Supporting Information

Totally Green Cellulose Conversion into Bio-Oil and Cellulose Citrate using Molten Citric Acid in an Open System: Synthesis, Characterization and Computational Investigation of Reaction Mechanisms

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| 1. | FT-IR spectra of cellulose citrate | S3 |
| 2. | Conductometric titration of cellulose citrate after different reaction times | S7 |
| 3. | Conductometric titration of cellulose citrate using different weight equivalents of citric acid | S7 |
| 4. | FT-IR spectra of cellulose citrate using different citric acid weight equivalents after 30 minutes of reaction at 155 °C | S8 |
| 5. | FT-IR spectra of esterified cellulose using other organic acids | S10 |
| 6. | Morphological characterization of cellulose citrate by SEM | S11 |
| 7. | Mass spectra of Bio-oil | S14 |
| 8. | ESI (+) MS/MS spectra | S24 |
| 9. | FT-IR spectra of the Bio-oil recovered after different reaction times | S28 |
| 10. | Determination of the pH, hydroxyl group content and total acid number of Bio-oil | S31 |
| 11. | FT-IR spectrum of complete esterification of the Bio-oil by phthalic anhydride | S31 |
| 12. | Elemental analysis of cellulose, Bio-oil and cellulose citrate | S32 |
| 13. | Free energy profile describing the esterification of cellulbiose in presence of CA by condensation when the hydroxyl group at C2 is involved. Relative energies are in kcal mol-1 and calculated with respect to the zero reference energy of separated reactants. | S33 |
1. FT-IR spectra of cellulose citrate.

FT-IR spectrum of cellulose-citrate stopping the reaction after 30 minutes at 155 °C.

FT-IR spectrum of cellulose-citrate stopping the reaction after 1 hour at 155 °C.
FT-IR spectrum of cellulose-citrate stopping the reaction after 2 hours at 155 °C.

FT-IR spectrum of cellulose-citrate stopping the reaction after 3 hours at 155 °C.
FT-IR spectrum of cellulose-citrate stopping the reaction after 5 hours at 155 °C.

FT-IR spectrum of cellulose-citrate stopping the reaction after overnight time at 155 °C.
Figure S1. Normalized spectral area of the carbonyl stretching vibration peak as a function of the reaction time.
2. Conductometric Titration of cellulose citrate after different reaction times.

Cellulose-citrate obtained after different reaction times was dispersed in distilled water at 2 mg/mL at room temperature for 30 min using a sonicator. Subsequently, the pH was adjusted to 10 with a solution 0.1 M of NaOH. The resulting solution was titrated with a solution 0.1 M of HCl, and the change in voltage was monitored using a conductivity meter. Average degree of substitution values were calculated according to ATSM D1439.\(^1\) This method consists in dispersing cellulose-citrate in a 0.1 M NaOH solution and titrating with a 0.1 M HCl solution. Degrees of substitution were calculated using the following equation: \(G = \frac{0.162A}{1 - XA}\) where \(A = \frac{BC - DE}{F}\) with \(B = mL\) of \(\text{NAOH}\) solution added, \(C = E = 0.1\) (molarities of \(\text{HCl}\) and \(\text{NaOH}\)), \(F = \text{amount of cellulose-citrate used in g}\), \(162 = \text{the molar mass of the AGU unit}\), and \(X = \text{increase in molecular mass for cellulose-citrate (176 for citrate modified cellulose)}\). Values obtained were divided by two due to the fact that each citrate unit introduces two free carboxylic acids.

After three hours esterified cellulose starts to decompose and the degree of substitution becomes lower. A time-dependent conductometric titration was carried out.

| Reaction time   | Degree of substitution |
|-----------------|------------------------|
| 30 minutes      | 0.46                   |
| 1 hour          | 0.46                   |
| 2 hours         | 0.46                   |
| 3 hours         | 0.46                   |
| 5 hours         | 0.35                   |
| Overnight time  | 0.20                   |

Feddersen, R. L.; Thorp, S. N. Standard Test Methods for Sodium Carboxymethylcellulose. *Ind. Gums.* 1993, 03, 537-578.

