

Polyols from the Lignocellulosic Waste of Biodiesel Production Process

Luis Serrano, Rodrigo Briones, Ainara Melus, Zsanett Herseczki, Jalel Labidi*
Chemical and Environmental Engineering Department,
University of the Basque Country
Plaza Europa, 1, 20018, Donostia-San Sebastián, Spain
jalel.labidi@ehu.es

The oxypropylation of rapeseed cake residue generated in the biodiesel production process was studied. The reaction was carried out by suspending the rapeseed cake residue in propylene oxide [30/70 ratio (w/v)] in the presence of a basic catalyst (10% KOH) and heating the resulting mixture at 160 °C in a nitrogen atmosphere. The chemical structure of the obtained polyol was studied by CHNS elemental analysis, infrared spectroscopy, and ¹H NMR spectroscopy, and other parameters such as viscosity, OH number, molecular weight (GPC), and thermal behaviour (DSC, TGA) were also measured. The obtained results showed an almost total conversion of the solid substrate into a polyol with good characteristics (OH number, 610 mg of KOH/g; viscosity, 84.23 Pa·s; and molecular weight, 33550 g/mol) for use in polyurethane, polyether, or polyester formulations.

1. Introduction

Biodiesel, fuel derived from renewable biological sources such as vegetable oils or animal fats, represents a promising source to substitute conventional diesel fuel because of its biodegradability, nontoxicity, low emission profiles, and environmentally beneficial characteristics (Dmytryshyn et al., 2004). However, in spite of its favorable impact, biodiesel production presents some drawbacks related to the economics of the process, which are highly dependent on feedstock costs (Yuan et al., 2008; Cetinkaya and Karaosmanoglu, 2004). Specifically, EU-25 biodiesel is mainly obtained from rapeseed whose demand for this use has increased considerably in the past several years (Piotrowska et al., 2008).

In the processing of rapeseed oil seeds for biodiesel production, 65% of the feedstock is converted into a lignocellulosic cake residue (Özçimen and Karaosmanoğlu, 2004). This product, which is rich in hemicelluloses and has a high content in hydroxyl groups, is currently used as cattle feed (canola variety) or for energy production (Çulcuoğlu et al., 2002). Nevertheless, the upgrading of this byproduct through its conversion to lowcost polyols by oxypropylation and their incorporation into polymer formulations could entail a considerable valorisation of the residue and, thus, economic and environmental improvements for the process.

This oxypropylation process does not require the removal of any solvent or other component, nor does it require any separation or purification procedure for the recovery of the final polyol mixture (Fernandes et al., 2005). The objective is to increase the OH functionality of the starting material by moving the hydroxyl groups to the chain end, making them much more accessible for further reaction (Gandini, 2008). The corresponding hydroxypropyl derivatives can be used as rheological modifiers, components in the manufacture of polyurethanes, and additives, as well as various other applications (Gandini, 2008; Gandini and Belgacem, 2008).

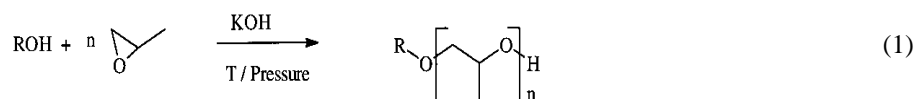
This article describes a preliminary study of the oxypropylation of rapeseed cake residue and the characterization of the ensuing polyols and rapeseed cake pellets.

2. Materials and Methods

2.1 Materials

Rapeseed cake pellets (RCPs) were supplied by ÖKO-Line Ltd., Budapest, Hungary. Characterization of rapeseed cake pellets were done according to standard methods. Chemical composition, given on an oven dry weight basis, was following: 5±0.1% ash (TAPPI T211 om-93), 16±5.2% lignin (TAPPI T222 om-98), 62±3.2% holocellulose (Wise et al., 1946), 18±1.2% α -cellulose and 44±0.5% hemicelluloses (Rowell, 1983).

2.2 Oxypropylation reaction



The oxypropylation reaction was carried out in a 1500 mL Parr stainless steel reactor equipped with a heating mantle, mechanical stirrer and manometer. Rapeseed cake pellets were preactivated with an ethanol/KOH solution at room temperature under nitrogen atmosphere. The dried activated substrate was mixed with 99.5 % propylene oxide and the reactor was heated to 160 °C under nitrogen atmosphere. From this initial status, the exothermic started and a progressive increase of pressure and temperature was observed. The reaction was considered finished when the pressure returned to atmospheric levels, reflecting the consumption of propylene oxide.

