**Supplementary material.**

1. Proximate assay.

1.1 Moisture.

For the determination of moisture in the coffee cherry waste sample, the technical report NREL/TP-510-42621 was used as a guide. One mass of 1,000 grams of both wet and air-dried biomass (milled) was weighed, put in a crucible, and inserted in a Memmert Oven at 105 °C for 24 hours. Afterward, the moisture of the samples was calculated using Equation S1.

$$\%Moisture = \frac{(Weight_{dry\ crucible\ plus\ dry\ sample} - Weight_{dry\ crucible})}{Weigh_{sample\ as\ recieved}} \quad \text{(S1)}$$

1.2 Ashes.

For the determination of ash in the coffee berry waste sample, the laboratory analytical report NREL/TP-510-42622 was followed. A total of 1,000 grams of both wet and air-dried (milled) biomass was weighed, put in a crucible, and inserted in a muffle furnace with the following program: hold at 105 °C for 12 minutes, ramp to 250 °C at 10°C / minute, hold at 250 °C for 30 minutes, ramp to 575 °C at 20 °C / minute, and hold at 575 °C for 180 minutes. Then, the temperature was allowed to drop to 105 °C, and it was weighted. This was performed in triplicates and calculated with Equations S2 and S3.

$$ODW = \frac{Weight_{air\ dry\ sample}\ x\ \%Moisture}{100} \quad \text{(S2)}$$

$$\%Ash = \frac{Weight_{Crucible+ash} - Weight_{crucible}}{ODW_{sample}} \quad \text{(S3)}$$

1.3 Volatile Matter.

For the determination of volatile matter in the coffee berry waste sample, the laboratory analytical report ISO-18123-2015 was followed. A sample of 1 g of dried (milled) biomass was taken and put in a crucible. Afterward, the muffle furnace was set at 900 °C, and the sample was introduced for 7 minutes, the time during which the volatile substances were released as gases or vapors. The weight loss experienced by the sample during this process represents the volatile matter content and is calculated with Equation S4.

$$Volatile\ Matter\ (\%) = (\frac{Weight_{sample+Crucible} - Weight_{(Residual\ weight)}}{Weight_{sample+Crucible}} \quad \text{(S4)}$$

1.4 Fixed Carbon.

The determination of the fixed carbon is not a laboratory procedure; it is a calculated value involving all the characterizations previously obtained. According to ASTM D 3172 – 89, the fixed carbon corresponds to Equation S5.

$$\%Fixed\ Carbon = 100\% - (moisture\ content\ \% - Ash\ content\ \% - Volatile\ matter\ \%) \quad \text{(S5)}$$

1.5 Reactors used for hydrothermal processes.

The LHW hydrothermal process was carried out in 100 mL batch reactors in which a ratio of 3 grams of biomass to 27 grams of water was added, and autogenous pressure was maintained (Ratio 1 biomass/ 9 water). The reactor has a Teflon jacket and is made of stainless steel with a screw-type closure; once the biomass was measured, the reactor was introduced into an oven with the respective temperature and reaction time. A switch to a different reactor was performed at higher temperatures due to the stability of Teflon.

2.

Image S1. LHW Batch 100 mL reactor for hydrothermal processes.

The reactions were carried out in 500 mL stainless steel batch reactors, which were filled with ratios of 10 grams of biomass and 90 grams of water (Ratio 1 biomass/ 9 water). Image S2 shows the implemented reactor, which consists of a jacket (A), where the 500 mL stainless steel vessel is placed, eight threaded studs (B) in the upper part that are adjusted; a heating blanket allows for the regulation of the reaction temperature (C and D), and the coil (I) is used for the circulation of water to stabilize the temperature with the operation of the chiller (F) and its respective pump (E). The nozzles (K) allow for the control of gas extraction, and if necessary, an inert gas can be added to add pressure to the system (J). Finally, the system pressure is monitored using the manometer located in the reactor (L).

Image S2. HTC 500 mL reactors for hydrothermal valorization.

