



# Improved utilization of crude glycerol from biodiesel industries: Synthesis and characterization of sustainable biobased polyesters



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## ABSTRACT

The present work describes the synthesis of biobased polyesters using glycerol of different purities and sources with the aim of understanding how glycerol composition can influence the resulting structure and properties of biobased polyesters. Glycerol and succinic acid based polyesters were synthesized using crude and technical grade glycerol obtained from biodiesel producing facilities. It was shown that the presence of impurities in crude glycerol can greatly decrease the yield of reaction and also lead to products with different chemical structure and composition than those derived from pure glycerol. In particular, the presence of fatty acids and soaps was shown to produce incorporation of fatty acid residues and formation of carboxylate residues in the polymer backbone respectively. The products synthesized from industrial technical grade glycerol with 95 wt% purity were similar to those formulated from pure glycerol, showing rubbery behavior at room conditions. The materials synthesized from crude glycerol showed different thermal and chemical properties due to incorporation of impurities from the glycerol source to the polymer backbone. It was concluded that technical glycerol could be used as an alternative to pure glycerol on the synthesis of polyesters without inducing major changes on the synthesis products.

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## 1. Introduction

Crude glycerol is the main co-product of biodiesel industry which has grown rapidly in the last decades due to environmental concerns about the usage of depleting fossil fuels. The expansion of biodiesel industry has led to a 100% increase in global crude glycerol production in the last ten years reaching a total annual production of 3.3 billion lbs in 2011. With such a drastic increase in the production of this co-product, its price has decreased dramatically from \$400 per ton in 2001 to less than \$100 per ton in 2011 (Quispe et al., 2013). Further increase of biodiesel production is foreseen in many countries around the globe with the associated production of crude glycerol as a co-product adding pressure to an already saturated glycerol market. By 2020, it is expected to double the amount of crude glycerol produced reaching a global production of 5.8 bil-

lion lbs. (Ayoub and Abdullah, 2012). If biodiesel industry aims for sustainable growth, this will be achieved in a biorefinery context, where crude glycerol could be utilized as a value added feedstock for synthesis of biobased chemicals, fuels or materials which can further extend the utilization of renewable resources.

Unlike pure glycerol, crude glycerol contains many impurities coming from the biodiesel production process. The main contaminants in crude glycerol are methanol, soaps, fatty acids, methyl esters of fatty acids and glycerides. The amount of each component in a crude glycerol sample depends both on the oil feedstock and the process employed for biodiesel synthesis. Crude glycerol samples with a glycerol content ranging from 20 to 80 wt% have been reported in the literature (Hu et al., 2012b; Thompson and He, 2006). This heterogeneous nature of the feedstock limits its application as a direct replacement for conventional processes requiring pure glycerol. Extensive purification is required to obtain a glycerol product meeting purity requirements (>99.5%) for being used in food, cosmetic, personal care and other products (Ayoub and Abdullah, 2012).

Unpurified crude glycerol has been traditionally used as animal feed or low grade burning fuel, limiting the commercial value

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of the feedstock and therefore compromising the sustainability of biodiesel production (Johnson and Taconi, 2007; Pachauri and He, 2006). Intensive research has been conducted in the past few years in order to find new applications for crude glycerol. These include its use as feedstock for biological or chemical conversion to value added products, use as low cost organic solvent and use as building block to biomaterial synthesis (Yang et al., 2012). A wide range of chemicals have been produced from crude glycerol through fermentative or reactive processes including hydrogen (Sabourin-Provost and Hallenbeck, 2009), polyhydroxybutyrate (Mothes, 2007), propanediol (Mu et al., 2006), ethanol (Oh et al., 2011), lipids (Liang et al., 2010) and propylene (Chiu and Dasari, 2006). In the field of biomaterial synthesis, crude glycerol has been employed for synthesis of biobased polyols and foams (Hu et al., 2012a; Luo et al., 2013). Crude glycerol shows a high potential for becoming a useful industrial feedstock, nevertheless, the variability on its composition remains as a barrier for the direct utilization of crude glycerol in commercial scale processes.

Biodegradable elastomeric polyesters have been synthesized using pure glycerol in polycondensation reactions followed by curing steps (Halpern et al., 2014; Li et al., 2013; Migneco et al., 2009; Nagata et al., 1999; 1996; Wang et al., 2002). These materials have been proposed as soft tissue replacement alternatives, due to the biocompatibility and biodegradable nature of its constituent monomers. Crude glycerol is not an alternative for replacement of pure glycerol in biomedical applications due to biocompatibility issues of impure glycerol. Nevertheless, for non-biomedical applications of these biodegradable elastomeric polyesters it is of interest to know if the composition of crude glycerol exerts any effect in the mechanical and thermal properties of glycerol based materials. A few authors have proposed the utilization of crude glycerol as a glycerol source for polyester synthesis (Brioude et al., 2007; Carvalho et al., 2011), but no data is available concerning the effect of changing the glycerol source from pure to crude on the structural and physical properties of glycerol based polyesters. Since glycerol composition has been shown to have an effect in the performance of biotechnological processes (Chatzifragkou and Papanikolaou, 2012), it is expected that the different composition of crude glycerol samples can influence the thermo-mechanical properties of biobased materials synthesized from them. Thus, the aim of this work is to provide insights about the feasibility of using glycerol of different purities for the synthesis of biobased materials and what changes are produced in the synthesis and properties of these materials by changing the glycerol source from pure to crude glycerol.