2.3 Polyol characterization

The viscous product obtained was analyzed in terms of elemental analysis for carbon, hydrogen and nitrogen in a Euro EA 3000 series elemental analyzer from Euro Vector SpA, Milano, Italy. Chemical structure was studied by Fourier transform infrared (FTIR) and ¹H NMR spectroscopies.

Gel permeation chromatography (GPC) was used to determine the average molecular weight of the oxypropylated product (M_w). The thermal stability of the samples was studied by thermogravimetric analysis (TGA), which measures the weight loss of samples in relation to the temperature of thermal degradation.

The glass transition temperature (T_g) of the oxypropylated product was determined using a Mettler DSC20 differential scanning calorimeter linked to a TC 15 TA processor and medium pressure pans.

The complex viscosity (η^*) and the hydroxyl index, or OH number (I_{OH}), are important parameters in the characterization of oxypropylated products.

3. Results

3.1 Chemical composition

The high hemicelluloses percentage found ensured the availability of hydroxyl groups and suggested the suitability of this material for the oxypropylation reaction. A high carbon percentage, 44.87 %, was found in the rapeseed cake residues. The oxypropylated product presented higher percentages of carbon (50.14 %) and hydrogen (9.12 %), but a lower percentage of nitrogen (1.93 %).

3.2 Yield

The weight of the product obtained was slightly lower than the reagents' weight, indicating a minimal quantity of unreacted PO. This finding was also in agreement with the total drop of the pressure in the reactor at the end of the reaction.

3.3 Infrared spectroscopy analysis

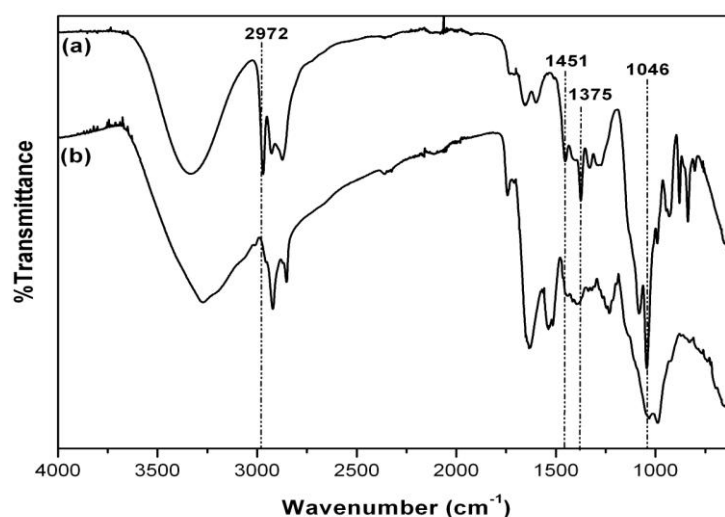


Figure 1: IR-ATR spectra of (a) oxypropylated product and (b) rapeseed cake pellets

Figure 1 shows IR-ATR spectra of RCPs and the obtained polyol. A comparison between the two spectra corroborates the high extent of the reaction as shown by the increase in absorption of the aliphatic C-H stretching region (2800-2990 cm^{-1}), including the appearance of a new peak at 2972 cm^{-1} associated with the methyl groups of the grafted oxypropylene units that was absent in the spectrum of rapeseed cake residue, a new peak at 1451 cm^{-1} attributed to CH_2 aliphatic groups, a new peak at 1375 cm^{-1} that confirms the presence of the CH_3 groups, and an increase and shift of the

absorption in the C-O stretching region ($1000\text{--}1100\text{ cm}^{-1}$) at 1046 cm^{-1} . The spectral intensity also changed as a function of the oxypropylation extent, which is also related to the kind of base employed to activate the hydroxyl groups (de Menezes et al., 2007).

