

# Scalable single-step synthesis of lignin-based liquid polyols with ethylene carbonate for polyurethane foams



A. Duval <sup>a, b, \*\*</sup>, D. Vidal <sup>a, b</sup>, A. Sarbu <sup>b</sup>, W. René <sup>b</sup>, L. Avérous <sup>a, \*</sup>

<sup>a</sup> BioTeam/ICPEES-ECPM, UMR CNRS 7515, Université de Strasbourg, 25 rue Becquerel, 67087, Strasbourg Cedex 2, France

<sup>b</sup> Soprema, 14 rue de Saint Nazaire, 67100, Strasbourg, France

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## ABSTRACT

A new method for the synthesis of lignin-based liquid polyols was developed. Organosolv lignin was reacted with ethylene carbonate in polyethylene glycol as solvent, leading to a full conversion of the phenolic OH into primary aliphatic OH groups. These aromatic polyols are obtained in a single step, without any purification. Upon modification of the polyethylene glycol molar mass, a wide range of hydroxyl values ( $I_{OH}$ ) can be covered. The polyols with up to 30%wt lignin have a viscosity suitable for the direct elaboration of polyurethane (PUR) foams. The method presents significant advantages over oxypropylation, the most common method for producing lignin-based polyols since it is performed at ambient pressure, without any toxic chemicals, does not require purification or post treatment, and allows to produce polyols with tunable properties. Four different aromatic polyols were then synthesized to produce rigid PUR foams, with substitution of up to 100% of a standard polyether polyol. The developed polyols showed very high reactivity, allowing to reduce the catalyst content in the PUR formulation by 75%. Rigid PUR foams prepared with 25% substitution of the standard polyol showed properties in the range of commercial PUR foams, with more than 90% closed cells and thermal conductivity of about  $25 \text{ mW m}^{-1}\text{K}$ , perfectly adequate for thermal insulation applications.

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## 1. Introduction

One-third of the worldwide energy consumption is used for the heating or cooling of buildings [1]. Thermal insulation thus appears as fundamental to reduce the global energy consumption and greenhouse gases emissions, to limit global warming according to the objectives of the Paris agreement [2]. Rigid polyurethane (PUR) foams are among the most efficient thermal insulating materials and are widely used by the building industry [3, 4]. PUR foams are conventionally obtained by the reaction between polyisocyanates and polyols [5]. To further reduce the environmental impact of PUR foams, aromatic or aliphatic bio-based polyols with different molecular architectures have been developed to replace their fossil-based counterparts [6,7]. These bio-based polyols are more and more used at an industrial level to develop sustainable materials [8].

Lignin is a natural polyphenol present in lignocellulosic biomass and in particularly high amount in wood. It is commonly separated from the other constituents of biomass, cellulose, and hemicelluloses by the paper pulp industry, as well as in lignocellulosic biorefineries. Although lignins are still very often burnt for the energy balance of the corresponding plants (e.g. Kraft), their commercial availability is growing [9], with a strong increase of the demand [10]. According to the botanical resource and the fractionation process, different lignins can be obtained. From a structural point of view, lignin is a multifunctional oligomer with a high content in aliphatic and phenolic OH groups and can be considered as an aromatic building block [11, 12]. Therefore, it is now recognized as a major potential feedstock for the synthesis of aromatic polymer materials, especially for crosslinked polymer networks [13–15].

The use of lignin in PUR foams has seen numerous developments in the past 20 years [16]. Several attempts have been made to directly incorporate neat lignins in PUR foams [17–22]. Lignin was mixed with polyether polyols, but the dissolution was often incomplete and led to a very fast increase of the viscosity with the lignin content [17–19]. It caused a reduced reactivity of the polyol resulting in foams with larger and less uniform cells, with

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [antoine.duval@unistra.fr](mailto:antoine.duval@unistra.fr) (A. Duval), [luc.averous@unistra.fr](mailto:luc.averous@unistra.fr) (L. Avérous).

decreased density and compressive strength [17,18,20,21]. In this case, lignin mostly acts as filler and do not take part in the formation of the PUR network because of the low reactivity of its phenolic OH groups with isocyanates [5]. Then, to use lignin as an efficient aromatic polyol, the best strategy is to convert the solid lignin into a liquid polyol and modify the native OH groups. For this purpose, two main processes have been largely described and studied in the literature: liquefaction and oxypropylation.

Liquefaction consists of thermal treatment of biomass in a polyol solvent, usually ethylene glycol, polyethylene glycol (PEG), or glycerol, at high temperature (usually above 150 °C) and in the presence of an acid catalyst, such as sulfuric acid [23, 24]. It was commonly applied to various lignocellulosic biomass, such as wood, agricultural crop residues, or straws [23–26], more scarcely to isolated lignins [27, 28]. During liquefaction, lignin is first decomposed into low molar mass products by solvolysis before condensation reactions lead to an increase in molar mass [24, 26, 29, 30]. Various reactions occur, among which acid-induced depolymerization, leading to an increase in the phenolic OH groups content [29]. However, the latter show poor reactivity with isocyanates [5], leading to the slow kinetics of PUR foam formation [31, 32].

Oxypropylation consists of the reaction of lignin OH groups with propylene oxide, leading to the grafting of poly (propylene glycol) onto lignin [33]. This process presents significant advantages for the preparation of PUR foams since oxypropylated lignin polyol (OLP) is a viscous liquid, and lignin phenolic OH groups are converted into more reactive and less sterically hindered aliphatic OH groups. Lignin oxypropylation was first developed by Glasser et al. in the 1980s [34–37] and has then been applied to many different lignin sources [21, 38–44]. Rigid PUR foams were successfully prepared using OLP as polyol, alone or in combination with polyether polyols. OLP usually shows a high reactivity, leading to faster foaming kinetics [21, 40, 44]. However, the synthesis of OLP suffers from significant drawbacks. PO is a highly toxic and carcinogenic compound, with low boiling point (34 °C) and potentially explosive vapors. In addition, the oxypropylation reaction is performed at high temperature (above 150 °C) and pressure (above 10 bar) and thus requires the use of pressurized reactors. It thus complicates the potential upscaling of OLP production. Indeed, despite almost 30 years since the seminal work of Glasser et al. and numerous developments at the laboratory scale, OLP has never been brought to a commercial scale.

In a series of previous studies, we focused on the use of cyclic carbonates as potential alternatives to alkylene oxides for the modification of polyphenols [45–48]. Cyclic carbonates, such as propylene or ethylene carbonate (EC), are non-toxic, high boiling compounds, with good solvency for polyphenols, allowing the modifications to be performed at atmospheric pressure without addition of other solvents. The modification of lignin with EC is particularly attractive as it yields a modified lignin that contains only primary aliphatic OH groups of high reactivity [47–50]. However, EC-modified lignin is still a solid and cannot be used directly as polyol for the preparation of PUR foams. Recently, Zhang et al. [51] modified Kraft lignin with EC using PEG as co-solvent and water as reactive additive, resulting in liquid polyols that were used for the preparation of PUR foams. However, their polyol synthesis requires a high temperature (170 °C) and the use of sealed reactor, leading to the same scale-up issues as for OLP synthesis.

In this study, we thus focused on developing a new protocol to prepare liquid polyols from lignin based on the reaction with EC. The reaction between lignin and EC was conducted in PEG of various molar mass to obtain liquid polyols with tunable properties in a single step. Complete polyols characterization was then performed, and different formulations were selected and scaled-up for

the preparation of rigid PUR foams for thermal insulation, which have been characterized in detail.

