Formulation of Bio-Based Adhesives with Industrial Application

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***Abstract*—Bio-based polyols are synthesized from wastes such as used cooking oils, and from compounds present on orange, tomato, and pine (i.e. (+)-limonene, lycopene, and α-pinene, respectively). In this work, we synthesized the polyols by using a one-pot reaction. To achieve this, a performic acid epoxidation (*in situ*) opens the epoxides with water at different reaction times in a temperature of 65°C at atmospheric pressure. The obtained polyols were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR) and the refractive index (n_D).The number of hydroxyl groups was determined a value in a range of 129 up to 215 mg KOH / g. The resultant polyurethane adhesives were synthesized adding methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) to the polyols. Preliminary adhesion tests with these polyurethanes indicated that it can be probably used to produce more ecological glue in the footwear industry. The economic evaluation shows that the investment has the potential to address the environmental and economic challenges of waste cocking oil contributing to improve the sustainability of glue industry.**

***Keywords*—Cooking oil, Natural waste, Polyols, Polyurethane adhesives, Footwear industry**

I. INTRODUCTION

Environmental concerns and increasing price of crude oil have led to increased interest in the development of material based on bio-based and renewable resources. Vegetable oils are one of the most promising sources due to their properties. The polyurethanes are polymers with a versatile range of properties and applications. The synthesis consists on the polyaddition of polyisocyanates (usually a diisocyanate) to polyols. In industry, limited types of polyisocyanates are available. However, there are a wide variety of petroleum-based polyols resources or bio-based resources. The most common source for bio-based polyol is vegetable oils. [1], [2]

The major constituents of vegetable oils are triglyceride molecules, which are fatty acids triesters of glycerol. The fatty acids commonly present in vegetable oils are palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3). The reactive sites of triglycerides are ester bonds, carbon-carbon double bonds (C=C) and hydroxyl groups (OH). The OH groups are among the most important groups to synthesize the polyols. [1], [2]

Although some vegetable oils have OH groups due to the presence of the fatty acid ricinoleic (C18:1 OH), the majority has to be functionalized. One of the most popular and effective routes to achieve it is through epoxidation. The epoxidation of vegetable oils is usually carried out with performic or peracetic acid formed in-situ by reaction of hydrogen peroxide and the fatty acid, in presence or absence of catalysts. [2], [3], [4], [5], [6], [7]

The used cooking oils (UCO) are the result of the frying process of cooking oils and are constituted mainly by vegetable oils, namely sunflower oil. This type of waste is obtained from domestic and restoration sectors and has to be treated. In Portugal, the UCO have, as the main destination, the sewage network causing problems in channeling and in performance and functioning of wastewater treatment plants. This waste is also disposed of illegally in landfills causing environmental impact with the pollution of the surroundings. Currently, there are companies that are responsible for the treatment and distribution of the UCO and also the transportation until the companies that recycle this waste. The main use of UCO in the industry is to produce biodiesel, soaps and animal feed. The market is saturated and is necessary to investigate other methods to reuse the UCO. The main difference between UCO and new cooking oil (NCO) is the composition of free fatty acids that is greater in UCO than NCO. As one of the reactive sites of triglycerides is the carbon-carbon double bonds (C=C), other components that have C=C are potential raw material. The (+)-limonene and lycopene are extracted from orange oil and tomato, respectively, that is also a waste that is produced in the large amount in Portugal due to agricultural activities. The α-pinene is also a compound with C=C that is present in pines, one of the major constituent of the Portuguese forest, that urgently need management solutions to control the fires. These compounds have the reactive sites that are required to hydroxylate the compounds.

In this study, a series of polyols were prepared by epoxidation/ring opening from different types of cooking oils, (+)-limonene, lycopene, and $\alpha - pineno$. The main goal of this work is to produce bio-based polyols starting from waste cooking oils (+)-limonene, lycopene, and α-pineno in order to obtain a more ecological adhesive formulation. The conversion of triglyceride double bonds to epoxide rings followed by their conversion to the hydroxyl groups occurs in a single step. Epoxidation is carried out by performic acid generated *in situ* with formic acid/hydrogen peroxide and ring opening by water in acidic media.

This work was developed in partnership with the company CIPADE. This company produces adhesives for several sectors, including the Footwear Industry.

