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# Development of silica-rich polyols from rice husk biomass

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## Introduction

Rice (*Oryza sativa*) is one of the most produced and consumed cereals in the world, being the main food for more than half of the world population. It contains, by weight, about 25% of husk and 10% of bran, which represent a high volume of residues. In fact, every year about 30 million tons of solid residues (husk and pulp) are produced, most of them inadequately disposed. The rice husk (RH) is a poor nutritional material, and is rarely used as animal feed. Their traditional uses comprise utilization as fertilizer additives, in stock breeding rags, as cooking fuel, and in landfill or paving applications. Other beneficial applications of RH include their use in composites and partition boards, biochar production, with only a small amount utilized for energy generation, and other applications such as silica production. The rice husk ash (RHA) has proved to be an important source material for manufacturing value-added silicon carbide, silicon nitride, silicon tetrachloride, magnesium silicide, pure silicon, zeolites, fillers for rubbers and plastic composites, corrosion resistant cements, adsorbents and support of heterogeneous catalysts [1].

The abundant presence of silica is considered an interesting feature of this lignocellulosic residue, which can be exploited in the production of silica-rich polyols. In this context, the oxypropylation of RH will enable the direct obtainment of polyols enriched with silica, which can find application as raw-materials for the synthesis of polyurethanes and other polymeric materials. The incorporation of silica in polyurethanes leads to an increase of crystallinity and polymer chain orientation [2]. Also, the incorporation of nanofillers like silica can provide materials with higher thermal, mechanical, optical properties, and flame retardancy properties. In fact, silica nanoparticles have received much attention due to their mild synthetic preparative conditions, large surface area, smooth nanoporous surface, high adsorption capacity and large pore volume [3]. In this context, and as a preliminary study to the topic, the oxypropylation process of RH will be presented and discussed.

## Experimental

The RH has been characterized in terms of moisture content, ashes, lignocellulosic composition and extractables. The lignocellulosic composition was obtained using the procedures described elsewhere [4]. The ash content was determined based on Tappi 211 om-93 method and the moisture content was determined according to the ASTM 1413-76 standard (ASTM, 1984). The extractables were quantified using a sequential extraction procedure in a soxhlet using n-hexane, dichloromethane, methanol and water.

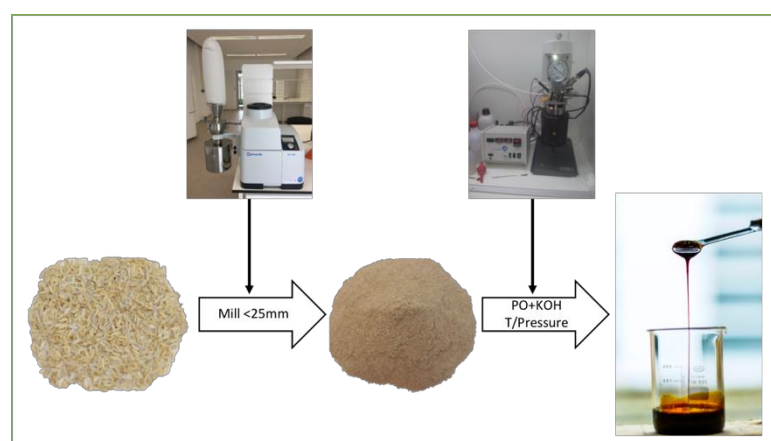
For the oxypropylation process a pressure reactor of 450 mL equipped with a heating mantle, mechanical stirrer, thermocouple and manometer, was used. Two Biomass/PO ratios were tested (20/80 and 10/90, w/v, g/ml) using 4 catalyst contents (5, 10, 15 and 20%, w/w, biomass-based). The polyols were characterized in terms of homopolymer content (HOMO, % (w/w)) according to the procedure described by Pavier and Gandini [5], viscosity (Pa.s, 20°C), hydroxyl number (IOH, mg KOH/g) according to the ASTM D4274 standard (ASTM, 2005),

unreacted biomass (UB, w/w, biomass-based) determined gravimetrically after dilution of the polyol in a suitable solvent, filtering and weighted. The silica content (SC) in the polyols was also estimated based on the content of silica present in the ashes (80-95%) [6].

## Results and discussion

The RH presented ash and moisture contents of 15.7% and 1.7%, respectively. The lignocellulosic composition (79.8%, dry-basis) comprises cellulose, hemicellulose and lignin at contents of 54.5%, 20.8% and 24.7%, respectively. Moreover, it presents 0.3% of fats (based on the n-hexane extractables), 0.3% of non-polar substances (based on the dichloromethane extractables), 1.7% of OH-bearing compounds (based on the methanol extractables) and 2.8% of more polar substances (based on the water extractables).

Oxypropylation occurred at moderate conditions of temperature, pressure and time giving rise to liquid polyols (Fig. 1) with the exception of the 20/80 series with catalyst contents of 5 and 10%, which resulted in a solid residue at the end of the reaction, i.e. minor biomass oxypropylation occurred being impossible to remove the product from the reactor for characterization. For the tested series, the homopolymer content ranged between 14-57%, the hydroxyl number between 225-357 mg KOH/g. Comparatively with the series 20/80, the series 10/90 presented lower viscosities; viscosities were over 300 Pa.s for the series 20/80, and between 1.7-64.0 Pa.s, for the series 10/90. In a general way, viscosity tend to increase with the increase of the RH/PO ratio, i.e. with RH increase. For the series 10/90, the maximum in homopolymer content was achieved for the polyol 10/90/5 (57%). For the series 20/80 a decrease of the homopolymer content was observed comparatively with the series 10/90. For the series 20/80, the IOH reached the maximum value for a catalyst content of 15% (357.1 mgKOH/g), and the polyol 10/90/5 (306.2 mg KOH/g) presented a IOH higher than the polyol 10/90/10 (225.8 mg KOH/g). The SC content in the polyol was estimated for the series 20/80 and 10/90 based on the values reported for the SC content in the ashes (95%), corresponding to a content of 14.6% in the RH. Thus, the theoretical values of silica in polyols were estimated as 4.38, 2.92 % (w/w) for the 20/80 and 10/90 polyols, respectively. According to literature several loads of silica were used in the synthesis of polyurethane foams. Namely, the presence of 5% (w/w) in rigid PU foams resulted in an increase in cell density, cell size reduction, but a decrease in compressive strength [7].



**Fig. 1.** Schematic representation of all the process of oxypropylation of rice husk.

The UB varied between 22.5 and 45.0% of the originally used biomass. The series 10/90 was the one that presented the higher amount of unreacted RH (26.0-45.0 %) independently of the used catalyst amount.

## Conclusions

To the best of our knowledge no other works concerning RH oxypropylation are available in the literature. In a general way, and comparatively with other oxypropylation studies dealing with other biomass substrates (e.g. almond shell and Brazilian pine fruit shell), the obtained polyols are characterized by higher viscosities, possibly associated to the high ash content of the RH (material rich in silica). However, further studies and other RH/PO ratios will be tested in the future. The presence of silica in the produced polyols was considered an interesting feature for the polyurethane industry since silica is often added to formulations to enhance properties, namely mechanical and thermal resistance [8]. The effect of silica content on the produced polyols will be further investigated in final applications (e.g. rigid polyurethane foams).

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