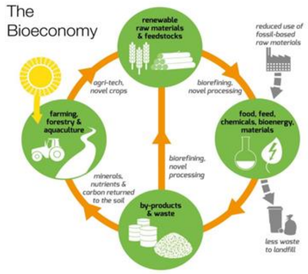
Fernando Climent Barba
Calum Birch
Luke Higgins

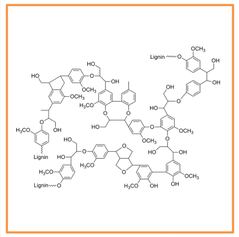
# High value products from Biomass

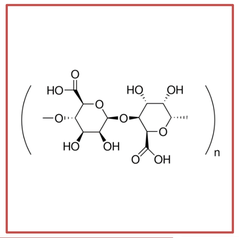
R. Blackburn., J. Blacker & C. Rayner
UNIVERSITY OF LEEDS

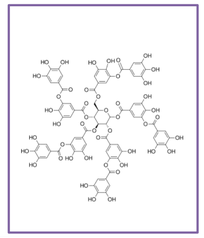
## Introduction

- High value products are necessary to reduce fossil fuel dependence and use renewable feedstocks to boost the Bioeconomy[1]
- Apart from energy and fuels, there is a need for building-block chemicals
- They are currently manufacture from petrochemicals, e.g. natural gas
- Lignocellulosic and algae surge as potential feedstocks to produce a wide range of commodities

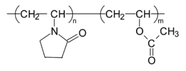



Lignin | Alginic Acid | Polyphenols

## Background

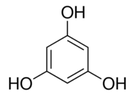
- Polyvinylpyrrolidone/ vinyl acetate (PVP/VA) is the main "ingredient" for hair-spray formulation → Heavily based on fossil fuels.

Walter Reppe's synthesis (PVP): chemistry of acetylene [2]



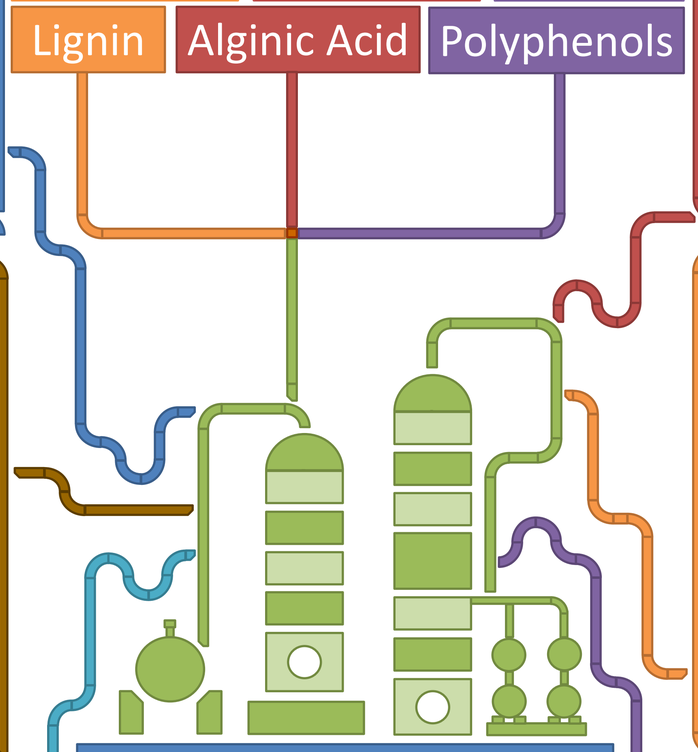
Addition of acetic acid to Acetylene (VA)

- Phloroglucinol[3] is an intermediary chemical used in the synthesis of many statin based drugs, in particular Fluvastatin. The synthesis is currently unsustainable, as it's derived from either TNT (Trinitrotoluene)[4] or 1,3,5-trinitrobenzene[5]. Deriving a natural alternative could be a key step in sustainable drug production.



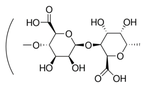

- Lignin is the largest natural source of aromatic compounds known to exist. An amorphous, three dimensional, recalcitrant polymer Lignin is used to bind hemicellulose and cellulose in biomass[6]. Kraft lignin, a waste product from the paper industry, is a good source of purified lignin and has been investigated for chemical production for many years through, base/acid hydrolysis, pyrolysis, gasification and combustion for many years[7]. The production of valorised products from lignin, especially vanillin[8] ( 2/3 of the worlds supply used to come from Kraft lignin), is an achievable goal.

