Supporting Information

# Improvement of Pelletability of Woody Biomass by Torrefaction under Pressurized Steam

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**Table S1.** Proximate and ultimate analyses of raw and torrefied acacia tree. (Corresponding to **Table 1** for rubber tree)

| | Proximate analysis (wt%-dry) | | | Ultimate analysis (wt%-d.a.f.) | | | | Atomic ratio (−) | | HHV |
|---|---|---|---|---|---|---|---|---|---|---|
| | Ash | VM | FC | C | H | N | O | H/C | O/C | (MJ/kg-d.a.f.) |
| Raw | 1.1 | 88.7 | 10.7 | 50.6 | 6.21 | 0.03 | 43.2 | 1.46 | 0.64 | 18.2 |
| DT250 | 1.1 | 76.9 | 22.0 | 56.9 | 6.03 | 0.09 | 36.9 | 1.26 | 0.49 | 21.2 |
| DT260 | 1.3 | 71.6 | 27.0 | 59.5 | 5.94 | 0.11 | 34.4 | 1.19 | 0.43 | 22.4 |
| DT270 | 1.5 | 67.5 | 30.9 | 61.1 | 5.62 | 0.14 | 33.1 | 1.09 | 0.41 | 22.7 |
| DT280 | 1.7 | 57.6 | 40.8 | 64.8 | 5.28 | 0.16 | 29.8 | 0.97 | 0.35 | 24.1 |
| WT180 | 0.5 | 87.9 | 11.2 | 52.4 | 6.30 | 0.00 | 41.3 | 1.43 | 0.59 | 19.3 |
| WT200 | 0.4 | 84.9 | 14.7 | 53.2 | 6.01 | 0.04 | 40.7 | 1.34 | 0.57 | 19.3 |
| WT220 | 0.5 | 81.6 | 17.9 | 56.7 | 6.23 | 0.05 | 37.0 | 1.31 | 0.49 | 21.4 |
| WT250 | 0.4 | 63.0 | 36.4 | 66.3 | 5.74 | 0.32 | 27.7 | 1.03 | 0.31 | 25.7 |
| PST180 | 0.6 | 87.1 | 12.4 | 50.8 | 6.17 | 0.21 | 42.8 | 1.45 | 0.63 | 18.3 |
| PST200 | 0.8 | 84.9 | 14.2 | 52.7 | 6.24 | 0.25 | 40.8 | 1.41 | 0.58 | 19.4 |
| PST220 | 0.7 | 79.7 | 19.6 | 54.2 | 6.20 | 0.22 | 39.4 | 1.36 | 0.55 | 20.1 |
| PST250 | 0.6 | 75.1 | 23.6 | 56.8 | 6.05 | 0.02 | 37.1 | 1.27 | 0.49 | 21.2 |

**Table S2.** Yield of volatiles from each pseudo component in pyrolysis of raw and torrefied acacia tree. TGA conditions: sample 3 mg, heating rate 5 °C/min, and $N_2$ 300 mL/min. (Corresponding to **Table 2** for rubber tree)

