



Valorization of crude glycerol as a novel transesterification agent in the glycolysis of polyurethane foam waste



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ARTICLE INFO

Article history:

Received 16 June 2015

Received in revised form

31 August 2015

Accepted 1 September 2015

Available online 8 September 2015

Keywords:

Polyurethane

Glycolysis

Crude glycerol

Flexible foam

Rigid foam

ABSTRACT

Glycolysis is the most widely used recycling process for PU. It consists of a transesterification reaction, in which the ester group joined to the carbonyl carbon of the urethane is interchanged by the hydroxyl group of a glycol. With a large molar glycol excess condition, the reaction product splits in two phases, where the upper layer is mainly formed by the recovered polyol, with a higher purity than in the case of single phase glycolysis processes, and the bottom layer by the excess of glycolysis agent and reaction by-products. However, this huge molar excess causes an important increasing of the operation costs what makes almost impossible the implantation of industrial glycolysis plants.

In this work, for the first time in literature, the feasibility of the glycolysis process of flexible PU foam scraps by means of using crude glycerol, a waste of the biodiesel production, as a novel, sustainable and economical (approximately 0.13 \$/kg) transesterification agent has been demonstrated, reducing approximately in ten times the operation costs associated to the transesterification agent.

Besides, crude glycerol has provided a glycolysis upper phase with a lower content of byproducts and transesterification agent than in the case of using the best transesterification agent described until this moment (DEG), as a consequence of its higher dielectric constant. Furthermore, as a result of the crude glycerol higher dielectric constant, the net yield in polyol of the glycolysis process increases due to the almost negligible presence of polyol in the bottom phase. Furthermore, once the washing of the glycolysis phases has been done, the glycolysis upper phase can be used to replace up to 25 parts per hundred (pph) of a raw flexible polyether polyol in the synthesis of new flexible PU foams. Besides, the glycolysis bottom phase can be valorized recycling it in the formulation of new PU insulating foam replacing partially the raw rigid polyether polyol.

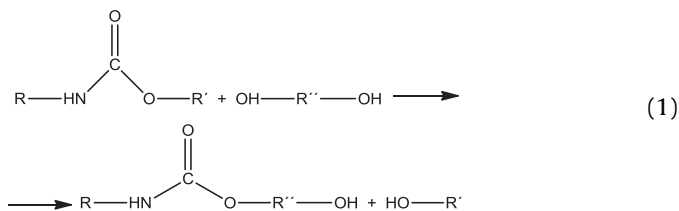
Hence, a global, sustainable and economical viable glycolysis process has been achieved by means of using two waste substances (flexible PU foam scraps and crude glycerol), obtaining valuable products of both glycolysis phases.

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1. Introduction

Glycolysis is the most widely used chemical recycling process for PU. It consists of a transesterification reaction, in which the ester group joined to the carbonyl carbon of the urethane is interchanged by the hydroxyl group of the glycol [1].

The main reaction that takes place is the following one:



All over the years a lot of different low weight glycols have been employed in the glycolysis process of polyurethane wastes. Borda et al. [2] described the glycolysis of elastomers based on polyether polyol and MDI using ethylene glycol (EG), 1,2-propylene glycol

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(PG), triethylene glycol (TEG) and poly(ethylene glycol) (PEG) as glycols. Modesti et al. [3] also described glycolysis reactions of flexible PU foams based on polyether polyol (mostly triol) and toluene diisocyanate (TDI) using ethylene glycol (EG) and glycolysis reactions of reinforced PU by means of using dipropylene glycol (DPG) [4]. However, Wu et al. [5] reported glycolysis reactions of flexible PU foams using diethylene glycol (DEG). On the other hand, Nikje et al. [6,7] carried out microwave assisted split-phase glycolysis reactions of flexible PU foam wastes using glycerine and a mixture of DEG-pentaerythritol (PER) as a new solvent-reactant mixture. Recently, Datta et al. [8–11] reported the glycolysis reaction of elastic PU foams using ethylene glycol (EG), propane 1,3 diol (PG), butane 1,4 diol (BDO), pentane 1,5 diol (GP) and 1,6 hexanediol HDO.

On the other hand, in a previous article in this series, our research group carried out a study to determine the optimal glycol to be used in the split-phase chemolysis reaction of flexible PU foams [12]. The foam used for that study was a conventional one based on glycerol based polyether polyol with a MW of 3500 Da. In that work, diethanolamine (DEA) was used as catalyst and monoethylene glycol (MEG), diethylene glycol (DEG), 1,2-propylene glycol (MPG) and dipropylene glycol (DPG) as low weight glycols. It was found that propylenic glycols increased the solubility between phases, worsening the phase separation. On the other hand, MEG provided a slow degradation rate, while DEG showed a good degradation capacity of the urethane chain requiring lower time to achieve their complete degradation and obtaining a polyol with properties similar to those of the raw one. As a consequence, DEG was the glycol selected to develop the split phase glycolysis process in all the papers published until this moment, including the ones carried out with foams containing polymeric polyols [13] and with viscoelastic ones [14].

