# DETERMINATION OF LIPOPHILIC EXTRACTIVES IN IONIC LIQUID EXTRACTS OF EUCALYPTUS PULP BY GAS CHROMATOGRAPHY - MASS SPECTROMETRY

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**ABSTRACT**

*Lipophilic wood extractives composition is currently a big concern of pulp and paper industries as well as for the environmentalists due to their negative impacts on the quality of pulp and the environment. Because of the shortcomings of different extraction procedures using volatile organic solvents in capturing residual lipophilic extractives in pulp, this study reports on the use of ionic liquids as an effective approach for such extraction. The capacity of two ionic liquids; 1-butyl-3-methylimidazolium acetate and 1-butyl-3-methylimidazolium chloride to recover wood extractives was compared and it was observed that ionic liquid with chloride anion recovered a higher amount of extractives. The effect of temperature of the added precipitating solvent during cellulose regeneration on the recovery of extractives was also studied. Recovery of extractives increased with increasing temperature of the added precipitating solvent and equilibrium was reached at 90$^{o}$C. Fatty acids (saturated, unsaturated and α-hydroxyl acids), sterols (β-sitosterol and stigmastanol), steroid hydrocarbons and ketones were the main compounds determined from bleached pulp using gas chromatography mass spectrometry. On the basis of the fact that ionic liquids are biodegradable and non-volatile, this approach of analysis is definitely a highly green process for the determination of lipophilic extractives in pulp.*

**Key words**: Dissolving pulp, Extractives, Gas chromatography-mass spectrometry, Green solvent, Ionic liquid

## INTRODUCTION

Although lipophilic wood extractives occupy a very small fraction among the plant constituents, yet they have a serious negative impact on the pulping process as well as on the final bleached pulp. During wood pulping for the production of chemical cellulose, extractives from wood cells such as resin canals and ray parenchyma (Gutiérrez *et al.* 2001) are released and removed during different pulping stages. Depending on the pulping process, chemical structures and bleaching chemicals used, these compounds do survive the process in differing amounts and composition (Gutiérrez *et al.* 2008). For instance, fatty acids, sterols and glycerides are predominant in acid sulphite cooked pulp than kraft pulp (Sithole *et al.* 2010), which is attributable to the inability of acidic condition used to dissolve and break down lipophilic wood extractives into soluble components (Sithole *et al.* 2010, Gutiérrez *et al.* 1999). Lipophilic extractives which exist to the final stages can deposit on the surface of the fibres thereby affecting the quality of pulp. They cause dark spots on the final sheet, affect the physico-chemical properties of fibers such as surface energy by decreasing the fiber-fiber bonding ability (Asikainen *et al.* 2010, Freire *et al.* 2006a, Freire *et al.* 2006b, Gutiérrez *et al.* 1998) and reduced reactivity

during viscose production. On the other hand, residual lipophilic extractives are deposited on the pulping equipment leading to the formation of pitch as colloidal particles. The pitch deposits on the machinery resulting into periodic closures of the plant for maintenance (Gutiérrez *et al.* 2001).

Previous studies on eucalyptus pulps has revealed the presence of fatty acids (mainly, saturated fatty acids, which are mostly present in the bleached pulp indicating their stability under bleaching conditions), long chain aliphatic alcohols and sterols (Freire *et al* 2006b). Most of the unsaturated sterols and fatty acids are reported to be significantly removed during bleaching stages, which can be attributed to the reaction with chlorine dioxide which favours oxidation reaction (Freire *et al* 2006b, Gutiérrez and del Río 2005).

Lipophilic extractives which survive the pulping process either stick to the fibres and/or are trapped in parts of the cellulose fibre structures which are difficult to access (Freire *et al* 2006b). There is therefore a need for investigating and devising a more effective analytical procedure which can effectively capture the residual lipophilic extractives while at the same time addressing the environmental issues. The extraction procedures which are currently used prior to instrumental analysis are either too laborious or use large amounts of organic solvents posing an increased environmental and health hazard (Gutiérrez *et al.* 2008, Freire *et al.* 2006a, Freire *et al.* 2005, Thurbide and Hughes 2000, Silvério *et al.* 2008). Among the extraction procedures, Soxhlet extraction is widely used; however, this approach is time consuming and uses large amounts of volatile organic solvents.

