Acid hydrolysis of anhydrosugars for glucose production

Paula H. Blanco

Aston University, CEAC, European Bioenergy Research Institute (EBRI), Birmingham, B4 7ET

Bioenergy Research Group
(BERG)

12th ECCRIA Conference, Cardiff University. September 2018

Outline

- Background
- Research project
- Results & Conclusions
- Future research

Bio-oil from fast-pyrolysis of biomass

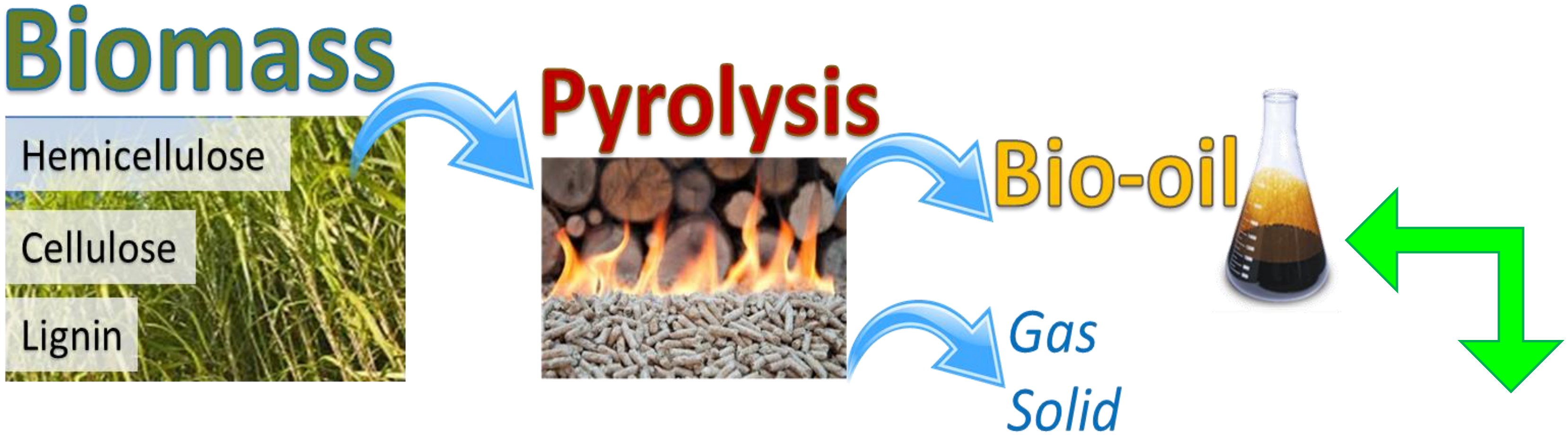
Biomass can be **pre-treated** via different methods to modify its properties.

Fast pyrolysis of biomass yields a gaseous, solid and a liquid fraction or **bio-oil**.

Upgrading of **bio-oil** can yield sugar platforms such as ***glucose***.

Bio-oil from fast-pyrolysis of biomass

Bio-oil composition depends upon the **type of biomass** as well as the **fast-pyrolysis conditions** used.



If the resulting **bio-oil** is heterogeneous, it can be segregated into **aqueous** and **non-aqueous** fractions (*i.e. via decantation*).

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Glucose form anhydrosugars

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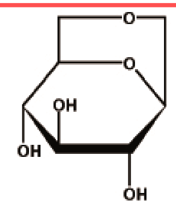
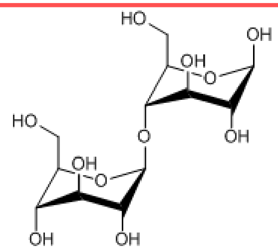
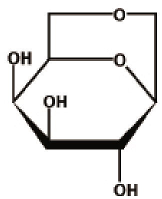
Examples of *anhydrosugars* found in the **bio-oil aqueous fraction**, include…



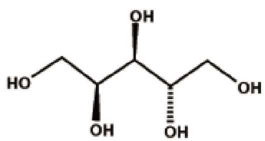
levoglucosan
(1,6-anhydro-beta-D-glucopyranose)