## 2. Materials and methods

### 2.1. Materials

Beech lignin was isolated from the aqueous acetone organosolv FABIOLA™ process [52] developed by TNO and performed at pilot-scale at Fraunhofer CBP (Leuna, Germany). After fractionation of beech wood, the lignin was precipitated from the liquor by dilution with three volumes of water and recovered by filtration using a chamber filter press. Lignin was dried overnight in a vacuum oven at 40 °C before use. Detailed characterization of this lignin has been reported in a previous publication [48]. It contains 1.89, 3.58, and 0.06 mmol/g of aliphatic OH, phenolic OH, and COOH, respectively.

Triethylene glycol, PEGs of average molar mass 200, 300, and 400 g/mol (PEG<sub>200</sub>, PEG<sub>300</sub>, PEG<sub>400</sub>) and ethylene carbonate (EC, 99%) were purchased from Acros Organics and used as received. Polymeric 4,4'-methylene bis-(phenyl isocyanate) (pMDI, Lupranat M 70 R, BASF), was used as polyisocyanate for the preparation of PUR foams. Its NCO content is 31% and average functionality is 2.9. Daltolac R570 (Huntsman) was used as a reference polyol. It is mainly composed of alkoxyated glycerol and has an  $I_{OH}$  of 570 mg KOH/g. N,N'-dimethylcyclohexylamine (DMCHA, Sigma-Aldrich) was used as catalyst and Tegostab B81048 (Evonik), a polyether – polydimethylsiloxane copolymer, was used as a surfactant. Tris (1-chloro-2-propyl) phosphate (TCPP, Shekoy) was used as flame retardant. Isopentane (bp 28 °C, Inventec-Dehon) or diethyl ether (bp 35 °C, Fisher Scientific) were used as physical blowing agents, and deionized water was used as chemical blowing agent.

### 2.2. Synthesis of lignin-based polyols

Lignin and PEG were introduced first into the reactor, with lignin content from 20 to 30 %wt based on the total mass of lignin and PEG. In a scaling-up approach, different reactors were used in the course of the study: (i) first tests were performed in a 50 mL three-necked round bottom flask with 10 g of lignin-PEG mixture; (ii) 250 mL three-necked round bottom flask were then used for a mass of 50 g; (iii) 1 L reactor was finally used for a mass of 200 g. The lignin-PEG mixture was stirred with a mechanical stirrer and EC (2 molar equivalents with respect to total OH groups in lignin) and K<sub>2</sub>CO<sub>3</sub> (0.1 molar equivalent to EC) were successively added. The mixture was placed under an argon flux and immersed into an oil bath regulated at 110 or 130 °C. Aliquots were withdrawn at regular intervals and the reaction was maintained for 4–6 h. The obtained homogeneous liquid polyols were used without further purification for the analysis and foam preparation.

### 2.3. Preparation of PUR foams

Lignin-based PUR foams were prepared in a two-steps process. First, predetermined quantities of standard polyol, lignin-based polyol, catalyst, surfactant, water, physical blowing agent and eventually flame retardant were added in a beaker and mixed at 5000 rpm. Second, polyisocyanate was added to the above homogeneous mixture, the mixture was then stirred for 5 s and poured into a mold where the foam was allowed to rise freely.

Preparation of PUR foams was performed at different scales. For continuous recording of the foaming parameters during the foam expansion, about 200 g of mixture was prepared. The mixture was poured in a cylindrical container (180 mm in height and 75 mm in radius) connected to the FOAMAT® apparatus, and in parallel, a small foam sample was prepared in order to determine the

characteristic foaming times for each formulation. For the preparation of larger foam samples used to determine the physical and mechanical properties, about 600–700 g of mixture were prepared and poured into a mold of  $20 \times 20 \times 60 \text{ cm}^3$ .

#### 2.4. Characterization of lignin-based polyols

$^1\text{H}$  and  $^{31}\text{P}$  NMR were performed using a Bruker 400 MHz spectrometer.  $^1\text{H}$  NMR (Nuclear Magnetic Resonance) was performed under quantitative conditions (15 s relaxation delay) in the presence of 2,3,4,5,6-pentafluorobenzaldehyde as internal standard. About 20 mg polyol samples were dissolved in 550  $\mu\text{L}$  DMSO- $d_6$ , and 100  $\mu\text{L}$  of a 0.5 M solution of pentafluorobenzaldehyde in DMSO- $d_6$  was then added. The amount of unreacted EC in the polyol was quantified by integration of the singlet at 4.48 ppm.

$^{31}\text{P}$  NMR was used to quantify the hydroxyl content of the polyols. 15–20 mg of polyol was derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane in pyridine/ $\text{CDCl}_3$  (1.6 : 1 v/v) in the presence of cholesterol as an internal standard, according to the standard protocol [53,54]. 128 scans were recorded with 15 s relaxation delay. The hydroxyl index  $I_{\text{OH}}$  was calculated according to Equation (1):

$$I_{\text{OH}} \left( \text{mg KOH g}^{-1} \right) = [\text{OH}] \times 56.1 \quad (1)$$

where  $[\text{OH}]$  is the polyol content in OH groups measured by  $^{31}\text{P}$  NMR (in mmol/g) and 56.1 is the molar mass of KOH (in g/mol).

Viscosity measurements were performed using a TA Discovery HR-3 rheometer equipped with Peltier plates at 25 °C, using 25 mm parallel plate geometry, for shear rates ranging from 0.1 to 100  $\text{s}^{-1}$ , where a Newtonian behavior was observed.

Size exclusion chromatography (SEC) was performed using a Waters Acquity Advanced polymer chromatography system, equipped with three 150 mm advanced polymer chromatography XT columns (a 45 Å, 1.7  $\mu\text{m}$ , a 200 Å, 2.5  $\mu\text{m}$ , and 450 Å, 2.5  $\mu\text{m}$ ) thermostated at 40 °C. Tetrahydrofuran (THF, HPLC grade, Fisher Scientific) was used as an eluent at a flow rate of 0.6 mL/min. The detection was performed by an Acquity refractive index detector and an Acquity TUV detector operating at 280 nm. To ensure a full solubility in THF, all samples were acetylated as previously reported [55]. They were then dissolved in THF at 5 mg/mL concentration and filtered through 0.2  $\mu\text{m}$  PTFE syringe filters prior to injection. The average molar mass ( $M_n$ ,  $M_w$ ) and dispersity ( $\text{Đ}$ ) were calculated from a calibration with polystyrene standards.

#### 2.5. Characterization of PUR foams

The main characteristic foaming times (cream, gel and the tack-free times) were recorded manually following the physical change of the expanding foam. The cream time corresponds to the start of bubble rise that causes color change of the mixture to become froth-like. Gel time is the starting point of a stable network formation by intensive formation of urethane and crosslinking reactions. At tack-free time, the outer surface of the foam loses its stickiness.

To follow the foaming process, the core temperature, foam height and expansion rate were continuously recorded using a Foamate® FPM 150 device (Messtechnik GmbH, Germany). The apparatus was equipped with a cylindrical container (180 mm in height and 75 mm in radius), an ultrasonic probe to record the foam height and a Pt sensor to follow the temperature evolution inside the foam.

Foams were conditioned 7 days prior to cutting samples for the different analyses. Apparent foam density was measured by

weighing parallelepipedal foam samples whose dimensions were measured with a caliper, according to EN 1602 standard.

Dimensional stability was measured after 48 h at 70 °C and 90% humidity rate, and after 48 h at –20 °C, according to EN 1604 standard.

Compression strength at 10% deformation was measured on  $100 \times 100 \times 60 \text{ mm}^3$  foam samples with an Instron 3367 dynamometer equipped with a 30 kN load sensor at room temperature, according to EN 826 standard.

Closed cells content was determined using a gas pycnometer (Ultrapyc 1200e, Quantachrome Instruments), according to EN ISO 4590 standard. Cubic foam samples (approximately  $25 \times 25 \times 25 \text{ mm}^3$ ) were used for the first measurement. They were then cut into eight smaller and equivalent pieces and a second measurement was performed to correct the closed cells content from the closed cells that were opened during the cutting step.