## Biorefineries



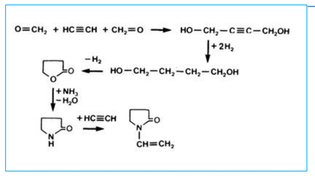
## Case Study 1: AA vs PVP LCA

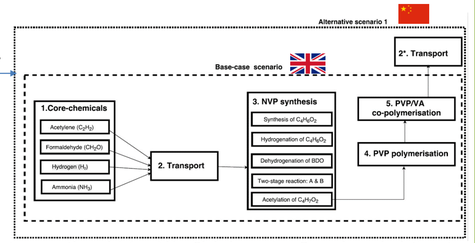
- Bio-based alternatives, Keracol Functional, natural, sustainable patented a hair-spray[9] (KeraStyle) with alginic acid.
- Copolymer extracted from brown seaweed made of β-D-mannuronic and/or α-L-guluronic acid blocks.



Life Cycle Assessment (LCA): to compare environmental impacts of PVP/VA and alginic acid production.

- Functional unit: 1 tonne for each compound.
- Tools: openLCA v. 1.5.0 and ecoinvent v. 3.1 as data-base.

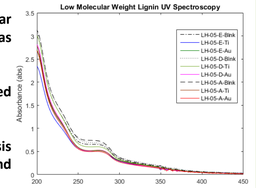


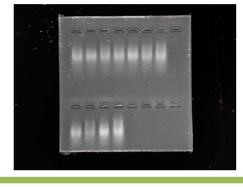



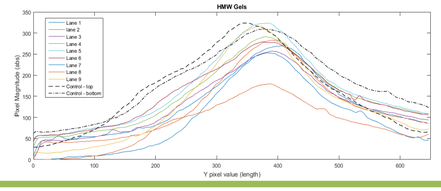

Walter Reppe's synthesis[1] Results: PVP/VA contributes more than alginic acid in: Global warming, Ozone layer depletion etc...

## Case Study 2: Lignin

- Kraft processed lignin with both high molecular weight (HMW 100g/L) and low molecular weight (LMW 15g/L) was diluted 1:1 with water and then 50mg of Au/$TiO_2$ catalyst was mixed under UV light, with compressed air bubbling and stirring for 2 hours[10].
- Results showed that whilst there was some evidence of degradation, this was not increased by using the gold catalyst over just titania, which is known to be photoactive.
- A novel method of characterising the breakdown of the lignin through Gel Electrophoresis (PAGE), was investigated. As well as using UV-vis spectroscopy, total phenolics assay and NMR.






## Conclusion

- LCA demonstrated an elevated global warming potential due to huge dependence of natural gas in PVP/VA compared to alginic acid. This co-polymer is based on complicated industrial processes, which involves higher temperature and pressure at industrial scale. Others aspects in PVP polymerisation, such as photolysis of hydrogen peroxide by UV light or manufacturing of catalysts were not included, which will accentuate its environmental impact over alginic acid.
- Au/TiO2 photocatalyst did not show any improvement over titania catalyst on its own. The project was useful in producing a method for using PA gel electrophoresis as a qualitative method for estimating degradation of lignin. A comprehensive review of literature on the degradation of lignin was also produced.
- Synthesis of phloroglucinol from seaweed derived polyphenols is possible through a base hydrolysis reaction using sodium hydroxide. Increasing the concentration of the base produces a crude product with a high phloroglucinol presence and purity. With no other aromatics present.
- Biorefineries have the potential to develop high value products from biomass, producing complex materials and chemicals from biological sources. This study indicates the feasibility of creating these sustainable alternatives, that not only do they reduce the carbon footprint from synthesis, but further shorten complex reaction procedures, having a twinned benefit to the manufacturer.

## References

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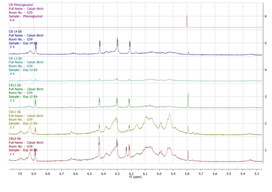
## Case Study 3: Polyphenols

- Seaweed derived Polyphenols were degraded through a base hydrolysis reaction to yield a crude product containing a naturally derived Phloroglucinol[11]. Several experiments were ran to determine factors effecting the presence of phloroglucinol and purity of the sample. With an overall outcome indicating a 4M NaOH concentration having the most advantageous impact.
- All samples were analysed using 1H NMR (500MHz) to determine the aromatic hydrogen environments within the sample. A further impactful result came from leaving the reaction stirring under Nitrogen after completion of the reflux period, but before extraction using ethyl acetate. This pre-extraction period proved effective at reducing the overall phenolic content[12].



(Right): Spectra indicating the effect on increasing the pre-extraction period

(Left): Spectra indicating the effect on increasing the NaOH concentration up to 4M