

ORANGE PEEL LIQUEFACTION MONITORED BY FTIR

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Abstract

The aim of this work was to test polyalcohol liquefaction for processing orange peel into value added products such as adhesives, foams, chemicals or even as liquid fuel.

Dry orange peel was liquefied using a mixture of ethyleneglycol and glycerol (50/50) as solvents catalysed by sulphuric acid (SA). A ratio of 9:1 solvent/lignocellulosic material (LM) was used and 3% of sulphuric acid (SA) was added based on the solvent mass. The liquefaction temperatures tested were 160°C, 180°C and 200°C. The time ranged between 60-120 min. The Initial peel, the liquefied material and the resulting solid residue were analysed by FTIR-ATR.

The liquefaction yield ranged from 79% to 92%. The results showed that it is possible to achieve a high liquefaction yield even at low temperatures. The solid residue and the original material have similar spectra, the main differences are observed between the original orange peel and the liquefied material.

Key words: Liquefaction, orange peel, FTIR

1. INTRODUCTION

Orange peel is a by-product of orange juice companies and although there are many uses for this product the amounts produced are high and companies would certainly benefit from its use in high value products. Due to the scarcity of fossil oil, the replacement of products that are usually made with fossil oil derivatives by new products based in lignocellulosic materials (preferably lignocellulosic wastes) is, more than a necessity, an obligation.

Polyalcohol liquefaction has proven before to be a good way to liquefy several lignocellulosic materials, like wood (Kobayashi et al. 2004; Kurimoto & Tamura 1999), wheat straw (Chen & Lu 2009), barks (D'Souza et al. 2015), corn bran (Lee, Yoshioka & Shiraishi 2000), etc.

Liquefied material was used with success to produce products like polyurethane foams (Alma & Shiraishi 1998; Gama et al. 2015; Esteves et al. 2017), polyester and polyurethane films (Budija et al. 2009; Kurimoto et al. 2001), adhesives (Esteves et al. 2015) and even as fuel (Seljak et al. 2012; dos Santos, Bordado & Mateus 2016).

This work was done in the frame of the project project Citrus (PROJ/CI&DETS/2017/31). The aim of this work was to test polyalcohol liquefaction for processing orange peel into a liquefied material that can later be used to produce value added products such as adhesives, foams, chemicals or even be used as liquid fuel.

2. MATERIAL AND METHODS

2.1 Material

Orange peel was dried at 105°C for 24 hours and afterwards split and crushed in a mill, sieved in a to separate the orange peel into fractions of >40, 40-60, 60- 80 mesh and powder which is the fraction remaining in the bottom of the sieve.

2.2 Liquefaction

Dry orange peel was liquefied in a double shirt reactor with heated oil using a mixture of ethyleneglycol and glycerol (50/50) as solvents catalysed by sulphuric acid (SA) (Figure 1).



Figure 1. Liquefaction apparatus

A ratio of 9:1 solvent/lignocellulosic material (LM) was used and 3% of sulphuric acid (SA) was added based on the solvent mass. The stirrer was placed at ± 70 rpm. The liquefied material was dissolved in methanol and separated from the solid residue using a paper filter. After filtration, the liquefied material was placed in a rotary evaporator to remove the solvents, water and methanol. Afterwards the liquefied material was placed in an oven at 105° C overnight to remove any water still remaining after evaporation. The solid residue was washed again with water to remove any glycerol still found in the residue. Then the residue was left to dry in an oven at 105°C overnight, removed and cooled in a desiccator. Liquefaction yield was determined in accordance to equation 1.

$$\text{Liquefaction yield (\%)} = \left(1 - \frac{\text{Solid residue(g)}}{\text{Dry Orange peel(g)}} \right) \times 100 \quad (1)$$

The liquefaction temperatures tested were 160°C, 180°C and 200°C (temperature of the oil in the jacket). The time ranged between 60-120 min.

2.3 FTIR-ATR

The Initial dried peel, the liquefied material and the resulting solid residue were analysed by FTIR-ATR. The samples were dried in an oven at 100°C for one week in order to assure that water was completely removed.