| | Yield (wt%-sample)[a] | | | Composition (wt%) | | | Yield (wt%-feedstock)[b] | | | $T_{peak}$ (°C)[c] | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Hemi | Cel | Lig | Hemi | Cel | Lig | Hemi | Cel | Lig | Hemi | Cel | Lig |
| Raw | 24.0 | 47.8 | 11.5 | 28.8 | 57.4 | 13.8 | 24.0 | 47.8 | 11.5 | 289 | 339 | 372 |
| DT250 | 1.0 | 49.0 | 20.9 | 1.5 | 69.1 | 29.5 | 0.8 | 39.1 | 16.7 | 271 | 340 | 382 |
| DT260 | 4.3 | 42.0 | 14.8 | 7.0 | 68.8 | 24.2 | 3.1 | 30.5 | 10.7 | 282 | 339 | 395 |
| DT270 | 3.2 | 35.0 | 17.7 | 5.8 | 62.6 | 31.6 | 2.1 | 22.7 | 11.5 | 271 | 339 | 395 |
| DT280 | – | 15.2 | 30.1 | – | 33.6 | 66.4 | – | 8.5 | 16.7 | – | 338 | 385 |
| WT180 | 16.6 | 51.2 | 17.2 | 19.5 | 60.2 | 20.2 | 12.4 | 38.4 | 12.9 | 322 | 364 | 356 |
| WT200 | 12.0 | 50.2 | 19.9 | 14.7 | 61.2 | 24.2 | 8.4 | 35.2 | 13.9 | 328 | 363 | 369 |
| WT220 | 11.1 | 42.6 | 24.6 | 14.1 | 54.5 | 31.4 | 7.6 | 29.2 | 16.8 | 329 | 361 | 370 |
| PST-A180 | 24.8 | 46.2 | 13.4 | 29.3 | 54.8 | 15.9 | 20.5 | 38.3 | 11.1 | 294 | 339 | 372 |
| PST-A200 | 17.2 | 40.4 | 21.6 | 21.7 | 51.0 | 27.3 | 11.3 | 26.7 | 14.3 | 304 | 338 | 341 |
| PST-A220 | 14.3 | 44.2 | 21.4 | 17.9 | 55.3 | 26.8 | 8.5 | 26.1 | 12.7 | 306 | 345 | 349 |
| PST-A250 | 4.7 | 38.4 | 28.3 | 6.5 | 53.8 | 39.6 | 2.4 | 19.5 | 14.4 | 312 | 359 | 376 |

[a] Yield on a torrefied sample mass basis. [b] Yield on a feedstock mass basis. [c] Peak temperature in DTG profile.

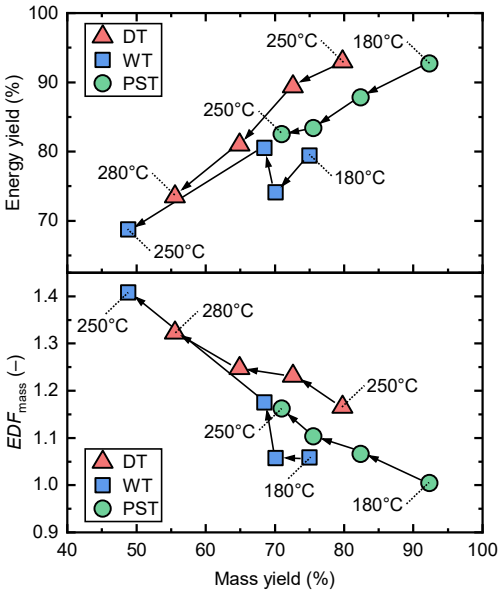


**Figure S1**. Energy yield and $EDF_{mass}$ plotted against mass yield for torrefied acacia tree. Torrefaction temperature: 250→260→270→280°C for DT and 180→200→220→250°C for WT and PST. (Corresponding to **Figure 2** for rubber tree)