### 3. Chromatographic Method

A Hitachi Elite LaChrom chromatograph coupled to a Hitachi L-2490 refractive index detector was used. In line with the objectives of the thesis, an isocratic method was developed with a SHODEX Sugar SH1821 column (ion exchange and size exclusion separation) at 60 ºC, 0.005M $H_2SO_4$ mobile phase, 0.5 mL/min flow rate, and RI detector at 40 ºC. It was developed with xylose, glucose, galactose, arabinose, levulinic acid, 5-HMF, furfural, acetic acid, and formic acid standards and their respective retention times (Table S1, Figure S1). It was observed that all sugars present had similar retention times and coeluted into a single peak at 16.985 minutes, and hence, quantification was performed by HPLC-IR as "Sugars" and not the individual species of glucose, xylose, fructose, galactose, and arabinose.

**Table S1.** Retention time for standards used.

| Platform chemicals | Retention time (minutes) |
|---|---|
| **Glucose** | 16.789 |
| **Xylose** | 17.179 |
| **Galactose** | 17.255 |
| **Arabinose** | 17.916 |
| **HMF** | 35.637 |
| **Levulinic acid** | 22.127 |
| **Formic acid** | 20.415 |
| **Furfural** | 51.349 |

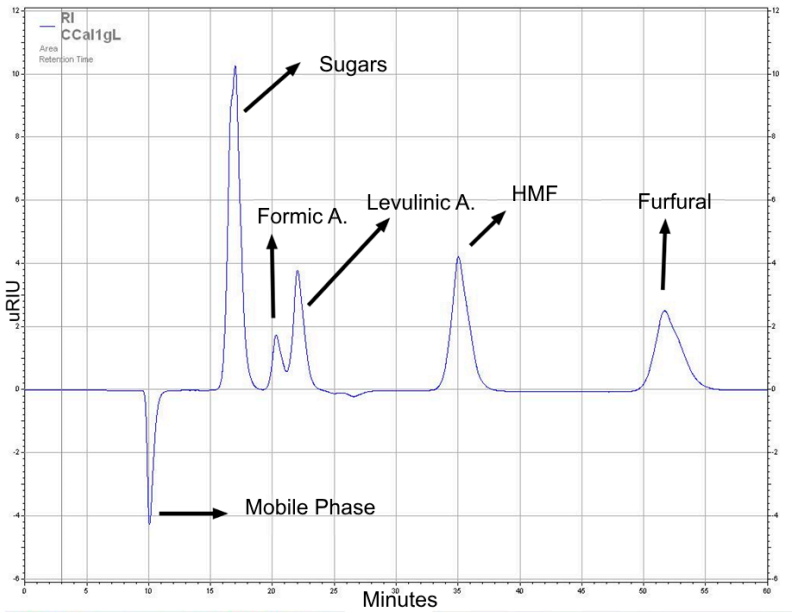


**Figure S1**. Standards used for analytic method development.

For the validation of the chromatographic analytical method and following the standards established by ISO 17025 in its technical note 17, "Guidelines for the validation and verification of quantitative

and qualitative test methods", the following validation parameters were evaluated: linearity; range; precision; accuracy; and limit of detection and quantification, robustness, and sample stability.

**Linearity**: Linearity establishes whether the response of the detector is proportional to the analyte concentration over a given range. To evaluate the linearity of the method, a standard calibration curve for the quantification of sugars, formic acid, levulinic acid, furfural, and HMF at five concentration levels (0.1, 1, 1, 3, 5, 8, 10 g/L) was performed in triplicate. Linearity was evaluated by means of linear regression to obtain the equation of the straight line of the data obtained at the different concentrations of the curve. This allows for obtaining the correlation coefficient (r), the intercept (b), and the slope of the regression line (m); on the other hand, the sum of residual squares was carried out to determine the homogeneity of the variances.

**Range:** Range evaluation in the validation of chromatographic analytical methods involves determining the concentration range within which the method is linear, accurate, and suitable for the intended use. This ensures that the method provides reliable results over a specific range of concentrations. The process involves selecting concentration levels, preparing reference samples or standards, performing experiments, constructing a calibration curve, and evaluating the linearity of the calibration curve using statistical tools. The range is defined as the concentration interval in which the relationship between concentration and detector response is linear and accurate, usually (and in this work) taken as the range in which a coefficient of determination (R2) is greater than 0.99. The upper and lower limits of the range are set according to the results, defining the minimum and maximum concentrations for which the method is valid.

