

Oxypropylation of Brazilian Pine-Fruit Shell Evaluated by Principal Component Analysis

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ABSTRACT: Pine-fruit shell (PFS) is a lignocellulosic residue derived from the fruit of *Araucaria angustifolia*, a coniferous tree native of South America, part of a whole vegetation of the Atlantic Forest, found in the South and Southwest of Brazil. In this work PFS will be characterized and used in the production of PFS-based polyols through oxypropylation. Three series were chosen (PFS/propylene oxide (PO) (w/v, g/mL) of 30/70, 20/80 and 10/90) with four catalyst levels (5%, 10%, 15% and 20%, (w/w, PFS based)). Oxypropylation occurred at moderate conditions of temperature, pressure and time giving rise to liquid polyols with a homopolymer content (PPO) ranging from 4-65%, a hydroxyl number (IOH) between 257-605 mg KOH/g and viscosities (V) varying from 0.76 Pa.s to 373.90 Pa.s (20°C) for the series 20/80 and 10/90, while for the series 30/70, the viscosity reached values higher than 500 Pa.s, 20°C. The unreacted PFS (UR) varied between 3.6% and 77.4% (PFS-basis). After the PFS-based polyols production and characterization, a principal component analysis (PCA) was performed in order to evaluate the established interactions between the used formulation variables and the obtained polyol properties. The PCA analysis allowed to clarify the interactions between PFS and PO contents and the final biopolyol properties (PPO, IOH, V and UR). This approach showed to be a simple method to rationally analyze the influence of the input formulation variables on the final polyol properties.

KEYWORDS: Principal components analysis, Brazilian pine-fruit shell (PFS), oxypropylation, polyols

1 INTRODUCTION

Presently, the prospect on the recovery and valorisation of low value agro-industrial and agroforestry residues, have attracted the interest of academia and industrials, with the purpose of their reuse to generate value-added products. In this context, the growing interest in the obtainment of macromolecular materials derived from renewable resources, having in view the development of polyols from biomass sources, represents a sought alternative for polymer production, where the search for sustainable processes and green chemistry became of utmost importance [1].

Oxypropylation is a polymerization process (base-catalysed anionic ring-opening polymerization), through which grafts of poly(propylene oxide) are formed from available biomass hydroxyls, leading to liquid polyols, as a result of the introduction of multiple

ether moieties. It corresponds to a chain-extension reaction occurring in bulk through the interaction between the gas phase (vaporized propylene oxide) and the solid phase (biomass) [2, 3]. Along the oxypropylation reaction, homopolymerization of the propylene oxide can occur due to the transfer reactions of the grafting mechanism [4]. Thus, the resultant polyols are a mixture of oxypropylated biomass, polypropylene oxide oligomers (POO) and, eventually, unreacted biomass (Figure 1). Usually, polypropylene oxide oligomers, which are bifunctional molecules, are kept in the polyol because they allow the reduction of the polyols' viscosity and the lowering of the glass transition temperature [5]. Theoretically, any biomass residue containing hydroxyl groups can be transformed by oxypropylation into a liquid polyol [6]. Considering this feature, several studies on residual biomass oxypropylation were published, namely the oxypropylation of sugar beet pulp [7], cork [8], rapeseed cake residue [9], olive stone [10], date seeds [11] or soy hulls [12].

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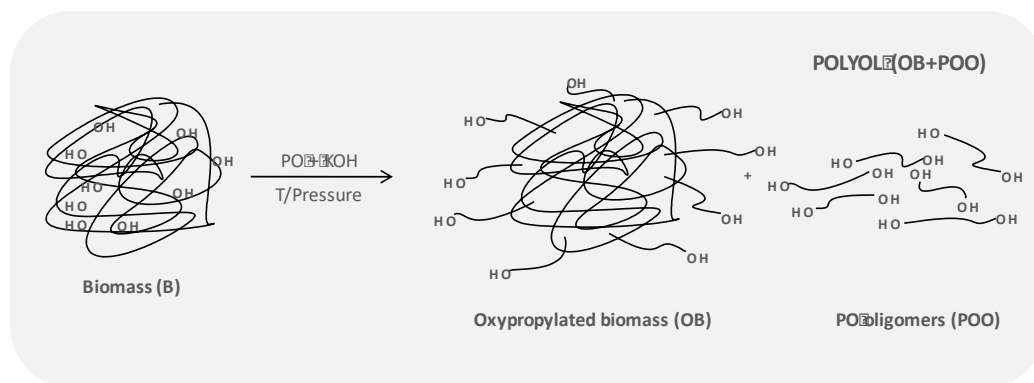


Figure 1 Schematic representation of biomass oxypropylation putting in evidence the composition of the polyol (mixture of oxypropylated biomass and PO oligomers).

