Electronic Supplementary Material (ESI) for Green Chemistry

Supplementary Materials for

High-pressure fast-pyrolysis, fast-hydropyrolysis and catalytic hydrodeoxygenation of cellulose: Production of liquid fuel from biomass

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Screw feeder design

The purpose of the screw feeders is to introduce biomass or biomass model compounds into the reactor system at high pressures of up to 68 bar. The screw feeder consists of a feed hopper containing the solids, an auger tube with the screw and a feed chamber, which is a stainless steel box on the right side of the screw feeder (as shown in Figure S.1). These different parts are connected using Conflat (CF) flanges. The material of construction of the screw feeder is stainless steel 316 except for the 1” glass window attached to the feed chamber. The window has a maximum working pressure of 95 bar at room temperature. The feed hopper and the feed chamber can be purged with inert gas prior to any experiment. The screw feeder is driven by an Applied Motion M400 electric servo motor which is connected to the feeder via magnetic coupling and therefore isolated from the high pressure environment. The screw feeder is capable of feed rates in the range of 0.1 to 20 g min^{-1}.

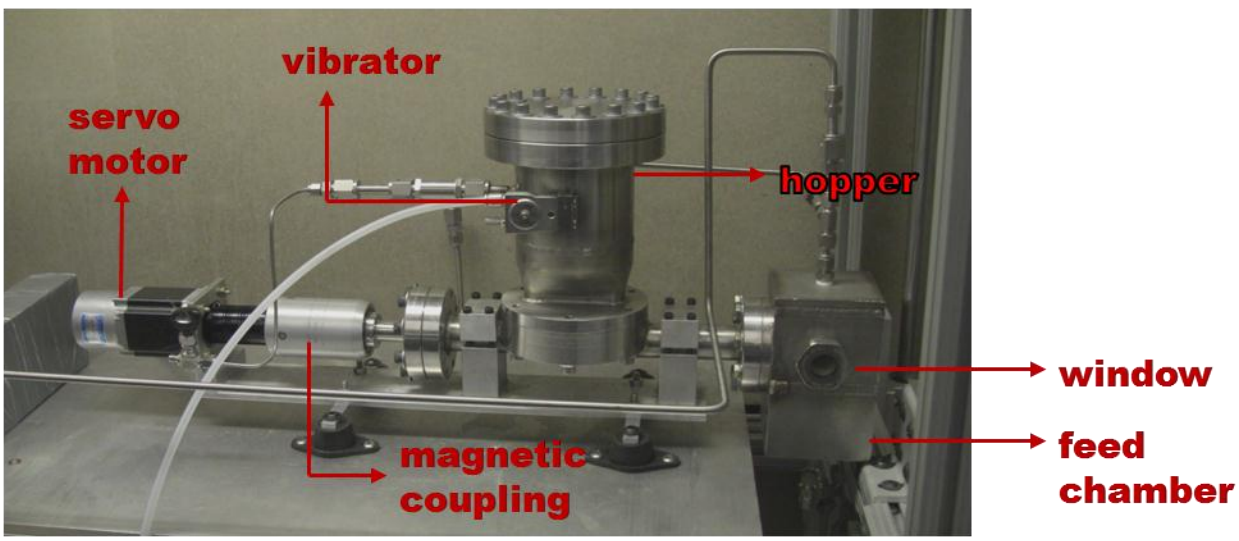

Figure S.1 Picture of high-pressure biomass screw feeder.

High-pressure reactor design

<u>Fast-hydropyrolysis Reactor</u>

A cross sectional view of the fast-hydropyrolysis reactor is shown in Figure S.2. The body of the cyclone reactor is machined from stainless-steel type-347 round bar and has an OD and ID maximum of 2.375” and 1.69” respectively, corresponding to schedule 160 pipe. At 650 °C, the basic allowable stress for TP347 seamless pipe is 4.4 ksi (5.9 ksi at 600 °C) which corresponds to an internal design pressure of 110 bar (or 145 bar at 600 °C). The flange connection at the top of the reactor is a F316H 2" #2500 B16.5 flange which has a maximum working pressure of 106.5 bar at 650 °C. At the bottom of the reactor, the OD and ID are 1.05" and 0.614" respectively which corresponds to schedule 160 pipe and has an internal design pressure of 179 bar. The bottom flange, which is used to connect to the char collector, is a F316H #1500 ¾" B16.5 flange which has a maximum working pressure of 106 bar at 593 °C.