For linearity, the correlation coefficients, intercept, and slope shown in Table S2 and Figure S2 were obtained.

**Table S2**. Information of calibration curves for platform chemicals (PC).

| PC | Slope (m) | Intercept (b) | Pearson correlation (R) | Coefficient of determination ($R^2$) |
|---|---|---|---|---|
| **Sugars** | 262400487.8 | 75704583.1 | 0.9978 | 0.9956 |
| **Formic A.** | 41380930.2 | 3784997.3 | 0.9978 | 0.9955 |
| **Levulinic A.** | 150296520.1 | 3912845.5 | 0.9994 | 0.9988 |
| **HMF** | 311724039.2 | 41994984.9 | 0.9968 | 0.9962 |
| **Furfural** | 210362509.3 | 28492710.7 | 0.9981 | 0.9959 |

Table S2 shows the Pearson correlation coefficients and the coefficient of determination ($R^2$); the $R^2$ is above 0.99 in all cases, an aspect that demonstrates linearity in all the calibration curves carried out and which is a suitable range for the implementation of this curve for quantitative purposes. On the other hand, and applying the data in Figure S2, a regression analysis was made applying ANOVA, where the F value and the critical F value were obtained through the sum of squares; the value obtained was less than 0.05 in all cases, which allowed us to conclude that the model had statistical

significance, and as the response coefficient test was less than 5%, we could safely say that it had linearity.