Araucaria angustifolia is a species of conifer native of South America, found in the South and Southwest of Brazil, part of a whole vegetation of the Atlantic Forest. Due to the intense deforestation, occurred in the last decades, its cultivation has received a strong incentive by environment and agriculture sectors from Brazil's governmental, state and federal municipalities [13]. The seeds of its fruit (Brazilian pine-fruit), called "pinhão" (pine), a seasonal product (April-August), are consumed after cooking or roasting [14-16] representing an important economic revenue for the local populations and originating a lignocellulosic by product (shell), which represents around 22% of the whole "pinhão" [17]. Even the consumption is most often done at domestic level, the industrialization of some pine-derived products (e.g. packed pine fruit cooked and grounded, beer, pickled pine fruit) is emerging, making this residue more attractive for industrial valorisation [18,19]. Its production is estimated at around 2120 ton per year [20].

The PCA (Principal Component Analysis) analyzes a data table presenting observations described by several dependent variables, which are, in general, inter-correlated. Its goal is to extract important information from the data table and express this information as a set of new orthogonal variables called principal components [21]. This analysis may reveal grouped observations, trends, and outliers, as well as uncover relationships between observations and variables and between the variables themselves [22]. This methodology is being applied with success to several studies such as high pressure polymerization of low density polyethylene [23], hydrothermal liquefaction of biomass [24] or lignin depolymerization [25], leading to the achievement of important conclusions. To the best of our knowledge PCA was never applied to the analysis of the oxypropylation process, neither this substrate (pine-

fruit shell) was studied for oxypropylation purposes. In the present work PFS residue was characterized in terms of its lignocellulosic composition, extractable fractions (using solvents of different polarity), and ash and moisture contents. Furthermore, the production of PFS-based polyols by oxypropylation was conducted by evaluating the effect of different PFS/PO ratios, and catalyst (KOH) contents on the resulting polyol's technical properties, namely homopolymer content (PPO), hydroxyl number (IOH), viscosity (V) and unreacted PFS (UR). The interaction between the formulation variables and the achieved polyol properties was analysed by PCA and the advantages of using this statistical tool discussed.

2 EXPERIMENTAL

2.1 Materials

Pine fruit shell (PFS) was acquired in a local market from Campo Mourão, Paraná (Brazil) in August 2015. The following reagents were used for PFS characterization, polyol production and characterization: Acetone (P.A., Panreac), glacial acetic acid (P.A., Panreac); sulphuric acid (H_2SO_4 , 95-97% P.A., Panreac), acetic anhydride (P.A., Carlo Erba), sodium borohydride ($NaBH_4$, P.A., Panreac), dichloromethane (P.A., Sigma Aldrich), ethanol (P.A., 99.9%, Panreac), potassium hydroxide (KOH, P.A., Panreac); sodium hydroxide (P.A., Panreac), potassium iodide (99.2%, Pronolab), potassium permanganate (99%, Riedel), hydrogen peroxide (P.A., 30%, Panreac), propylene oxide (PO, P.A., $\geq 99.5\%$, Aldrich), hydrochloric acid (P.A., 37%, Panreac), phthalic anhydride (P.S. 98%, Panreac), sodium carbonate (99%, Sigma Aldrich), n-hexane (P.A. $>99\%$, Carlo Erba), potassium hydrogen phthalate (P.A. Panreac) and pyridine (P.A., Panreac).

2.2 Pine Fruit Shell Preparation

For PFS shell recovering, 525 g of pine fruit seeds were cooked in 1 L of boiling water during 50 min, simulating the typical boiling for pine consumption. Then, the internal edible seeds were removed and the shells dried in an oven (Nova Ética, Brazil) under forced air convection for 24 h at 40°C. Thereafter, the dried shells were grinded in a bench-top knife mill (Solab, Brazil) and sieved, being selected the material retained in mesh Tyler 20 (0.85 mm). Figure 2 shows the PFS residue aspect: Dried shells before grinding (A) and powdered form after grinding (B). The last one was the form used for both characterization and oxypropylation studies.