FTIR-ATR spectra were taken in a Perkin Elmer UATR Spectrum Two with 72 scans/min with a resolution of 4.0 cm⁻¹ over the 4000 to 400 cm⁻¹ range. After performing the background, the sample was placed over the crystal. Solid samples were pressed against the crystal. The average of three spectra was used.

3. RESULTS

3.1 Temperature optimization

Figure 2 presents the liquefaction yield at temperatures ranging from 140°C to 200 °C. The liquefaction yield was around 85%, for 140°C, 79% for 160°C, 87% for 180°C and 92% for 200°C.

Overall, a higher temperature lead to a higher liquefaction yield. Nevertheless the results showed that it is possible to achieve a high liquefaction yield even at low temperatures. This is important because higher temperatures involve more money and in some cases more expensive heating media.

The liquefaction yields are slightly higher than the liquefaction yields achieved with other materials at similar conditions. For example, tests made with cork, liquefied with a mixture of glycerol and Polyethylene glycol achieved liquefaction yield around 40% at 150°C and 75% at 170°C (Esteves et al. 2017). This differences are probably due to the different chemical composition that influences the liquefaction yield.

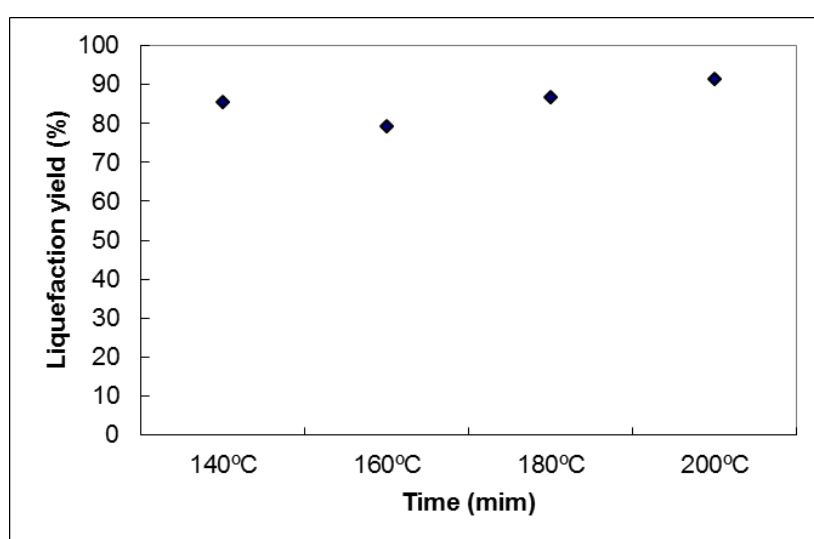


Figure 2. Liquefaction yield (%) at temperatures ranging from 140°C to 200 °C.

3.2 Time optimization

The ideal process is a process that takes the less amount of time possible, since time consuming processes are more expensive. There must be an equilibrium between time consumption and liquefaction yield in order to optimize resources. Figure 3 presents the liquefaction yield at 200°C for times ranging from 15 to 120 min. The results show that the best liquefaction yield was achieved at around 60 min (94.27%). However good liquefaction yield could be achieved with only 30 min. The use of times higher than 60 min seems to bring no improvement to the liquefaction yield and might even be prejudicial due to recondensation reactions. Although there is a slight decrease for 120 min reaction time this does not mean that there has been recondensation. It has been suggested before that re-condensation happens when both cellulose and lignin are liquefied but that this reaction could be inhibited by the addition of low-molecular weight glycols, such as glycerol (Kurimoto & Tamura 1999). In this study, the high amount of glycerol used (50%) should inhibit this re-condensation reactions.