Scanning electron microscopy (SEM) was carried out to determine the size of the cells using a Jeol IT-100 equipment and an in-house statistical imaging analysis software based on Image J. Cubic foam samples were cut with a microtome blade and analyzed in longitudinal (*i.e.* parallel to foam rise) and transverse (*i.e.* perpendicular to foam rise) directions.

Thermal conductivity was measured 21 days after foaming using a heat flowmeter (HFM 446, Netzsch), according to EN 12939 standard. Foam samples of  $175 \times 175 \times 60 \text{ mm}^3$  have been used for the determination of the thermal conductivity coefficient  $\lambda$  at 10 and 20 °C.

Flammability tests were performed according to EN ISO 11925-2 standard, measuring the maximum flame height on the sample after exposition to a direct flame.

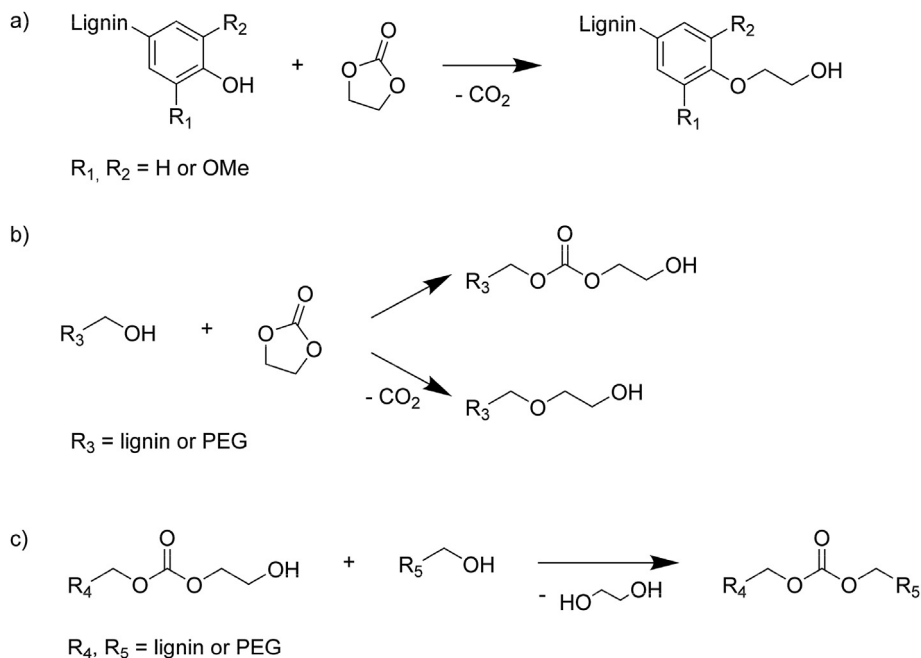
### 3. Results and discussions

#### 3.1. Synthetic strategy for lignin-based polyols

The modification of lignin with EC has been previously developed in our laboratory [47,48] and others [49,50,56]. It is attractive for PUR synthesis as it allows the conversion of all the lignin phenolic OH groups into primary aliphatic OH groups (Scheme 1a), which are much more reactive with isocyanates. Recently, we reported that Fabiola™ organosolv lignin could be easily modified with EC under mild reaction conditions [48]. However, the resulting modified lignin is a solid, which prevents the direct use as polyol for the preparation of PUR foams, where liquid polyols with viscosities in the range of 2–10 Pa s are required.

Interestingly, the grafting of ethylene oxide groups makes the EC-modified lignin highly soluble in PEGs. Homogeneous liquid polyols could thus easily be obtained with up to 35%wt lignin upon simple mixing of EC-modified lignin and PEG. However, this approach requires two steps. Lignin needs to be purified by precipitation and filtration after chemical modification to remove excess EC [47,48], which compromises the potential scale-up. We thus developed a single-step, purification-free synthesis of liquid lignin-based polyols, where lignin was first mixed with PEGs of various chain lengths before reacting with EC. In our previous work, EC was used in large excess (10 molar equivalents with respect to lignin OH groups) to act as both reagent and solvent of the lignin [47,48]. Here, the mixture of lignin and PEG is a homogeneous viscous liquid, and EC does not have to be used in large excess. Consequently, no purification is required to remove it after the reaction.

Since the reaction is conducted directly on a mixture of lignin and PEG, several reactions can occur. EC reacts with the phenolic OH groups of lignin, according to the pathway shown on Scheme 1a. It can also react with aliphatic OH groups, which are present on the lignin and on the PEG chain ends, as shown on Scheme 1b, forming



**Scheme 1.** Reaction of EC with lignin and PEG: (a) reaction with lignin phenolic OH groups, (b) reaction with lignin or PEG aliphatic OH groups, (c) chain coupling by trans-carbonation. EC, ethylene carbonate; PEG, polyethylene glycol.

ether and/or carbonate linkages. Once the latter are formed, trans-carbonation reactions can lead to chain coupling, involving either lignin-lignin, PEG-PEG or PEG-lignin couplings (Scheme 1c).

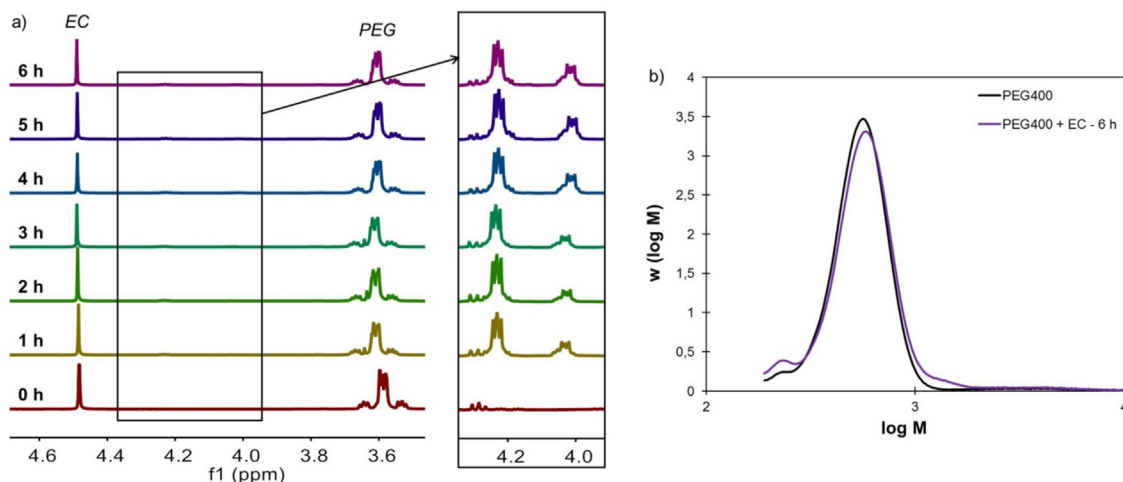
To evaluate the reactivity of PEG with EC, preliminary experiments were conducted in the absence of lignin. PEG<sub>400</sub> and EC were reacted in bulk at 110 °C in the presence of K<sub>2</sub>CO<sub>3</sub>, and the reaction was followed by <sup>1</sup>H NMR and SEC (Fig. 1). <sup>1</sup>H NMR shows a progressive decrease of the signal related to EC at 4.48 ppm indicating that about 40% of the EC reacts with PEG under these conditions. The corresponding integrations are given in the Supporting Information (Figures S1 and S2). The appearance of new multiplets at 4.0 and 4.2 ppm confirms the formation of carbonate linkages (Scheme 1b and c) [57]. SEC reveals an increase in PEG molar mass after the reaction (Fig. 1b). The main peak is slightly shifted, which can be caused by grafting of ethylene oxide or EC units onto the PEG chain ends (Scheme 1b). The presence of a shoulder for higher molar

mass indicates the potential occurrence of chain coupling, as shown in Scheme 1c.