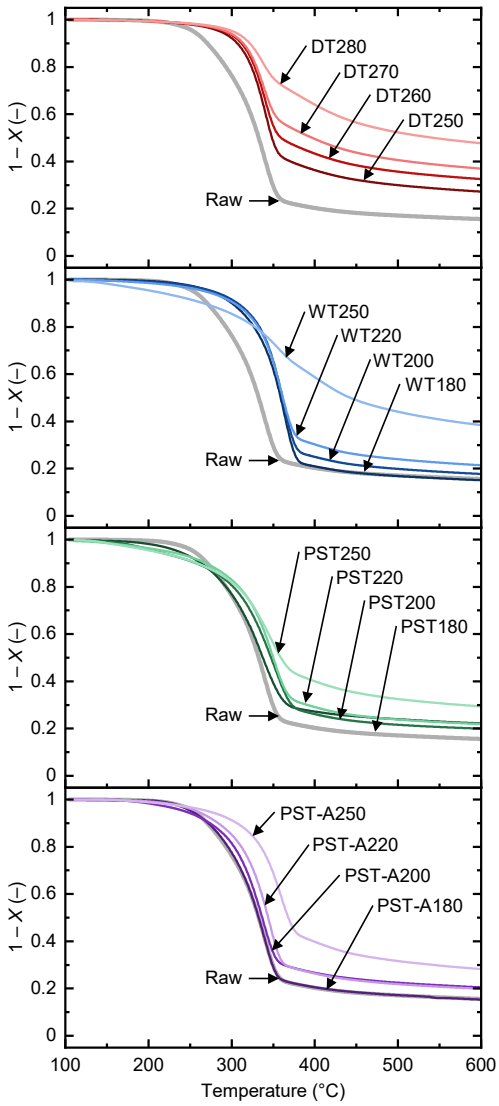


**Figure S2**. Mass release curves for pyrolysis of raw and torrefied acacia tree. TGA conditions: sample 3 mg, heating rate 5 °C/min, and $N_2$ 300 mL/min. (Corresponding to **Figure 3** for rubber tree)

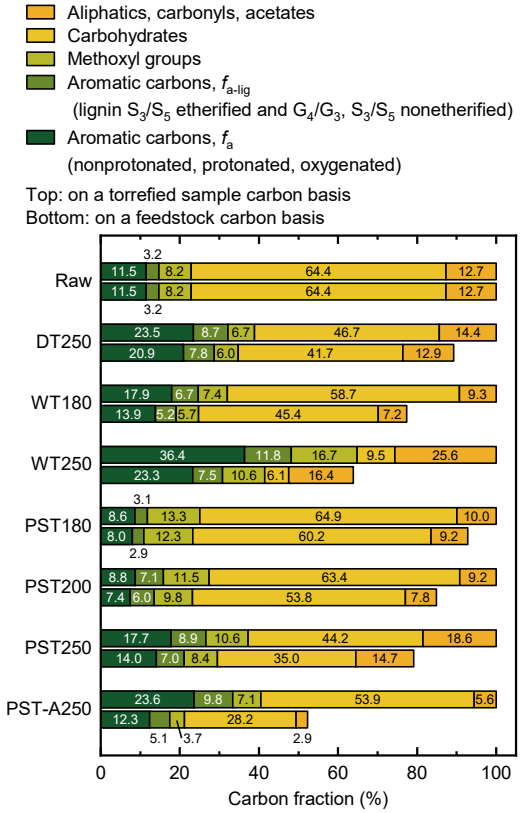


**Figure S3.** Fraction of carbon moieties analyzed by solid-state $^{13}C$ NMR for selected fuels from acacia tree. (Corresponding to **Figure 4** for rubber tree)

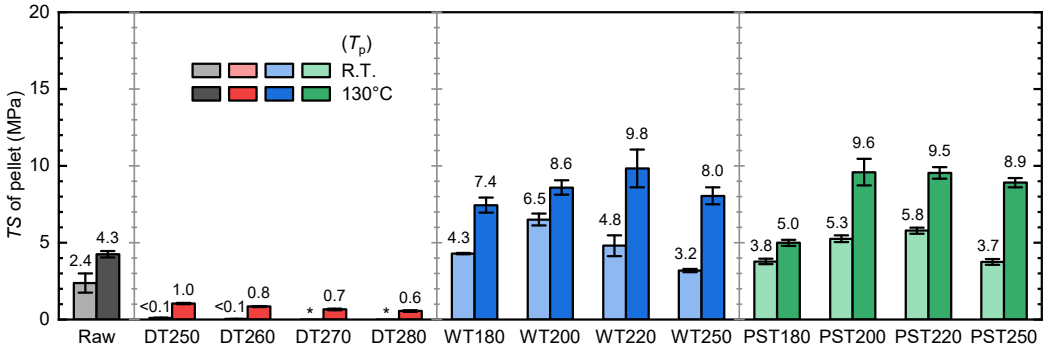


**Figure S4.** *TS* of pellets from raw and torrefied acacia tree. Asterisk presents that pellet could not be prepared. (Corresponding to **Figure 5** for rubber tree)