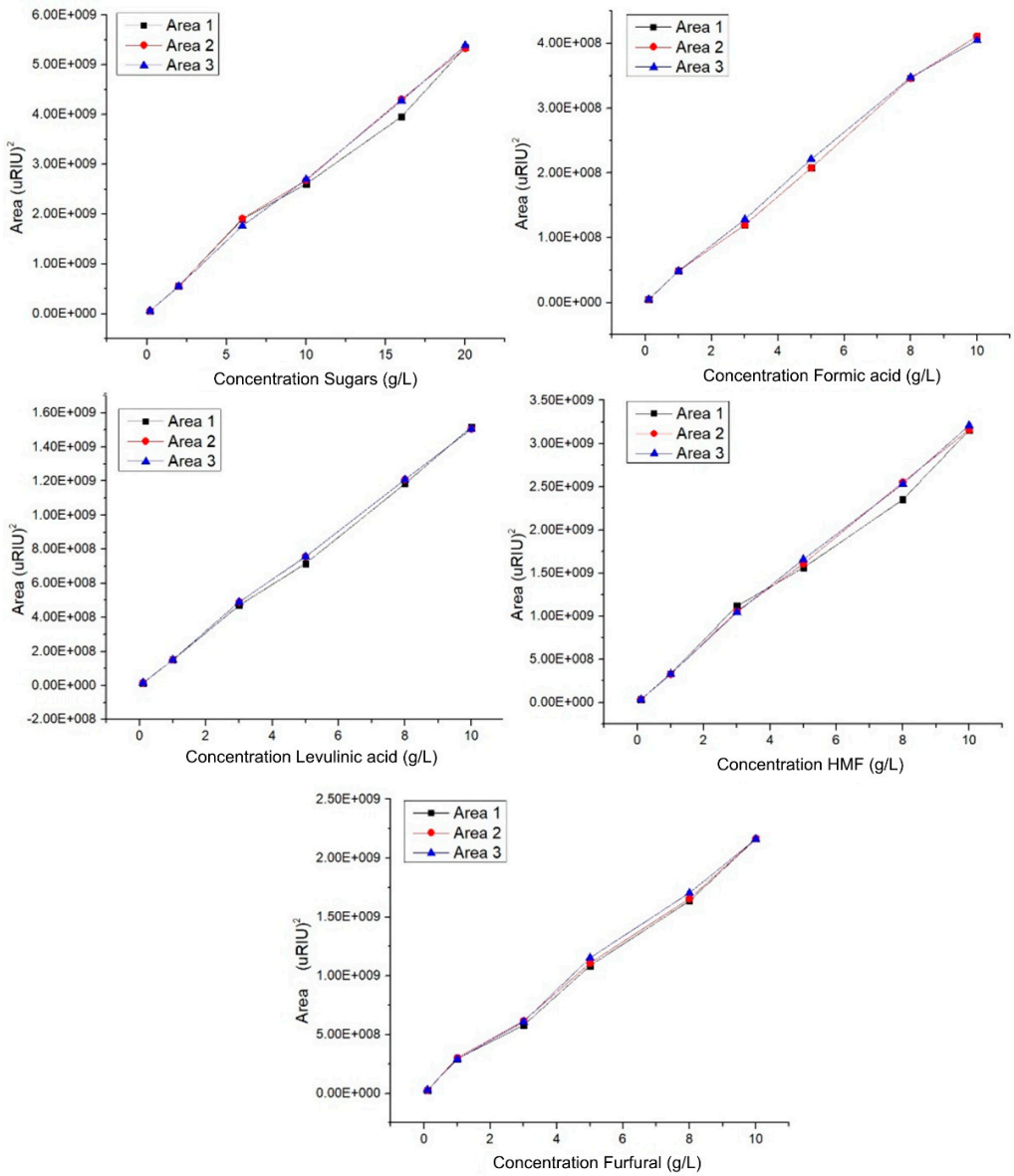


**Figure S2**. Calibration curves performed for every PC.

On the other hand, the homogeneity of the variances was evaluated through the residuals of each of the calibration curves (Figure S3). This allows us to affirm the homoscedasticity of the method; i.e., for this linear regression model, the estimation errors are constant throughout the different concentration points of the calibration curve, and having a constant variance makes the model more reliable.