## 2. Materials and Methods

### 2.1. Materials

Succinic acid (99+ wt%, KIC Chemicals, UK) and pure glycerol (100 wt%, Fisher Scientific, Canada) were used as received. Technical glycerol was kindly donated by BIOX Corporation (Canada) specified as a 98 wt% glycerol content feedstock obtained through purification of industrial crude glycerol by provider. Crude glycerol 1 was kindly donated by Methes Energies International Ltd. (Canada) specified as an unpurified industrial crude glycerol. Crude glycerol 2 was kindly donated by Veenstra Farms (Canada) specified as unpurified crude glycerol from farm biodiesel production. Refined glycerol was prepared by purification of crude glycerol 2 feedstock following the method described by Manosak et al. (2011). Briefly, crude glycerol was acidified using concentrated phosphoric acid until pH 2. At this point, two phases were in samples, corresponding to separated non-polar (oil rich) top phase and polar (glycerol rich) bottom phase. The bottom phase was collected and

neutralized using a 5 mol L<sup>-1</sup> potassium hydroxide (KOH) solution until pH 6. The excess of water was removed by means of vacuum distillation and the product was filtered to eliminate excess precipitated salt. The refined glycerol was analyzed through gas chromatography to determine its glycerol content and stored in a plastic capped bottle until further use.

### 2.2. Glycerol characterization

Glycerol samples were characterized in order to determine their content of free glycerol, fatty acid methyl esters (FAMES), free fatty acids (FFAs) and soaps. Free glycerol, FAMES and glycerides were determined through gas chromatography (GC) of samples, according to procedure described by Hu et al. (2012b) using a Shimadzu 2014 GC–FID (Shimadzu, Canada) equipped with a flame ionization detector (FID) and a MXT-Biodiesel TG column (15 m, 0.32 mm ID, 0.10 μm, Restek, USA). Butanetriol was used as internal standard and helium as a carrier gas at a flow rate of 3 mL min<sup>-1</sup>. Briefly, a sample of glycerol (10–20 mg) was placed in a glass tube and mixed with 100 μL of 1:1 v/v HCl solution in water. 10 mL of pyridine were added to the tube and the sample was dissolved by shaking. After dissolution, an aliquot of 100 μL of the mixture was placed together with 100 μL of butanetriol standard solution (1 mg mL<sup>-1</sup>) in a 2 mL glass vial and derivatized in presence of *N*-Methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA, Restek, USA) for 20 min in the closed vial. Once derivatization was complete, 800 μL heptane were added to the vial and well mixed. Samples were injected at an injection volume of 1 μL into GC. Injector and detector temperatures were held constant at 240 °C and 380 °C. Oven program employed was: hold temperature at 50 °C for 1 min, ramp temperature at 15 °C min<sup>-1</sup> to 180 °C, ramp temperature at 7 °C min<sup>-1</sup> to 230 °C, ramp temperature at 30 °C min<sup>-1</sup> to 380 °C, hold temperature at 380 °C for 5 min. Free fatty acids were determined by titration according to ASTM standard method D4662-08. Soaps were determined by titration and ash was determined by burning samples at 750 °C following the procedures described by Hu et al. (2012b). Methanol content was determined by subjecting the samples to evaporation at 70 °C until constant weight was reached. Water content was determined by Karl–Fischer titration using a T70 automatic titration system (Mettler Toledo, Canada). Table 1 presents the main components of the glycerol samples employed.

### 2.3. Polyester synthesis

Crude glycerol and succinic acid were mixed together without catalyst or solvent to a total mass of 180 g in a four neck 1 L glass reactor equipped with temperature control and stirring. The mixture was heated to 180 °C and stirred constantly at 250 rpm under atmospheric pressure. Water produced in the polycondensation was collected in a Dean Stark apparatus allowing the equilibrium of the reaction to shift to product formation. When the solution reached the preset synthesis temperature (180 °C) this was recorded as time zero of the reaction. The reaction was continued until visible gelation occurred when the material changed from a liquid to a rubbery consistency and stopped flowing as a consequence of stirring. Immediately after gelation onset, the reactor was removed from the heating source and allowed to cool down at room temperature. Pure glycerol, technical glycerol and refined glycerol produced only solid products after reaction. When crude glycerol was used as starting material, the synthesis procedure was analogous, but due to high amount of FAMES present in crude glycerol, a liquid and a solid phase were recovered after reaction was completed. The end product of the reaction, composed of a liquid and a solid phase, was cooled by removing the reactor from the heating source and allowing the two phases to separate by gravity.

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