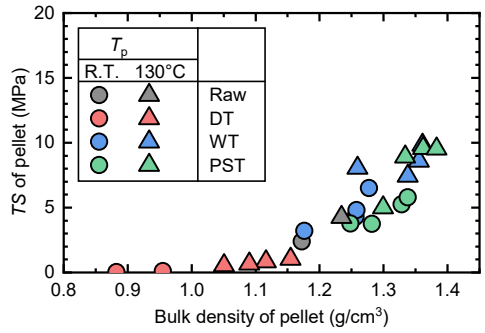


**Figure S5.** *TS* of pellet plotted against its bulk density for raw and torrefied acacia tree. (Corresponding to **Figure 6** for rubber tree)

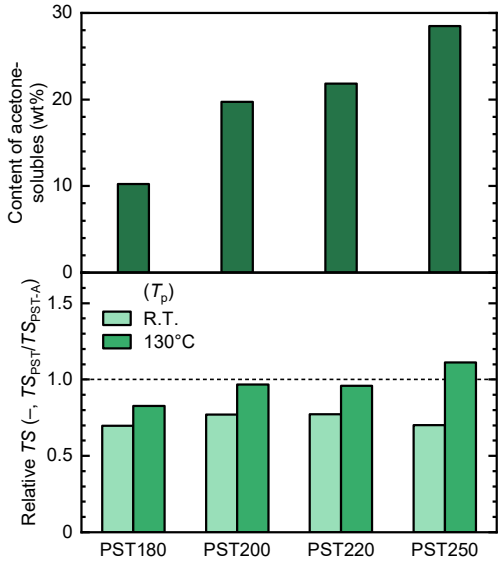


**Figure S6.** Content of acetone-soluble portion in PST180–250 (top) and relative *TS* of pellet from PST fuel to that from PST-A fuel (bottom) for acacia tree. (Corresponding to **Figure 8** for rubber tree)

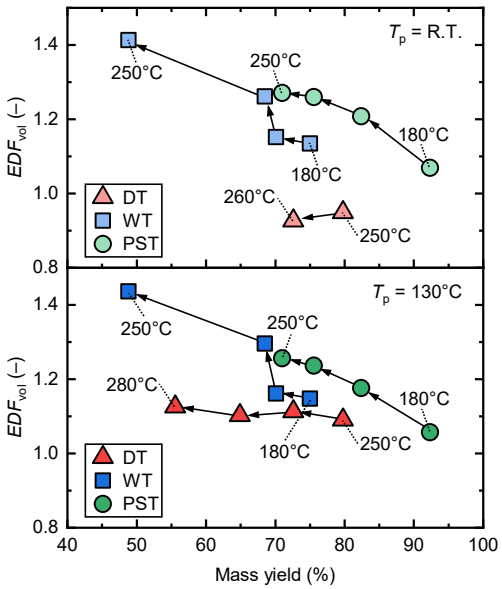


**Figure S7.** $EDF_{vol}$ of pellets plotted against mass yield in torrefaction for torrefied acacia tree. (Corresponding to **Figure 9** for rubber tree)

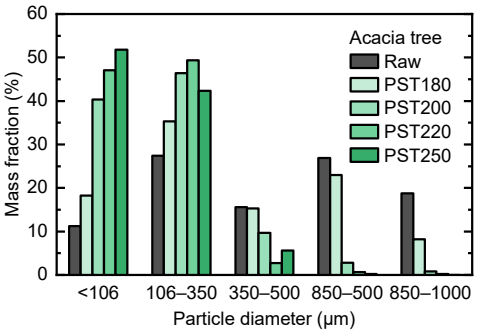


**Figure S8.** Particle size distribution of ground raw and PST fuels from acacia tree. 10 g of pellets before or after PST was ground by a crusher for a predetermined duration and then subjected to sieving.