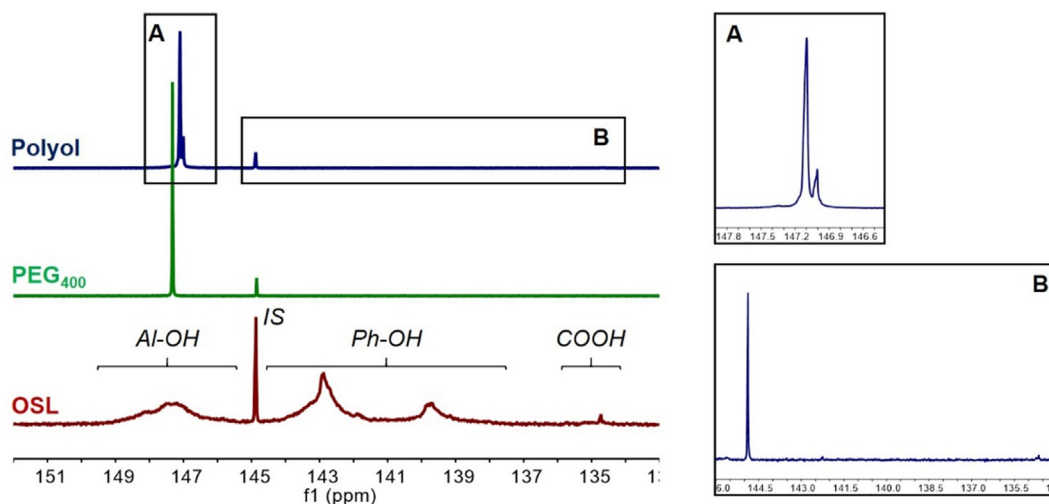
### 3.2. Influence of lignin content and PEG chain length on polyols properties

To account for the partial consumption of EC by reaction with PEG, lignin-based polyols were synthesized using a two-fold excess of EC with respect to lignin reactive groups, *i.e.* the sum of OH and COOH groups. To evaluate the influence of the lignin content and the PEG chain length, various polyols were synthesized in 10 g scale. <sup>31</sup>P NMR showed the complete disappearance of lignin phenolic OH groups, and the formation of new aliphatic OH groups, as a result of the successful modification of lignin by EC (Fig. 2).

Polyols were synthesized with 4 different PEG, with *M<sub>n</sub>* from 150 (triethylene glycol) to 400 g/mol, and a lignin content of 20, 25, or



**Fig. 1.** <sup>1</sup>H NMR (a) and SEC (b) of the product of the reaction between PEG<sub>400</sub> and EC, depending on the reaction time. EC, ethylene carbonate; PEG, polyethylene glycol; SEC, size exclusion chromatography.



**Fig. 2.**  $^{31}\text{P}$  NMR spectra of OSL, PEG<sub>400</sub> and the polyol prepared from 25%wt lignin and 75% PEG400, with details of the aliphatic (a) and phenolic OH (b) regions of the polyol. IS = internal standard (cholesterol). PEG, polyethylene glycol; OSL = Organosolv Lignin.

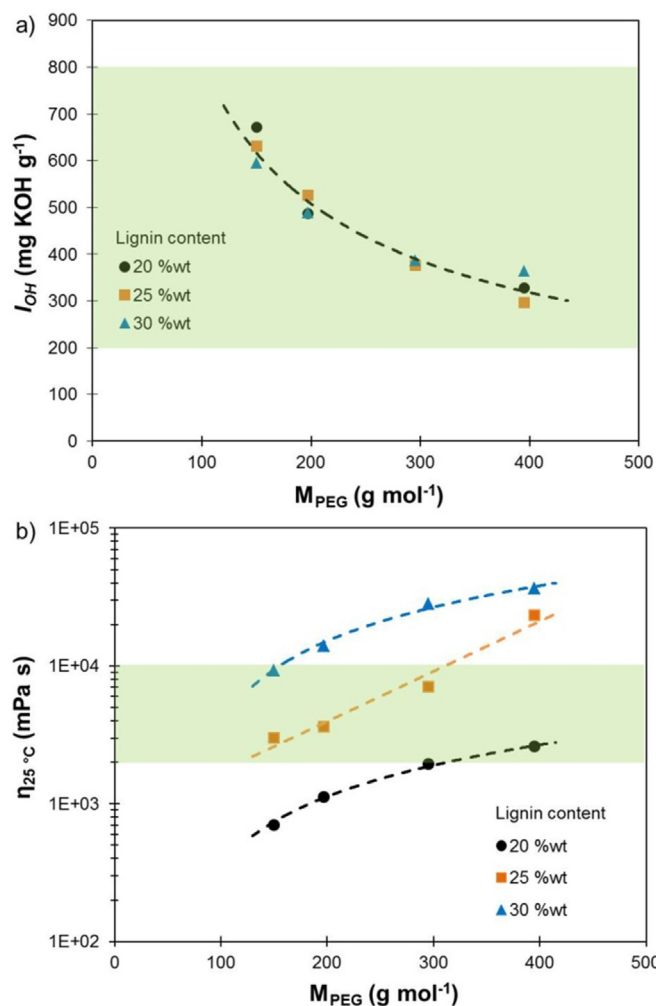
30%wt. The hydroxyl value  $I_{OH}$  and viscosity of the polyols are presented in Fig. 3. The  $I_{OH}$  is highly dependent on the PEG molar mass, but almost unaffected by the lignin content. Indeed, the majority of the OH groups of the polyol are brought by the PEG chain ends (more details are given in SI, Figure S3), therefore the  $I_{OH}$  is inversely correlated to the PEG molar mass. The amount of lignin has thus a limited effect on the total OH content of the polyol, but it contributes to increase the polyol functionality thanks to the high functionality of lignin. A wide range of  $I_{OH}$  is accessible depending on the chosen PEG, which gives the opportunity to easily tune the polyol properties depending on the target applications. The covered  $I_{OH}$  range (about 300–700 mg KOH/g) is much larger than reported values for OLP (usually between 200 and 400 mg KOH/g, depending on the lignin source) [39–44,58,59].

The viscosity of the polyols increases with the PEG chain length and the lignin content (Fig. 3b). Depending on the chosen PEG, lignin contents between 20 and 30 %wt allow reaching viscosity values within the target range for the elaboration of rigid PUR foams. It is high compared to lignin-based polyols prepared by other methods. For instance, the direct incorporation of unmodified lignin led to viscosity values higher than 9 Pa s with only 10 %wt lignin [18]. Lignin-based polyols prepared by liquefaction in PEG – glycerol had an optimal lignin content between 16 and 20 %wt [28]. For OLP, the viscosity increases sharply with the lignin content, and above 20 or 25 %wt lignin the polyol viscosity is usually too high to be used as sole polyol for the preparation of PUR foams [21,38,39,42,44]. Higher lignin content in OLP were reported (up to 70 %wt), but at the cost of long and energy-intensive pretreatments [58,59].

The developed synthesis thus gives a lot of flexibility to obtain lignin-based polyols with tailored properties. The opportunity to play on the PEG chain length and the lignin content allows to cover a much larger range of  $I_{OH}$  than usually reported for lignin-based polyols, while maintaining viscosity values within the adequate range for the elaboration of PUR foams.

### 3.3. Scale-up of lignin-based polyol synthesis and detailed characterization

Based on the  $I_{OH}$  and viscosity results, 4 polyols were selected for the scale-up and production of rigid PUR foams. They were selected



**Fig. 3.** Hydroxyl value  $I_{OH}$  (a) and viscosity  $\eta$  at 25 °C (b) of the lignin-based polyols depending on the lignin content and the average PEG molar masses. The green zones represent the target  $I_{OH}$  (200–800 mg KOH/g) and viscosity (2–10 Pa s) ranges for the production of rigid PUR foams.