Ionic liquids are organic salts made of cations and anions and most of them are liquids at room temperature (Kubisa 2004, Kiefer *et al.* 2008). They have been reported to have high ability to dissolve polymers such as cellulose, and various organic compounds (Kiefer *et al.* 2008, Kilulya *et al.* 2011, Kline *et al.* 2010, Swatloski *et al.* 2002). They are able to interact with the biopolymer matrix which results in the formation of hydrogen bonding between hydroxyl groups and the anions of the solvent (Swatloski *et al* 2002). Ionic liquids provide an attractive choice due to the fact that they are capable of dissolving cellulose and regenerate pure cellulose after the addition of polar solvents. These attributes enables the release of all residual extractives into ionic liquid-aqueous filtrate which can be easily extracted using a small amount of non polar solvents. Ionic liquids are considered to be environmentally friendly due to their properties such as negligible vapour pressure, non-flammable and biodegradability (Kline *et al.* 2010, Fort *et al.* 2007, Earle and Seddon 2000, Zhu *et al.* 2006).

In this paper, we report the results of the comparative study of two ionic liquids (1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium acetate) which were observed to be suitable solvents for dissolving pulp in initial experiments. Their ability to extract lipophilic extractives is compared. Characteristics of determined lipophilic extractives are discussed. The effect of temperature of the added cellulose precipitating solvent (water in this case) on the recovery of different components of extractives is presented.

## MATERIALS AND METHODS

### Sample collection

Pulp samples were pulped at CSIR-Forestry and Forestry Products Research Centre Laboratories in Durban, South Africa. Samples were then obtained from two bleaching stages (Pre- and Post-oxygen delignification (PR-$O_2$ and PO-$O_2$)) of

elemental chlorine free (ECF) bleaching sequence.

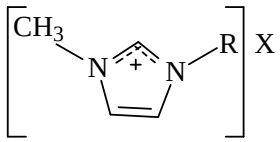
**Chemicals and Reagents**

The following chemicals were used in this study and were all purchased from Sigma Aldrich (Steinheim, Germany): 1-butyl-3-methylimidazolium chloride [BMIM]Cl (98.0% purity), 1-butyl-3-methylimidazolium acetate [BMIM]Ac (97.0% purity), 1-ethyl-3-methylimidazolium chloride [EMIM]Cl (98.0% purity), 1-ethyl-3-methylimidazolium acetate [EMIM]Ac (97.0% purity), 1-butyl-3-methylimidazolium methylsulphate [BMIM]$MeSO_4$, 1-butyl-3-methylimidazolium hexafluoro phosphate [BMIM] $PF_6$ (97.0% purity), HPLC grade acetone (≥ 99.8% purity), hexane (85.0% purity), ethyl acetate (99.7%) undecanoic acid (99.0% purity), hexadecanoic acid methyl ester, cholesterol (95.0%, purity), stigmasterol (95.0%, purity), stigmastanol (97.4%, purity), HPLC grade methanol (≥ 99.9% purity), ethyl acetate (99.7%, purity), hydrochloric acid (37.0% purity), anhydrous sodium sulphate (99 to 100.5% purity) and ammonium solution (25.0%).

**Experimental Procedure**

**Selection of ionic liquids**

Based on the dissolution of pulp in imidazolium-based ionic liquids, the results of which were reported in Kilulya *et al.* (2011), two imidazolium-based ionic liquids, namely 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium acetate were selected for this study. In the screening experiments, four anions were considered, namely chloride ($Cl^-$), acetate ($CH_3COO^-$), hexafluorophosphate ($PF_6^-$) and methylsulphate ($CH_3SO_4^-$), (Scheme 1).



