Industrial Crops & Products 109 (2017) 1–7

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

Methanolysis of epoxidized soybean oil in continuous flow conditions

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ARTICLE INFO

Keywords:
ESO
Bio-based
Polyol
Soybean oil
Flow mode

ABSTRACT

Bio-polyols synthesized from vegetables oils are a great alternative to petrochemical polyols for polyurethanes industry. The simplest approach to bio-polyols synthesis involves epoxidation of carbon–carbon double bond of unsaturated fatty ester moieties and subsequent epoxide ring-opening by nucleophilic reagents. In order to improve the latter process by increasing both productivity and product quality, the advantages of flow chemistry were exploited, such as facile automation, reproducibility, improved safety and process reliability, investigating for the first time in the literature the methanolysis reaction of epoxidized soybean oil (ESO) in a continuous flow mode.

Compared with batch reaction, flow mode allowed the cut of the reaction time from 30 min to 2 min, and the reduction of catalyst concentration by an order of magnitude, which brought significant benefits in terms of cost efficiency and eco-sustainability, rendering the method suitable for industrial applications.

1. Introduction

Oil reserve depletion and increasing market prices have led researchers worldwide to seek renewable resources to replace petrochemical derivatives (Choi et al., 2015). New green technologies have to be developed assuring the use of renewable resources as an alternative to petrochemical products. Vegetable oils such as soybean (Changa et al., 2017), palm (Khatuna et al., 2017), linseed (Calvo-Correas et al., 2015), castor (Mutlu and Meier 2010) etc., are promising alternatives since they are relatively inexpensive and renewable sources.

In this context, bio-polyols synthesized from unsaturated fatty esters are suitable substitutes of petrochemical polyols for polyurethanes industry (Desroches et al., 2012). Since from the pioneering work of Petrović on the synthesis of polyols from vegetable oils (Petrović 2008), there has been an explosion of interest on this topic (Petrović et al., 2008; Alagi and Hong, 2015; Tan et al., 2011; Datta and Głowinska 2014; Bloise et al., 2012; Longobardi et al., 2013; Mele et al., 2014; Annese et al., 2014; Dai et al., 2009; Annese et al., 2011; Pantone et al., 2017; Lozada et al., 2009). The simplest approach involves epoxidation of carbon–carbon double bond of unsaturated fatty ester chains and subsequent epoxide ring-opening reaction (hydroxylation) by nucleophilic reagents (Scheme 1).

The epoxidation of oils is a well-known technique used in the production of epoxidized soybean oil (ESO), which is used as plasticizer, lubricant, cross-linking agent, stabilizer etc. (Fenollar et al., 2009). Petrović et al. patented the alcoholysis of epoxidized oils using tetrafluoroboric acid as a catalyst with different hydroxylated molecules like water, monoalcohols (methanol, ethanol, propanol and butanol) and their mixtures (Petrović et al., 2000; Petrović et al., 2002).

In order to improve the hydroxylation process and increase the productivity of the process itself, the methanolysis reaction of epoxidized soybean oil (ESO) under continuous flow conditions was investigated (Scheme 2).

In fact, while studies of the epoxidation of soybean oil in continuous mode have been reported (He et al., 2013), the methanolysis of ESO under flow conditions remained totally unexplored (Almena et al., 2013).

In the past two decades, flow chemistry has received a growing interest due to the several advantages provided to synthetic processes such as facile automation, secured reproducibility, improved safety and process reliability (Hartman et al., 2011; Elvira et al., 2013; Schwalbe et al., 2002; Mason et al., 2007; Razzaq and Kappe 2010; Wegner et al., 2011). Moreover, reaction parameters such as temperature, concentration, composition of reactants established for the small scale flow process can be transferred directly to larger flow reactors, without the need for chemical assessments (Wegner et al., 2011).

Note of mention, the use of pressure-resistant reactors enables to

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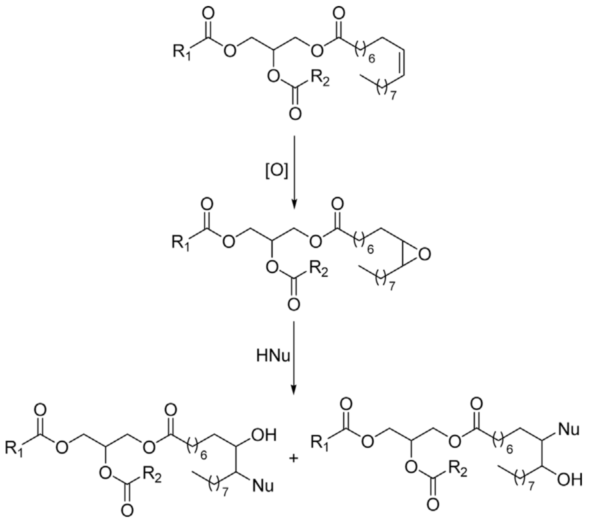
http://dx.doi.org/10.1016/j.indcrop.2017.08.001
Received 30 May 2017; Received in revised form 31 July 2017; Accepted 1 August 2017



Scheme 1. Representation of a typical chemical approach to the conversion of soybean oil into polyol.

work at temperatures much greater than the boiling point of the solvent until reaching supercritical conditions, thus leading to very short reaction times (Razzaq et al., 2010).

In this work, reaction conditions of methanolysis of ESO carried out in flow were optimized by means of the response surface methodology (RSM), a strategy generally used for modeling and optimizing the experimental parameters in physical and chemical processes. By using this approach, relationship between the input variables temperature (T) and residence time (RT) and the response data was determined, highlighting advantages obtained by the use of flow chemistry in this process (Leardi, 2009; Bezerra et al., 2008).