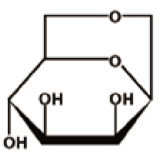
CELLOBIOSE



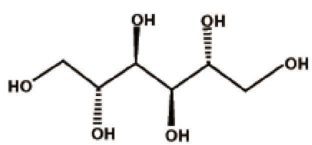
mannosan
(1,6-anhydro-beta-D-mannopyranose)



arabitol
((2R,4R)-pentane-1,2,3,4,5-pentol)

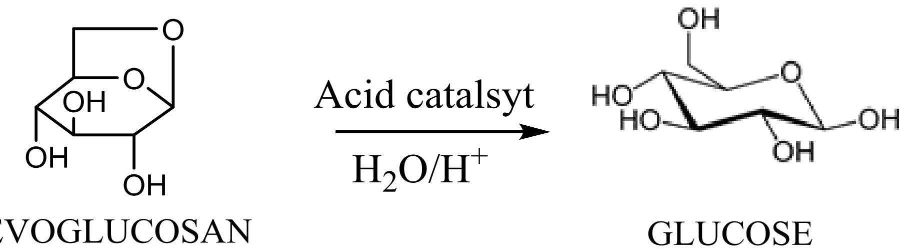


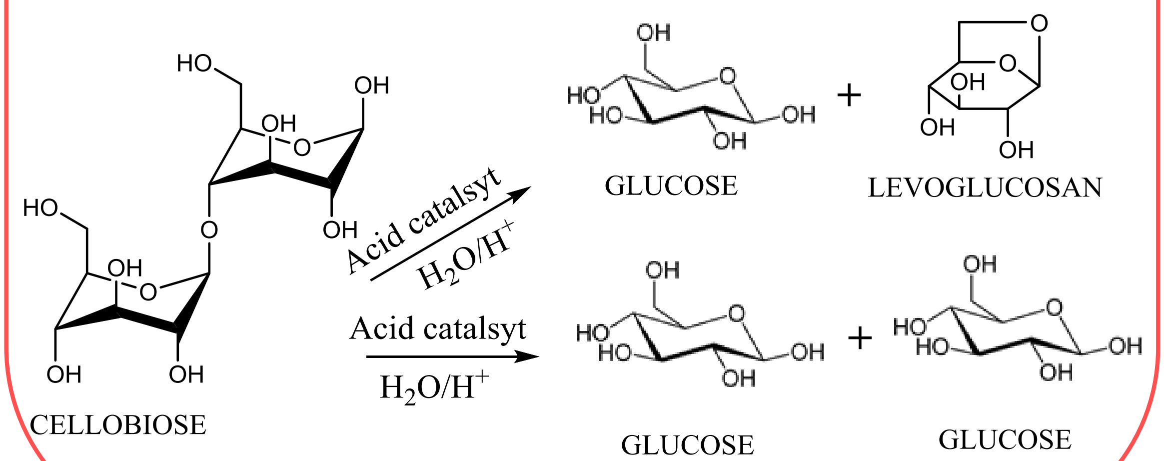
galactosan
(1,6-anhydro-beta-D-galactose)



mannitol
((2R,3R,4R,5R)-hexane-1,2,3,4,5,6-hexol)

Acid hydrolysis (liquid or solid catalysts) to produce **GLUCOSE**

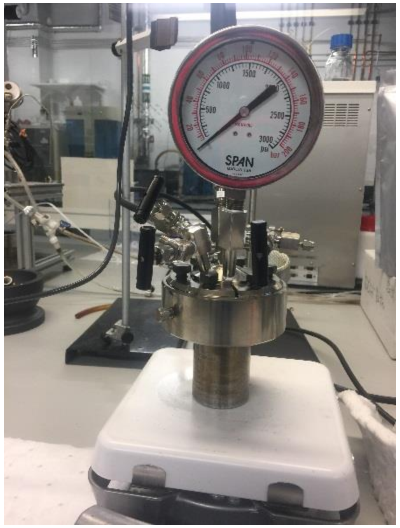


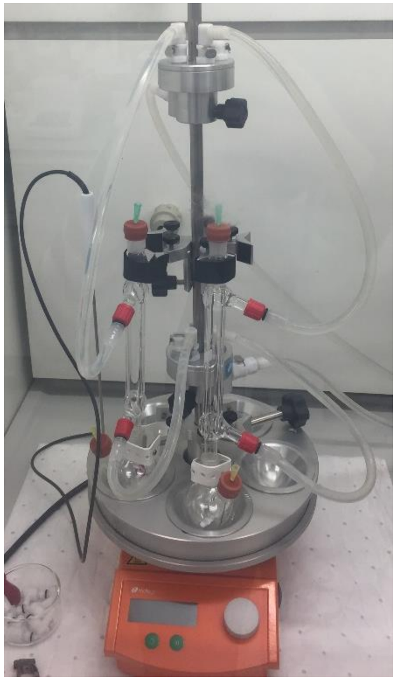


Acid hydrolysis of anhydrosugars

Anhydrosugars contained in the **aqueous fraction** of **bio-oil**, can be converted into **glucose** via acid hydrolysis.