II. RELATED WORK

The epoxidation/oxirane ring opening methods have been widely investigated for the preparation of bio-based polyols for polyurethane production. In these methods occurs the epoxidation of unsaturated bonds, followed by ring-opening reactions of the oxirane rings. The nucleophilic reagents can be amines, carboxylic acids, halogenated acids or alcohols. [7]

In some developed researches water, mono-hydroxy alcohols and poly-hydroxy alcohols were used as nucleophilic reagents for ring-opening of epoxides. The ring-opening reaction is frequently catalyzed with inorganic acids, such as phosphoric acid, sulphuric acid, fluoroboric acid and Lewis acids. [8], [9], [10] In [4] was prepared a series of polyols from ESO using methanol, glycol, and 1,2-propanediol as ring-opening nucleophiles. The prepared polyols had a range of OH number varying from 148 to 240 mg KOH/g. Using a similar pathway, in [11], [12] were prepared polyols through ring-opening epoxidized vegetable oils using bio-based 1,2-propanediol and 1,3-propanediol. In [13] methanol was used to ring-open epoxidized *Jatropha* oil to prepare polyols with hydroxyl content from 171 to 179 mg KOH/g. In this study, the authors also reported that the application of more concentrated hydrogen peroxide in the solvent-free epoxidation process accelerated the epoxidation reaction, resulting in minimum side reactions and the maximum value of oxirane rings content. In [14] bio-based polyols were prepared by ring-opening of epoxidized rapeseed oil using diethylene glycol.

Using greener nucleophiles, in [2] was used water as a reagent for ring-opening of epoxidized vegetable oils. It was also reported that epoxidation and the hydroxylation of vegetable oils can be performed in one single step using performic acid prepared *in situ* with the reaction between hydrogen peroxide and formic acid.

III. MATERIALS AND METHODS

A. Synthesis of bio-based Polyols

Chemicals

The used cooking oils were obtained by domestic utilities, the linseed oil was purchased from the brand *Emile Noel*, the cooking oil was purchased from the brand *fula*, (+)-limonene was extracted by steam distillation from orange oil purchased from *Sumol*, lycopene was extracted by Soxhlet extraction from tomatoes and α-pinene was purchased from *Fluka Chemie AG*. Formic acid 98% and sodium bisulfite were purchased from *Merck*. Hydrogen peroxide solution 30%, diethyl ether and magnesium sulfate anhydrous were purchased from *Panreac*. Sodium carbonate was purchased from *Univar*. All chemicals are analytical grade and were used without further purification.

Procedure

Cooking oils (35g, 0,19 mol of double bonds) were mixed with 21,5 mL (1,11 mol) of formic acid. A solution of H_2O_2, 30% (25,3 mL; 0,28 mol) was slowly added dropwise to the mixture at room temperature over 30 min, under strong mechanical stirring. When the H_2O_2 addition was completed, the mixture was heated at 65°C, Figure 1. The procedure was repeated with reaction times between 1-5 hours. After the required time, the reaction mixture was washed firstly with a sodium bisulfite 10% (w/v) solution and after with sodium carbonate, 10% (w/v) solution until neutralization had occurred. Lastly, diethyl ether was added to separate the organic phase. The organic phase was dried overnight with magnesium sulfate anhydrous. The solvent was removed under vacuum using a rotatory evaporator.

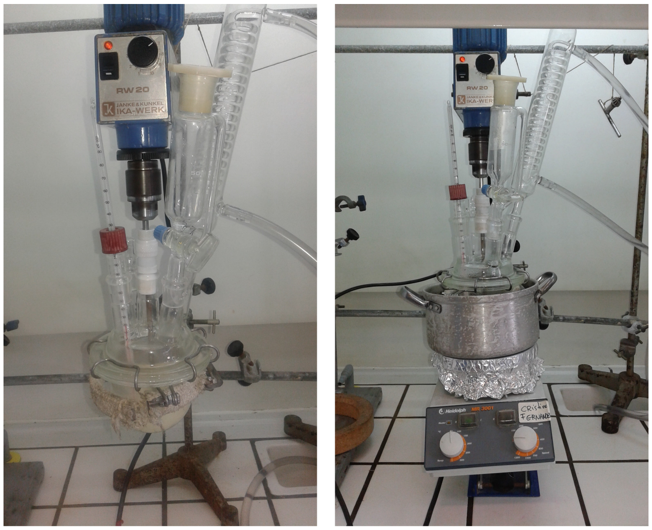
(a) (b)

Fig. 1. Experimental apparatus were is possible see the reactor (a) and the heating system (b).

