.6 | 821.0 |
| 15 | 96.8 | 175.6 | | | |

and the Figure 2 shows the influence of the time, temperature, and the concentration of catalyst on the hydroxyl number.

Based on the figures above and bearing in mind an hydroxyl number between 300 and 800 mg KOH/g optimal conditions were obtained for the maximum liquefaction yields: 155°C, 5 min, 3% of catalyst (polyol 10) and 155°C, 5 min, 1% of catalyst (polyol 24). Finally, the polyol 24 was selected presenting the highest liquefaction yield and hydroxyl number.

Attenuated-Total Reflection Infrared Analysis (ATR-IR) Spectroscopy

ATR-IR was used to study the structural changes of the lignin after the reaction of liquefaction. Figure 3. shows the spectra of the organosolv lignin and the optimized products of the liquefaction.

In the polyols spectra at 3390 cm^{-1} the vibration caused by the stretching of the O—H group increased remarkably due to the presence of PEG and glycerol. In the lignin spectra the vibration of C—H in the methyl and methylene groups at 2929 and 2830 cm^{-1} , all increased in the polyols spectres.²⁴

The most significant bands in the lignin structure at 1325 cm^{-1} was related to the breathing of the syringyl (S) ring with C—O stretching and at 1218 cm^{-1} was associated to the breathing of the guaiacyl (G) ring with C—O stretching. Also, it was a vibration caused by the deformation of the C—H bond in the syringyl (S) substructure at 1110 cm^{-1} and the characteristic band of the hemicelluloses at 1026 cm^{-1} converted to only one

Table III. Snedecor's F Values for the Obtained Equation in the Experimental Design. R^2 and R^2 -adjusted Values Obtained from the Adjusted Model Eqs. (6) and (7)

| Equation | Snedecor's F | R^2 | R^2 -adjusted |
|------------------|----------------|-------|-----------------|
| I_{OH} | 0.43 | 18.59 | - |
| X_C | -0.34 | | |
| X_T | 0.85 | | |
| X_t | -1.41 | | |
| X_C^2 | 0.05 | | |
| X_T^2 | 0.87 | | |
| X_t^2 | 0.28 | | |
| $X_C \times X_T$ | -0.66 | | |
| $X_T \times X_t$ | 0.12 | | |
| $X_C \times X_t$ | -0.34 | | |
| Yield | 1.02 | 35.15 | 0.82 |
| X_C | -0.19 | | |
| X_T | 1.51 | | |
| X_t | -1.61 | | |
| X_C^2 | 0.79 | | |
| X_T^2 | -1.26 | | |
| X_t^2 | -0.63 | | |
| $X_C \times X_T$ | 0.42 | | |
| $X_C \times X_t$ | -1.07 | | |
| $X_T \times X_t$ | 0.04 | | |