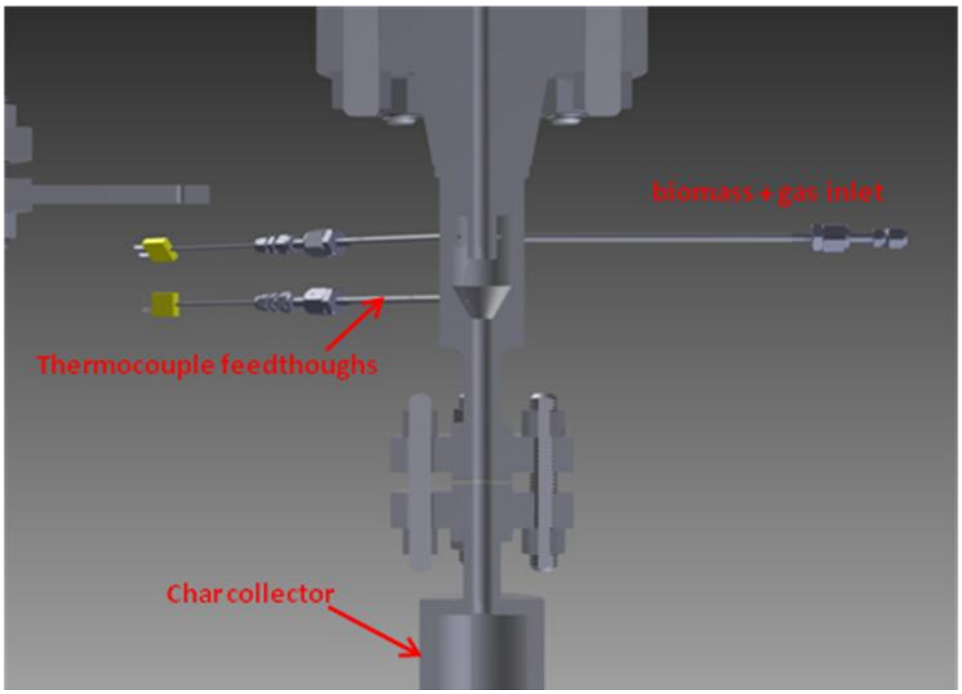

Figure S.2 Cross section view of high-pressure cyclone-type fast-hydropyrolysis reactor.

The char collector was machined from stainless-steel type-316 round bar and has an OD of 3.5" and an ID of 2.626", equivalent to schedule 160 pipe. At 315 °C, the char collector body has an internal design gage pressure of 381 bar. The bottom of the collector uses F316H #600 3" B16.5 flanges for access to the inside of collector if needed. These have a maximum working pressure of 100 bar at 40 °C.

Downstream Fixed-bed Vapor-phase Hydrodeoxygenation (HDO) Reactor

The HDO reactor, shown in Figure S.3, itself is simply an empty tube with a porous metal frit that supports the catalyst bed. It is made from ½" schedule 80 A312 TP316 piping and socketwelded to F316H #1500 B16.5 flange connections. The pipe has an internal design gage pressure of 236 bar at 650 °C. The flanges have maximum working pressure of 106 bar at 593 °C. The connector from the cyclone reactor to the downstream HDO reactor is made from ½" schedule 80 A312 TP316 piping and uses ½" F316H #1500 and 2" F316H #2500 B16.5 flange connections. Again, these flanges have a maximum working pressure of 132 bar and 106.5 bar at 650 °C respectively.