3.4 ^1H NMR Analysis

The ^1H NMR spectrum of the oxypropylated product presented a higher contribution of the ether-type peaks. The peaks at around 1.1, 3.5, and 3.8 ppm were attributed to $\text{CH}_3\text{-O}$, $\text{CH}_2\text{-O}$, and CH-O groups, respectively. It is worth noting that the doublet in the case of the methyl signal of the monomer (PO) cannot be seen because of the broadening effect of the molecular size of the oligomeric and polymeric structure of the PO homopolymer chains. Indeed, it is well-known that, in the NMR spectra of polymers, peaks become large and lose their multiplicity with increasing macromolecular size (Nadji et al., 2005).

3.5 Viscosity

The viscosity of the oxypropylated product was $84.23\text{ Pa}\cdot\text{s}$. The viscosity of oxypropylated products has been demonstrated to be influenced by the catalyst concentration and solid-to-PO ratio. If these parameters are high, hydroxyl activation is favored, as all of the chains have the possibility of adding new monomer and growing, resulting in the formation of a short graft chain product with a lower hydrodynamic volume and, thus, a higher viscosity (Cateto et al., 2009). Different applications can be envisaged for these materials, but if these materials they were to be used in the manufacture of polyurethanes, only those with viscosities lower than about $300\text{ Pa}\cdot\text{s}$ would be viable. Products with higher viscosities would require the addition of a more fluid copolyol (Nadji et al., 2005).

3.6 Gel permeation chromatography (GPC)

The molecular weight of the oxypropylated product (M_w) was 33550 g/mol , indicative of a high yield in the oxypropylation reaction, as this molecular weight is higher than that of the PO homopolymer (about 220 g/mol); this is entirely reasonable considering the different architectures between the two products.

3.7 Hydroxy index (I_{OH})

I_{OH} was found to be 610 mg of KOH/g determined following the ASTM D4274-88 standard. The quite high obtained I_{OH} value indicates that the initial residue is an OH-rich substrate. It is an adequate OH number considering the polyol requirements in view of its use in rigid of polyurethane foam synthesis [hydroxyl index (I_{OH}) between 300 and 800 and viscosity below $300\text{ Pa}\cdot\text{s}$] (Cateto et al., 2009).

3.8 Differential scanning calorimetry (DSC)

The oxypropylated product exhibited a T_g value of $33\text{ }^\circ\text{C}$ (this point was determined by the change in signal slope). This value is in agreement with the T_g value reported by Pavier and Gandini (2000) in the oxypropylation of sugar beet pulp.

3.9 Thermogravimetric analysis (TGA)

The DTG curve is presented in Figure 2. The extent of the first mass loss, from room temperature to about $150\text{ }^\circ\text{C}$, associated with the evaporation of water present in the samples, decreased considerably with the oxypropylation reaction; that is, the hydrophilic character of the sample decreased correspondingly. The curves presented

two zones of degradation; the introduction of propylene oxide (PO) induced a decrease in the degradation temperature of the oxypropylated product (from 338 to 198 °C and from 385 to 315 °C), given the higher thermal fragility of the polyether (de Menezes et al., 2007).

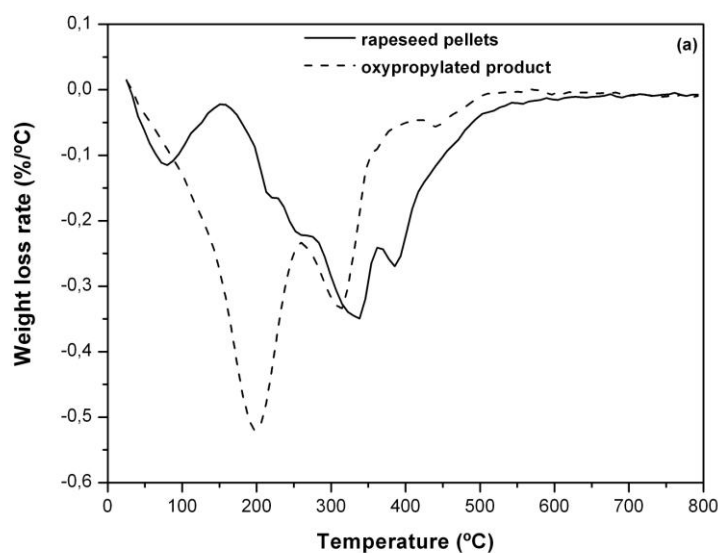


Figure 2: DTG curves of rapeseed cake pellets and oxypropylated product

4. Conclusions

The transformation of rapeseed cake residue into a viscous polyol with appropriate properties to be used in polyurethane, polyether, or polyester formulations was done by a solvent-free process with no extra separation or purification procedures and high reaction extent close to total conversion. Polyurethane foams are widely used in thermal insulation, adhesives, paints, condoms, furniture, and many other applications.

