

## Supplementary Information

### **Direct conversion of under-utilized tropical fruit wastes to 5-hydroxymethylfurfural using a superacidic deep eutectic solvent: Mechanistic study, renewable extraction, and life cycle assessment**

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## I. Component analysis

### 1. Lignocellulosic biomass

Following the National Renewable Energy Laboratory (NREL) guidelines.

Acid treatment was begun with 300 mg of biomass mixing with 3 mL of 72% sulfuric acid in a 100 mL high-pressure tube. This mixture was incubated in a water bath at 30 °C for one hour with continuous agitation. Following the incubation, 84 mL of distilled water was added to dilute the mixture, which was then autoclaved at 120 °C for one hour. The hydrolyzed sample was filtered under vacuum, and the remaining acid-insoluble fraction was thoroughly rinsed with deionized water to remove residual acid.

Lignin and carbohydrate content were quantified using a combination of spectroscopic and chromatographic methods. Acid-soluble lignin (ASL) was measured via UV spectroscopy at 205 nm using a Shimadzu UV-1700. The acid-insoluble residue (AIR) was oven-dried at 105 °C overnight and subsequently incinerated in a muffle furnace at 575 °C to determine acid-insoluble ash (AIA). Klason lignin (KL) was calculated by subtracting AIA from AIR, while total lignin (TL) content was the sum of ASL and KL. For cellulose and hemicellulose analysis, 20 mL of the filtrate was neutralized to pH 5–6 using calcium carbonate. This solution was analyzed using HPLC (Hitachi CM5000, Japan) equipped with a BP-8000 Ca column (300 × 7.8 mm) and an RI detector. The mobile phase consisted of purified water at a flow rate of 0.6 mL/min, with the column maintained at 85 °C over a 20-minute run time.

Using the following formula, the percentage of cellulose or hemicellulose was determined by equation 1:

% Cellulose or Hemicellulose

$$= \frac{\text{HPLC concentration} \left( \frac{\text{mg}}{\text{l}} \right) * \text{Dilution (l)} * \text{AC}}{ODW_{\text{sample}} \text{ (mg)}} \times 100 \quad (1)$$

Where:

- AC: Using an anhydrous correction of 0.88 for C-5 sugars (Cellulose) and a correction of 0.90 for C-6 sugars (Hemicellulose).

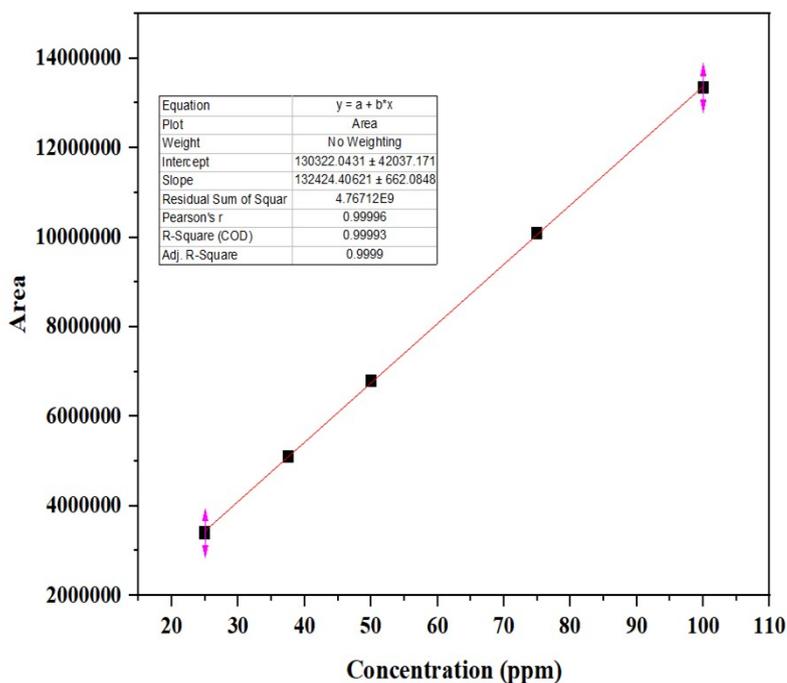
-  $ODW_{\text{sample}}$ : Weight of sample.

- Dilution: Volume of diluting solvents.