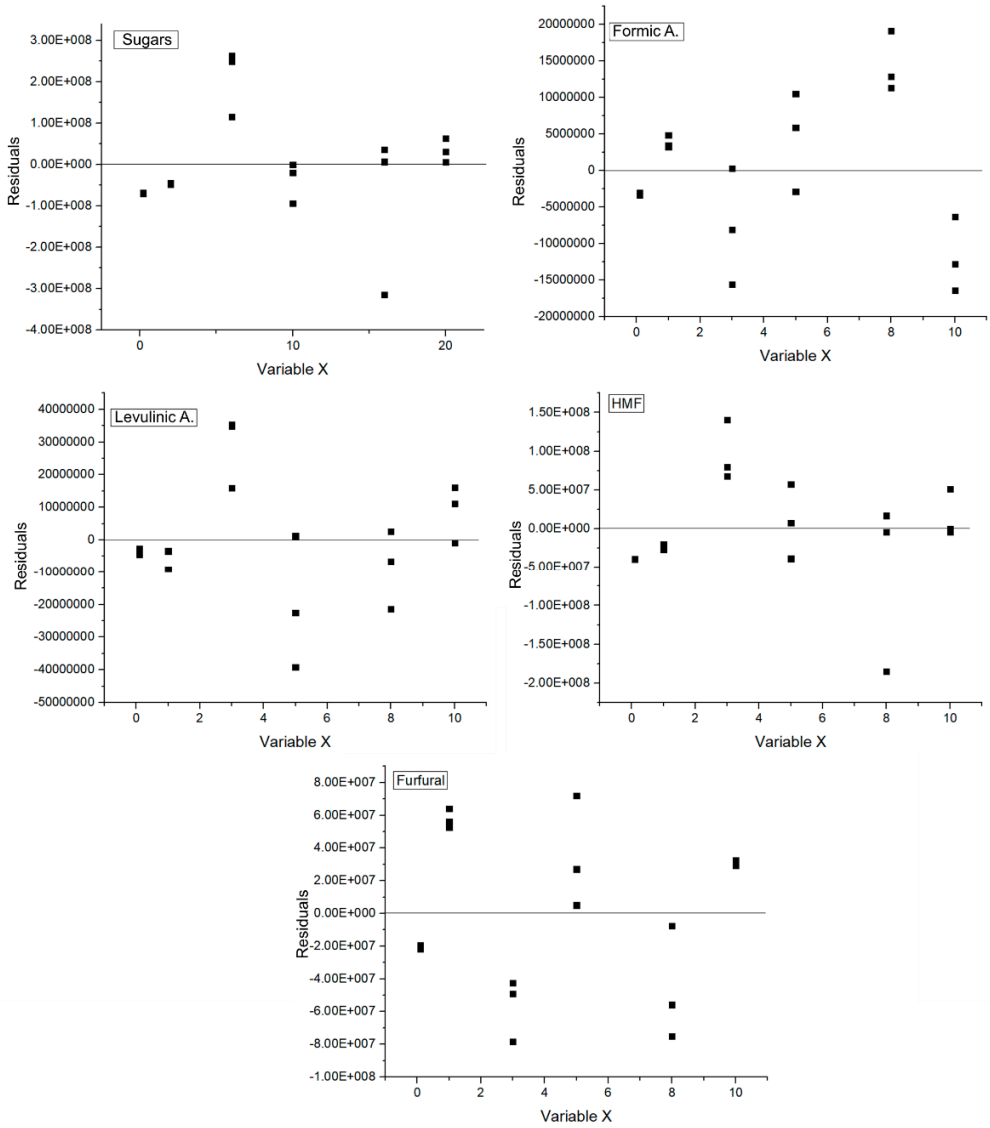


**Figure S3.** Residuals of calibration curves.

From the above, it can be concluded that the method has linearity (R2 greater than 0.99) and homogeneity in its variances, as well as being a model with statistical significance, all this for the working range from 0.1 g/L to 10 g/L.

**Accuracy:**

**Repeatability of the system:** Two standards were prepared from a multi-pattern solution at a concentration of 1 g/L and 10 g/L. They were injected into the HPLC-IR apparatus five consecutive times each, and the coefficient of variation in the responses obtained in the five repetitions of each standard was calculated.

Tables S3 and S4 present the results for the repeatability of the system, in which a high precision in the retention times of the analytes and an acceptable repeatability within the criteria for the analytical responses of the compounds are observed.

**Table S3.** Repeatability of the system based on the retention time.

| **Acceptance criteria** | **Sugars (%)** | | **Formic A. (%)** | | **Levulinic A. (%)** | | **HMF (%)** | | **Furfural (%)** | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Retention time (Minutes) | | | | | | | | | |
| | 1 g/L | 10 g/L | 1 g/L | 10 g/L | 1 g/L | 10 g/L | 1 g/L | 10 g/L | 1 g/L | 10 g/L |
| **CV < 2%** | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0,12 | 0,07 |

**Table S4.** Repeatability of the system based on the area.

| **Acceptance criteria** | **Sugars (%)** | | **Formic A. (%)** | | **Levulinic A. (%)** | | **HMF (%)** | | **Furfural (%)** | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Analytical response (Area) | | | | | | | | | |
| | 1 g/L | 10 g/L | 1 g/L | 10 g/L | 1 g/L | 10 g/L | 1 g/L | 10 g/L | 1 g/L | 10 g/L |
| **CV < 2%** | 0,44 | 0,53 | 1,79 | 1,25 | 1,78 | 0,57 | 0,98 | 0,97 | 1,69 | 0,07 |

**Repeatability of the method:** It was evaluated by injecting the standard calibration curve and a sample of coffee hydrolysate liquid fraction five times for the quantification of the platform chemicals. Analyte concentrations and standard deviation were determined and compared with the acceptance criteria reported in the literature to determine precision.

Table S5 shows the repeatability of the method for each analyte, and the results obtained meet the acceptance criteria, implying that the analytical method developed is repeatable.

**Table S5.** Results for the repeatability of the method.

| **Acceptance criteria** | **Sugars (%)** | **Formic A. (%)** | **Levulinic A. (%)** | **HMF (%)** | **Furfural (%)** |
|---|---|---|---|---|---|
| **CV < 2%** | 1.04 | 1.39 | 1.88 | 0.82 | 1.25 |

**Intermediate precision**: The same procedure for the determination of method precision was replicated but performed by a different analyst on a different day than previously. Data were taken from the two analysts; the percentage of the platform chemical compounds and the standard deviation of these were determined and finally compared with the established acceptance criteria.