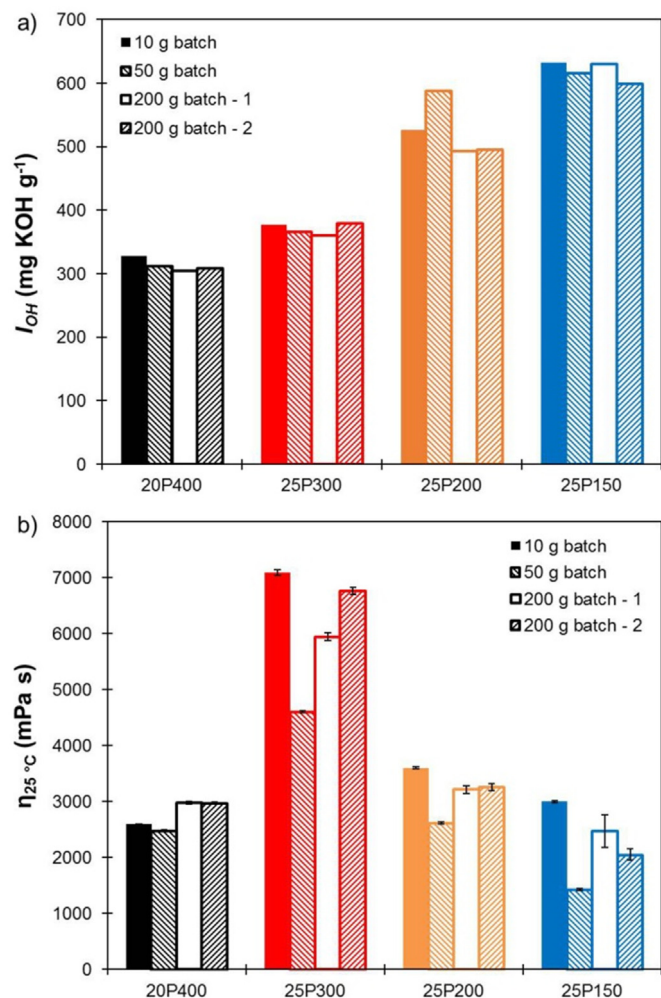
**Table 1**  
Composition of the polyols selected for scale-up and preparation of PUR foams.

Polyol	PEG type	PEG (%wt)	Lignin (%wt)
25P150	TEG	75	25
25P200	PEG <sub>200</sub>	75	25
25P300	PEG <sub>300</sub>	75	25
20P400	PEG <sub>400</sub>	80	20

to have viscosities between 2 and 10 Pa s. Their composition is given in Table 1. They were prepared with 25 %wt lignin, except with PEG<sub>400</sub>, where the lignin content was limited to 20 %wt to avoid too high viscosity.

First scale-up runs were performed on 50 g batches at 110 °C for 4 h <sup>31</sup>P NMR confirmed the full conversion of lignin phenolic OH groups. The second scale-up was performed on 200 g batches with similar conditions. In this case, <sup>31</sup>P NMR revealed that some of the lignin phenolic OH groups did not react (spectra are available in SI, Figure S4). Additional experiments were then performed at 130 °C, resulting in homogeneous polyols where all the lignin phenolic OH groups were converted (spectra are given in SI, Figure S5). Two distinct batches of 200 g of each polyol were finally prepared in these conditions (4 h at 130 °C) to evaluate the repeatability.

Fig. 4 shows the comparison of the  $I_{OH}$  and viscosities of the polyols prepared at different scales. The inter-batch reproducibility



**Fig. 4.** Hydroxyl value  $I_{OH}$  (a) and viscosity  $\eta$  at 25 °C (b) of the polyols prepared on different scales.

of  $I_{OH}$  is excellent. For unknown reasons, some polyols prepared in 50 g batch size present significantly lower viscosities. However, the reproducibility is satisfactory between the smaller (10 g) and the larger (200 g) batches and even excellent between the 2 distinct 200 g batches, thus confirming the scalability of the developed process.

<sup>1</sup>H NMR was used to quantify the presence of unreacted EC in the polyols, by integration of the singlet at 4.48 ppm (spectra are available in SI, Figure S6). About 80% of the EC reacted, either with lignin or PEG, leading to polyols that contain 2.8 to 4.3 %wt of remaining unreacted EC (Table 2). This should be considered for the PUR formulation, as EC can react with isocyanates forming oxazolidones while releasing CO<sub>2</sub> [60], and can thus be considered as a chemical blowing agent.

The polyols were then analyzed by SEC, using 2 complementary detectors. The refractive index (RI) detector analyzes the whole polyol, while the UV detector only detects the lignin fraction because of the absorption of the UV light at 280 nm by the aromatic rings. Fig. 5a shows the comparison of the SEC of polyol 25P300 with PEG<sub>300</sub> and the neat lignin. Similar data for the other polyols are given in SI (Figure S7). Two distinct domains are visible on the SEC of 25P300, corresponding to the PEG (visible only with RI) and the EC-modified lignin (visible on both RI and UV detections). The SEC distribution of the lignin fraction is shifted toward higher molar masses as a result of the grafting of ethylene oxide units. The comparison of the SEC of the different lignin-based polyols presented in Fig. 5b shows that the molar mass distribution of the modified lignin fraction is similar in all polyols, and does not depend on the PEG. This shows that coupling reactions between lignin and PEG should be limited, if any, and that PEG mostly acts as an unreactive solvent in the modification of lignin with EC.

#### 3.4. Detailed monitoring of lignin-based polyol synthesis

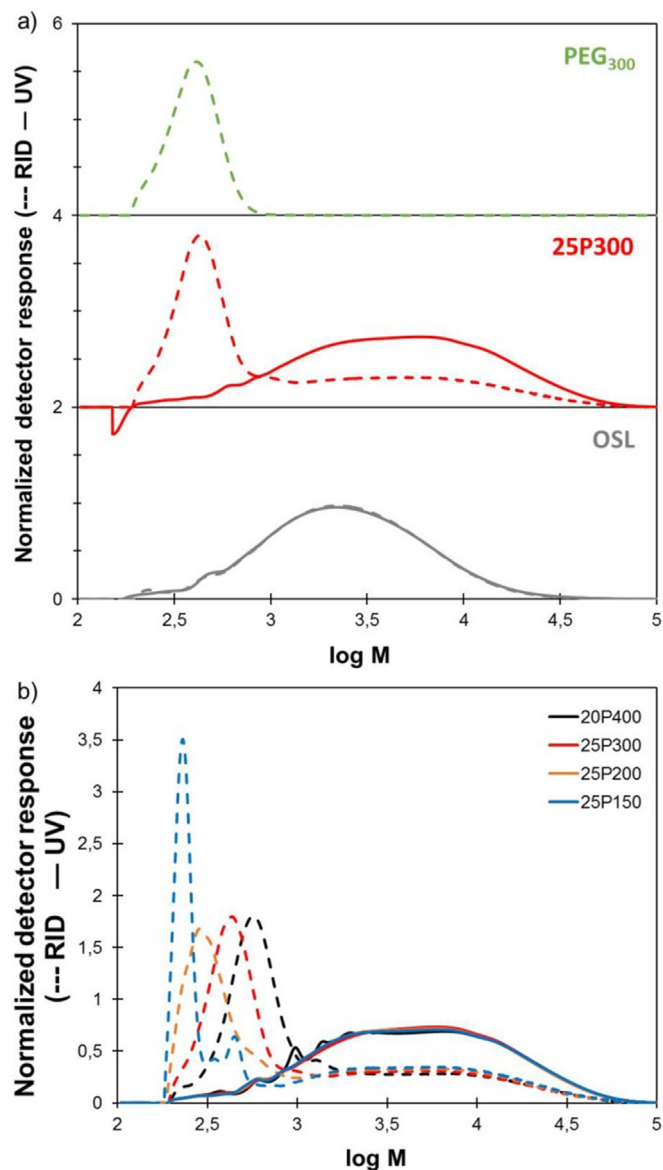
During the synthesis of the 200 g batches, aliquots were withdrawn every hour to follow the evolution of the conversion of lignin phenolic OH groups, the SEC distributions, and the viscosity. <sup>31</sup>P NMR reveals that full conversion of lignin phenolic OH groups is already achieved after 1 h and that the  $I_{OH}$  remains stable over the 4 h of reaction. The corresponding results are given in SI (Figure S8).

