The extraction and depolymerisation of lignin from vine shoots using a ternary deep eutectic solvent in combination with microwave irradiation

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Introduction

The growing concern stemming from the use of fossil-fuels has become more prominent over-time. The environmental pollution it causes, together with the rapid decline of their reserves has demanded the need for more sustainable alternatives. One such alternative is lignin which is the second most abundant material and the most naturally abundant aromatic material found on earth. Lignin is located mainly in the cell walls of plant biomass species and the largest commercial supplier of lignin is as waste effluents from pulp and paper mills. However, lignin obtained from these mills have altered chemical structures and are byproducts of numerous intense processes and harsh chemicals. The high carbon content and chemical structure of lignin means it can replicate many of the precursing functions that fossil-fuels currently possess.

Rapid growth in the human population has led to increased demands on the agricultural sector, of which vinification (winemaking) is a major contributor and consequently generates proportional amounts of organic waste. The waste generated is not intrinsically harmful, but the high concentrations from periodic productions are not ideal. Vine shoots play no part in the grape processing and if not burnt as a cheap fuel source, are discarded after pruning and destemming which leaves its high lignin and carbohydrate contents unutilised. The aim of this study was thus to extract and depolymerise lignin from table grape vine shoots, using aluminium chloride: choline chloride: 1,4-butanediol ($AlCl_3$: ChCl: BDO) as a ternary deep eutectic solvent (DES), in combination with microwave-assisted extraction (MAE). Each DES comprised of 2% $AlCl_3$ (w/v) and the power output used for microwave irradiation was 100 W.

Experimental methodology

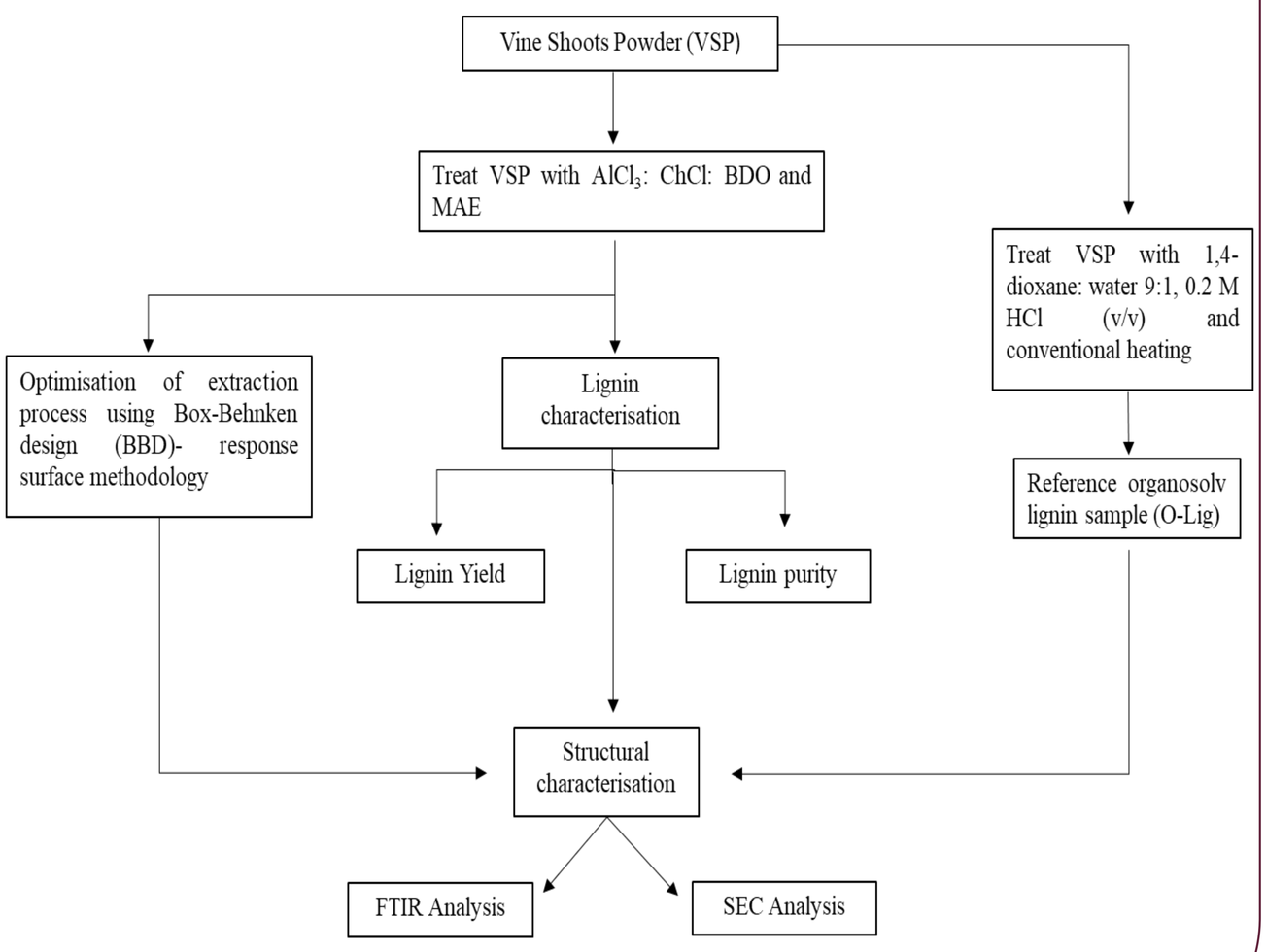

Figure 1: The experimental methodology for the extraction and characterization of lignin.