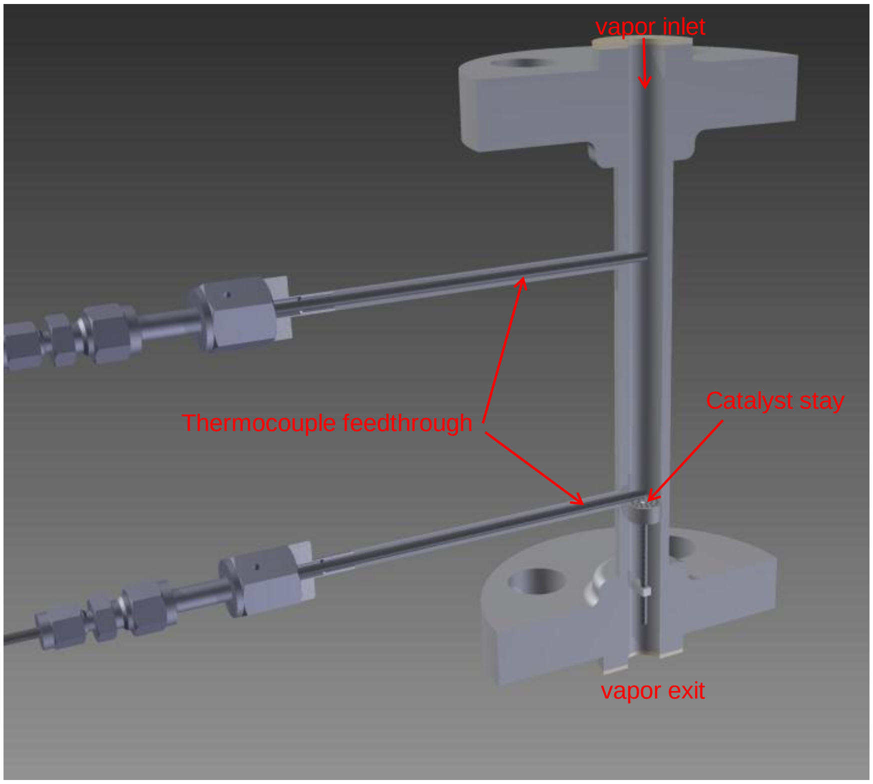

Figure S.3 Cross-section view of downstream fixed-bed vapor-phase HDO reactor.

<u>Condenser and Gas/Liquid Separation</u>

The purpose of this step is to cool and condense the pyrolysis vapors to 15-20 °C and then separate them from the permanent gas stream. The vapor quenching system consists of a concentric-tube countercurrent condenser. Gas and vapors pass through the center tube which is cooled by circulation of 50/50 mixture of ethylene glycol and water at 5°C. The condensed vapors are separated from permanent gases in a Swagelok coalescence filter, which utilizes a glass fiber filter element to help coalesce liquids and is rated to 68 bar at ambient temperature. After passing through the filter, gases are passed through a stainless steel trap, which is cooled using ice-water mixture to collect any remaining condensable liquids. The gas stream is then depressurized via a backpressure regulator and sent to exhaust and GC analysis streams.

The tube portion of the shell and tube condenser is made from schedule 80 A312 TP316 piping and connects to the HDO reactor with a ½" #1500 B16.5 flange. The pipe has an internal design gage pressure of 236 bar at 650 °C. The flanges have maximum working pressure of 106 bar at 593 °C. The exit of the condenser connects to the coalescence filter via ¼" A312 TP316 tube with a wall thickness of 0.028" welded to a ¼" fVCR connector which has an allowable working pressure of 275 bar at 100 °C

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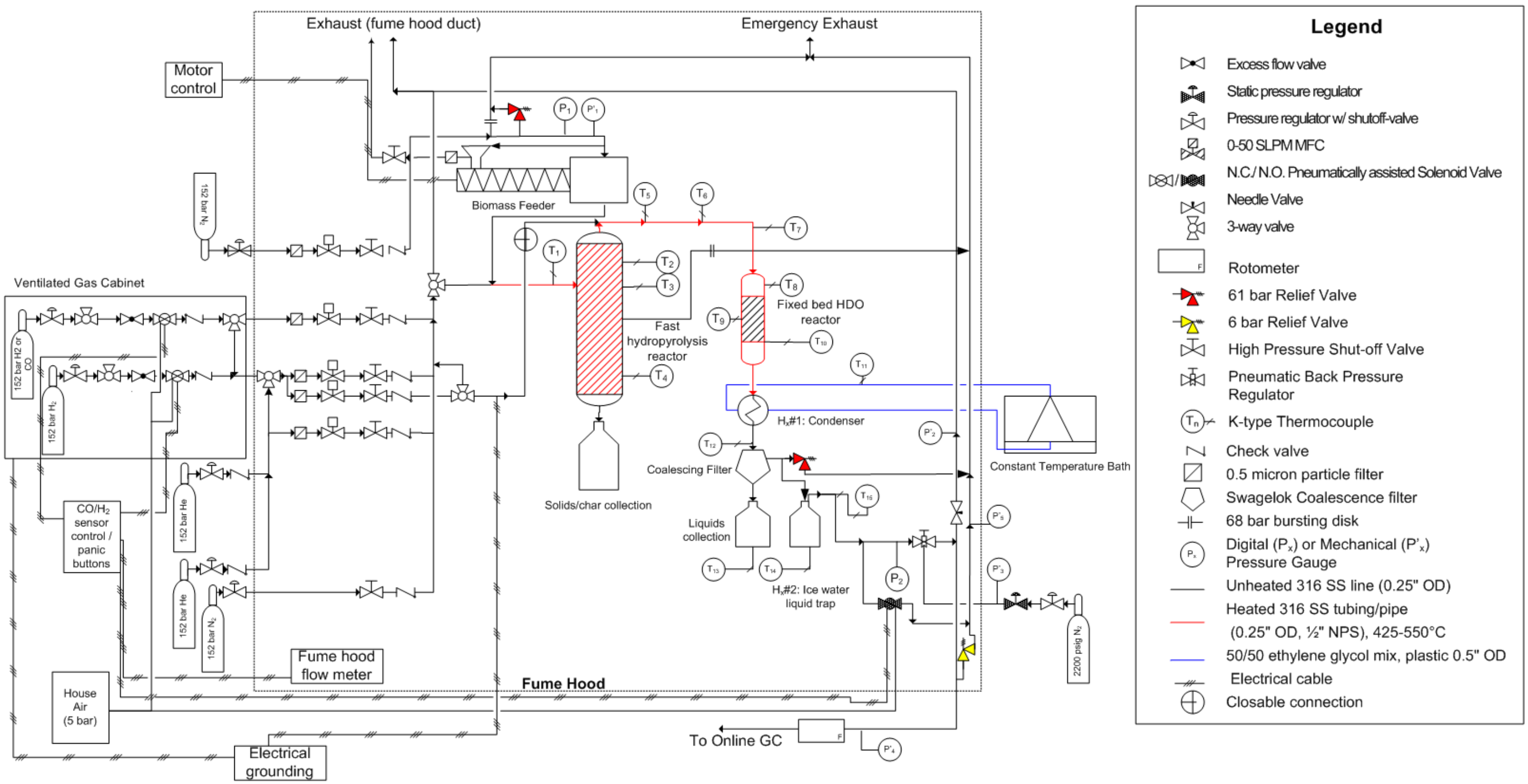