Fig. 6a shows the evolution of the viscosity of the lignin-based polyols during the synthesis. The viscosity increases sharply during the first hour of reaction, before stabilizing and reaching a plateau after 2–3 h. The strong increase in viscosity is probably caused by the consumption of the EC during the reaction. Recently, Liu et al. [61] proposed a method based on the measurement of the CO<sub>2</sub> evolution for in-line continuous monitoring of the modification of lignin with EC. In addition to this technique, continuous recording of the viscosity, for instance, by recording the torque of the stirring motor could potentially be applied here to precisely monitor the polyol synthesis.

SEC distributions of polyol 25P300 were recorded at different reaction times (Fig. 6b). The results show that after 2 h, the

**Table 2**  
EC consumed during polyol synthesis and final content in EC of the polyols.

Polyol	EC consumed (%)	Unreacted EC in the polyol (%wt)
25P150	80.8	3.6
25P200	77.6	4.3
25P300	77.7	4.2
20P400	82.2	2.8

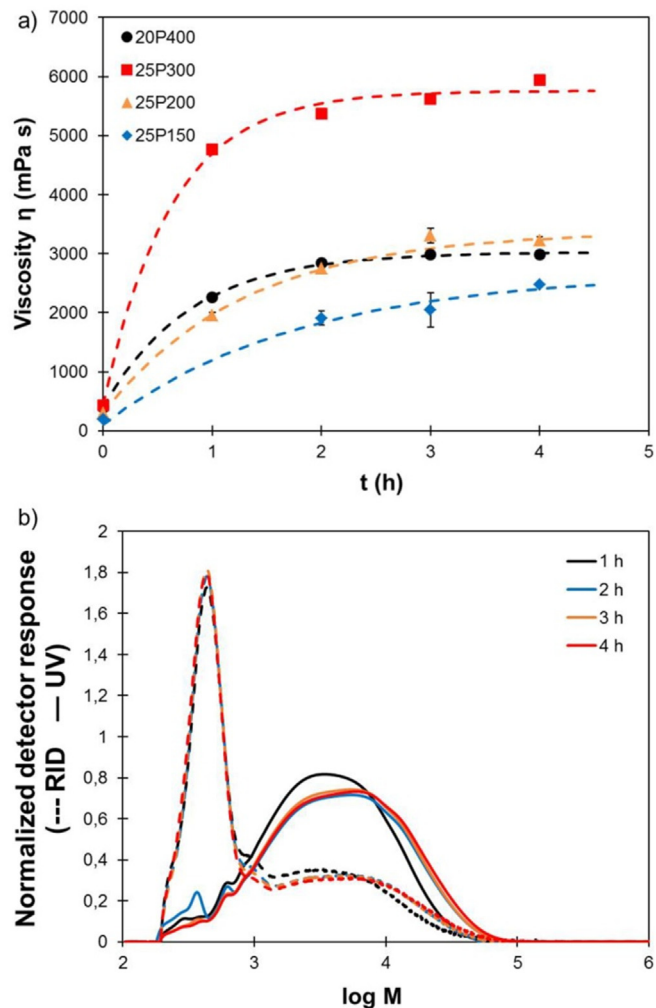


**Fig. 5.** comparison of SEC of polyol 25P300 with PEG<sub>300</sub> and OSL (a), and comparison of SEC of lignin-based polyols (b). PEG, polyethylene glycol; SEC, size exclusion chromatography.

distribution becomes stable, which is consistent with the observed evolution of the polyol viscosity. Interestingly, expanding the reaction time does not seem to cause lignin crosslinking, which is commonly observed during the reaction of lignin with EC [48, 49, 56], probably because EC is not used in large excess and the lignin is diluted in PEG. These results show that the polyol synthesis could effectively be reduced to only 2 h at 130 °C since the final polyol properties are already achieved.

### 3.5. Study of the foaming kinetics

The 4 lignin-based polyols were then tested in PUR foams formulations. The chosen formulations were kept simple in order to limit the number of components and easily evaluate the influence of the lignin-based polyols on the foaming kinetics; they are thus not fully representative of the industrial process for insulation panels. The lignin-based polyols were used in the replacement of a



**Fig. 6.** The evolution of the viscosity of lignin-based polyols during the synthesis (a), and the evolution of the SEC distribution of polyol 25P300 with reaction time (b). SEC, size exclusion chromatography.

commercial polyether polyol at substitution rates ranging from 25 to 100 %wt. Typical formulations are given in Table 3.

The expansion of the foams was followed using an ultrasonic sensor. The expansion curves are given in SI (Figures S9 to S12), together with optical and SEM pictures of the corresponding foams. The introduction of lignin-based polyols led to a faster expansion. The rise time decreases rapidly with the introduction of lignin-based polyols, as shown on Fig. 7a. It also decreases when the molar mass of the PEG used in polyols synthesis increases, especially for high substitution ratios. The maximum expansion rate increases very rapidly with the introduction of lignin-based polyols and reaches a maximum at 50–75% substitution (Fig. 7b). For 20P400 and 25P300, the maximum expansion rate could not be measured above 25% or 75% substitution, respectively, because the expansion was too fast and could not be fully recorded (see the expansion curves in SI, Figure S11 and S12).

The lignin-based polyols thus show high reactivity, which leads to a very fast foam expansion. However, the expansion is even too fast for the preparation of larger foams samples. It was thus decided to reduce drastically the catalyst content in the formulations to achieve a better control of the foam expansion. The amount of catalyst was reduced from 1.6 to 0.8 or even 0.4 parts in formulations with lignin-

**Table 3**

PUR foams formulations used for the study of foaming kinetics. Parts per hundred (pph) are given with respect to the total polyols content.

Component	Type	Parts (pph)
Standard polyol	Polyether polyol	100–0
Lignin-based polyol		0–100
Surfactant	Silicone	2.5
Chemical blowing agent	Water	1.6
Physical blowing agent	Diethyl ether	15.0
Catalyst	DMCHA	0.4–1.6
Polyisocyanate	pMDI	Adjusted to a constant NCO index (115)