Table S6 presents the intermediate precision values for the different analytes on 3 different days with two different analysts; all data obtained are below the acceptance criteria, and therefore, the intermediate precision parameter is accepted.

**Table S6**. Results for intermediate precision for the method developed.

| | Day | Acceptance criteria | Sugars (%) | Formic A. (%) | Levulinic A. (%) | HMF (%) | Furfural (%) |
|---|---|---|---|---|---|---|---|
| **Analyst X** | 1 | CV < 2% | 1.04 | 1.39 | 1.88 | 0.82 | 1.25 |
| | 2 | | 0.81 | 1.52 | 1.64 | 1.24 | 1.56 |
| | 3 | | 1.20 | 1.22 | 1.52 | 1.15 | 0.74 |
| **Analyst Y** | Day | Acceptance criteria | Sugars (%) | Formic A. (%) | Levulinic A. (%) | HMF (%) | Furfural (%) |
| | 1 | CV < 2% | 1.15 | 1.39 | 1.88 | 0.62 | 1.25 |
| | 2 | | 0.91 | 1.78 | 1.55 | 1.57 | 1.67 |
| | 3 | | 0.62 | 1.23 | 0.63 | 0.93 | 0.54 |

**Accuracy**: This was evaluated by enriching a matrix of biomass from a hydrothermal process at low temperature, with a multi-pattern standard, in order to have a known concentration of the analyte that could be quantified so as to be able to quantify the amount added using the method and confirm that it corresponds to the amount added to the standard of the method. The matrix was enriched with multi-pattern standards of concentrations of 5 and 10 g/L, which were subsequently injected into the equipment together with the calibration curve in order to quantify the multi-patterns, their recovery percentage, and the standard deviation of the three replicates of each concentration level. The values obtained were compared with acceptance criteria for this criterion reported in the literature.

Table S7 shows the recovery percentages versus the concentration added to the matrix for quantification using the method developed. It shows that all the analytes are within the acceptance criteria and, therefore, the method is accurate.

**Table S7.** Accuracy of the results obtained for the method.

| **Acceptance criteria (% of recovery)** | **Sugars** | | **Formic acid** | | **Levulinic acid** | | **HMF** | | **Furfural** | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Concentration added to the matrix | | | | | | | | | |
| | 5 g/L | 10 g/L | 5 g/L | 10 g/L | 5 g/L | 10 g/L | 5 g/L | 10 g/L | 5 g/L | 10 g/L |
| **90 %< x < 110%** | 105 | 102 | 106 | 98 | 104 | 101 | 99 | 97 | 107 | 102 |

Limit of detection (LOD) and limit of quantification (LOQ): The calibration equation can be used to estimate the instrumental LOD. Using the estimate of LOD as the blank plus three standard deviations of the blank, the instrument response to a blank is taken as the intercept of the calibration curve (a), and the standard deviation of the instrument response is taken as the standard error of the calibration (sy/x). Therefore, from the calibration equation, $y_{LOD} = a + 3\ S_{y/x} = a + bx_{LOD}$ ; then, xLOD = $x_{LOD} = 3\ S_{y/x}/b$. This equation is widely used in analytical chemistry.

Several conventions have been applied to estimate the LOQ. Depending on the level of certainty required, the most common recommendation is to quote the LOQ as the blank value plus 10 times

the repeatability standard deviation, or 3 times the LOD (which gives largely the same figure), or as 50% above the lowest fortification level used to validate the method.

The limit of detection and limit of quantification were calculated and recorded in Table S8. The values of both LOD and LOQ are below the values of the measured samples, so it can be said that the detected concentrations were reliably obtained by the proposed analytical method.