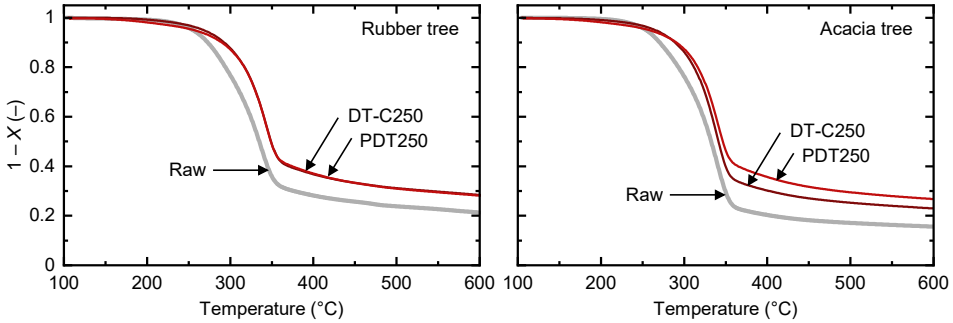


**Figure S9.** Mass release curves for pyrolysis of raw and torrefied fuels. Torrefaction was carried out in the autoclave loaded with $N_2$ at atmospheric pressure (DT-C250) or 3.9 MPa (PDT250). TGA conditions: sample 3 mg, heating rate 5 °C/min, and $N_2$ 300 mL/min.