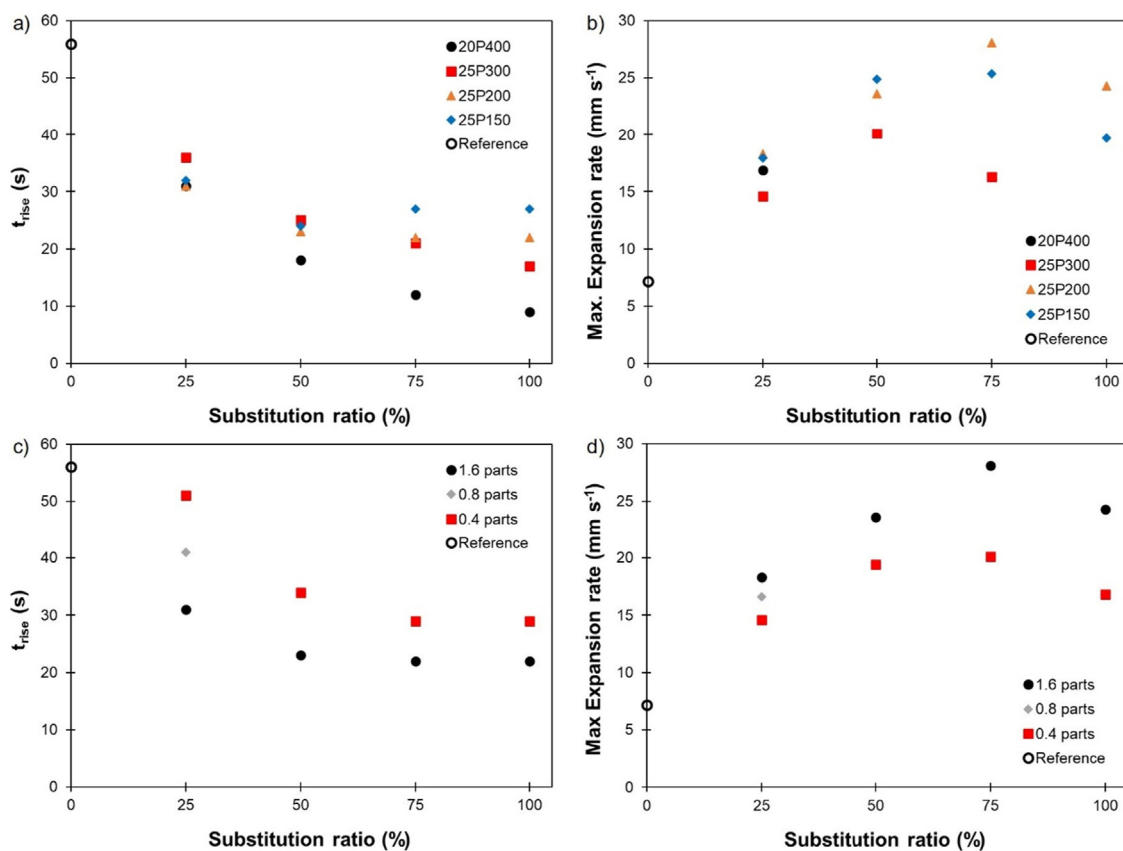
based polyol 25P200. The foaming kinetics was then evaluated for the different substitution ratios. The rise time and maximum expansion rates are shown in Fig. 7c and d, and the expansion curves are given in the SI (Figure S13). As expected, the reduction in catalyst allows slowing down the foam expansion. At 25% substitution ratio, the rise time is close to the reference when the catalyst content is divided by 4 compared to the standard formulation. However, for higher substitution ratios, even with a four-fold catalyst reduction, the rise times remain very short, which might compromise the preparation of larger foam samples. Further reduction of the catalyst content led to a reduced foam expansion, probably because the network formation becomes too slow to retain the blowing agent inside the structure. The maximum expansion rates decrease with the reduction of catalyst content (Fig. 7d), but they remain at least twice as high as the reference, confirming the very high reactivity of the developed lignin-based polyols.

### 3.6. Preparation and characterization of lignin-based rigid insulation foams

Given the above results, it was decided to prepare larger foam samples and perform detailed characterizations for 25% substitution ratio of the standard polyol. The foams were prepared with a four-fold reduction of catalyst content compared to the standard formulation, as shown on Table 4. The NCO index was maintained constant at 115, leading to a reduced proportion of polyisocyanate for polyols 25P200, 25P300, and 20P400, which have a lower  $I_{OH}$  than the standard polyol. Pictures of the obtained foams are shown on Fig. 8.

Characteristic foaming times, shown in Fig. 9a, confirm the high reactivity of the lignin-based polyols. Even with a reduced amount of catalyst, the gel and tack-free times decrease, whereas the cream time is constant. The expansion rate and temperature inside the foam were continuously recorded during the foam expansion. The corresponding curves are shown in Fig. 9b. Foams prepared from lignin-based polyols show a maximum expansion rate twice as high as that of the reference, indicating a faster expansion and confirming the results of the kinetics study (Fig. 7). The temperature inside the lignin-based foams also increases much faster than in the reference and reaches higher final values. The increase in temperature is caused by the well-known exothermicity of the reaction between isocyanates and alcohols. These results confirm that the lignin-based polyols have a higher reactivity than the standard polyether polyol.

Large foam samples ( $200 \times 200 \times 600 \text{ mm}^3$ ) were then prepared, and samples were cut out for the different characterizations.



**Fig. 7.** Rise time (a) and maximum expansion rate (b) of PUR foams prepared with the different lignin-based polyols, depending on the substitution ratio of the standard polyol. Maximum expansion rates could not be measured above 25% for 20P400 and above 75% for 25P300. Rise time (c) and maximum expansion rate (d) of PUR foams prepared with polyol 25P200 and various amounts of catalyst, depending on the substitution ratio of the standard polyol. PUR, polyurethane.



**Table 4**

Formulations of the lignin-based PUR foams. Parts per hundred (pph) are given with respect to the total polyols content.

Component	Type	Reference	LF-150 (25P150)	LF-200 (25P200)	LF-300 (25P300)	LF-400 (20P400)
Standard polyol	Polyether polyol	100.0	75.0	75.0	75.0	75.0
Lignin-based polyol		0	25.0	25.0	25.0	25.0
Surfactant	Silicone	2.5	2.5	2.5	2.5	2.5
Chemical blowing agent	Water	1.6	1.6	1.6	1.6	1.6
Physical blowing agent	Isopentane	15.9	16.0	15.8	15.1	14.9
Catalyst	DMCHA	2.0	0.5	0.5	0.5	0.5
Flame retardant	TCPP	10.0	10.0	10.0	10.0	10.0
Polyisocyanate	pMDI	Adjusted to a constant NCO index (115)				

The properties of the obtained lignin-based foams are compiled in Tables 5 and 6. The lignin-based foams present a significantly lower density (10–15% reduction) than the reference foam. Consequently, the compressive strength, which is directly correlated to the foam density, is reduced. There is no significant trend on the influence of the PEG molar mass used in polyol synthesis on the mechanical properties. All the lignin-based foams show very good dimensional stability, at high or low temperatures.

The foam structure was characterized using SEM. The average cells diameters of the lignin-based foams are similar to reference (200  $\mu\text{m}$ ), but the cells are more elongated (Table 6). This is probably related to the higher expansion rate measured during foaming. Except for LF-300, the closed cells content is above 90%, which is adequate but slightly lower than the reference formulation but higher than previously reported for equivalent foams prepared with OLP (86–88%) [44]. The thermal conductivity was measured at 10 °C and 20 °C, showing similar values for all the lignin-based foams. The thermal conductivity at 10 °C, which is a standard value for industrial insulation panels, is about 25  $\text{mW m}^{-1}\text{K}$  for all the lignin-based foams, slightly higher than the reference foam. The difference might come from the more elongated cells, as the measurement of the thermal conductivity is performed in the cells longitudinal direction, i.e. in the direction of the cells height axis. Indeed, the radiation component of the conductivity is maximized by higher distance in the measurement axis. The measured thermal conductivity of the lignin-based foams is, however, in the range of commercially available rigid PUR foams. It is also much lower than values reported for foams based on OLP with similar substitution ratio and *n*-pentane (28–32  $\text{mW m/K}$ ) [42] or acetone (29–38  $\text{mW m/K}$ ) [58,59] as physical blowing agents or water as chemical blowing agent (33–38  $\text{mW m/K}$ ) [62]. Lower values were reported by Nadji et al. [38], but using hydrochlorofluorocarbon (HCFC) 141b as physical blowing agent.