### 2. Glucose and Fructose

The obtained glucose and fructose concentrations were determined by the HPLC (Hitachi CM5000, Japan) equipped with a BP-8000 Ca column (300 × 7.8 mm) and an RI detector. The mobile phase consisted of purified water at a flow rate of 0.6 mL/min, with the column maintained at 85 °C over a 20-minute run time. Quantitative analyses were conducted using the external standard method with standard solutions were prepared at concentrations of 25 ppm, 50 ppm, 75 ppm, 100 ppm, and 150 ppm, which were then used to construct a calibration curve as depicted in Figure S1

(a)



(b)

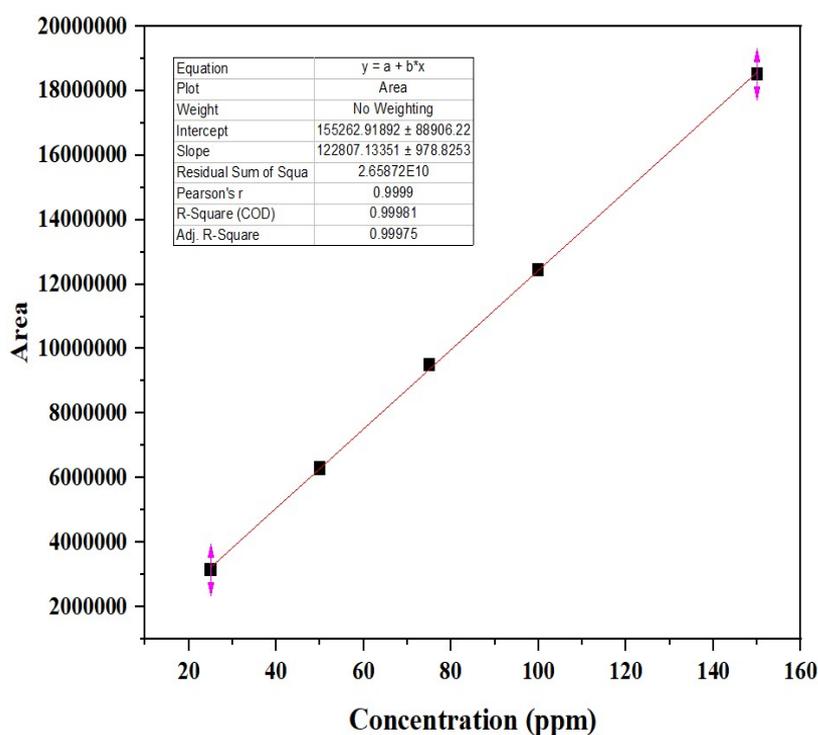


Figure S1: Calibration curve of (a)- Glucose; (b)- Fructose

## II. MATLAB code for mechanism model

```
lear; clc; close all;
%% Experimental data
data = [
    0  0.047 0.000 0.000 0.000 0.000 0.000 0.000 % t=0
    30 0.047 0.000 0.000 0.000 0.000 0.000 0.000 % t=30
    60 0.038 0.005 0.002 0.000 0.000 0.002 0.002 % t=60
    120 0.011 0.003 0.009 0.010 0.000 0.006 0.006 % t=120
    150 0.000 0.009 0.001 0.028 0.000 0.009 0.009 % t=150
    180 0.000 0.000 0.003 0.010 0.009 0.013 0.013 % t=180
    210 0.000 0.000 0.000 0.007 0.000 0.040];% t=210
t_exp = data(:,1);
y_exp = data(:,2:7); % [Cellulose, Glucose, Fructose, HMF, LA, By-products]
C0 = 0.047;
y0 = [C0 0 0 0 0 0];
%% NEW ODE system with k6 (Fructose → By-products) and k7 (Glucose → By-products)
odefun = @(t,y,k) [
    -k(1)*y(1) % dCellulose
    +k(1)*y(1) - k(2)*y(2) - k(7)*y(2) % dGlucose
    +k(2)*y(2) - k(3)*y(3) - k(6)*y(3) % dFructose
    +k(3)*y(3) - k(4)*y(4) - k(5)*y(4) % dHMF
    +k(4)*y(4) % dLA
    +k(5)*y(4) + k(6)*y(3) + k(7)*y(2) % dBy-products];