Reaction systems used for acid hydrolysis tests





Multivariable approach: identify **hydrolysis conditions** (Temperature, Reaction time, catalyst/substrate molar ratio) **to achieve glucose yields higher than 90%**.

Experimental set up & Design of Experiments

Catalyst

H_2SO_4 0.5 M (for all the experiments). The c/s ratio was varied by changing volumes of substrate and/or catalyst.

Substrate

Real mixture: anhydrosugars contained in **bio-oil** aqueous fraction

*T = 80, 100, 120º C;
RT = 20, 40, 60min;
c/s = 0.2, 0.6, 0.9

*Some tests T = 135 º C

Coded factor matrix: 3 variables, 3 degrees of freedom

Experiment	Temperature (°C) X_1	Reaction time (min) X_2	Catalyst/substrate molar ratio X_3
1	-1	-1	-1
2	-1	-1	0
3	-1	-1	1
4	0	-1	-1
5	0	-1	0
6	0	-1	1
7	1	-1	-1
8	1	-1	0
9	1	-1	1
10	-1	0	-1
11	-1	0	0
12	-1	0	1
13	0	0	-1
14	0	0	0
15	0	0	1
16	1	0	-1
17	1	0	0
18	1	0	1
19	-1	1	-1
20	-1	1	0
21	-1	1	1
22	0	1	-1
23	0	1	0
24	0	1	1
25	1	1	-1
26	1	1	0
27	1	1	1

Acid hydrolysis of bio-oil aqueous fraction

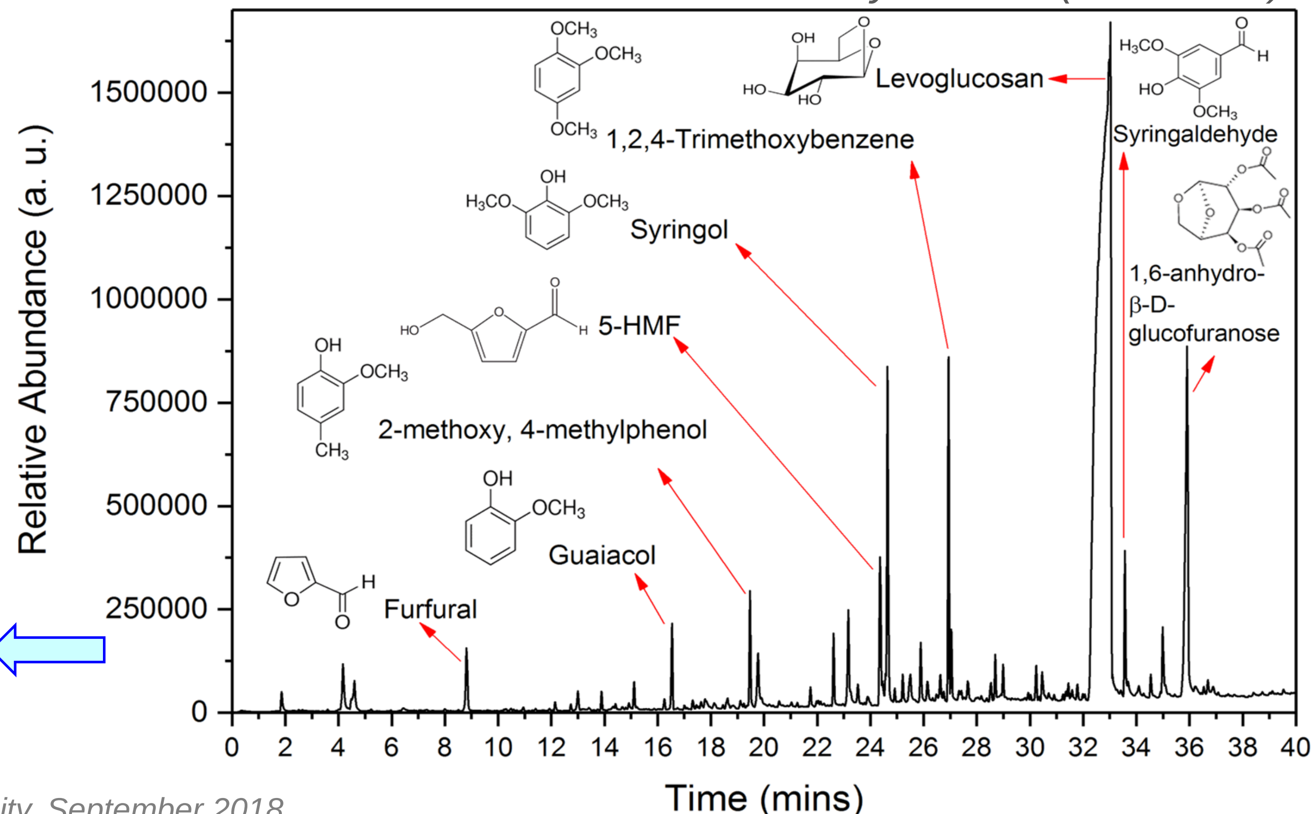
- **Bio-oil** was obtained from the fast pyrolysis of birch wood (400°C) and using superheated steam.