Figure 2 Empty shells of pine fruit (A) and after grinding (B).

2.3 Pine Fruit Shell Characterization

Pine fruit shell was characterized regarding ash and moisture contents, lignocellulosic composition (cellulose hemicellulose, holocellulose and lignin) and extractables, following general protocols adopt in our laboratory and briefly described below. More details about the used procedures can be found elsewhere [10]. All the determinations were done at least in duplicate.

For ash and moisture contents, pre-weighted samples (1.0 g, for both tests) were put in a muffle furnace at 525°C during 5 hours (TAPPI T211 om-07) or in an oven at 105±5°C during 24 h (ASTM 1413-76), respectively. Results (% w/w) were expressed as the ratio between the sample weight lost (initial weight-final weight) and the initial sample weight.

The cellulosic composition determination started with holocellulose extraction by the peracetic acid method. The extraction was carried out at 90°C during 40 minutes, under stirring and reflux using 4 g of PFS suspended in 100 mL of peracetic acid (prepared from hydrogen peroxide (30% solution) and acetic anhydride using a 1:1 volume ratio). The obtained sample was filtered and washed with distilled water (55°C) until a neutral pH was reached, followed by a 1:1 (v/v) acetone:ethanol mixture (55°C). Hemicellulose A was extracted at room temperature

during 2 h, with 100 mL of a 10% KOH solution containing 14 mg of NaBH₄, using 3 g of the previously recovered holocellulose. The resulting solution was filtered and washed with ethanol and the obtained residue used to extract hemicellulose B with 100 mL of a 24% KOH solution containing 14 mg of NaBH₄, under the previous described conditions. The α-cellulose was obtained as the remaining insoluble fraction. Results were expressed as weight fractions relative to the corresponding PFS sample weight (% w/w).

The insoluble lignin (Klason lignin) was determined according to the standardized method of Klason, described in standard TAPPI T222 om-08, with some modifications. Briefly, 1 g of PFS was treated with 15 mL of a 72% H₂SO₄ solution at 20°C under stirring for 2.5 h. Thereafter, the resulting mixture was completed with water up to 300 mL and refluxed for 2 h. Finally, it was filtered and the obtained solid residue washed with boiling water until a neutral pH was reached, and then dried. Lignin content was expressed relative to the corresponding PFS sample weight (% w/w).

The extractables were quantified by soxhlet extraction from 10 g of PFS, using the following sequential procedure: 300 mL of n-hexane for 6 h (to remove the fatty residues), 300 mL of dichloromethane (to remove non-polar substances), 300 mL of methanol (to remove the hydroxylated substances), and 300 mL of water (to remove the most polar components). The isolated fractions were concentrated in a rotary evaporator (Buchi AG, Flawil, Switzerland), then dried in an oven at 105±5°C for 2 h and weighed. The content of each isolated fraction was expressed relative to the initial PFS sample weight (% w/w).

2.4 Pine Fruit Shell Oxypropylation Procedure

The oxypropylation reaction was carried out in bulk using a 450 mL Parr autoclave model 4560 (Illinois, USA) equipped with a reaction vessel, heating mantle, mechanical stirrer, thermocouple and manometer. Three series were chosen (PFS/propylene oxide (PO) (w/v, g/mL)) of 30/70, 20/80 and 10/90 with four catalyst levels (5, 10, 15 and 20%, (w/w, PFS-basis)), implemented at a scale of 100 g. The desired amount of PFS, PO and KOH were placed in the reactor, thereafter closed and heated (set point temperature of 160°C). In a typical oxypropylation reaction, pressure reaches a maximum value (P_{max}) from which a decrease is observed, reflecting the propylene oxide consumption. During this process, temperature also attains a maximum value (T_{max}). Upon relative pressure get to zero (finishing of the reaction), the reactor was cooled to room temperature under stirring, and the polyols collected for further

characterization. The following terminology was used to identify the samples: PFS/PO/CAT. For example, a formulation designated 30/70/20 means a formulation prepared with 30 g of PFS, 70 mL of PO and 20% (w/w, PFS-basis) of catalyst.