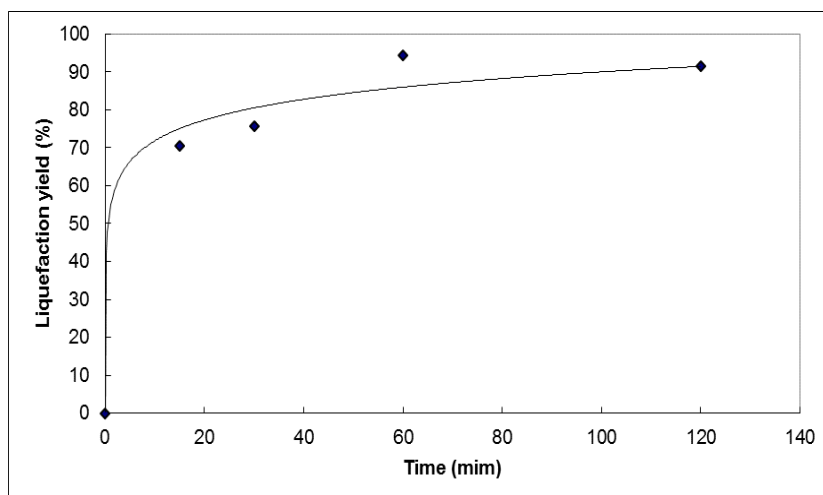


Figure 3. Liquefaction yield at 200°C for times ranging from 15 to 120 min.

3.3 FTIR-ATR monitoring

Figure 4 presents FTIR spectra of the initial orange peel, liquefied material and solid residue for a liquefaction reaction conducted at 200°C for 60 min. All the spectra have high absorption at about 3300 cm^{-1} corresponding to OH stretching vibrations of phenols and alcohols, a double peak at about 2900 cm^{-1} of the CH stretch vibrations present in lignin, cellulose and hemicellulose. These two peaks have a higher absorption for the liquefied orange peel probably due to the contribution of the polyalcohols used as solvent. The peak around 1720 cm^{-1} is due to unconjugated C = O groups while conjugated C = O absorbs at a lower wavelength (about 1600 cm^{-1}). There is a clear decrease in the ratio between the peak at 1600 cm^{-1} and 1720 cm^{-1} in both liquefied and solid residue, showing that there is a higher percentage of unconjugated C = O bonds. Bands between $1300\text{--}1000\text{ cm}^{-1}$ are assigned to CO groups which are present in lignin and polysaccharides, with a peak absorption of about 1200 cm^{-1} for the liquefied material, the peak around 1030 cm^{-1} is attributed to the COC deformation. Monitoring these liquefaction reactions through FTIR-ATR seems to be very difficult due to the significant amount of different reactions happening at the same time leading to the change of most bands associated to lignin and polysaccharides.

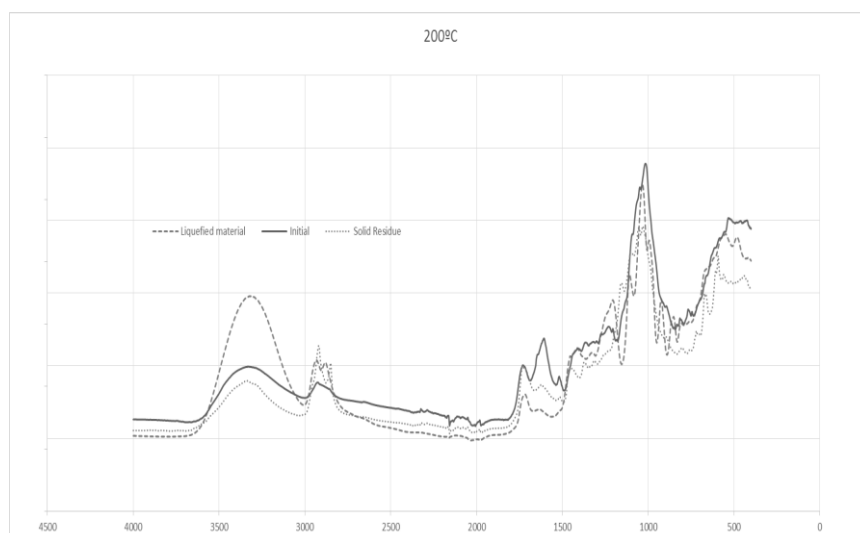


Figure 4. FTIR spectra of initial orange peel, liquefied material and solid residue for a liquefaction reaction conducted at 200°C for 60 min.

4. CONCLUSIONS

Overall liquefaction yield increases with time and temperature but the results showed that it is possible to achieve a high liquefaction yield even at low temperatures. The solid residue and the original material have similar spectra, the main differences are observed between the original orange peel and the liquefied material.

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