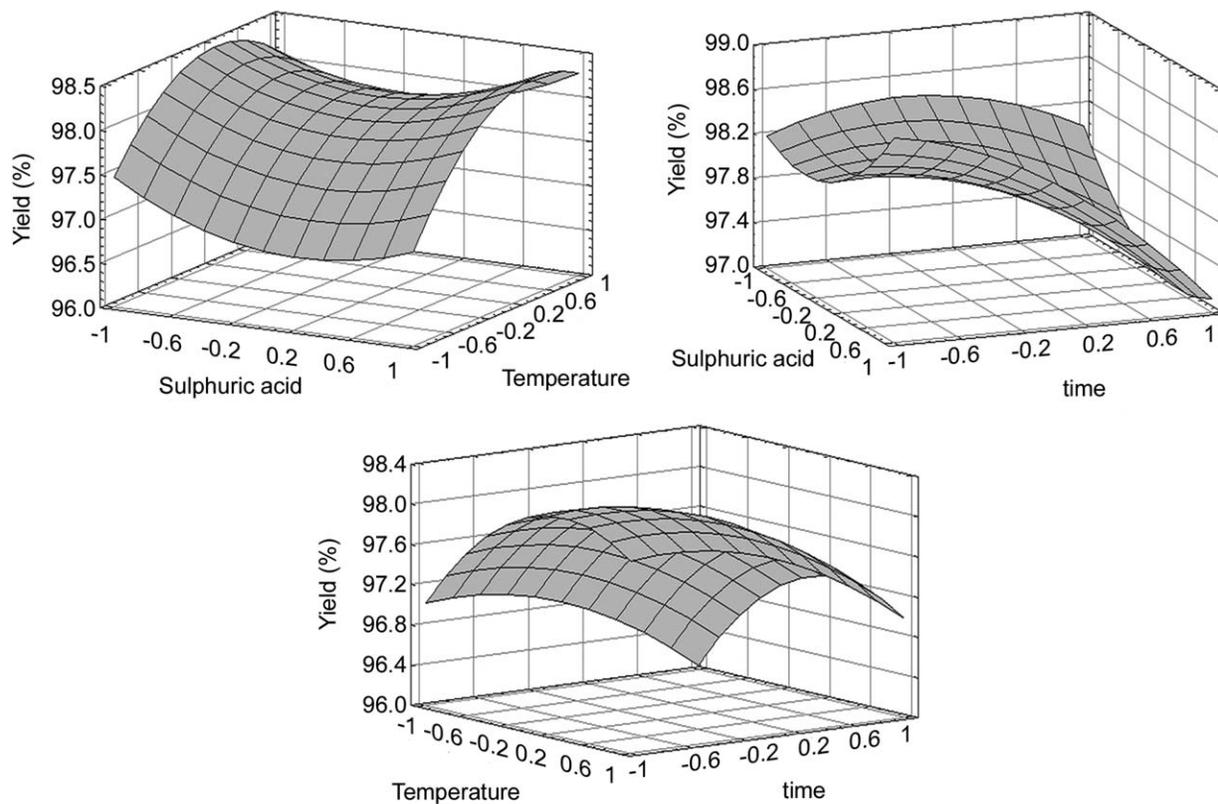


Figure 1. Variation of the liquefaction yield with the temperature, time and the concentration of the catalyst.