2.5 Polyols Characterization

Polyols were characterized in terms of homopolymer content (PPO, % (w/w)), Hydroxyl number (IOH, mg KOH/g), viscosity (η , Pa.s, 20°C) and unreacted biomass (UR, %w/w) (expressed as PFS-basis (UR_S) and polyol-basis (UR_P)) following general protocols adopt in our laboratory and briefly described below. All the characterizations were done in duplicate. More information considering the used protocols can be found elsewhere [5].

PPO was quantified through its complete removal from the polyol mixture with n-hexane under reflux during 8 hours, according to the procedure described by Pavier and Gandini [7]. Briefly, 5 g of polyol were weighted and 50 ml of n-hexane used. The n-hexane was removed from the recovered fractions (oxypropylated PFS and PPO) using a rotary evaporator (Buchi AG, Flawil, Switzerland) followed by vacuum-drying until a constant weight was achieved. The PPO content (% w/w) was determined as the ratio between the achieved weight of PPO relative to the used polyol sample weight.

IOH was determined according to the ASTM D4274 standard. For that, the polyol sample was refluxed during 1h at 115°C using 25 mL of a phthalation reagent solution, as well as a blank sample (phthalation reagent without polyol). The phthalation reagent was prepared by mixing 140 g of phthalic anhydride and 2 L of pyridine. Next, the flasks were left to cool at room temperature before adding 50 mL of pyridine. The obtained mixture was back titrated with NaOH solution (0.5 N). The titrations were carried out in an automatic titrator (TitroLine 6000, SI Analytics) equipped with a glass electrode. IOH (mg KOH/g) was determined according to Equation (1), where V_1 is the NaOH volume required for the blank titration (mL), V_2 is the NaOH volume required for the polyol sample titration (mL), C is the NaOH concentration (mol/L) and W is the polyol weight (g). When needed the correction for acidity or alkalinity was performed.

$$\text{IOH} = \frac{(V_1 - V_2) \times C \times 56.1}{W} \quad (1)$$

Unreacted PFS was determined by weighing 1.0 g of polyol into an Erlenmeyer followed by the addition of 50 mL of dichloromethane. The mixture was filtered through a GF/A 1.6 μm filter under vacuum. The obtained solid residue (unreacted biomass) was washed several times with dichloromethane and then

dried in a vacuum oven at 40°C until constant weight was achieved. The UR content (% w/w) was determined as the ratio between the achieved unreacted biomass relative to the used polyol weight sample (UR_P) or the corresponding PFS (UR_S).

Viscosity was measured at 20°C with an Analogic Rheometer Malvern CVO 100 (Westborough, MA, USA) operating at stress-controlled mode, using a 40 mm diameter, 4° top-angle cone plate with a gap of 150 μm . The data acquisition was done in the range of shear stress of 15-3500 Pa, and by collecting 50 points.

2.6 Principal Component Analysis

Principal Component Analysis (PCA) was used to explore the relationship between the used experimental oxypropylation conditions and the properties of the obtained polyols. PCA was performed with MATLAB R2015b (MathWorks Inc., Natick, MA, USA). For that, the results obtained for IOH (mg KOH/g), PPO (%w/w), viscosity (Pa.s, 20°C), URs and URp, as well as the defined formulation variables (PFS, PO and KOH content), were placed in columns and the experimental runs used as the rows. Before analysis, each column was mean centered and divided by its variance, resulting in a scaled matrix. The first principal components with eigenvalues higher than 1.0 were used to evaluate the samples distribution in the new projection space [26]. Also, an outlier detection was performed using the Mahalanobis distance. The PCA score biplot was used to determine whether the produced polyols could be grouped into different classes. A regression analysis was also performed to evaluate the correlations among the variables and experimental results (Pearson's correlation coefficient, r).

3 RESULTS AND DISCUSSION

3.1 Pine-fruit Shell Characterization

The composition of the PFS sample used in this study is characterized by a moisture and ash content of 5.0% and 1.9%, respectively. The extractables (dry-basis) revealed a prominence of OH-bearing compounds (6.3%, based on the methanol extractables) and of more polar substances (7.5%, based on the water extractables). Moreover, it presents 0.3% of fats (based on the n-hexane extractables) and 0.2% of non-polar substances (based on the dichloromethane extractables). The high amount of OH-bearing compounds, as well as of water soluble substances, can be related with the presence of flavonoids and phenolic compounds [17]. According to D'Souza and collaborators [3], their presence can influence oxypropylation reaction by acting as preferable sites for reaction initiation. In fact, these compounds are

readily accessible, reacting even before lignin and cellulose.