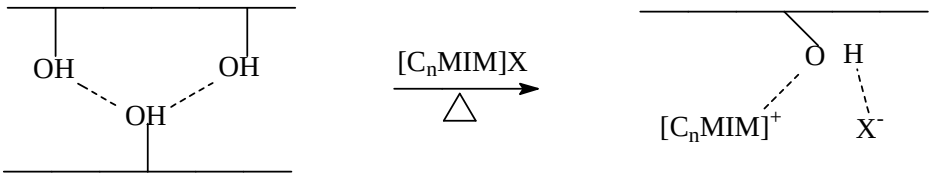

$X = Cl^-, CH_3COO^-, PF_6^-, CH_3SO_4^-$

$R = C_4H_9, C_2H_5$

**Scheme 1**: General chemical structure of imidazolium-based ionic liquids investigated

Among the ionic liquids that were found to have cellulose solvation properties, the dissolution trend was in the following order; 1-butyl-3-methylimidazolium acetate > 1-ethyl-3-methylimidazolium acetate > 1-butyl-3-methylimidazolium chloride > 1-ethyl-3-methylimidazolium chloride (Kilulya *et al.*2011). This can be explained by the strength of interaction of ionic liquid anions with cellulose (Guo *et al.* 2010).

From the cellulose dissolution trends given above, the best two ionic liquids were then selected for further investigation of their ability to extract lipophilic extractives based on their anions, since the dissolution of cellulose in ionic liquid is due to the hydrogen bonding from the hydroxyl groups of the cellulose and the anions of the solvent (scheme 2) (Swatloski *et al.* 2002).




**Scheme 2**: Schematic diagram showing dissolution of cellulose in ionic liquid [$C_n$MIM]X (Swatloski *et al.* 2002, Kosan *et al.* 2008).

These two anions ($Cl^-$ and $CH_3COO^-$) of the selected ionic liquids are all strong hydrogen bonding acceptors (Swatloski *et al.* 2002, Spiridon *et al.* 2010, Feng and Chen 2008) and therefore have an ability to disrupt the extensive hydrogen bonding network of cellulose thus leading to its dissolution.

**Method**

Pulp samples weighing about 0.3 g were dissolved in about 5.7 g of 90 °C molten ionic liquid. Dissolution was performed at 90 °C while stirring until a clear and less viscous solution was formed and thereafter 25 mL of distilled water at a temperature of 90 °C was added to regenerate the cellulose. Investigation of effect of temperature of added water on the recovery of extractives was initially performed by varying temperature between 25 °C and 90 °C. After regeneration of the cellulose the samples were filtered while hot using glass fibre filters. Then, the retained cellulose on the filter paper was washed using 5 mL of acetone. The pH of the filtrates was adjusted to pH 2 using 1 M HCl and/or ammonium solution before extraction. The filtrates were then extracted using hexane (20 mL) followed by hexane: ethyl acetate (2:1 v/v, 2 x 10 mL), by first sonicating for 5 minutes and then shaken on the autoshaker for 20 min. The extracts were combined and evaporated to dryness using a rotary evaporator at 40 °C. Dried extracts were then weighed and dissolved in 0.5 mL of acetone for derivatization before GC and GC-MS analysis.

**Derivatization procedures**

Derivatization by acid alcoholysis for methylation and breaking down of bound compounds (ie. steryl esters and fatty acid esters) was performed prior to GC-FID and GC-MS using 3 M methanolic HCl which was added to the sample at a ratio of 1:2 then heated at 60 °C for 1 h in a water bath. Samples were then cooled at room temperature. The solvent was evaporated to dryness using nitrogen gas and then re-dissolved in HPLC grade methanol for GC-FID and GC-MS analysis.

**GC-FID and GC-MS Analysis**

The GC–FID instrument used to monitor all the optimization procedures and for the separation and detection of the extractives was a Shimadzu (GCMS-QP2010, Kyoto, Japan) GC-FID with ZB-1MS column [30 m x 0.25 mm i.d., 0.25 µm film thickness] using hydrogen as a carrier gas, injection temperature was set at 250 °C while the detector temperature was set at 350 °C. Injection volume was 1 µL, at a flow rate of 1.0 mL/min; initial oven temperature was 60 °C (held for 1 min), ramped up to 290 °C at a ramp-up rate of 15 °C/min and held for 10 min.