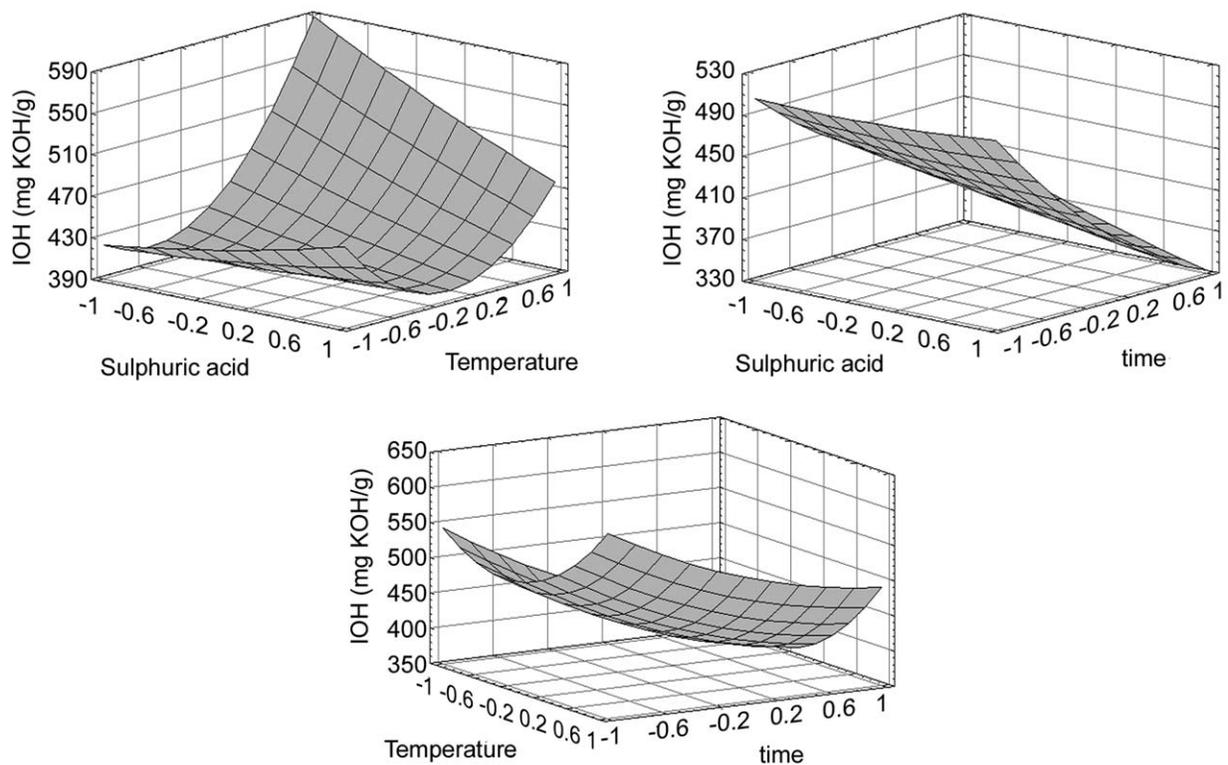


Figure 2. Variation of the hydroxyl number with the temperature, time, and the concentration of catalyst.

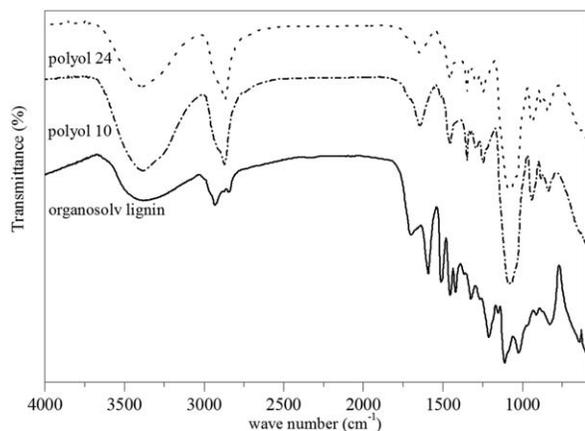


Figure 3. ATR-IR spectra of the polyol 24, 10 and organosolv lignin.

peak at 1097 cm^{-1} of C—O—C stretching of ether which could indicate that the hemicelluloses reacted. In addition, the linkage of C—C of the aromatic skeleton had peaks was around $1600\text{--}1424\text{ cm}^{-1}$ and in the polyols spectra the intensity of these peaks decreased because in the first stage of the liquefaction lignin degraded to lower molecular weight structures.^{24,27}

Thermogravimetric Analysis (TGA)

The rates of change in weight (DTG) curves under N_2 atmosphere of liquefied lignin organosolv and lignin are shown in Figure 4.