An analog procedure was done for linseed oil, (+)-limonene, lycopene, and $\alpha - pinene$ with an adjustment of the reagents quantity (Table I).

TABLE I
QUANTITY OF REAGENTS.

	Mass (g)	Formic Acid (mL)	Hydrogen Peroxide (mL)
linseed oil	35	30,8	36,2
(+)-limonene	35	29,6	34,8
lycopene	35	49,0	58,0
$\alpha - pinene$	35	15,1	17,7

B. Determination of Hydroxyl Value of Polyols

Chemicals

Potassium hydroxide (KOH) 0,1 N and 0,5 N were purchased from *Fluka*. 4-N, N-dimetilaminopiridine, phenolphthalein, and thymolphthalein were purchased from *Merk*. Acetic anhydride and tetrahydrofuran (THF) were purchased from *Sigma*.All chemicals are analytical grade and were used without further purification.

Procedure

The hydroxyl (OH) content of the polyols was determined by titration methods. To determine the hydroxyl value is also necessary to obtain the acid value (AV). To obtain the AV, 40 mL of THF and 3 drops of pH indicator phenolphthalein were added into 1 g of the polyols. The mixture was titrated with a KOH 0,1 N solution. For each polyol, the procedure was done in triplicate. The AV has determined accordingly with Equation 1.

$$AV = \frac{V_{KOH} \times N \times MW_{KOH}}{w_{sample}} \quad (1)$$

where $MW_{KOH} = 56,1 g.mol^{-1}$, V_{KOH} is the titrant volume, N is the titrant concentration and w_{sample} is the sample weight used

To determine the OH value it was necessary to prepare 3 solutions:

1) Catalyst solution: 1% 4-N,N-dimetilaminopiridine in THF;
2) Acetyl solution: 12,5% of acetic anhydride in THF;
3) pH indicator solution: 1% thymolphthalein in THF.

At 1g of polyols was added 40 mL of THF, 10 mL of catalyst solution and 10 mL of acetyl solution. The mixture was stirred for 10 minutes. Then 2 mL of distilled water was added and the mixture was stirred for more 30 minutes. After the stirred time, 3 drops of thymolphthalein solution were added and the mixture was titrated with KOH 0,5 N. For each polyol, the procedure was done in triplicate. The OH value was calculated accordingly with Equation 2.

$$OH = \frac{MW_{KOH} \times N \times (V_S - V_{KOH})}{w_{sample}} + AV \quad (2)$$

where $MW_{KOH} = 56,1 g.mol^{-1}$, V_{KOH} is the titrant volume,V_S is the volume of standard sample (all the reagents were added except the polyols), N is the titrant concentration, w_{sample} is the sample weight used and AV is the acid value previously determined.

C. *Refractive Index*

Instrumentation

The refractive index of the polyols was measured in an Abbe refractometer from *CARL ZEISS*.

D. *Fourier Transfrom Infrared Spectroscopy*

Instrumentation

The Fourier Transform Infrared Spectroscopy (FTIR) spectrum was determined using sodium chloride disks (NaCl) and the equipment FTIR-8400S from *SHIMADZU*. The spectra were obtained with 32 scans and a resolution of 4,0.

E. *Proton Nuclear Magnetic Resonance Spectroscopy*

Instrumentation

The Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H RMN) spectra were determined using the equipment *Bruker 300* $Ultrashield^TM$ type *Magnet System* 300 MHz/54 mm.

F. *Synthesis of Polyurethane Adesives*

Chemicals

Methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) were supplied by CIPADE.

Procedure

To obtain the polyurethane adhesives were added a percentage of di-isocyanate at 4 g of the polyols. Accordingly to CIPADE the amount of di-isocyanate added is 5% of total weight of the polyols sample. This value is used for the petroleum-based polyols that this company produce. To know the percentage of di-isocyanate to add, the OH values of the CIPADE polyols were determined and compared with the OH values of the bio-based polyols. In the Table II the mass percentages over the total amount of polyol of di-isocyanate to add at bio-based polyols obtained from new cooking oil (NCO), used cooking oil (UCO), very used cooking oil (VUCO) and new linseed oil (NLO) for reaction times of 1h, 3h and 5h are showed.