The lignocellulosic fraction (corresponding to a content of 83.7% of the original material, dry-basis) comprises cellulose, hemicellulose and lignin at overall contents of 34.9%, 17.8% and 47.3%, respectively. In the work of Sampaio and co-workers [27], dealing with the characterization of *Araucaria angustifolia* seeds teguments, a result of 32.4% (wet-basis) for lignin quantification was achieved, representing a quite high lignin content when compared with seeds from other tree species. In the present work, a value of 36.6% (wet-basis) was achieved.

3.2 Pine-fruit Shell Oxypropylation

A summary of the oxypropylation reaction conditions (P_{\max} , T_{\max} , time to P_{\max} , time to T_{\max} , and total time),

registered for each formulation, is given in Table 1. It was observed that the values for maximum temperature and pressure varied from 199.2 until 289.4°C, and 19.0 to 28.8 bar, respectively. Moreover, the highest values for both variables were registered for the series with lower PFS and the highest catalyst contents, (10/90/15 and 10/90/20). Generally, the lowest P_{\max} values were obtained for the 30/70 formulations, independently of the used catalyst content. Considering the total reaction time, the formulation 30/70/10 was the longer one, since it lasted 2.2 h. Comparatively, the series 20/80 and 10/90 had shorter reaction times (1.5 h to 1.2 h and 1.6 h to 1.5 h, respectively), with time decreasing as the catalyst content increases. This behaviour is similar to the one reported by Cateto et al. [5], who also registered the highest T_{\max} and P_{\max} values for formulations with low biomass/PO ratios and high catalyst contents.

Table 1 Formulations and operating conditions used in the oxypropylation study.

Run	PFS/PO (w/v)	Catalyst (w/w)	T_{\max} (°C)	P_{\max} (bar)	Time to T_{\max} (min)	Time to P_{\max} (min)	Reaction time (h)
1	30/70	5	225	*	31	*	1.4
2	30/70	10	216	20.1	31	24	2.2
3	30/70	15	222	21.4	30	20	2.1
4	30/70	20	225	19.0	29	18	1.3
5	20/80	5	199	22.2	37	25	1.5
6	20/80	10	288	22.3	29	25	1.4
7	20/80	15	260	22.0	25	18	1.1
8	20/80	20	257	21.8	24	17	1.2
9	10/90	5	240	23.4	45	40	1.6
10	10/90	10	263	23.3	28	25	1.3
11	10/90	15	287	28.8	22	18	1.5
12	10/90	20	289	28.8	20	17	1.5

* Not registered.

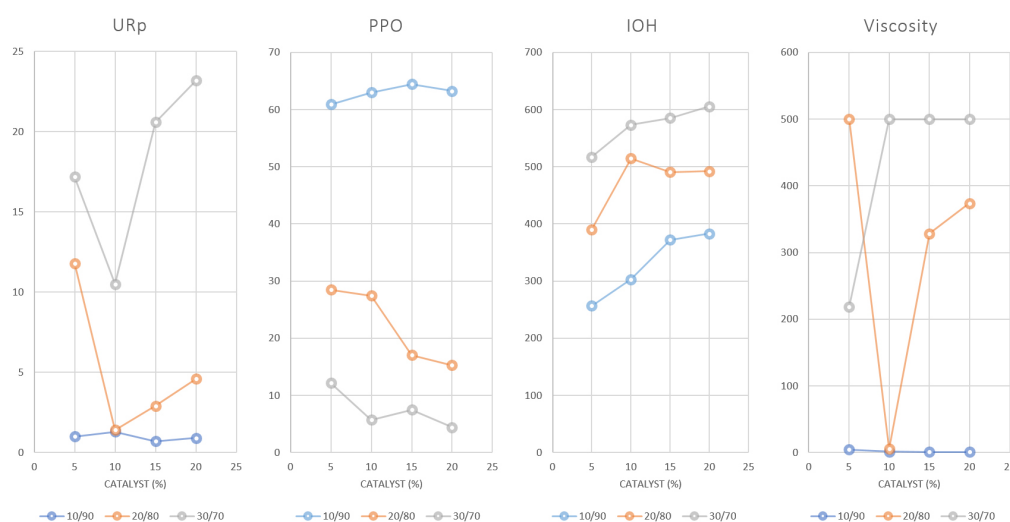


Figure 3 Evolution of UR_p (% w/w, polyol-basis), PPO (% w/w), IOH (mg KOH/g), and viscosity (mPa.s) as a function of catalyst content for each series (PFS/PO of 10/90, 20/80 and 30/70). (*) Viscosity values represented as 500 mPa.s are over this value (high viscosity polyols).