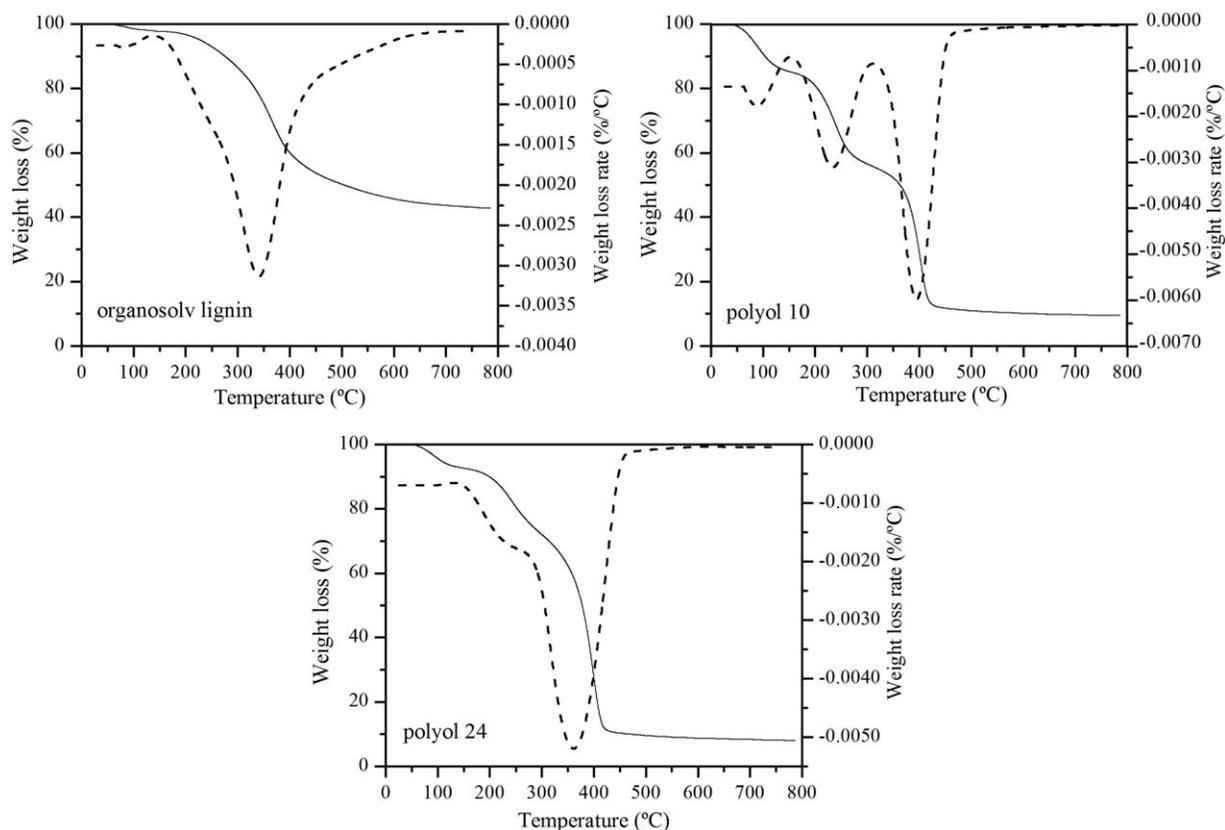


Figure 4. TGA and DTG curves of the organosolv lignin and the optimized polyols 10 and 24.

Organosolv lignin showed a low weight loss around 70°C that was associated with the moisture presented in the lignin samples. The high quality of the lignin was checked by the low hemicelluloses contamination presented between 185 and 260°C , it confirms the composition analysis in sugars (0.7%). Finally, lignin degradation happened slowly in a wide range of temperatures with a maximal mass loss rate between 300 and 400°C , this fact being associated with the complex structure of lignin with phenolic hydroxyl, carbonyl groups, and benzylic hydroxyl, which are connected by straight links.²⁸

According to Briones et al., 2012,²⁹ DTG analysis of pure PEG:Glycerol presented a glycerol decomposition from 153 to 267°C and PEG decomposition from 267 to 392°C . DTG curves of optimized polyols presented similar pattern with peaks ranging from 155 to 287°C and 287 to 489°C (polyol 24); from 154 to 310°C and from 310 to 464°C (polyol 10). So, it could be assumed that the two peaks presented in the polyols curves are due to the presence of glycerol and PEG in the final product. These results confirm the combination of the lignin and liquefying solvents, but the introduction of the chemicals reactants retarded the degradation temperature of the liquefied product.

CONCLUSIONS

The microwave system could substitute the conventional heating systems because it reduces the reaction times and the heat penetrates directly in the bulk of the material. A process was

developed for the optimization of polyol production from lignin obtained by organosolv treatment of the olive tree pruning by the use of microwave heating. The optimization ensured high liquefaction yield and a polyol with suitable hydroxyl number to be used as a precursor in polyurethane foam synthesis. Optimized polyols were characterized by FTIR and TGA to check the introduction of liquefying solvents. In future works, it would be desirable to evaluate the synthesis of polyurethane foams using polyols generated through liquefaction olive tree pruning lignin. Also it would be desirable to measure the acoustic, mechanic, and thermal properties of the created polyurethane foams.

ACKNOWLEDGMENT

Authors would like to thank the Department of Agriculture, Fishing and Food of the Basque Government (scholarship of young researchers training), University of the Basque Country and the Spanish Ministry of Economy and Competitiveness (Juan de la Cierva contract JCI-2011-09399) for financially supporting this research project.

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