TABLE II
MASS PERCENTAGE OF DI-ISOCYNATE TO ADD AT BIO-BASED POLYOLS.

Polyols	MDI (%)	TDI (%)
UCO 1h	26	49
UCO 3h	15	29
UCO 5h	23	43
VUCO 1h	19	35
VUCO 3h	17	32
VUCO 5h	11	21
NCO 1h	18	34
NCO 3h	5	9
NCO 5h	19	35
NLO 1h	39	72
NLO 3h	15	27
NLO 5h	13	24

G. *Glue Tests*

The glue tests were done using a specific paper that was supplied from CIPADE. This paper is the same that they use to test their own adhesives.

The polyurethane adhesives were applied to the paper using an applicator as shown in Figure 2.

The paper was cut into strips (Figure 3). After 30 minutes one of the strips was evaluated by separating the ends of the paper. The same procedure was done every one hour until the paper rips when being taken off, a positive result.

IV. RESULTS AND DISCUSSION

A. *Synthesis and Characterization of the Polyols*

In this work, the bio-based polyols were synthesized from different types of raw materials. Regarding the viscosity, the polyols synthesized from NLO and VUCO showed a higher viscosity, than others. Regarding the smell, the cooking oil polyols had no odor of used oil, as well as the lycopene and $\alpha - pinene$ polyols. On the other hand, the polyols synthesized from (+)-limonene preserved the characteristic

Fig. 2. Application of the polyurethane adhesives at the test paper.

Fig. 3. Rips of paper glued by bio-based polyurethane adhesives.

odor of its compound, indicating that (+)-limonene did not react completely.

In terms of coloring, the polyols from vegetable oil presented a colorless appearance, except for the polyols obtained from VUCO and NLO, which in this case had a yellow coloration. The yellow coloration was expected, once the oil was exposed to a long frying time at high temperatures causing a change in its color, consequently, in the obtained polyol. So, the (+)-limonene polyols showed a brown coloration while the lycopene and $\alpha - pinene$ polyols showed a yellow coloration. The Figure 4 shows some polyols samples along with its respective coloration.

B. Synthesis and Characterization of the polyurethane Adhesives

The color can be an important factor to choose an adhesive among other, especially in the footwear context. If the adhesive is used to attach the tops of the shoes to the sole, its color may not affect the choice of the polyol. Although if the adhesive is used to paste exposed areas of the shoes, it is necessary to ensure that the design of the shoes are not affected by the color of the polyols.

The smell is another important factor to take into consideration because it can drastically affect the consumer demand. In general, the cooking oil polyols meets the smell and color requirements, as they are promising for the adhesives formulation and application to the shoes. While the other residues used for polyol synthesis are also promising, it is necessary to research more methods for its synthesis that includes the addition of color and odor-eliminating components.

Fig. 4. Polyols obtained from NCO, UCO and VCO, from left to right

The polyols were synthesized from new cooking oil (NCO), used cooking oil (UCO), very used cooking oil (VUCO) and new linseed oil (NLO) with yields between 23% and 91%. The differences among yelds values are caused by experimental errors. Table III shows the yields according to its reaction time. Comparing the yields with the reaction time, it is possible to infer that the yield generally reaches its maximum value with 3 hours of reaction.

TABLE III
THE YIELD OF THE SYNTHESIS PROCESS OF THE POLYOLS THROUGH DIFFERENT TYPES OF RAW MATERIALS ALONG WITH DIFFERENT REACTION TIMES. *NS NOT SYNTHESIZED, *RQ RESIDUAL QUANTITIES

Yield (%)	**1h**	**2h**	**3h**	**4h**	**5h**
NCO	75	61	60	62	64
UCO	63	56	82	73	43
VUCO	23	37	55	49	48
OLN	80	49	91	57	46
(+)-limonene	ns	ns	rq	ns	27
$\alpha - pinene$	ns	ns	38	ns	15
Lycopene	ns	ns	rq	ns	rq

Regarding the (+)-limonene and $\alpha - pinene$ polyols, the obtained yields are between 15% and 38%. The quantity of polyol obtained from lycopene was residual, making it impossible to calculate its yield. Due to the low yields obtained from these compounds, we decided to proceded the study only considering the polyols obtained from oils.