A Shimadzu GC – MS instrument was used, with a ZB-1MS column [30 m x 0.25 mm i.d., 0.25 µm film thickness] using helium as a carrier gas. Injection volume was 1 µL, flow rate 1.0 mL/min. The injector temperature was 250 °C; the initial oven temperature was 60 °C, (held for 1 min), ramped up to 290 °C at a ramp-up rate of 15 °C/min and held for 10 min at a linear velocity of 36.4 cm/s. The interface

temperature was 250 °C and an ion source temperature of 240 °C was used. The MS was operated in full scan mode under electron ionization mode. Compounds were identified by comparison of the mass spectra with those in NIST libraries (NIST 2005), by mass fragmentation and by comparison with standard compounds for those standards which were available.

**RESULTS AND DISCUSSION**

It was observed that in the dissolution of cellulose in the two ionic liquids, namely 1-butyl-3-methylimidazolium chloride [BMIM]Cl and 1-butyl-3-methylimidazolium acetate [BMIM]Ac, cellulose degradation was occurring at higher temperature and prolonged dissolution. It was further observed that cellulose was more easily degraded in 1-butyl-3-methylimidazolium acetate compared with 1-butyl-3-methylimidazolium chloride. The degradation was clearly observed by a deep coloration of the solution (deep brownish colour) (Vitz *et al.* 2009), at which the regeneration of cellulose was not possible. Dissolution of pulp was therefore, performed at 90 °C to avoid higher temperature which would result into cellulose degradation. Effect of the temperature of the added precipitating solvent for cellulose regeneration on the amount of extractives obtained was studied. It was found that the amount of extractives increased with temperature of the precipitating solvent (water) added (Fig. 1). Comparison of [BMIM]Cl and [BMIM]Ac for the yield of total extractives was also performed at this stage and it was found that [BMIM]Cl enabled extraction of more extractives than [BMIM]Ac (Fig. 1). The difference could be attributed to the nature of the anions of the two ionic liquids; acetate is basic in nature while chloride ionic liquid is acidic. Another observation was that, acetate ionic liquid solution was forming a buffer filtrate solution; the buffering capacity makes it difficult to lower the pH to a more appropriate value which could have an effect on the extractability of the dissolved extractives. However, more investigation is needed on this fact. The difference was further performed by computing the total amount of lipophilic extractives fraction from GC-MS results (Fig. 2).

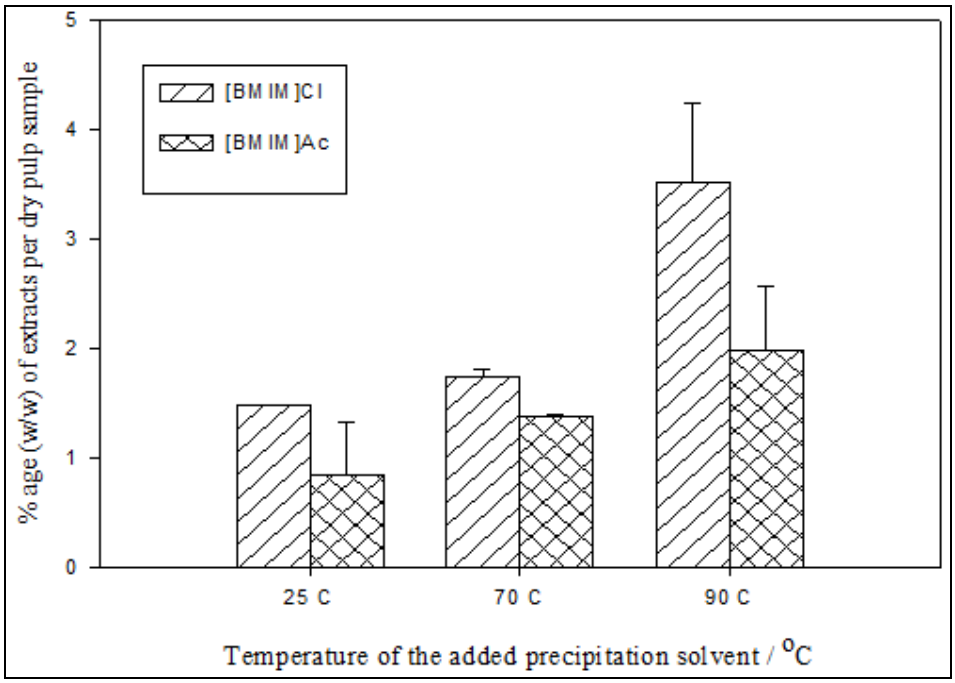



**Figure 1**: Comparison of [BMIM]Cl and [BMIM]Ac in the recovery of lipophilic extractives at temperatures 25 °C, 75 °C and 90 °C of the added cellulose precipitating solvent (water).