- **Bio-oil aqueous fraction** segregated by simple decantation.

Non-aqueous

Aqueous

Bio-oil characterisation by GC-MS (and HPLC)

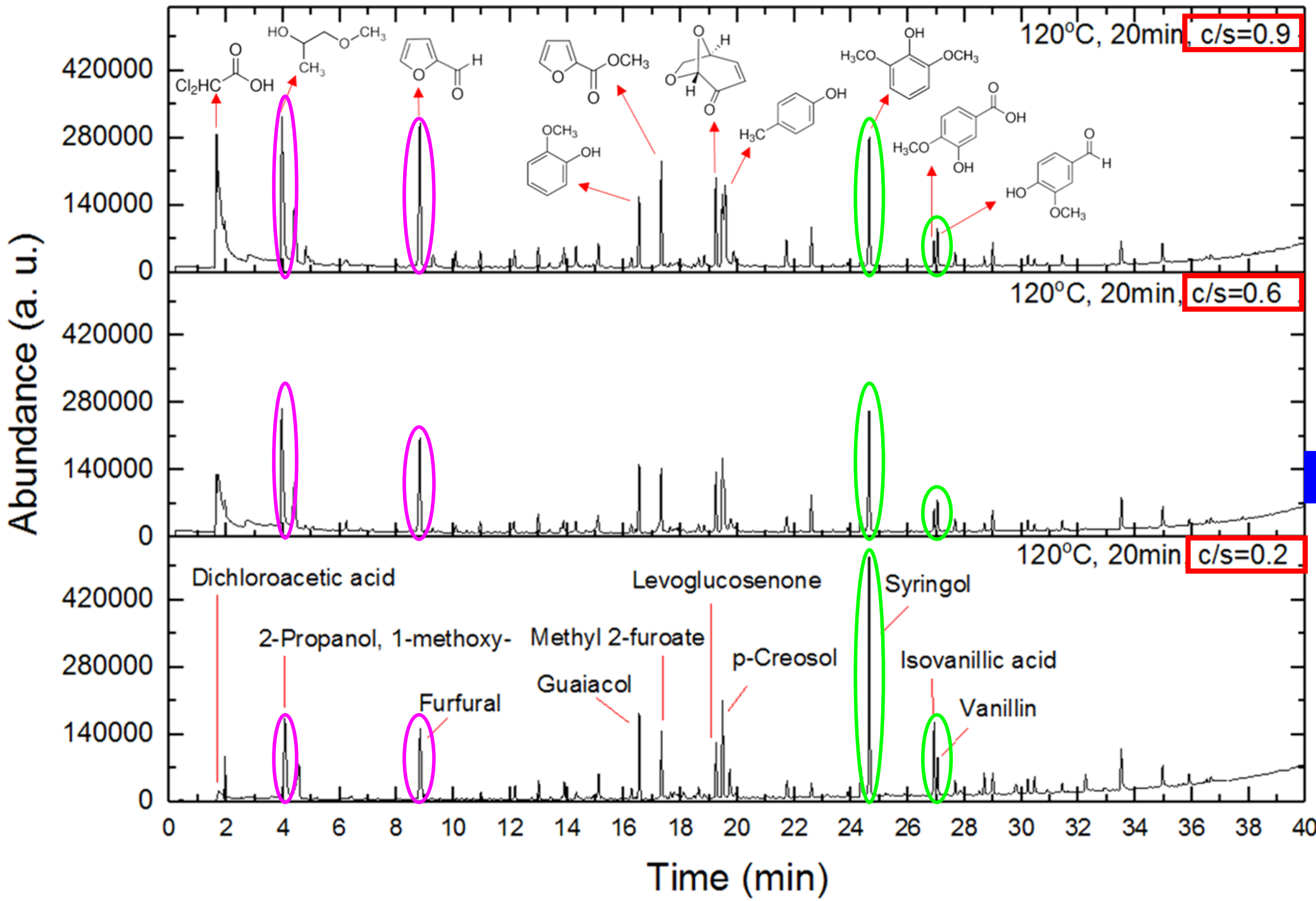


Initial concentrations:

Levoglucosan 31 g L^{-1}
Cellobiosan 2.1 g L^{-1},
and other compounds

Influence of varying c/s ratio in bio-oil hydrolysis

GC-MS bio-oil hydrolysis: T=**120 °C**, time = **20 min**, catalyst/ substrate ratios **0.6-0.9**