3.3 Polyols Characterization and Overall Analysis

After polyol production, and as a regular procedure, the unreacted biomass was determined and expressed as PFS-basis and polyol-basis, UR_S and UR_P , respectively. Thereafter polyols were characterized for their technical properties (PPO, IOH and V). The obtained results for each series (10/90, 20/80 and 30/70), as a function of catalyst content, are presented in Figure 3. UR_S is not represented since it follows a similar trend as UR_P .

Regarding UR_P , the series 30/70 was the one showing the higher values (17.2% to 23.2%). Additionally, an amount of 11.8% was achieved for the assay 20/80/5. For the series 10/90, the unreacted biomass amounts in the polyol were inferior to 1.0%. As expected, the same tendency was observed for the biomass-basis values (UR_S) (data not shown). In brief, for the studied series, the amount of unreacted biomass in the final polyol was less than 25% (23.2% for the assay 30/70/20), but reaching values as low as 0.7% (assay 10/90/15).

Concerning the homopolymer content, the 10/90 series presented the higher amount (above 60%). Moreover, only a slight variation was observed when the catalyst content varied from 5% to 20%. This series correspond to the one with the lower unreacted PFS (less than 10%) which pointed out for a high extent of the PFS oxypropylation. For the series 30/70, the homopolymer amount diminished from 12.2 to 4.4%, as the catalyst content increased from 5 to 20%. Additionally, for the 20/80 series the same pattern was observed (from 28.5% to 15.3%).

The IOH values, in a general way, increased with catalyst content increase, being this behavior markedly identified for the low-PFS content formulations (10/90 and 20/80). For the 10/90 series the IOH varied from 256.6 mg KOH/g to 383.0 mg KOH/g, while for the 20/80 series the increase was from 390.2 mg KOH/g to 492.1 mg KOH/g. Concerning the 30/70 series, this effect was attenuated. Additionally, for the same catalyst content, the IOH value increased with the increase of the PFS/PO ratio. Similar observations were made by Nadji et al. [4] and Cateto et al. [5], with experiments conducted with lignin. It is worth to mention that oxypropylation render biomass hydroxyl groups more accessible [12]; the IOH content variation is therefore related with the amount of hydroxyl groups present in the PFS, their level of activation by the catalyst, and the formed homopolymer amount. Comparing the IOH values obtained in the present work, they are generally inferior to the ones published in similar works. By

using the 20/80/10 formulation, Serrano and co-workers [9] produced a polyol based on rapeseed cake with an IOH of 610 mg KOH/g, while Briones and collaborators [11] produced a date seed-based polyol with an IOH of 779 mg KOH/g. In this work, a value of 514.3 mg KOH/g was obtained.

For product viscosity, an increment was observed with catalyst content increase. This effect is more visible in the series with low PFS content (10/90 and 20/80). The series 30/70 using catalyst contents of 10, 15 and 20% presented the higher values (above 500 Pa.s, 20°C), being similar to the series 20/80 with 5% of catalyst. Relatively to the series 20/80, and for the assay using 10% of catalyst, the viscosity value was 5.3 Pa.s, value similar to the one registered by Briones and co-workers [11] (6.9 Pa.s) with date seeds. For 15% and 20% of catalyst, and 20/80 series, viscosity was 328.5 Pa.s and 373.9 Pa.s, respectively. This pattern was related with the effect of the catalyst content on the PFS hydroxyl activation; a higher amount of catalyst can activate more hydroxyls, reducing the length of the grafted molecular chains thus resulting in more viscous polyols. This finding is in accordance with the analysis made by Cateto and co-workers [5]. Regarding the series 10/90, low viscosity values were obtained, being this fact related with the presence of a high homopolymer content.