Flammability tests, detailed in the SI (Figure S14), showed no significant differences between the lignin-based foams and the reference. Indeed, apart from rare examples [63], neat lignins do not usually provide fire resistance to polymer materials and

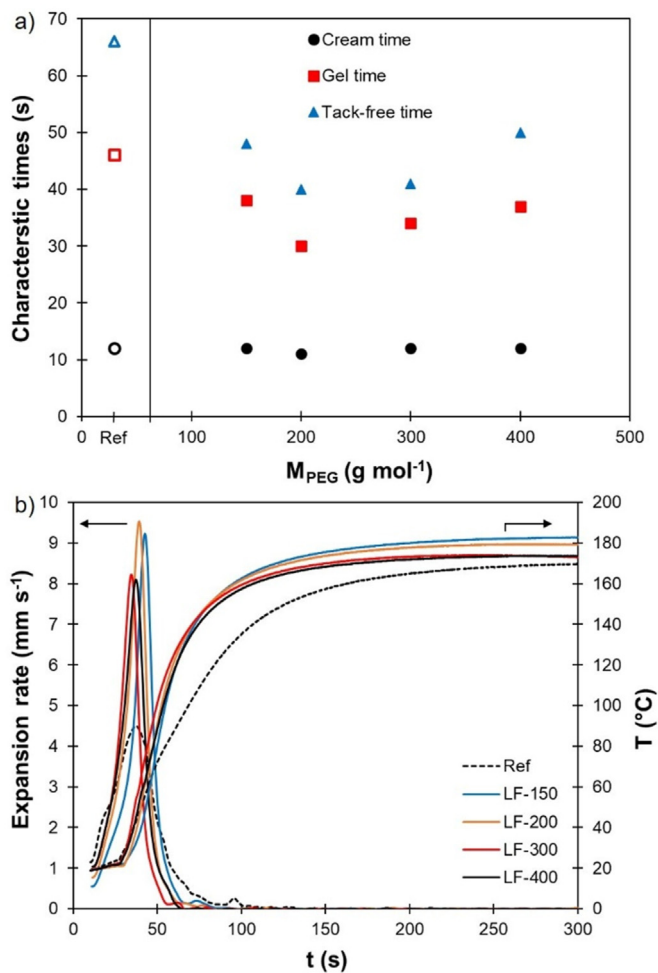


Fig. 9. Characteristic foaming times (a), expansion rate and temperature recorded during the foam rise using a Foamat device (b) for reference and lignin-based foams.

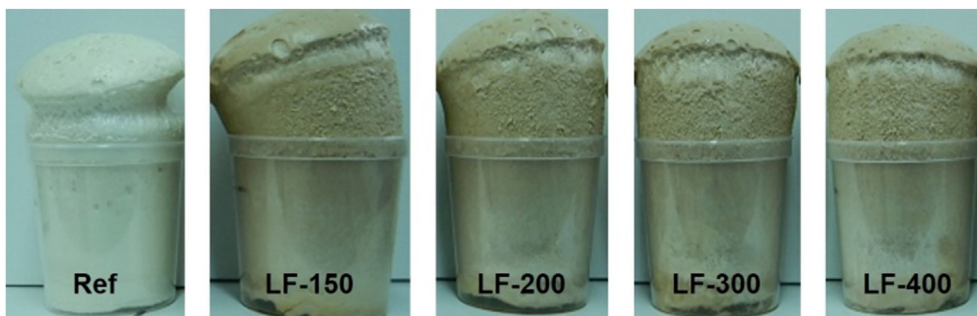


Fig. 8. Pictures of reference (Ref) and lignin-based PUR foams (LF-150 to LF-400). PUR, polyurethane.

**Table 5**

Density, mechanical properties, and dimensional stability of reference and lignin-based foams. Negative values on dimensional stability indicate a shrinkage phenomenon.

Foam	Density (kg/m)	Compressive strength (kPa)	Dimensional stability at 70 °C, 90 %RH (%)			Dimensional stability at - 20 °C (%)		
			L	l	e	L	l	e
Ref.	31.9	381 ± 38	2.2	2.2	- 0.6	- 0.2	0.3	- 2.4
LF-150	27.0	214 ± 21	1.6	1.8	- 0.2	- 0.4	- 0.1	- 1.4
LF-200	27.2	233 ± 23	1.7	1.9	- 0.8	- 0.0	0.0	- 2.3
LF-300	27.7	225 ± 23	1.5	1.7	- 1.0	0.0	0.0	- 1.1
LF-400	28.5	244 ± 24	1.9	2.0	- 1.4	0.0	- 0.0	- 0.2

**Table 6**

Thermal conductivity, closed cells content, and dimension of the cells of reference and lignin-based foams.

Foam	$\lambda_{10^{\circ}\text{C}}$ (mW m <sup>-1</sup> /K)	$\lambda_{20^{\circ}\text{C}}$ (mW m <sup>-1</sup> /K)	Closed Cells content (%)	Average cells diameter (μm)	Average cells height (μm)
Reference	23.9	24.8	99	200 ± 50	320 ± 50
LF-150	25.3	26.6	92	200 ± 50	410 ± 145
LF-200	25.4	26.8	92	200 ± 40	405 ± 130
LF-300	25.2	26.5	87	210 ± 50	345 ± 85
LF-400	25.6	26.9	92	200 ± 50	435 ± 150

chemical modifications with flame-retardant elements such as P and N are required to achieve an improvement [64].

#### 4. Conclusion

A new process for a greener synthesis of liquid lignin-based polyols has been successfully developed. These aromatic polyols are suitable for the elaboration of rigid PUR foams with high performance, for instance, for building insulation. Lignin was reacted with EC in the presence of PEG, leading to the synthesis of liquid polyols only containing primary aliphatic OH groups. Upon modification of the PEG molar mass, it is possible to obtain polyols covering a wide range of  $I_{OH}$ , between 300 and 700 mg KOH/g. Polyol viscosity suitable for manufacturing PUR foams is achieved with up to 30 %wt lignin. This new green and safe synthetic strategy presents significant advantages over previously reported lignin-based polyols, such as those obtained by oxypropylation. First, the polyol properties are easily tunable thanks to the modification of the PEG molar mass, leading to the easy production of polyols covering a much larger  $I_{OH}$  range, thus opening a lot of perspectives for PUR applications (rigid or flexible foams, coatings, adhesives and so on). Second, the polyols present a lower viscosity than polyols prepared from oxypropylated lignin, allowing the introduction of higher lignin content while keeping the viscosity below acceptable limits for suitable processing. Finally, the synthesis is performed at low temperature (110–130 °C) and more importantly at atmospheric pressure, according to green chemistry principles. Thus, it does not require any specific equipment, such as pressurized reactors used for oxypropylation, giving great perspectives for upscaling to industrial production.

The process was successfully scaled up and four different polyols were synthesized and used in the preparation of PUR foams. PUR foams with up to 100% substitution of standard polyether polyol were produced. The developed lignin-based polyols show a very high reactivity, allowing a reduction in the catalyst content by 75%. Foams with 25% substitution of standard polyol were prepared in a large scale and characterized. The obtained foams show properties in the range of commercially available PUR foams for insulation, with more than 90% closed cells and thermal conductivity around 25 mW m<sup>-1</sup>/K. In the next step toward industrial development, adjustments in the formulation could be made to allow better control of the foaming kinetics and ultimately prepare foams with higher levels of substitution of the standard polyol.

#### Credit author statement

**Antoine Duval:** Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Validation; Visualization; Roles/Writing – original draft; Writing – review & editing.

**David Vidal, Alexandru Sarbu and William René:** Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Writing – review & editing.

**Luc Averous:** Conceptualization; Funding acquisition; Project administration; Resources; Supervision; Validation; Writing – review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mtchem.2022.100793>.

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