**GC-FID and GC-MS analysis of the lipophilic fraction of extractives**

For further comparison on the performance of the two ionic liquids on the extraction ability of lipophilic extractives and investigating the characteristics of lipophilic extractives, extracts obtained after the addition of cellulose precipitating solvent at 90 °C were analysed by GC-MS.

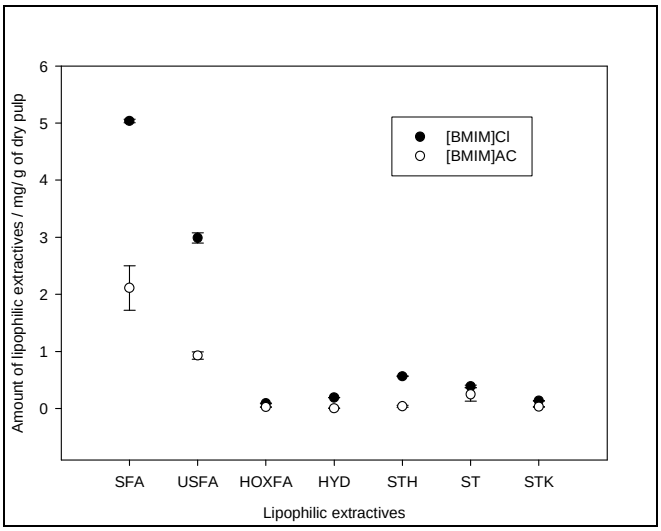



**Figure 2**: Amount of extractives from post-oxygen delignification pulp samples extracted using [BMIM]Cl and [BMIM]Ac at 90 °C of the added cellulose precipitating solvent (water) (SFA = saturated fatty acids, USFA = unsaturated fatty acids, HOXFA = Hydroxyfatty acids, HYD = hydrocarbons, STH = steroid hydrocarbons, ST = sterols, STK = steroid ketones).

The amount of lipophilic extractives identified in the dissolving pulp samples collected after oxygen delignification (PO-$O_2$) bleaching stage of the "elemental chlorine free" (ECF) bleaching sequence was computed and compared. Saturated fatty acids, unsaturated fatty acids, sterols, steroid hydrocarbons and steroid ketones were the main components. The results obtained showed that [BMIM]Cl extracted more lipophilic extractives than [BMIM]Ac as shown on Fig. 2. All of the main components of lipophilic extractives observed (saturated fatty acids (SFA), unsaturated fatty acids (USFA), hydroxyfatty acids (HoxyFA), sterols (ST), hydrocarbons (HYD), steroid hydrocarbons (STH) and steroid ketones (STK)) were higher in [BMIM]Cl extracts.

To further understand the characteristics of lipophilic extractives in the cellulose-ionic liquid solution with increasing temperature of precipitating solvent the main components of lipophilic extractives identified in GC-FID results were used to study the variation in trend with increasing temperature. The peak areas of 9-hexadecenoic acid, hexadecanoic acid, 9,12-octadecadienoic acid, 9-octadecenoic acid, octadecanoic acid, β-sitosterol and steroid ketones were used for this investigation. The increasing trend was observed to attain its equilibrium point at 90 °C where there was no further increase (Fig. 3 and 4). The increase in the amount of extracted lipophilic extractives with temperature of the added precipitating solvent can be explained by the fact that, at low temperature of the added solvent, lipophilic extractives precipitate on the surface of the fibres due to their hydrophobicity. At low temperature of added solvent, such as 25 °C, very little amount of extractives was extracted; and only trace amounts of steroid ketones were detected at this temperature. To avoid the problem of extracted extractives depositing or precipitating on the surface of fibre