3.4 Principal Component Analysis

To the best of our knowledge, the principal component analysis was never applied to the study of biomass oxypropylation. As input variables, PFS, PO and catalyst content were considered. Based on this information, the principal component analysis (PCA) determined that the first two PCs (principal components) presented eigenvalues higher than 1, as can be observed in Figure 3. The remaining six generated PCs (from 3 to 8) yielded progressively lower eigenvalues and did not explain data variability (<10.79% total). Therefore, according to Kaiser's rule [28], only the first two PCs were used for further study. An outlier detection was performed considering the two selected PCs, with the Mahalanobis distance [29]. The results can be observed in Figure 4, where no outlier could be detected in the analyzed dataset. After this evaluation, the scores of PFS oxypropylation results were submitted to the PCA and the obtained biplot is shown in Figure 5.

It can be observed that the two PCs explained 89.21% of the variability in the data. Analyzing the relations between the evaluated variables in this study, it can be observed a strong correlation between the PO amount and the homopolymer content (POO), as well as among viscosity, hydroxyl number, PFS amount and

unreacted PFS (both PFS-basis and polyol-basis). The interactions between these variables can be observed in Table 2, where the Pearson's correlation values (r) are presented. The influence of both, the used amounts of PFS and PO, in the defined responses (PPO, IOH and V), are considered strong since the r values are near 1. On the other hand, no linear correlation can be defined between the used catalyst amount and the observed results, since the r values are equal to

zero. Probably, the catalyst amount presents a significant influence in the reaction kinetics, but not in the results evaluated here (final product properties). Considering all the analyzed results, this is an unexpected outcome. In this sense, it can be concluded that to obtain materials from PFS with different characteristics, for different technological applications, the amount of catalyst can be kept in the lowest concentration, with varying PFS and PO.

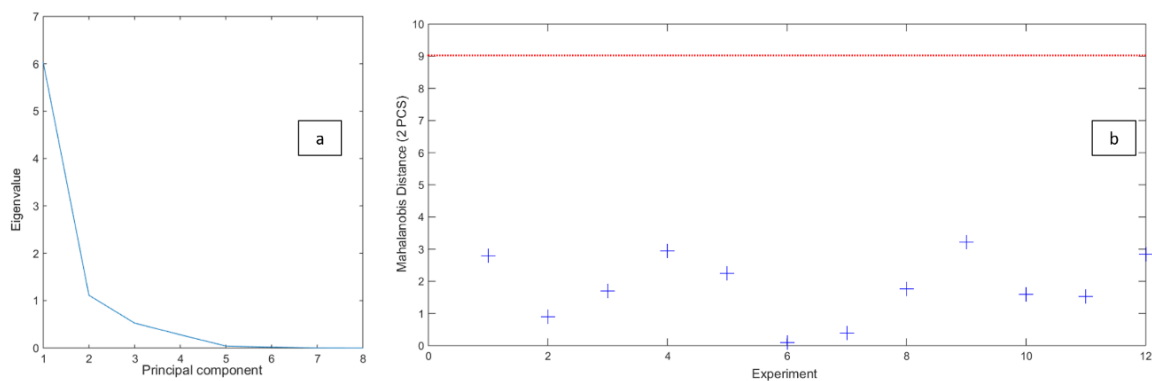


Figure 4 a) Screen plot of eigenvalues obtained for the PFS polyols production results; b) Mahalanobis distance of the experimental results considering 2 PCs.