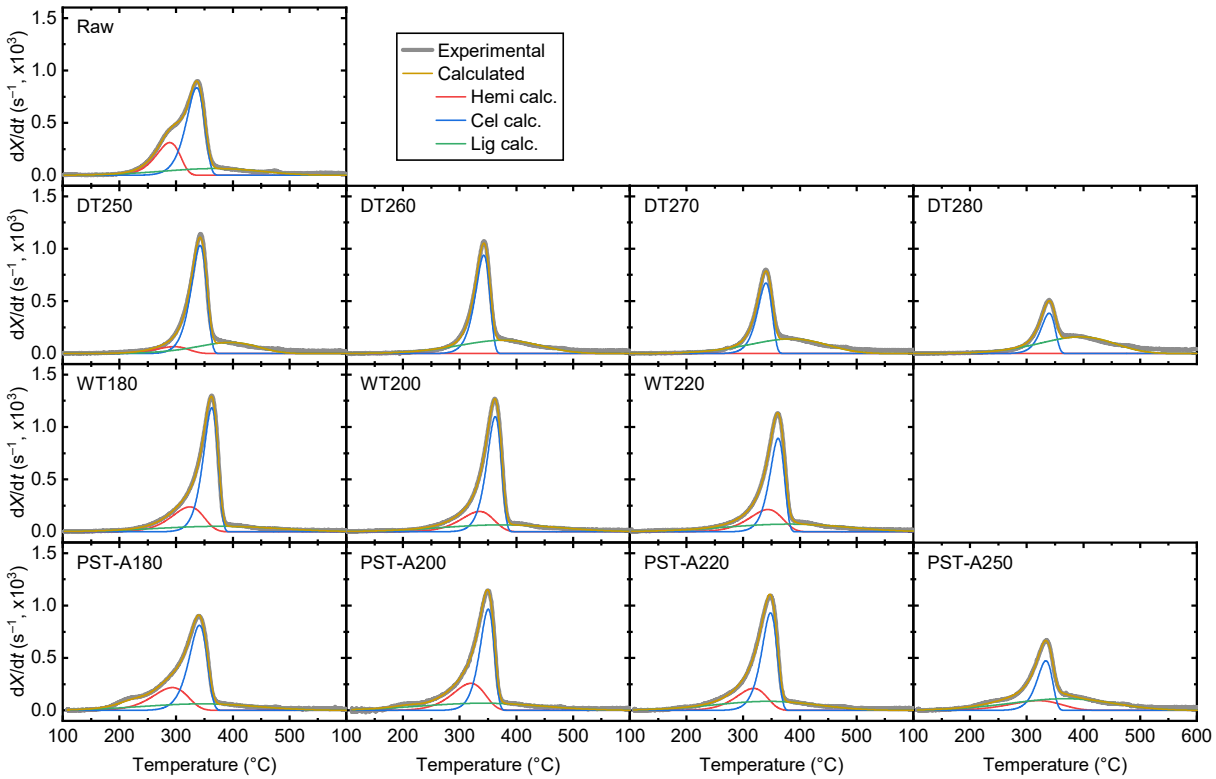


**Figure S10**. Deconvolution of DTG profile of raw and torrefied rubber tree.

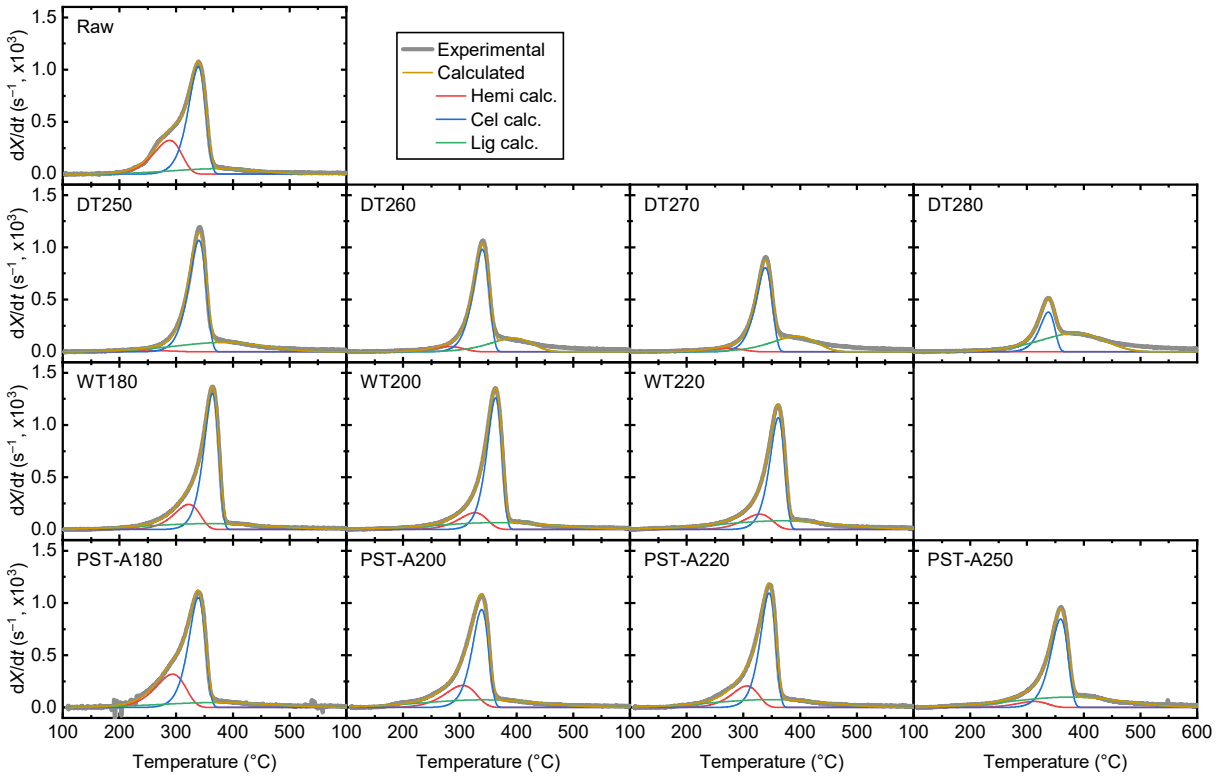


**Figure S11**. Deconvolution of DTG profile of raw and torrefied acacia tree.

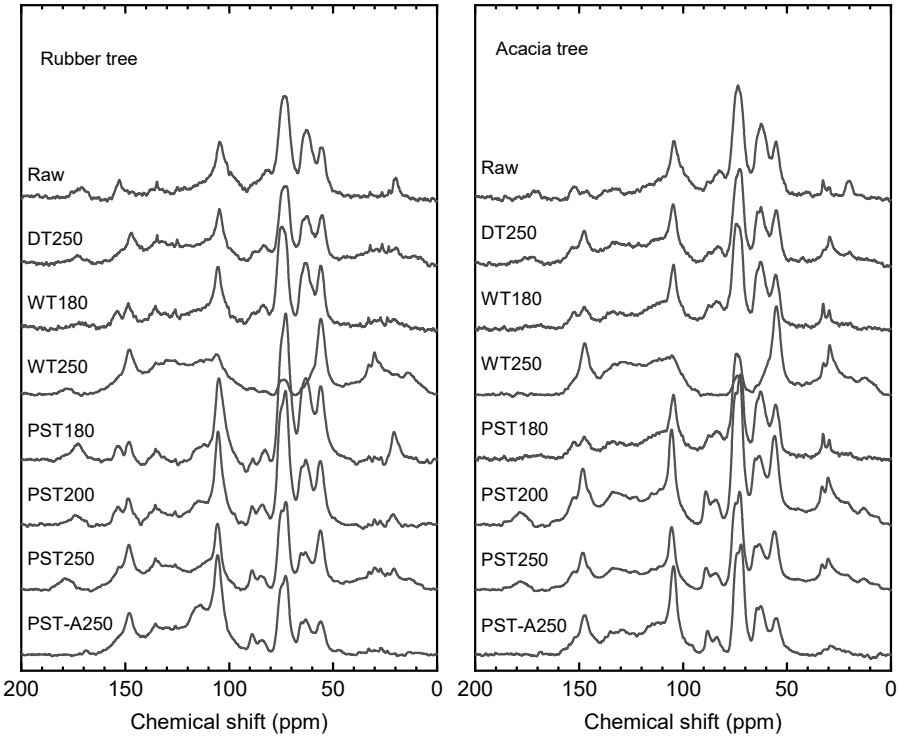


**Figure S12.** Solid-state $^{13}C$ NMR spectra of selected fuels.

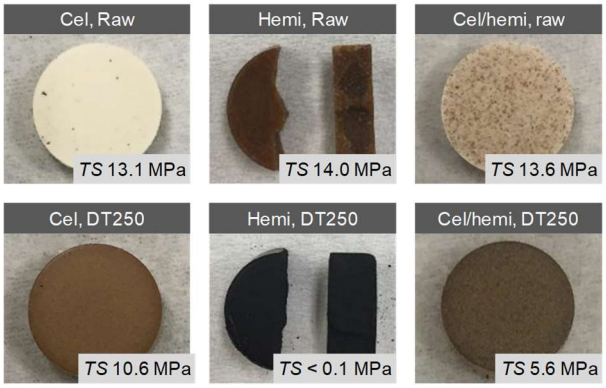


**Figure S13.** Photographic image of pellet (or fractured pellet) prepared at $T_p$ = 130°C from model compounds of cellulose, hemicellulose, and their mixture (hemicellulose 30 wt%-dry) with and without DT at 250°C.