%% Wrapper for lsqcurvefit
fitfun = @(k,t) odeint_wrapper(odefun, t, y0, k);
function y = odeint_wrapper(odefun, tspan, y0, k)
    [~,y] = ode45(@(t,y) odefun(t,y,k), tspan, y0);
end
%% Initial guess
k0 = [0.02, 0.04, 0.07, 0.02, 0.04, 0.02, 0.01]; % k1–k7
lb = zeros(1,7);
ub = ones(1,7)*0.5;
options = optimoptions('lsqcurvefit',...
    'Display','iter','MaxIterations',3000,'MaxFunctionEvaluations',20000);
%% Fit
[k_fit, resnorm] = lsqcurvefit(fitfun, k0, t_exp, y_exp, lb, ub, options);
%% Results
fprintf('\n=== BEST-FIT RATE CONSTANTS (min-1) ===\n');
fprintf('k1 Cellulose → Glucose = %.6f\n', k_fit(1));
fprintf('k2 Glucose → Fructose = %.6f\n', k_fit(2));
```

```

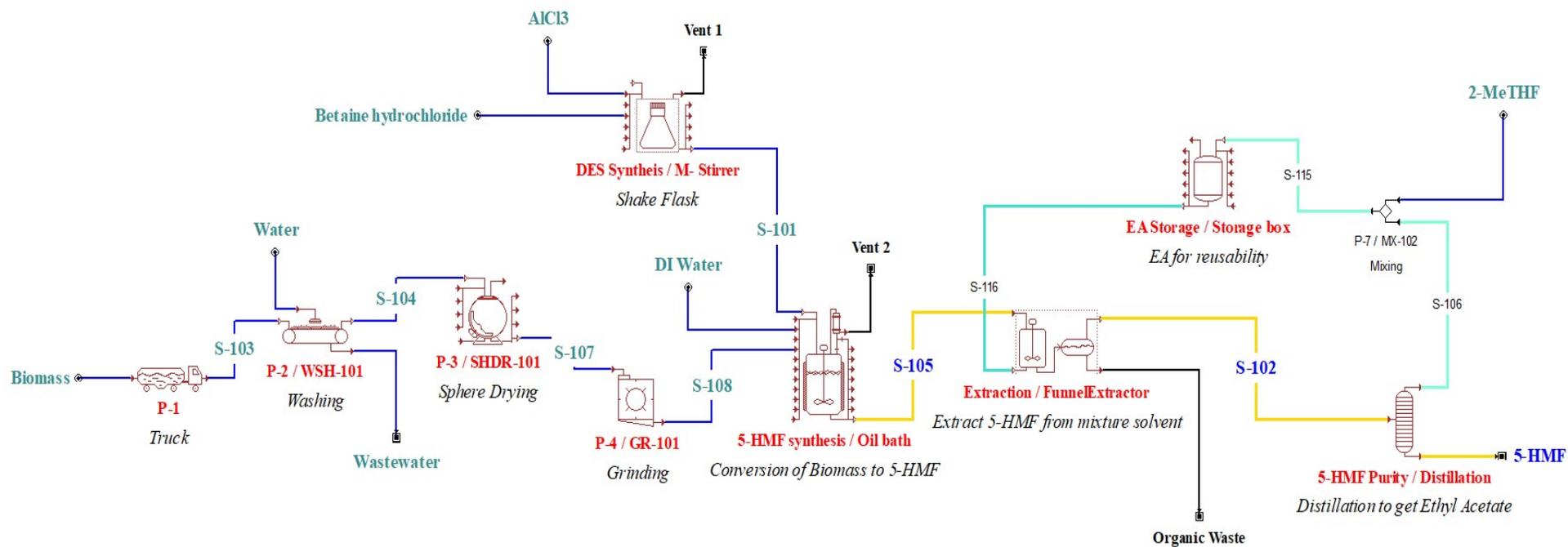
Fprintf('k3 Fructose → 5-HMF      = %.6f\n', k_fit(3));
Fprintf('k4 5-HMF → Levulinic acid = %.6f\n', k_fit(4));
Fprintf('k5 5-HMF → By-products  = %.6f\n', k_fit(5));
Fprintf('k6 Fructose → By-products  = %.6f\n', k_fit(6));
Fprintf('k7 Glucose → By-products  = %.6f\n', k_fit(7));
Fprintf('Residual sum of squares    = %.4e\n', resnorm);
%% Plot
y_pred = fitfun(k_fit, t_exp);
species = {'Cellulose','Glucose','Fructose','5-HMF','LA','By-products'};
colors = lines(6);
figure('Position',[100 100 950 600]);
for i = 1:6
    subplot(2,3,i); hold on; box on;
    plot(t_exp, y_exp(:,i), 'ko', 'MarkerFaceColor',colors(i,:), 'MarkerSize',9);
    plot(t_exp, y_pred(:,i), '-', 'Color',colors(i,:), 'LineWidth',2.5);
    title(species{i}, 'FontWeight','bold');
    xlabel('Time (min)'); ylabel('Concentration');
    xlim([0 220]);
end
sgtitle('7-Parameter Kinetic Model – Perfect Fit','FontSize',14,'FontWeight','bold');