during cellulose regeneration by adding water at room temperature, the possibility of using polar organic solvents as cellulose precipitating solvents (such as acetone, methanol, ethanol and acetonitrile), was considered. However, most of these organic solvents boil at low temperature while the dissolution temperature in this work was 90 °C a temperature at which any added organic solvent would evaporate and result into serious pollution and other risks. For these reasons as well as for the sake of addressing environmental issues where the chemistry processes are supposed to be 'green' as much as possible, the use of water was retained as the only plausible choice. Another possibility was to allow the cellulose-ionic liquid solution to cool down before addition of organic solvent to precipitate the cellulose, but this was also not possible because the solution became very thick and viscous with decreasing temperature, such that it would result in trapping the extractives in such a way that they could not be accessed by the added solvent.

At this stage bleached pulp from the pre- and post-oxygen delignification stages of the "elemental chlorine free" (EFC) bleaching sequence was analysed. These samples were preferred in order to study the effect of matrix in this extraction protocol of lipophilic extractives. It should be noted that pulp samples from pre-oxygen delignification contain more lignin, which is also dissolved by the ionic liquid hence reducing the solubility of cellulose fibres. This might have an impact on the amount of extractives captured. On the other hand, post-oxygen delignified pulp contain relatively lower amounts of lignin, most of which is already oxidised during oxygen delignification to water soluble compounds and washed out of the pulp. Oxygen delignification reduces Kappa number by about 50%, thus, PO-$O_2$ pulp was easily dissolved by ionic liquid, because of lower amounts of lignin. However, the trend of increase of the amount of the main components of lipophilic extractives was similar to that observed in PR-$O_2$ pulp and reached equilibrium at 90 $^{o}$C. Because of the effect of less matrix interference in PO-$O_2$ pulp, equilibrium of the extracted amount of the main lipophilic extractives compounds was clearly observed (Fig. 3) unlike that of PR-$O_2$ pulp (Fig. 4).

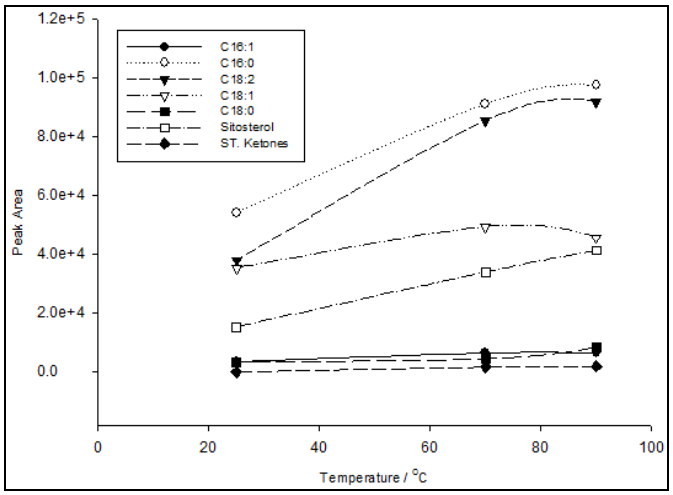



**Figure 3**: Effect of temperature of the added water during cellulose regeneration on the extraction of extractives from post-oxygen delignification (PO-$O_2$) pulp sample, (C16:1 = 9-hexadecenoic acid, C16:0 = hexadecanoic acid, C18:2 = 9, 12-octadecadienoic acid, C18:1 = 9-octadecenoic acid, C18:0 = octadecanoic acid, ST. Ketones = steroid ketones (stigmasta-3,5-dien-7-one and stigmast-4-en-3-one).