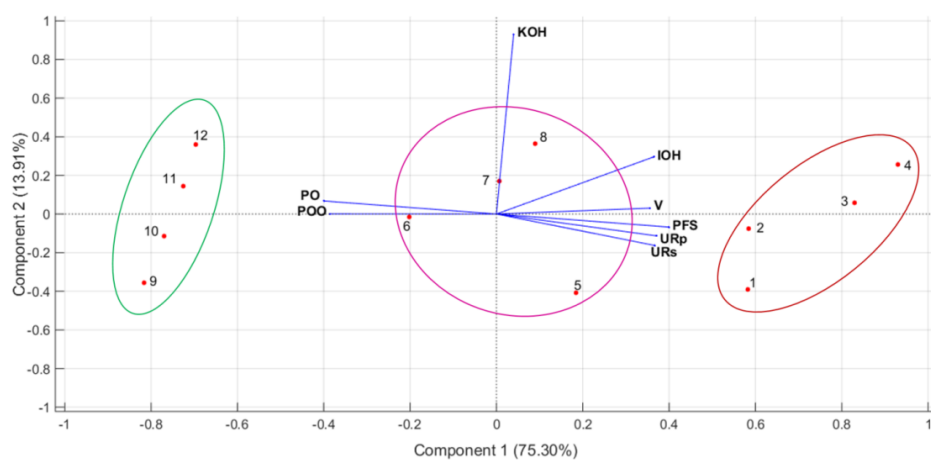


Figure 5 Principal component analysis biplot of the scores of PFS oxypropylation results: PO- propylene oxide, PFS-pine fruit shell, KOH- catalyst content, PPO- homopolymer content, IOH- hydroxyl number, V-viscosity, URs- unreacted biomass in relation to the original biomass, URp- unreacted biomass in the final polyol.

Table 2 Pearson's correlation (r) values obtained for the analyzed variables and responses of PFS oxypropylation process.

	PFS	PO	KOH	POO	IOH	V	URs	URp
PFS	1	-1	0	-0.9621	0.9062	0.7957	0.8288	0.8587
PO	-1	1	0	0.9621	-0.9063	-0.7957	-0.8288	-0.8587
KOH	0	0	1	-0.0499	0.3454	0.1320	-0.0142	0.0341
POO	-0.9621	0.9621	-0.0499	1	-0.8976	-0.8103	-0.7490	-0.7538
IOH	0.9062	-0.9063	0.3454	-0.8976	1	0.6976	0.6532	0.7039
V	0.7957	-0.7957	0.1320	-0.8103	0.6976	1	0.8130	0.7566
URs	0.8289	-0.8288	-0.0142	-0.7490	0.6532	0.8130	1	0.9800
URp	0.8587	-0.8587	0.0341	-0.7538	0.7039	0.7566	0.9800	1

Another point to be noted is that the experiments were grouped in three clusters. The first one comprises the experiments numbered from 9 to 12, which corresponds to the 10/90 series with 5%, 10%, 15% and 20% of catalyst. These experiments resulted in higher PPO contents, due to the higher amounts of PO which favor homopolymerization occurrence. On the other hand, these experiments presented the lowest viscosity results due to the high homopolymer content, as well as the low unreacted biomass fractions. Experiments from 5 to 8, which correspond to the 20/80 series, presented intermediary characteristics.

The experiments from 1 to 4 (30/70 series) presented high viscosities, high hydroxyl content, as well as high unreacted biomass content.

In fact, and according to the interaction between variables (Table 2), evaluating the influence of PFS content on biopolyol properties, it can be stated that: (i) Homopolymer content: Since higher biomass content implies higher amount of available hydroxyls for the oxypropylation reaction, available PO for homopolymerization reaction is reduced; (ii) IOH content: once higher PFS content will represent more hydroxyl groups available for oxypropylation, it resulted in biopolyols with increased IOH; (iii) Viscosity: Since this property is related with chain size, where the presence of a higher amount of hydroxyl groups increases the amount grafted molecular chains, but shorter in size, resulting in more viscous polyols; (iv) Unreacted biomass: The presence of higher amounts of PFS will increase the unreacted residue for the different formulations when using the same catalyst level. Analyzing the interaction between variables (Table 2) from the PO content perspective, it can be noticed that it is related with: (i) Homopolymer content: higher PO contents promotes the homopolymerization reaction; (ii) IOH: Higher PO content represents more oxirane rings available for the grafting reaction (depending on the biomass content), resulting on polyols with higher IOH contents; (iii) Viscosity: Higher PO contents results in more homopolymer formation, which in turn reduces the biopolyol viscosity; (iv) Unreacted biomass: the presence of higher PO amounts allows the maximization of the biomass conversion to polyol, diminishing the unreacted fraction present on the polyol.

CONCLUSIONS

In this work, the PFS residues were characterized aiming at propose novel solutions for their use, particularly in the field of polymeric materials (production of bio-polyols). Moreover, the study of the PFS oxypropylation evidenced that, depending on the

established formulations, biopolyols with different technical properties can be obtained. The performed PCA analysis allowed a clarification of the interaction of the PFS and PO contents on the final biopolyols properties. In brief, PCA has been proved to be a powerful tool for describing and visualizing the oxypropylation process, with possibility to be extended to other types of biomass or by integrating different input variables.

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