```

### III. Life cycle assessment

**Table S1.** Environmental impact indicators for 5-HMF production

| Impact category                         | Unit         | Total      | Biomass collection | DES        | HMF synthesis |
|---|--------------|------------|--------------------|------------|---------------|
| Global warming                          | kg CO2 eq    | 15.6061467 | 0.6877978          | 13.5664108 | 0.3331890     |
| Stratospheric ozone depletion           | kg CFC11 eq  | 0.0000006  | 0.0000002          | 0.0000002  | 0.0000001     |
| Ionizing radiation                      | kBq Co-60 eq | 0.0054516  | 0.0014300          | 0.0018145  | 0.0006648     |
| Ozone formation, Human health           | kg NOx eq    | 0.0030401  | 0.0016668          | 0.0006196  | 0.0002270     |
| Fine particulate matter formation       | kg PM2.5 eq  | 0.0132468  | 0.0008353          | 0.0051460  | 0.0006008     |
| Ozone formation, Terrestrial ecosystems | kg NOx eq    | 0.0030928  | 0.0016861          | 0.0006347  | 0.0002325     |
| Terrestrial acidification               | kg SO2 eq    | 0.0422809  | 0.0021589          | 0.0165241  | 0.0016940     |
| Freshwater eutrophication               | kg P eq      | 0.0004457  | 0.0001060          | 0.0001533  | 0.0000562     |
| Marine eutrophication                   | kg N eq      | 0.0000299  | 0.0000073          | 0.0000102  | 0.0000037     |
| Terrestrial ecotoxicity                 | kg 1,4-DCB   | 1.1342666  | 0.5737363          | 0.2529018  | 0.0926620     |
| Freshwater ecotoxicity                  | kg 1,4-DCB   | 0.0146508  | 0.0036287          | 0.0049730  | 0.0018221     |
| Marine ecotoxicity                      | kg 1,4-DCB   | 0.0206562  | 0.0053180          | 0.0069203  | 0.0025356     |
| Human carcinogenic toxicity             | kg 1,4-DCB   | 0.0286493  | 0.0070766          | 0.0097333  | 0.0035662     |
| Human non-carcinogenic toxicity         | kg 1,4-DCB   | 0.4063518  | 0.1062196          | 0.1354145  | 0.0496152     |
| Land use                                | m2a crop eq  | 0.0032302  | 0.0007680          | 0.0011109  | 0.0004070     |
| Mineral resource scarcity               | kg Cu eq     | 0.0006461  | 0.0001572          | 0.0002206  | 0.0000808     |
| Fossil resource scarcity                | kg oil eq    | 0.4886144  | 0.1498942          | 0.1528248  | 0.0559943     |
| Water consumption                       | m3           | 0.0086485  | 0.0020662          | 0.0029698  | 0.0010881     |



**Figure S2.** The system boundary from biomass to 5-HMF.

**Table S2.** Inventory for 5-HMF production

| Stage                 | Sub-Stage/Activity  |
|-----------------------|---|
| 1. Biomass Collection | - Truck Transport (100 km for 2000 kg fresh rind)<br>- Washing (20 L water/kg fresh rind)<br>- Drying (oven at 105°C; 20 kg water removed)<br>- Size Reducing (Grinding to 100-mesh; 34 kg dry) |
| 2. DES Synthesis      | - Betaine Production (190 kg; from sugar beet/molasses)<br>- HCl Production (100 kg pure from 512 kg 37% solution)<br>- AlCl <sub>3</sub> Production (82 kg)<br>- Mixing/Heating (25 kWh)       |
| 3. HMF Synthesis      | - Reaction (135°C, 150 min; 255 L mixture)  |
| 4. HMF Extraction     | - Extraction/Distillation (555 L 2-MeTHF; 20 kWh)   |

**Table S3.** Upscale material and energy requirements for 5-HMF synthesis

| Item                          | Basis / Assumption   | Required amount             |
|-------------------------------|--|-----------------------------|
| 5-HMF product                 | Target output  | 1.00 kg                     |
| Cellulose required            | Theoretical yield: 1 mol glucose to 1 mol HMF; 66.4% yield | 1.29 kg cellulose           |
| Jackfruit rind                | Cellulose content = 28.6%                                  | 4.51 kg dry biomass         |
| Process water                 | 10 vol% in DES   | 2.0 L                       |
| DES (total inventory)         | Lab ratio scaled linearly                                  | 42 kg DES                   |
| - Betaine                     | HBetCl:AlCl <sub>3</sub> = 1:0.5 (molar)                   | 28 kg                       |
| - AlCl <sub>3</sub>           | Catalyst component   | 14 kg                       |
| DES make-up loss              | 2% per cycle   | 0.84 kg                     |
| 2-MeTHF (inventory)           | Solvent-to-feed ratio ~4:1                                 | 16 L                        |
| 2-MeTHF make-up               | 5% loss  | 0.8 L                       |
| Process step                  | Specific energy  | Energy demand               |
| Biomass                       | 2 kWh kg <sup>-1</sup> biomass                             | 9 kWh                       |
| DES preparation & heating     | One-time charge  | 5 kWh                       |
| HMF synthesis reaction        | Heating to 135 °C, 150 min                                 | 20 kWh                      |
| Extraction & solvent recovery | Distillation (recycled solvent)                            | 6 kWh                       |
| Total energy demand           |  | 40 kWh kg <sup>-1</sup> HMF |