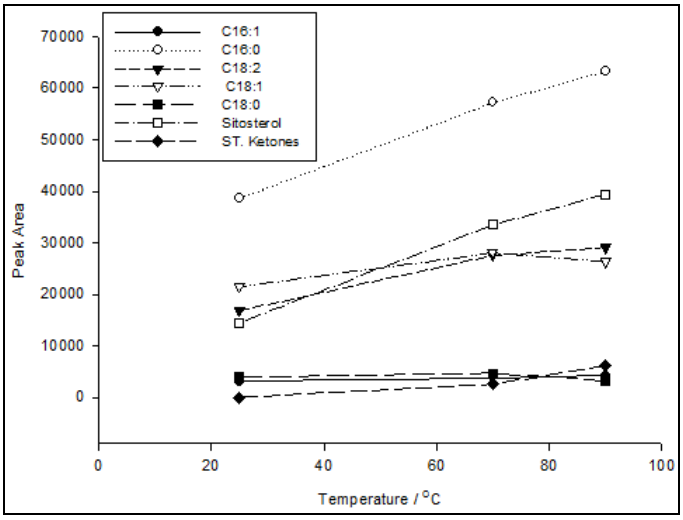



**Figure 4**: Effect of temperature of added water during cellulose regeneration on the extraction of extractives from pre-oxygen delignification (PR-$O_2$) pulp sample, (C16:1 = 9-hexadecenoic acid, C16:0 = hexadecanoic acid, C18:2 = 9, 12-octadecadienoic acid, C18:1 = 9-octadecenoic acid, C18:0 = octadecanoic acid, ST. Ketones = steroid ketones (stigmasta-3,5-dien-7-one and stigmasta-4-en-3-one).

Based on this analysis it was therefore concluded that [BMIM]Cl is a more suitable ionic liquid for the extraction of lipophilic extractives compared to [BMIM]Ac. Following this conclusion [BMIM]Cl was then selected for the remainder of the experiments. GC-MS chromatograms on Fig. 5, show the lipophilic extractives identified from PO-$O_2$ pulp samples using [BMIM]Cl in which the cellulose precipitating solvent temperature was at 90 °C. The amount of lipophilic extractives obtained from PR-$O_2$ and PO-$O_2$ samples using GC-MS were compared as it is shown on Fig. 6.

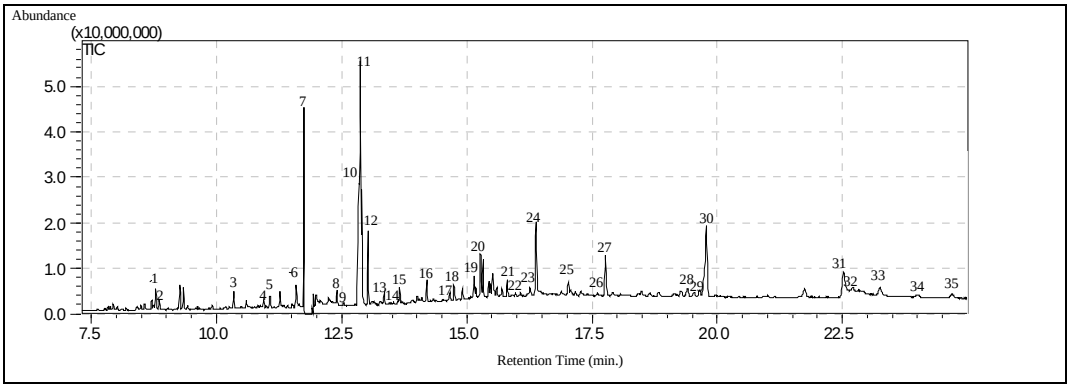



**Figure 5**: GC-MS chromatograms showing some of the lipophilic extractives from PO-$O_2$ pulp sample extracted using [BMIM]Cl at 90 °C added cellulose precipitating water