**Table S3.** Carbon fraction of main moieties in raw and torrefied hardwoods.

| Component (%-C) | Raw | DT250 | WT180 | WT250 | PST180 | PST200 | PST250 | PST-A250 |
|---|---|---|---|---|---|---|---|---|
| *Rubber tree* | | | | | | | | |
| *Carbohydrate carbons* | | | | | | | | |
| $C_1$ | 15.9 | 11.0 | 13.9 | 2.4 | 17.4 | 19.1 | 11.6 | 20.0 |
| $C_2$, $C_3$, $C_5$ | 23.6 | 15.7 | 20.4 | 2.7 | 27.3 | 24.0 | 16.5 | 12.9 |
| $C_4$ | 9.1 | 5.9 | 6.7 | 1.3 | 1.1 | 6.2 | 3.8 | 5.0 |
| $C_6$ | 15.4 | 9.9 | 14.2 | 1.8 | 15.3 | 11.5 | 7.2 | 8.7 |
| *Lignin carbons (methoxyl, aromatic carbons linked to oxygen)* | | | | | | | | |
| Methoxyl | 5.8 | 8.4 | 8.4 | 15.2 | 13.1 | 11.7 | 10.0 | 5.2 |
| $G_4/G_3$, $S_3/S_5$ nonetherified | 1.2 | 6.9 | 5.4 | 9.2 | 3.3 | 4.5 | 7.8 | 6.6 |
| $S_3/S_5$ etherified | 3.4 | 1.8 | 2.6 | 2.7 | 2.7 | 2.8 | 2.9 | 2.8 |
| *Other carbons* | | | | | | | | |
| Aliphatic | 8.4 | 14.4 | 8.6 | 21.7 | 8.9 | 3.3 | 14.9 | 2.9 |
| Aromatic | 11.9 | 22.0 | 16.3 | 40.9 | 5.5 | 14.1 | 22.5 | 34.5 |
| Carbonyl, acetate | 5.5 | 4.1 | 3.6 | 2.0 | 5.4 | 2.7 | 2.8 | 1.5 |
| *Acacia tree* | | | | | | | | |
| *Carbohydrate carbons* | | | | | | | | |
| $C_1$ | 15.2 | 10.4 | 14.7 | 2.8 | 16.9 | 18.0 | 11.4 | 17.8 |
| $C_2$, $C_3$, $C_5$ | 23.9 | 18.3 | 20.4 | 3.7 | 27.0 | 27.7 | 18.5 | 20.8 |
| $C_4$ | 8.5 | 5.1 | 9.4 | 0.0 | 4.8 | 5.3 | 5.2 | 5.9 |
| $C_6$ | 16.8 | 12.9 | 14.1 | 3.0 | 16.2 | 12.5 | 9.0 | 9.4 |
| *Lignin carbons (methoxyl, aromatic carbons linked to oxygen)* | | | | | | | | |
| Methoxyl | 8.2 | 6.7 | 7.4 | 16.7 | 13.3 | 11.5 | 10.6 | 7.1 |
| $G_4/G_3$, $S_3/S_5$ nonetherified | 1.1 | 6.1 | 4.3 | 9.8 | 1.3 | 5.1 | 6.6 | 7.7 |
| $S_3/S_5$ etherified | 2.1 | 2.6 | 2.5 | 1.9 | 1.8 | 2.0 | 2.3 | 2.1 |
| *Other carbons* | | | | | | | | |
| Aliphatic | 9.2 | 11.2 | 7.7 | 25.1 | 10.0 | 6.0 | 16.6 | 5.1 |
| Aromatic | 11.5 | 23.5 | 17.9 | 36.4 | 8.6 | 8.8 | 17.7 | 23.6 |
| Carbonyl, acetate | 3.5 | 3.2 | 1.6 | 0.6 | 0.0 | 3.2 | 2.0 | 0.5 |

Assignment [chemical shift (ppm)]: carbohydrates $C_1$ (105, 104−96); carbohydrates $C_2$, $C_3$, $C_5$ (74); carbohydrates $C_4$ (88.5, 84); carbohydrates $C_6$ (64); methoxyl groups (56.2); lignin $G_4/G_3$, $S_3/S_5$ nonetherified (150−144); lignin $S_3/S_5$ etherified (154−152); aliphatics (10-50); aromatics (141−120, 116−110, 108−106); carbonyls, acetates (>154).