Acknowledgments

The authors thank the University of the Basque Country (2008 Postdoctoral researcher specialization program), the Spanish Agency for the International Cooperation for Development (MAEC-AECID, 2008-2009 period, Program II.A), and the Basque Government for financially supporting this research project.

References

Dmytryshyn S. L., Dalai A. K. and Chaudhari S. T., 2004, Synthesis and characterization of vegetable oil derived esters: Evaluation for their diesel additive properties, *Bioresource Technology* 92(1), 55–64.

- Yuan X., Liu J., Zeng G., Shi J., Tong J. and Huang G., 2008, Optimization of conversion of waste rapeseed oil with high FFA to biodiesel using response surface methodology, *Renewable Energy* 33, 1678–1684.
- Cetinkaya M. and Karaosmanoglu F., 2004, Optimization of base-catalyzed transesterification reaction of used cooking oil, *Energy Fuels* 18, 1888–95.
- Piotrowska P., Zevenhoven M., Hupa M., Davidsson K., Åmand L. E., Kassman H. and Zabetta E. C., 2008, Fate of alkali metals during cocombustion of biodiesel residues with coal in a semi-industrial CFB boiler. In *Circulating Fluidized Bed Technology IX (CFB9): Proceedings of the 9th International Conference on Circulating Fluidized Beds*; Werther, J., Nowak, W., Wirth, K.-E., Hartge, E.-U., Eds.; TuTech Innovation GmbH: Hamburg, Germany.
- Özçimen D. and Karaosmanoğlu F., 2004, Production and characterization of bio-oil and biochar from rapeseed cake, *Renewable Energy* 29, 779–787.
- Çulcuoğlu, E., Ünay, E. and Karaosmanoğlu, F., 2002, Rapeseed Cake as a Biomass Source, *Energy Sources* 24, 329–336.
- Fernandes S., Rocha Freire C. S., Pascoal Neto C. and Gandini A., 2005, The bulk oxypropylation of chitin and chitosan and the characterization of the ensuing polyols, *Macromol. Mater. Eng.* 290, 1009.
- Gandini A., 2008, Polymers from renewable resources: A challenge for the future of macromolecular materials, *Macromolecules* 41(24), 9491–9504.
- Gandini A. and Belgacem M. N., 2008, Partial or total oxypropylation of natural polymers and the use of the ensuing materials as composites or polyol macromonomers. In *Monomers, Polymers and Composites from Renewable Resources*; Belgacem, M. N. Gandini, A., Eds.; Chapter 12, Elsevier: Amsterdam.
- TAPPI Test Methods, 2007, TAPPI Press: Atlanta, USA.
- Wise L. E., Murphy M. and D'Adieco A. A., 1946, Chlorite holocellulose, its fractionation and bearing on summative wood analysis and on studies on the hemicelluloses, *Paper Trade J.* 122 (2), 35–43.
- Rowell R., 1983, *The Chemistry of Solid Wood*; Advances in Chemistry Series; American Chemical Society: Washington DC, pp 70-72.
- de Menezes, A. J., Pasquini, D., Curvelo, A. A. S. and Gandini, A., 2007, Novel thermoplastic materials based on the outer-shell oxypropylation of corn starch granules, *Biomacromolecules* 8 (7), 2047–2050.
- Nadji H., Bruzzése C., Belgacem M. N., Benaboura A., and Gandini A., 2005, Oxypropylation of lignins and preparation of rigid polyurethane foams from the ensuing polyols. *Macromolecular Materials and Engineering* 290(10), 1009–1016.
- Cateto, C. A., Barreiro, M. F., Rodrigues, A. E. and Belgacem, M. N., 2009, Optimization Study of Lignin Oxypropylation in View of the Preparation of Polyurethane Rigid Foams, *Ind. Eng. Chem. Res.* 48, 2583–2589.
- Pavier C. and Gandini A., 2000, Oxypropylation of sugar beet pulp. 2. Separation of the grafted pulp from the propylene oxide homopolymer, *Carbohydrate Polymers* 42, 13–17.