Figure S.4 Process flow diagram of the complete reactor system along with the hydrogen safety systems like hydrogen detectors, automatic shut-off valves, excess flow valves, redundant pressure relief and emergency exhaust.

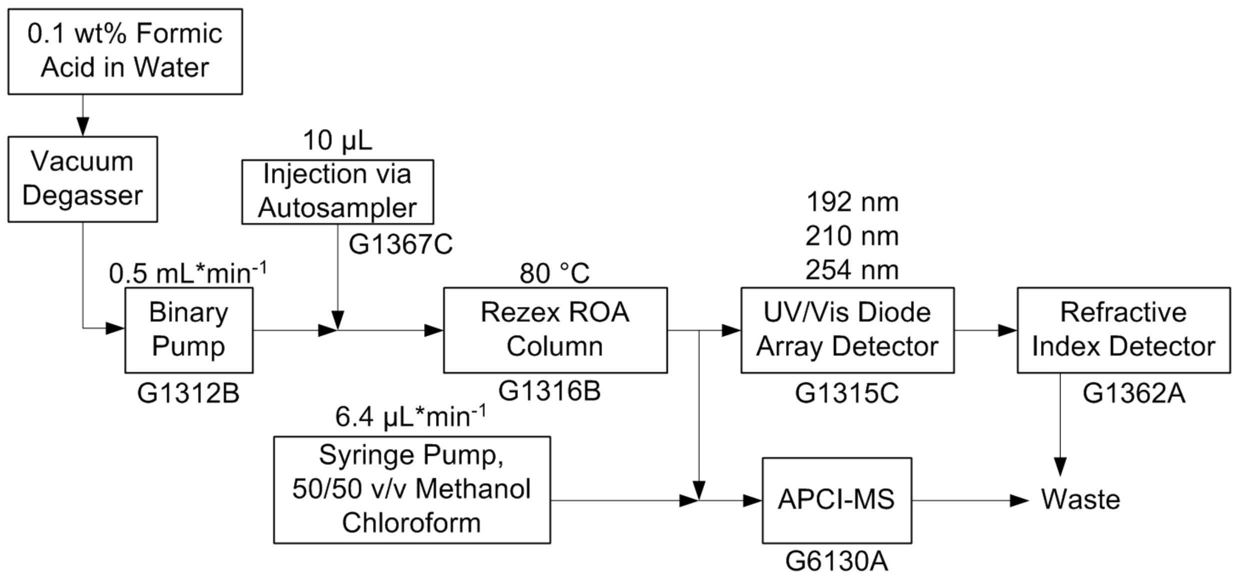

Figure S.5 Simplified schematic of the LC-MS setup for the analysis of liquid products from all experiments. Model numbers of the Agilent LC-MS modules are shown below each unit. Relevant analysis method parameters are shown above each unit.

Table S.1 Chemical compounds identified and quantified for LC-MS analysis of liquid products from all experiments.