The results obtained from the titration procedures indicate that the bio-based polyols have an amount of hydroxyl groups (OH) of 129-293 mg KOH/g and an acid value (AV) between 13-106 mg KOH/g (Table IV). The determined OH values are similar to those obtained in the literature. [4], [11], [12], [13], [2]. It is important to note that the different amounts of OH and AV between the bio-based polyols and the CIPADE polyols (which are obtained from petroleum sources) have lower OH and AV values. The differents AV and OH values are due to the higher molecular weight of CIPDADE polyols (4000-6000 g/mol) compared to bio-based polyols (1650-2000 g/mol). CIPADE produces specific polyols for each type of diisocyanate. For example, the polyol CIPADE 1 is specific for MDI addition while and the Polyol CIPADE 2 is specific for TDI addition. We can conclude that the obtained bio-based polyols have OH groups which can be used in the preparation of polyurethane adhesives.

TABLE IV
ACID VALUES AND HYDROXYL GROUPS PRESENT IN SYNTHESIZED POLYOLS FROM VEGETABLE OILS.

Polyols	AV (mg KOH/g)	OH (mg KOH/g)
UCO 1h	72	170
UCO 3h	42	162
UCO 5h	63	138
VUCO 1h	51	129
VUCO 3h	46	140
VUCO 5h	30	185
NCO 1h	49	215
NCO 3h	13	170
NCO 5h	52	223
NLO 1h	106	293
NLO 3h	40	218
NLO 5h	36	254
Polyol CIPADE 1	8	14
Polyol CIPADE 2	2	7

Figure 5 shows the evolution of refractive index of the bio-based polyols (y-axis) with the reaction time (x-axis) applied to each type of raw material.At reaction time zero, the refractive index values correspond to the cooking oils before any reaction. In this situation, the NLO and VUCO have the highest refractive index, while NCO is the oil with the lowest refractive index. In terms of used cooking oils, it is possible to verify that the frying time is directly related to the refractive index. The longer frying time, the higher refractive index, due to the higher viscosity.

Analyzing the behavior of the refractive index of the bio-based polyols, it is possible to verify that the polyols obtained from NLO and VUCO have a similar refractive index, due to higher polymerization. It has been previously shown that the polyols obtained from these oils had a yellow coloration and the highest viscosity. The refractive indexes of the NCO and UCO polyols are also similar, suggesting that their composition is alike, having the higher refractive index for 3h reaction.

Analyzing the UCO FTIR spectra and its respective polyols (Figure 6) it is possible to verify that the main difference between the spectra of the oil and the bio-based polyols is the disappearance of the band at 3010 cm^-1. Then, appears a large band at 3450 cm^-1 assigned to the OH group. In this way, it proves that the double bonds react completely, giving rise to the epoxide groups. Consequently, the ring opens leading to the desired functionalization with the OH group formation. The spectra of the polyols show that regardless the reaction time the band corresponding to the C-H (present in the double bonds) disappears, indicating that all the unsaturations were functionalized. The FTIR spectra of the remaining polyols show similar results and are in agreement with the literature. [4], [11], [12], [13], [2]

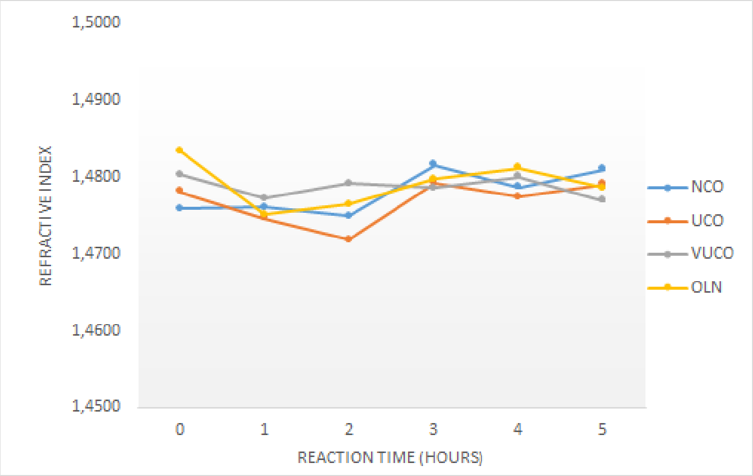

Fig. 5. Evolution of the refractive index with the reaction time.