The identified compounds were (**Note**, fatty acids were identified as their fatty acids methyl esters): **1**-dodecanoic acid, **2**-nonanedioic acid, **3**- tetradecanoic acid, **4**-9-methyltetradecanoic acid, **5**-pentadecanoic acid, **6**- 7-hexadecenoic acid,, **7**- hexadecanoic acid, **8**- heptadecanoic acid, **9**- 2-hydroxyhexadecanoic acid, **10**- 9,12-octadecadienoic acid, **11**- 9-octadecenoic acid, **12**- octadecanoic acid, **13**- 9,12-octadecadienoic acid (isomer), **14**-docosane, **15**- nonadecanoic acids, **16**-eicosanoic acid, **17**- tetracosane, **18**-heneicosanoic acid, **19**- 13-docosenoic acid, **20**- docosanoic acid, **21**- tricosanoic acid, **22**- 2-hydroxydocosanoic acid, **23**-heptacosane, **24**- tetracosanoic acid, **25**-pentacosanoic acid, **26**- nonacosane, **27**-hexacosanoic acid, **28**- steroid hydrocarbon, **29**- octacosanoic acid, **30**- stigmastan-3,5-diene, **31**- β-sitosterol, **32**- stigmastanol, **33**-stigmastan-3-one, **34**- stigmasta-3,5-dien-7-one, **35**- stigmast-4-en-3-one.

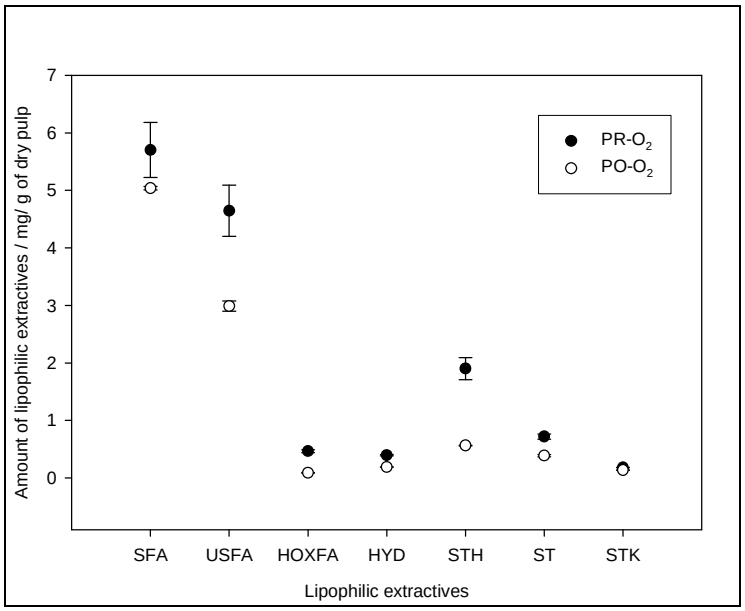



**Figure 6**: Amount of lipophilic extractives obtained from GC-MS results of PR-$O_2$ and PO-$O_2$ pulp samples. (SFA = saturated fatty acids, USFA = unsaturated fatty acids, HOXFA = Hydroxyfatty acids, HYD = hydrocarbons, STH = steroid hydrocarbons, ST = sterols, STK = steroid ketones)

Lipophilic extractives identified in this extraction approach were similar to what have been reported elsewhere using traditional and/or recently discovered extraction methods. It was observed that fatty acids were the dominant class. Sterols (β-sitosterol and stigmastenol) and steroid hydrocarbons (mainly; stigmasta-3,5-diene) were of significant amounts. With these results, the type and composition of these components were not affected by the use of ionic liquids. It can therefore be concluded that lipophilic extractives in ionic liquids extracts are similar to what has been reported previously using different extraction methods.

## CONCLUSION

This study has demonstrated the usability of imidazolium-based ionic liquids in analytical procedures of lipophilic extractives from dissolving pulp. Lipophilic extractives determined using this extraction approach were similar to those that have been reported using other extraction approach, which reveals that there is no reaction between extractives and ionic liquids, and therefore, ionic liquids in this case are just solvents. On the basis of the fact that ionic liquids are biodegradable, non-volatile and non-flammable this approach of analysis is a highly promising green process for the determination of lipophilic extractives in dissolving pulp. Among the two imidazolium-based ionic liquids investigated, 1-butyl-3-methylimidazolium chloride was observed to be a more suitable ionic liquid for the extraction of lipophilic extractives than 1-butyl-3-methylimidazolium acetate. Thus, the effectiveness of the ionic liquid in this process was due to the anion and not the cation of the solvent. The temperature of the added cellulose precipitating solvent (water)

was found to be crucial in the recovery of lipophilic extractives and the amount increased with increasing temperature up to the equilibrium point at 90 °C.

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