Chemical Compound	Retention Time / min	Calibration Range / g L^{-1}
Cellobiosan	11.3	0 - 0.7
Levogalactosan	15.5	0 - 8.0
Levoglucosan	16.1	0 - 6.2
Glycolaldehyde	17.0	0 - 3.2
Formic Acid	18.0	0 - 6.1
Acetic Acid	19.3	0 - 3.2
1,6:2,3-Dianhydro-β-D-mannopyranose (DAMP)	20.9	0 - 2.0
Hydroxyacetone	21.5	0 – 1.9
Methanol	24.3	0 - 4.3
Acetone	26.9	0 - 2.8
Ethanol	27.6	0 - 2.0
Levoglucosenone	33.5	0 - 2.2
5-Hydroxymethylfurfural (5-HMF)	33.9	0 - 1.0
Furfural	47.3	0 - 0.6

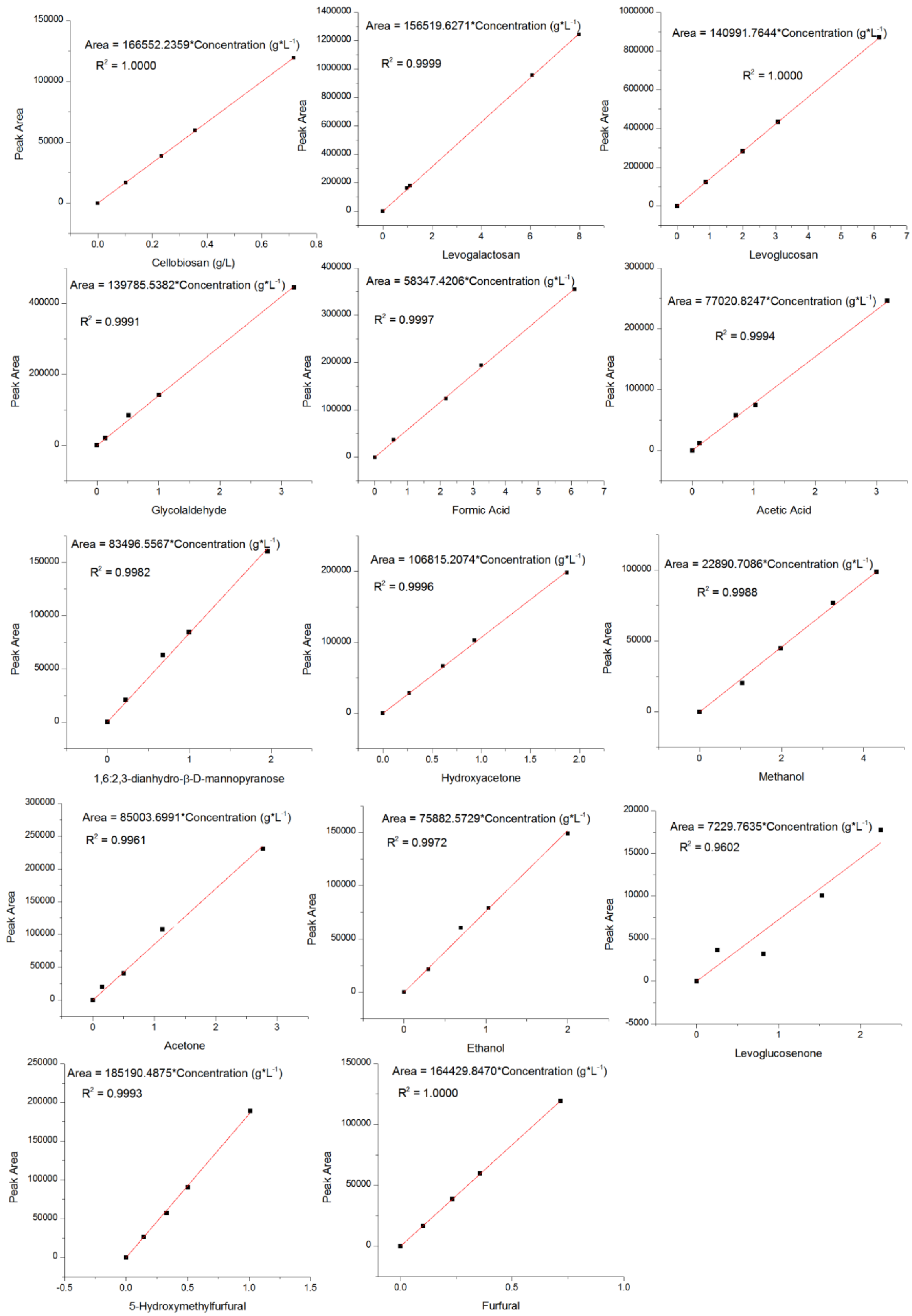

Figure S.6 LC-MS calibrations of the 14 chemical compounds used for quantification