The average **glucose** concentration determined by HPLC, was **30 g L^{-1}** for all the hydrolysates

Syringol & Furfural, are regarded as **inhibitors** for further fermentation of glucose

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Influence of varying reaction time in bio-oil hydrolysis

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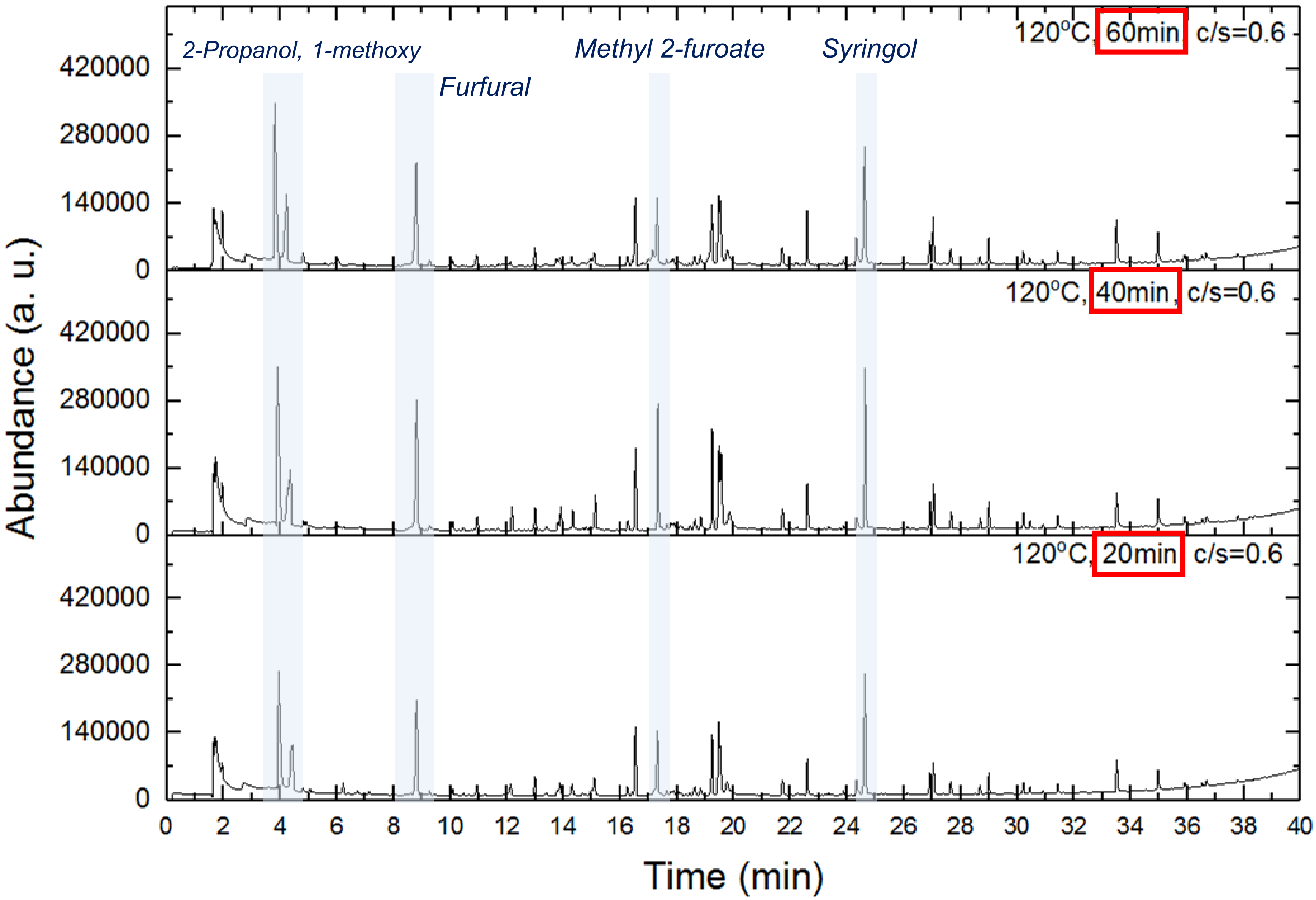
GC-MS bio-oil hydrolysis: T=**120 °C**, **catalyst/ substrate ratio 0.6**, time = **20-60 min**