**Table S8.** Detection and quantification limit for the method.

| PC | Sugars | Formic acid | Levulinic acid | HMF | Furfural |
|---|---|---|---|---|---|
| **LOD (g/L)** | 0.0139 | 0.0129 | 0.0169 | 0.0034 | 0.015 |
| **LOQ (g/L)** | 0.0436 | 0.0431 | 0.0563 | 0.0114 | 0.051 |

**Robustness:**

To evaluate this parameter, a multi-pattern standard was prepared at a concentration of 1 g/L and injected into the HPLC-IR equipment in duplicate at the chromatographic conditions proposed in the analytical method. After this, slight variations (±2 %) were made to the conditions (flow, temperature, and mobile phase) and injected in duplicate to each of the modifications in order to determine the peak retention times of the standards.

- Composition of the mobile phase: (±1mM).

Condition 1: $H_2SO_4$ 4mM, Condition 2: $H_2SO_4$ 6mM, condition 3: $H_2SO_4$ 5mM;

- Chromatographic column temperature (±2 ºC).

Condition 1: 58 ºC, Condition 2: 62 ºC, Condition 3: 60 ºC;

- Mobile phase flow rate ( ± 0,1 mL/min).

Condition 1: 0.4mL/min, Condition 2: 0.6mL/min, Condition 3: 0.5mL/min.

**Table S9.** Results for robustness of the method.

| Condition | Sugars | Formic A. | Levulinic A. | HMF | Furfural |
|---|---|---|---|---|---|
| **Composition MP** | Retention time (Minutes) | | | | |
| **$H_2SO_4$ 4mM** | 17.789 | 21.182 | 23.123 | 35.232 | 53.093 |
| **$H_2SO_4$ 5mM** | 16.985 | 20.285 | 22.029 | 34.732 | 51.048 |
| **$H_2SO_4$ 6mM** | 15.79 | 18.222 | 19.989 | 33.551 | 48.832 |
| **Temp. Column** | | | | | |
| **58ºC** | 16.989 | 20.232 | 21.023 | 34.723 | 50.089 |

| | | | | | |
|---|---|---|---|---|---|
| **60ºC** | 16.985 | 20.285 | 22.029 | 34.732 | 51.048 |
| **62ºC** | 17.001 | 20.320 | 22.103 | 34.791 | 52.099 |
| **Flow FM** | | | | | |
| **0,4mL/min** | 18.934 | 22.238 | 23.183 | 36.239 | 52.8239 |
| **0,5mL/min** | 16.985 | 20.285 | 22.029 | 34.732 | 51.048 |
| **0,6mL/min** | 13.239 | 16.239 | 17.232 | 30.239 | 45.2392 |

Table S9 shows that the method is robust since the variations in retention times in no case exceed a CV of more than 1%, demonstrating that small variations in the system do not affect the elution of the compounds.

**Sample stability.**

Solution stability was assessed by preparing a sample solution of hydrothermal coffee hydrolysate and multi-pattern solution (10g/L) that was injected into the HPLC-IR equipment every hour for a period of 12 hours to quantify the amount of platform chemicals at each time and, thus, observed the time the solutions can remain prepared without changing their concentration versus the initial time.

All samples taken over 12 hours maintained their physicochemical characteristics and did not change in the concentration of the analytes or in the retention times of the analytes, so the samples were stable over the injection times.

It can be said that the method developed to quantify PQP by HPLC-IR is linear, repeatable, accurate, precise, robust, and stable over time. The LOD and LOQ are also reported to ensure that all measurements obtained are above these values so that they can be reliably reported.

4. Hydrothermal valorization yields and concentrations.

**Table S10**. Yield of platform chemicals produced from LHW valorization.

| Temperature (°C) | [ ] of sugars (g/L) | Yield based on biomass (%) | Yield based on lignocellulosic structure (%) |
|---|---|---|---|
| 120 | 0.087 | 0.066 | 0.167 |
| 130 | 0.111 | 0.085 | 0.213 |
| 140 | 0.170 | 0.129 | 0.323 |
| 150 | 1.237 | 0.941 | 2.347 |
| 160 | 1.258 | 0.959 | 2.391 |
| 170 | 1.394 | 1.064 | 2.654 |
| 180 | 1.424 | 1.086 | 2.709 |