2. Experimental section

2.1. Materials and methods

A Vapourtec R-series flow reactor was used for flow chemistry experiments (Vapourtec. https://www.vapourtec.com/it/(Accessed May 20, 2017)). The reactor consists of a PFA tube having a total volume of 10 mL, wrapped in spire and housed inside a quartz enclosure, which is connected to the heating unit and to the temperature sensor for continuous monitoring of this parameter.

The “reagent in” port of the reactor coil was connected to the pump with a length of PFA tubing. The “reagent out” port was then directly interfaced with a 8 bar back pressure regulator after which there is a length of PFA tubing leading to a collection flask.

The instrument has several digital control displays for all variables. For example, it is possible to control the flow rate from which the residence time of reagents is dependent on. The RT can be varied in the range of 10 s – 200 min.

Temperature can be accurately controlled (± 1 °C), through a feedback system, in the range of room temperature − 150 °C.

^1H NMR spectra were recorded on a Agilent 500 MHz spectrometer, operating at 11.74 T, corresponding to the resonance frequency of 499.73 MHz for the ^1H nucleus. The NMR samples were prepared by dissolving 0.2 mL oil in 0.7 mL $CDCl_3$ and analyzed in 5 mm NMR tubes. The chemical shifts are reported in ppm referenced to residual isotopic impurity of $CDCl_3$ (7.26 ppm). Typical parameters for ^1H NMR spectra were: 45° pulse, 4 s acquisition time, 8.01 kHz spectral window, 8 scans, 16 K data points. The FID was not processed prior to Fourier transformation.

Conversions of ESO in bio-polyol were evaluated based on the ^1H NMR signal integral of residual epoxide protons at 3.15–2.74 ppm (Fig. 1b). All integral values were determined assuming the signal at 2.2 ppm as reference (with integral value equal to 6), being it assigned to protons of the α-position of fatty acyl groups ($-O-CO-CH_2-$) that remain unvaried during methanolysis. On these bases, the integral value of epoxide protons (at 3.15–2.74 ppm) in the spectrum of the starting material (ESO) was found to be 7.94 (Fig. 1a).

In a typical calculation, the conversion of epoxide in polyol was evaluated by Eq. (1):

$$\text{Conversion \%} = \left(1 - \frac{I_{3.15-2.74}}{7.94}\right) \times 100 \tag{1}$$

where $I_{3.15-2.74}$ is the integral value of residual epoxide protons at 3.15–2.74 ppm in the spectrum of reaction mixture (Fig. 1b).

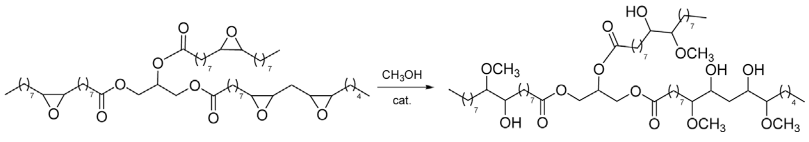
A Viscometer Cannon-Fenske reverse flows YNT instrument was used to determine the viscosity using the standard method ASTM D445 (Standard Test Methods for Kinematic Viscosity of Transparent and Opaque Liquids). The determination of density was obtained with the pycnometer method EN ISO 1675. Iodine number value, oxirane number (ON) and hydroxyl number were determined by EN ISO 661, ASTM D1652, and ASTM D4274 methods, respectively. (Dai et al., 2009; Pantone et al., 2017)

Commercial starting materials were purchased in highest purity available from scientific chemicals suppliers (Aldrich) and were used without purification. ESO was provided by Greenswitch S.r.l. (iodine number of 1.2 g I_2/100 g, oxirane number of 6.3 g O/100 g, mean Molecular Weight Mn of 943.80656 g/mol).

2.2. General batch mode methanolysis of ESO

Methanol 8.2 mL (0.2031 mol) and 34 μL (2.7×10^{-4} mol) of 48% aqueous solution of HBF_4 (or other catalyst such as H_3PO_4 85%, *p*-toluenesulfonic acid monohydrate 98%, HCOOH and 1,8-Diazabicyclo [5.4.0]undec-7-ene DBU) were added to a 50 mL, two-necked flask equipped with a condenser, a stirrer, and a thermometer. (Dai et al., 2009; Pantone et al., 2017) To the refluxing mixture, heated with a bath, 5 mL (5.3×10^{-3} mol) of ESO (oxirane oxygen 6.3 g O/100 g) were added and left to react for 30 min.

Reactions performed in batch mode at a higher temperature than the boiling temperature of methanol were carried out in a 55.6 mL stainless steel autoclave mounted in an electrical oven having a magnetic stirrer on its base. Reagents were introduced in a glass vial (~20 mL) and placed into the autoclave, in order to avoid any contact with metal walls. In a typical experiment the glass vial was charged with methanol (8.2 mL, 0.2031 mol), ESO (5 mL, 5.3×10^{-3} mol) and HBF_4 (or other catalysts), the vial was introduced into the autoclave which was sealed (Casiello et al., 2015). After cooling to room temperature, the reaction mixture was neutralized with small amounts of aqueous ammonia (30%) and then washed into a separating funnel with water (to remove inorganic by-product NH_4BF_4). The organic layer was subjected to heating at 98 °C under a low vacuum on a rotatory evaporator to remove the excess of methanol and the water residue. (Dai et al., 2009; Pantone et al., 2017). The reaction progress was monitored by ^1H NMR and by evaluating both the hydroxyl and oxirane numbers.



Scheme 2. Representation of ESO methanolysis reaction.