*If **RT increased**, the **glucose** concentrations:*

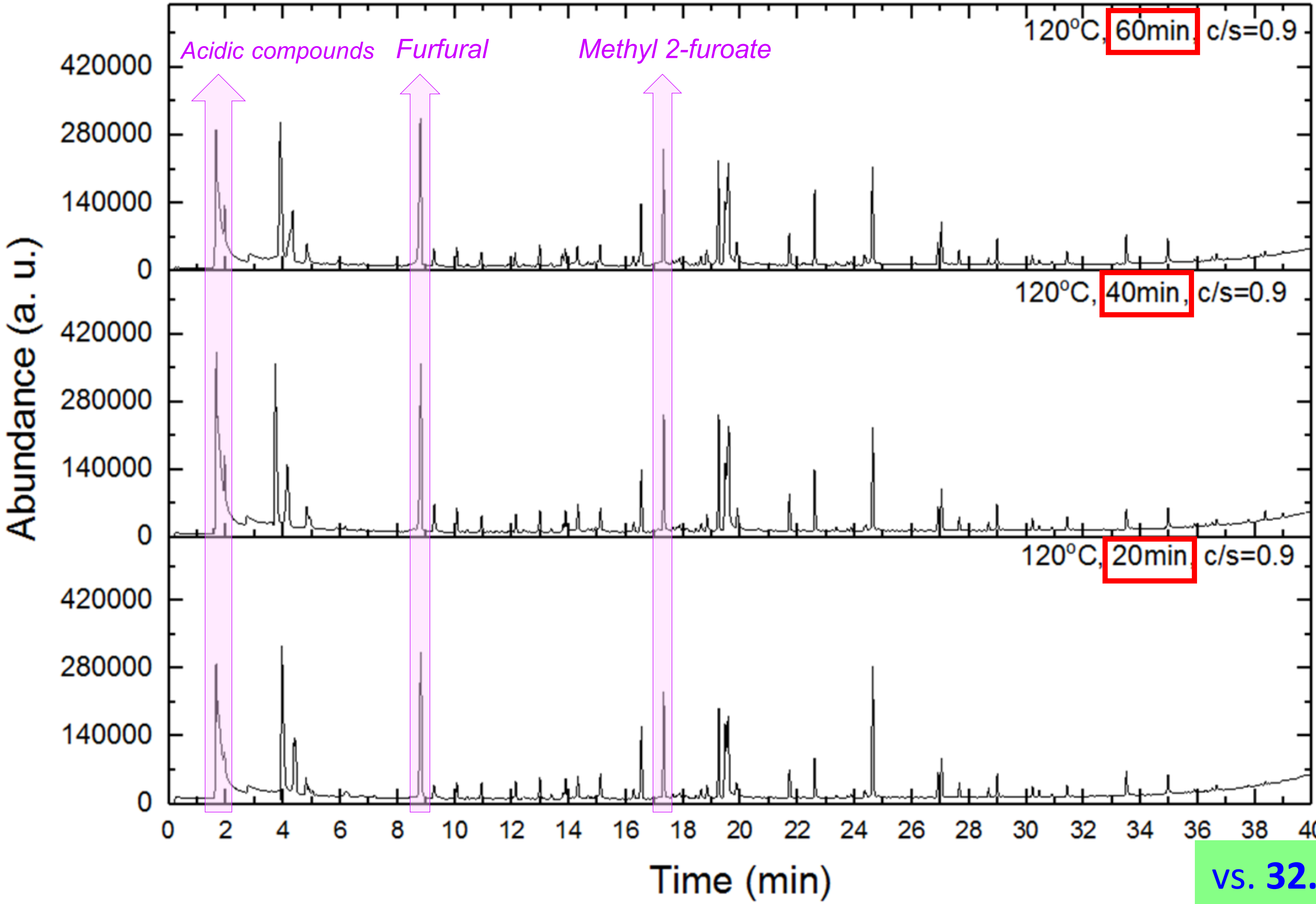
29.8 g L^{-1}

31.2 g L^{-1}

32.5 g L^{-1}

Will the glucose yield increase by increasing the c/s ratio?

GC-MS bio-oil hydrolysis: T=**120 °C**, **catalyst/ substrate ratio 0.9**, time = **20-60 min**



RT increased*, *glucose* *concentrations:

30.7 g L^{-1} (60 min)

30.7 g L^{-1} (40 min)

30.6 g L^{-1} (20 min)

vs. **32.5 g L^{-1}**
@120°C, 20min c/s=0.6

Suitable hydrolysis conditions (120°C)

20 minutes reaction time and a c/s of 0.6 seemed more suitable hydrolysis conditions:

- ✓ The increase in RT will reduce the glucose yields
- ✓ The increase in the c/s ratio promoted higher concentrations of potential inhibitors such as furfural (glucose degradation product).

Similar observations were made for the other temperatures tested and all the results were integrated looking at potential glucose yields.

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Results: acid hydrolysis using bio-oil aqueous fraction