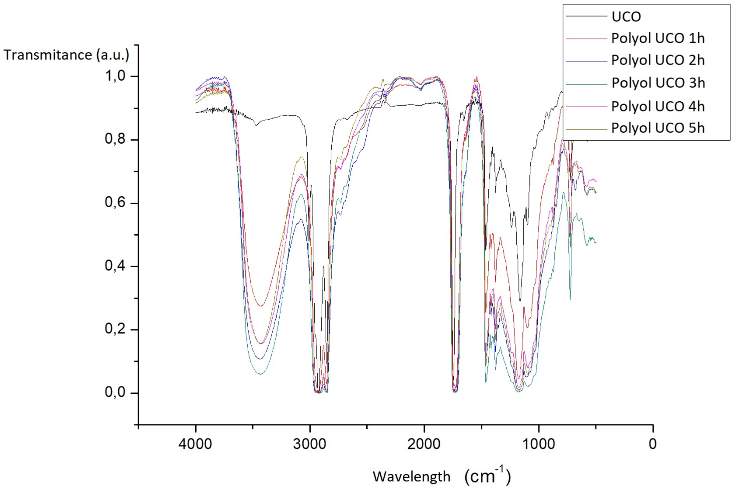

Fig. 6. FTIR spectra of the UCO and its respective polyols.

In the ^{1}H NMR spectra of UCO (Figure 7) it is visible a hydrogen signal in the region 5,2-5,5 ppm assigned to the C=C double bonds. In the polyols spectra, this signal does not appear. Instead, it appears a hydrogen signal at 2,6-2,9 ppm assigned to the epoxy groups for the polyol UCO 1h and a hydrogen signal in the region 3,8-4,2 ppm assigned to the OH groups for polyols UCO 1h and UCO 5h. In the spectra of polyol UCO 5h, the hydrogen signal related to the epoxy groups does not appear showing that all the epoxy rings were opened. For the other polyols, a similar result was obtained. These results are also in agreement with the literature. [4], [11], [12], [13], [2]

Once this work aims to synthesize bio-based polyols to replace petroleum-based polyols, we compared the FTIR spectra of the CIPADE petroleum-based polyols with FTIR spectra of the bio-based polyols (Figure 8). Note that the differences in the region of OH groups are expected because

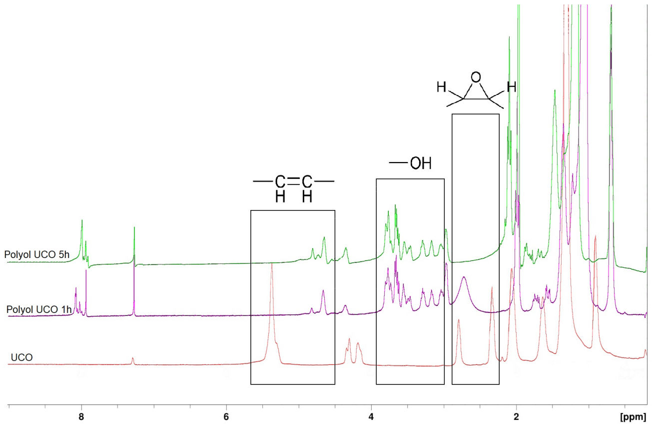

Fig. 7. ^{1}H NMR spectra of the UCO and its respective polyols.

of the smaller amount of OH value in CIPADE polyols. This spectrum shows that the choice of the diisocyanate (according to the composition of the polyol) has a significant influence on the synthesis of the polyurethane. It is unclear which the diisocyanates are the most suitable for adding to the bio-based polyols once none of the polyols of CIPADE have similar spectra.

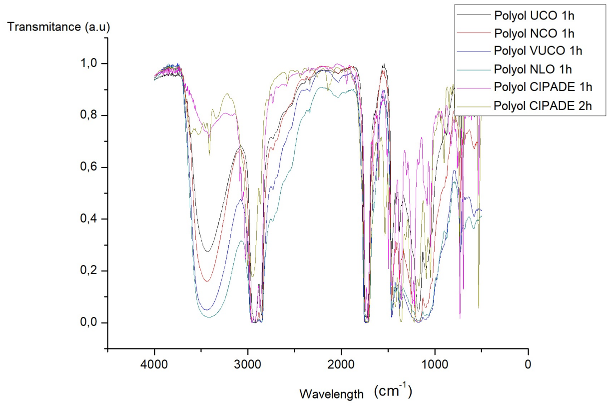

Fig. 8. FTIR spectra of the bio-based polyols and CIPADE polyols.