Optimisation of lignin extraction process

Table 2: The predicted, and experimental yields and purity of the optimised lignin sample using response surface methodology.

Output response	Molar ratio (ChCl:BDO)	Temp (°C)	Time (Min)	Predicted value (%)	Experimental value (%)
Yield	1:5.33	110	15	72.76	87.95 ± 0.70
Purity	1:5.33	110	15	95.12	91.37 ± 1.45

Structural characterisation: FTIR

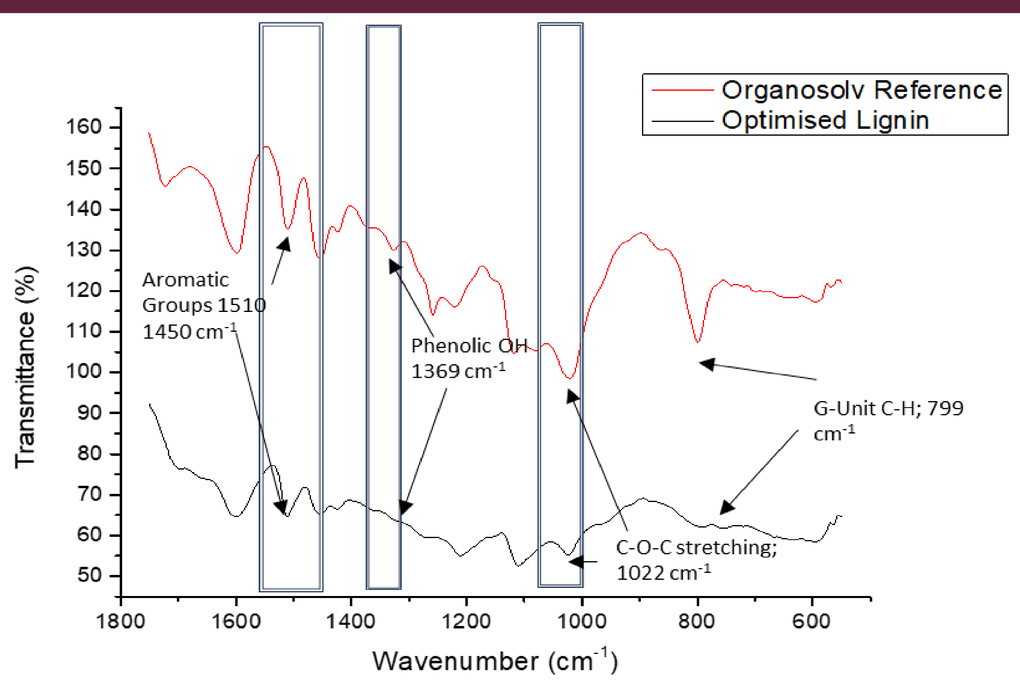

Figure 2: The FTIR spectra of the optimised lignin sample and the organosolv reference measured between 1800- 550 cm^{-1}

Results: Lignin yield and purity

Table 1: The lignin yields and purity of lignin extracted from VSP using $AlCl_3$: ChCl: BDO and MAE, at different conditions using a BBD.

Molar Ratio (ChCl: BDO)	Temperature (°C)	Time (min)	Lignin Yield (%)	Lignin Purity (%)
1:12	95	15	65.82 ± 0.60	92.67 ± 6.32
1:2	95	15	74.64 ± 2.88	88.07 ± 1.54
1:12	115	15	75.41 ± 0.94	80.17 ± 1.59
1:2	115	15	70.84 ± 1.60	89.45 ± 1.25
1:12	105	5	58.06 ± 1.67	80.11 ± 0.04
1:2	105	5	57.69 ± 0.28	87.32 ± 0.61
1:12	105	25	74.93 ± 3.52	86.97 ± 1.45
1:2	105	25	66.71 ± 6.62	89.51 ± 2.74
1:7	95	5	50.27 ± 8.38	84.68 ± 0.89
1:7	115	5	79.71 ± 0.21	87.94 ± 2.08
1:7	95	25	66.89 ± 5.99	86.00 ± 10.31
1:7	115	25	57.12 ± 2.74	91.25 ± 1.02
1:7	105	15	71.68	94.55
1:7	105	15	72.61	94.50
1:7	105	15	70.45	89.87

Structural characterisation: Molecular weight

Table 3: The weight- (Mw), number-average (Mn) molecular weights, and molecular weight distribution (Đ) of the optimised lignin sample and the organosolv reference lignin sample.

Sample	Mw (g/mol)	Mn (g/mol)	Đ
Optimised DES lignin	10490	4830	2,2
Organosolv reference	16100	9400	1,7

Conclusions

- High yields (87,95%), of high quality (91,37%) lignin was extracted from table grape vine shoots using green and sustainable methods.
- The extraction process was optimised which allowed for accurate prediction of the lignin purity, but not the yield.
- The lignin extracted using $AlCl_3$: ChCl: BDO and MAE was simultaneously depolymerised during the extraction process having lower molecular weights (10490 and 4830 g/mol) than lignin extracted using conventional procedures (16100 and 9400 g/mol) and showing an altered chemical structural indicative of lignin depolymerisation.
- The extracted lignin was also considered to have a moderately uniform chemical structure having a molecular weight distribution of 2.2 which suggested more irregularity in its chemical structure than the organsolv reference which had a distribution of 1.7.
- The lignin extraction process developed proved that grape waste, specifically vine shoots can be considered as an abundant source of lignin.