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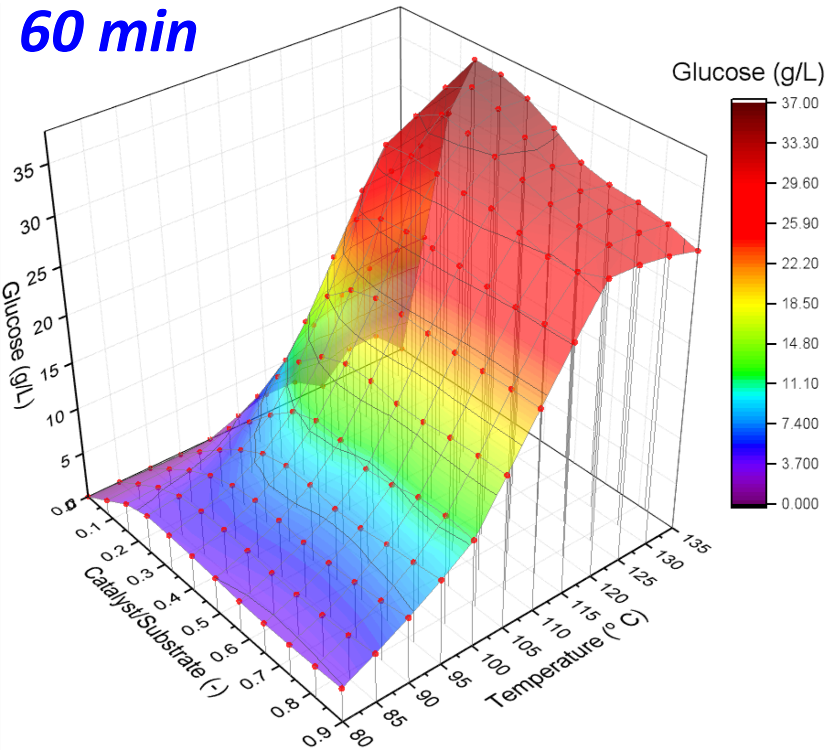
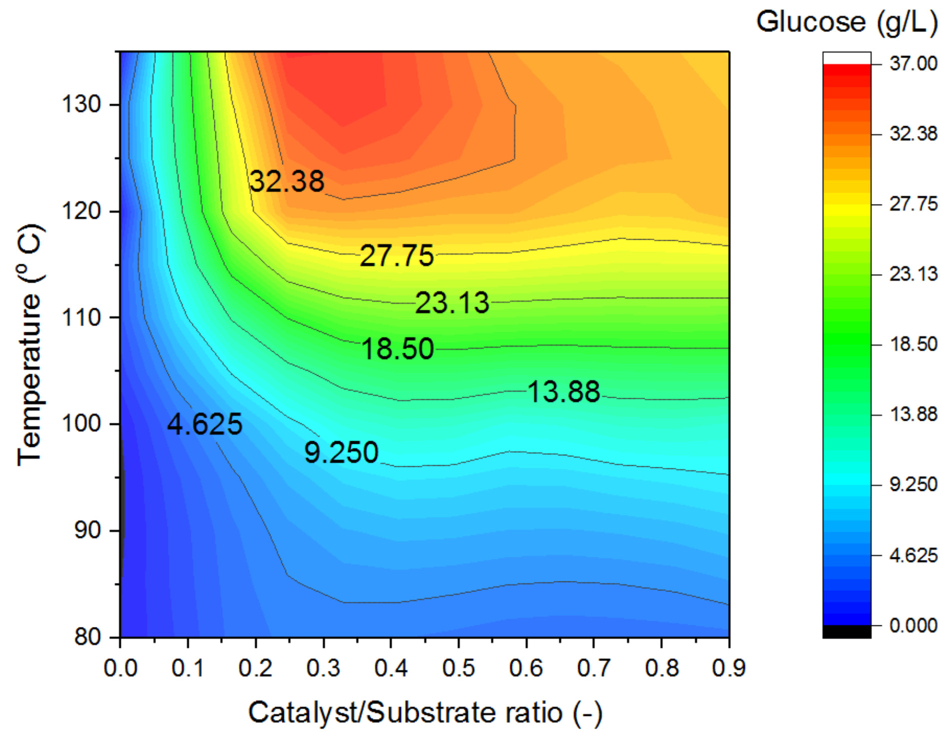
3D graph (left) and contour plot (right): glucose concentration from acid hydrolysis of bio-oil aqueous fraction and using H_2SO_4 (0.5M)

60 min





Glucose conc. **> 35 g/L** (*117% LG yield*), can be achieved at ***c/s* 0.25-0.425, and T 126°C-135°C**

Other anhydrosugars in the aqueous fraction also contribute to form glucose.

Conclusions

- The multivariable nature of hydrolysis experiments requires a large number of tests to be carried out, which is time-consuming and expensive.

- The hydrolysis tests should be carried out defining the hydrolysis parameters to be varied together with design of experiments (DoE).

- A detailed analysis of the presence of inhibitors in the resulting hydrolysates as well as segregation of target compounds such as glucose should be further explored.

- Tests related to the stability of hydrolysates should also be considered.

Future research and project development

To explore greener routes to obtain **glucose** as sugar platform:

- Use of **commercial solid acid catalysts** (A15, IR-120, etc.), potential .
- Development, synthesis, and characterisation of **novel solid acid catalysts** (i.e. carbon-based containing sulfonic groups).
- Study of **life-cycle tests** using solid acid catalysts (reuse and recycle).
- Envisage **more sustainable routes to obtain sugar platform** as well as bio-chemicals and bio-fuels.
- Explore alternative lignocellulosic biomass feedstocks.

Future research and project development

CHALLENGES:

- *Reaction yields and kinetics*
- *Presence of inhibitors for fermentation*
- *Isolation of sugar platform*
- *Multi-stage process (cascade)*

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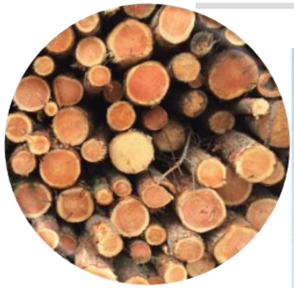
Thanks for your attention



Q & A

Published work:

Blanco PH et al, 2018. *ACS Sustainable Chem. Eng.* **DOI: 10.1021/acssuschemeng.8b02202**