The polyurethane adhesives (PUR) were synthesized with the addition of MDI and TDI at polyols. The reaction scheme for the synthesis of the polyols by epoxidation/ring opening and addition of diisocyanate for the formulation of the PUR is shown in Figure 9.

Analyzing the physical characteristics of PUR, we found that they have a yellow coloration when the MDI diisocyanate is used while they are colorless when TDI is added. Figure 10 shows a PUR sample formulated from polyol UCO 5h.

Analyzing the FTIR spectra of PUR samples (Figure 11), it is possible to verify the appearance of a band in the region 2200-2240 $cm^{-}1$ assigned to N=C group of the diisocyanates. These spectra were traced after 1h of PUR synthesis. The band at 3450 $cm^{-}1$ is still visible showing that the OH groups have not reacted completely. After 24h is expected that this signal disappears due to the complete reaction of the diisocyanate with the OH groups of the polyols. The similarity is observed between the spectra of the PUR samples, being unclear which diisocyanate (MDI or TDI) must be used. These spectra are in accordance with the literature. [2]

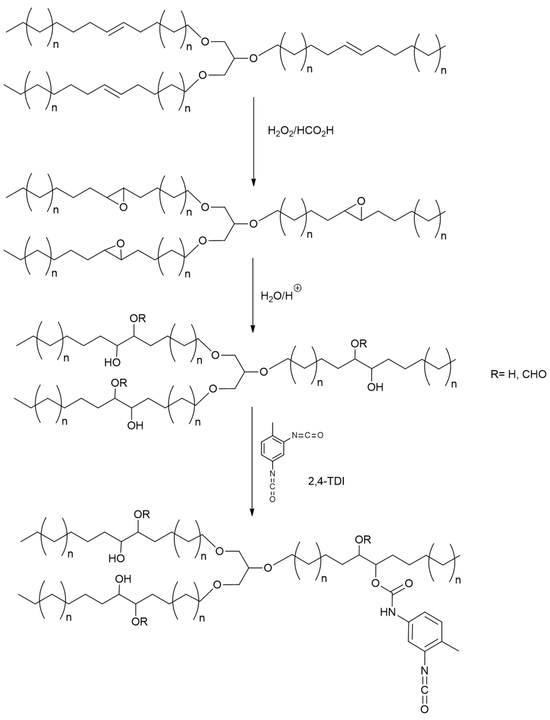

Fig. 9. Reaction scheme for the PUR formulation.

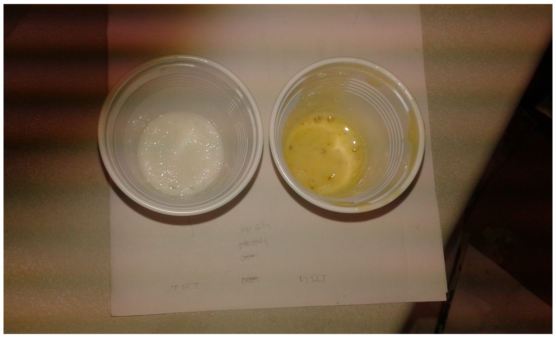

Fig. 10. PUR adhesives by adding TDI (left) and MDI (right) to the polyol UCO 5h.

The PUR were submitted to glue tests 30 minutes after the application. All the samples obtained negative results in this period. The same analyses were performed every 1 hour for 7 consecutive hours, during this period the results remained negative. After 24 hours, some of the samples already presented positive results, (i.e. the paper was torn when taking off). The glue tests results are summarized in Table V.

The Figure 12 shows a positive and a negative test.

The PUR obtained through the polyols NLO 1h, NLO 3h, NLO 5h, VUCO 1h, VUCO 3h, VUCO 5h and UCO 5h present positive results regardless of the type of diisocyanate used. This can be related to the high viscosity of these polyols. The PUR obtained from the polyol UCO 1h has a positive test when TDI is added. This result highlights the importance of choosing a suitable diisocyanate.