It is really important to remember that split phase glycolysis process allows recovering the polyol with a higher purity than in the case of single phase processes due to the upper layer is mainly formed by the recovered polyol and the bottom one by the excess of glycolysis agent and reaction by-products, but it is mandatory the employment of a large glycol excess to ensure that the reaction product splits in two phases [1]. It means that for recovering the raw polyol (approximately value 2.5 \$/kg [15]) from the PU foam wastes it is necessary a huge quantity of glycol (approximately value 1.24 \$/kg [16]) what makes difficult the implantation of industrial glycolysis plants. For this reason they have been scaled up to pilot plant but they have not achieved the commercial scale due to the cost of operation do not get paid through the disposal fees that the shredder operators are willing to pay. However, small scale commercial chemolysis plants exist in; Italy (shoe soles), Austria (elastomeric foam), Germany (Reaction Injection Molding, RIM) and UK (Flexible slab stock) [17] but employing mainly single phase glycolysis processes with the impurity of recovered polyol that they cause. As a consequence, these processes yield polyols which are only able to replace the virgin polyols in semi-rigid foams but not in flexible ones [17].

Therefore, novel alternatives, economical and environmentally friendly, of glycolysis agents are a high priority topic for researchers involved with polymer recycling processes.

Hence, with the aim of carrying out the transesterification reaction that implies the glycolysis process, it is necessary to look for new alternatives to the historical glycols employed all over the last decades. These new alternatives should own end hydroxyl groups to be able to produce the interchange with the PU ester group and should be insoluble in the recovered polyols to ensure a proper split phase glycolysis process.

A very promising alternative from an economical and environmental point of view to the common glycolysis agents, would be

the employment of crude glycerol, coming from the biodiesel production, as a novel transesterification agent.

Biodiesel production can be defined as a transesterification reaction in which 3 mol of methanol reacts in three steps with glycerides [18] in the presence of a catalyst (sodium hydroxide and potassium hydroxide are the most commonly used) to give as a result methyl esters and glycerol. In the first reaction step, methanol reacts with triglycerides to form diglycerides and methyl ester. After that, methanol reacts again with diglycerides to form monoglycerides and methyl ester. Finally these monoglycerides react again with methanol to obtain glycerol and methyl esters (biodiesel). Crude glycerol is normally generated at the rate of one mol of glycerol for every three mol of methyl esters synthesized. Approximately, glycerol as a by-product on biodiesel production means about 10 wt.% of the total product [19].

It is really important to take into account that in the last decades, the energy demand has been increased in a large extension promoting a serious energy crisis as a consequence of the non renewable energy sources extinction risk. Therefore the transition of the non renewable energy sources to the sustainable and renewable ones is an urgent task to be developed. One of the most known alternatives is the biodiesel. For this reason, biodiesel has become an attractive option due to it is made from renewable biological sources such as vegetable oils and animal fats. Furthermore it is biodegradable and nontoxic, has low emission profiles and of this way is environmentally friendly.

Hence, the growing extension of biodiesel production has provided a crude glycerol oversupply, and consequently the commercial price of glycerol has fallen down drastically. As a result of the low prices of glycerol, traditional producers such as Dow Chemical and Procter and Gamble Chemicals, decided to stop the glycerol production. Dow closed 140 million pound synthetic glycerin plant early 2006 [20] due to it was impossible to compete under these market pressures.

As a consequence of the glycerin oversupply, the development of the biodiesel industry is deeply affected since low prices of glycerol affect negatively the economy of biodiesel producers. Besides, crude glycerol represents a huge byproduct stream to be economically disposed of. Therefore, finding alternatives to mitigate this environmental and economical problem is an urgent task and for this reason the investigation of new applications of glycerol is a high-priority topic for managers and researchers related to the production of biodiesel.

The process to purify crude glycerol (that includes filtration, chemical steps, and filtration vacuum distillation) and convert it in technical grade glycerol (>97% pure, used for industrial type applications) or even in refined USP (United States Pharmacopeia) grade glycerol (>99.7% pure, used in cosmetics, pharmaceuticals or food) is mostly non viable from an economical point of view [21]. A proposal to solve the crude glycerin problem was to sell this glycerol to refineries. Nevertheless, glycerol producers have to pay for shipping the byproduct to refineries and it is important to take in mind that, due to the big oversupply of the crude glycerol, transportation costs equal or exceed the price of this product [22]. Hence, novel alternatives of valorization of this waste are one of the most demanded research topics at present, with the final aim of improving the economic viability of the biodiesel industry.

Therefore, in this paper a novel application for the crude glycerol is widely commented. It consists of using this low cost byproduct (approximately 0.13 \$/kg [23]), as a new transesterification reactive in the glycolysis of flexible polyurethane (PU) foam wastes with the final aim of recovering the raw polyol. As a consequence, the obtention of a value added product would be achieved using as reactivities waste substances (PU scraps and crude glycerol), providing an economical and environmental friendly solution to

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