**Table S11**: Yields and concentration of platform chemicals produced at 180 °C for 1–5 hours.

| Time (H) | Sugars | | Levulinic acid | | Formic acid | | HMF | | Furfural | | Total Yield (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | [ ] g/L | R (%) | [ ] g/L | R (%) | [ ] g/L | R (%) | [ ] g/L | R (%) | [ ] g/L | R (%) | |
| 1 | 1,424 | 2,716 | | | | | | | | | 2,716 |
| 2 | 1,896 | 3,209 | | | | | | | | | 3,209 |
| 3 | 3,453 | 4,855 | 0,423 | 0,862 | 0,862 | 1,785 | | | | | 7,502 |
| 4 | 5,072 | 6,036 | 1,853 | 3,775 | 6,078 | 12,38 | 0,322 | 0,656 | 0,159 | 0,718 | 23,56 |
| 5 | 6,789 | 8,554 | 1,482 | 3,019 | 4,919 | 10,02 | | | | | 21,59 |

**Table S12**. HTC yields and concentration.

| Temperature (ºC) | Total Yield (%) | Concentration (g/L) | | | | |
|---|---|---|---|---|---|---|
| | | Sugars | Levulinic A. | Formic A. | HMF | Furfural |
| 200 | 18.486 | **2.461** | 1.613 | 4.866 | 0.104 | 0.093 |
| 220 | 20.151 | 2.209 | **1.837** | **5.531** | 0.119 | 0.124 |
| 240 | 19.499 | 1.350 | 1.594 | 5.210 | 0.120 | 0.119 |
| 260 | 21.311 | 0.992 | 1.172 | 4.868 | 0.106 | 0.104 |

**Table S13**. HTC yields and concentration at 200ºC.

| Time (hours) | Total yield (%) | Concentration (g/L) | | | | |
|---|---|---|---|---|---|---|
| | | Sugars | Levulinic A. | Formic A. | HMF | Furfural |
| 1 | 18.483 | **2.461** | 1.613 | 4.865 | 0.104 | 0.093 |
| 2 | 14.519 | 2.510 | **1.234** | **3.054** | | 0.104 |
| 3 | 16.165 | 2.594 | 1.393 | 4.224 | | |
| 4 | 19.169 | 2.863 | 1.557 | 4.605 | | |
| 5 | 21.049 | 3.333 | 1.495 | 4.886 | | |

## 5. Catalysts yield and concentrations.

**Table S14.** Yields and concentrations of PC using homogeneous catalysts.

| Catalyst | Time (hours) | Total yield (%)* | Concentration g/L | | | | |
|---|---|---|---|---|---|---|---|
| | | | Sugars | Formic | Levulinic | HMF | Furfural |
| Without | 1 | 2.716 | 1.424 | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $H_2SO_4$ | 1 | 16.444 | 6.203 | 3.080 | 0.649 | | |
| $CH_3COOH$ | 1 | 12.252 | 0.922 | | 3.774 | | |
| KOH | 1 | 9.120 | 2.570 | 2.668 | | | |
| $NaHCO_3$ | 1 | 12.552 | 2.121 | 3.699 | 1.332 | | |
| Without | 2 | 3.616 | 1.896 | | | | |
| $H_2SO_4$ | 2 | 15.018 | 6.661 | 2.333 | 0.550 | 0.031 | 0.353 |
| $CH_3COOH$ | 2 | 12.754 | 1.007 | | 4.586 | | |
| KOH | 2 | 5.845 | 1.575 | 1,938 | | | |
| $NaHCO_3$ | 2 | 16.044 | 3.384 | 4,842 | 1,125 | | |
| Without | 3 | 7.116 | 3.453 | 0,877 | 0,423 | | |
| $H_2SO_4$ | 3 | 18.576 | 4.073 | 4,023 | 1,341 | 0,289 | 0,373 |
| $CH_3COOH$ | 3 | 13.528 | 1.249 | | 4,739 | | |
| KOH | 3 | 18.328 | 3.808 | 3,963 | 0,997 | | |
| $NaHCO_3$ | 3 | 17.014 | 3.582 | 5,239 | 1,094 | | |