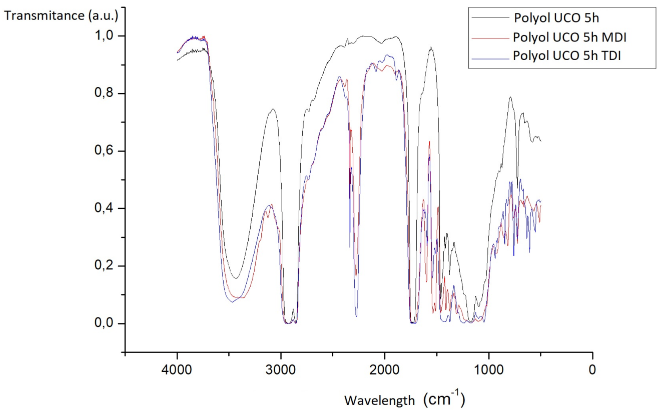

Fig. 11. FTIR spectra of the polyol UCO 5h and the respective polyurethane adhesives (PUR).

TABLE V
RESULTS OF GLUE TESTS.

Polyols	MDI	TDI
UCO 1h	-	+
UCO 3h	-	-
UCO 5h	+	+
VUCO 1h	+	+
VUCO 3h	+	+
VUCO 5h	+	+
NCO 1h	-	-
NCO 3h	-	-
NCO 5h	-	-
LNO 1h	+	+
LNO 3h	+	+
LNO 5h	+	+

Fig. 12. Glue tests result.

The polyols obtained from NCO have OH values higher than the UCO and VUCO polyols. However, none of the PUR samples synthesized with NCO polyols have positive tests. This result is unrelated with the polyols OH value because the positive tests are expected to occur on the polyols with the highest OH value. It can be related with the diisocyanate ratio and type and also with the fact that some of the OH groups are from the formic acid that not react completely.

These results show that the PUR obtained using used cooking oils, the VUCO particularly, had a better behavior in the glue test than the NCO. This is in agreement with the objectives to be reached with this work.

To finally conclude, these tests have many variables that can influence the results. To enhance the PUR performance it is necessary to optimize reagent quantities and reaction conditions.

V. INDUSTRIAL APPLICATION

To investigate if the formulation of polyurethane adhesives (PUR) from used cooking oils (UCO) has industrial viability, a scale-up of the process and an economic evaluation was performed. The economic evaluation methods used estimated the process profitability at an early stage.

A. *Scale-up*

To synthesize bio-based polyols from UCO at industrial scale using a laboratory similar method, the equipment was sized for an annual capacity of 10 kton. The amount of polyol produced is 1,263 ton/h, consuming 2,140 ton/h of UCO. In the process proposed, the reaction occurs in a stirring reactor, the neutralization and solvent extraction happens in tanks and the aqueous phase is eliminated in decanter vessels. The operations solid dry with magnesium sulfate anhydrous and rotary evaporation were replaced with a flash distillation column. The proposed flowsheet is shown in Figure 13.

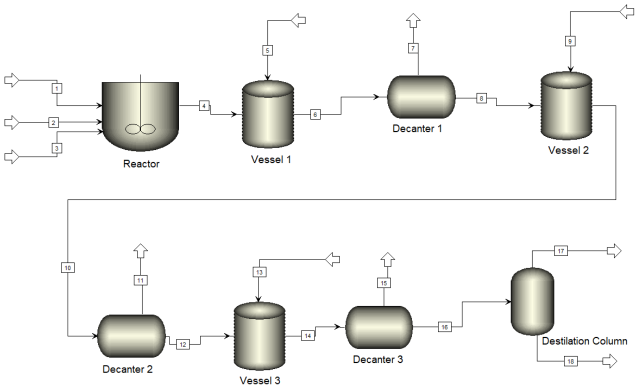

Fig. 13. Process Flowsheet to synthesize the polyol at industrial scale.

B. *Economical Evaluation*

The economic evaluation of the process indicated in a first analysis that the process is profitable with a profitability index of 1,6. The capital is recovered in 6 years. The break-even at 11% show that is possible reduces the plant capacity until 11% keeping the viability.

VI. CONCLUSIONS

The bio-based polyols synthesized from epoxidation/ring opening of cooking oils presented an average hydroxyl value (OH) of 129-293 mgKOH/g and an acid value (AV) between 13-106 mgKOH/g. FTIR and ^{1}H NMR analysis showed the presence of OH groups, confirming the conversion of the fatty acids double bonds (C=H). The glue tests results showed that the polyols with higher viscosity (higher refractive index), results in polyurethane adhesives (PUR) with positive tests. The process scale-up is economically viable. However, more investigation is needed to achieve the required PUR performance.

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