3. Conductometric titration of cellulose-citrate using different weight equivalents of citric acid.

The degree of substitution of cellulose-citrate using different citric acid weight equivalents after 30 minutes of reaction at 155 °C was reported.

| Citric acid weight equivalents | Degree of substitution |
|-------------------------------|------------------------|
| 0.5                           | 0.12                   |
| 0.8                           | 0.21                   |
| 1                             | 0.46                   |
| 1.2                           | 0.46                   |
| 1.5                           | 0.46                   |

From the table above, using higher than 1 citric acid weight equivalents, the degree of substitution of cellulose-citrate remains the same. The excess of citric acid is recovered inside the bio-oil.
4. FT-IR spectra of cellulose citrate using different weight equivalents of citric acid after 30 minutes of reaction at 155 °C.

FT-IR spectrum using 0.5 weight equivalents of citric acid

FT-IR spectrum using 0.8 weight equivalents of citric acid
FT-IR spectrum using 1.2 weight equivalents of citric acid

FT-IR spectrum using 1.5 weight equivalents of citric acid
5. FT-IR spectra of esterified cellulose using other organic acids.

FT-IR of cellulose esterified with adipic acid

FT-IR spectrum of cellulose esterified with benzoic acid (no esterification)
6. Morphological characterization of cellulose citrate by SEM

The ultrastructural morphology of the cellulose citrate was characterized by SEM analysis (Scanning Electron Microscope) (Figure S2). The morphological analysis performed on the microcrystalline cellulose shows the typical cellulose structure made of cylindrical fibrils forming indented and disordered aggregates. As the reaction with citric acid proceeds with time, a progressive loss of the above structures occurs. At low reaction times (within the first 3 h) the fiber structure is almost retained but the fibrils are smaller, either in diameter or in length, indicating that the reaction with citric acid induces a cellulose fragmentation. This process ultimately leads to a significant loss of the fibrils structure and the formation of very amorphous and smoothed aggregates where the cylindrical morphology is no longer detectable.
Cellulose citrate obtained after 1h minute of reaction

Cellulose citrate obtained after 2h of reaction

Cellulose citrate obtained after 3h of reaction
Figure S2. SEM analysis of cellulose and citrate cellulose at different reaction times
7. Mass spectra of Bio-oil

ESI (+) full scan spectrum of Bio-oil recovered after 30 minutes

Full scan 70-213

| Compound | m/z+H⁺ | m/z+NH₄⁺ | Relative abundance (%) |
|----------|--------|-----------|------------------------|
| ![Compound 1] | 110+H⁺ = 111 | - | 28 |
| ![Compound 2] | 128+H⁺ = 129 | - | 37 |
| ![Compound 3] | 138+H⁺ = 139 | - | 97 |
| ![Compound 4] | 140+H⁺ = 141 | - | 100 |
| ![Compound 5] | 142+H⁺ = 143 | - | 33 |
| ![Compound 6] | - | 126+NH₄⁺ = 158 | 47 |
| ![Compound 7] | - | 192+NH₄⁺ = 210 | 35 |
ESI (+) full scan spectrum of Bio-oil recovered after 1 hour at 155 °C.

Full scan 70-213

| Compound | m/z+H<sup>+</sup> | m/z+NH₄<sup>+</sup> | Relative abundance (%) |
|----------|----------------|-----------------|------------------------|
|         | 110+ H<sup>+</sup> = 111 | - | 43 |
|         | 128+ H<sup>+</sup> = 129 | - | 17 |
|         | 138+ H<sup>+</sup> = 139 | - | 100 |
|         | 142+ H<sup>+</sup> = 143 | - | 78 |
|         | - | 126+NH₄<sup>+</sup> = 158 | 47 |
ESI (+) full scan spectrum of Bio-oil recovered after 2 hours at 155 °C.

Full scan 70-213

| Compound | m/z+H⁺  | Relative abundance (%) |
|----------|---------|------------------------|
| ![Compound 1](image_url) | 110+ H⁺= 111 | 26 |
| ![Compound 2](image_url) | 138+ H⁺= 139 | 100 |
| ![Compound 3](image_url) | 142+ H⁺= 143 | 18 |
ESI (+) full scan spectrum of Bio-oil recovered after 3 hours at 155 °C.

Full scan 70-213

| Compound | m/z+H⁺ | Relative abundance (%) |
|----------|--------|------------------------|
| ![Molecule 1](image1.png) | 110+ H⁺ = 111 | 32 |
| ![Molecule 2](image2.png) | 138+ H⁺ = 139 | 100 |
| ![Molecule 3](image3.png) | 142+ H⁺ = 143 | 48 |
ESI (+) full scan spectrum of Bio-oil recovered after 5 hours at 155 °C.

Full scan 0-500

| Compound | m/z+H⁺ | Relative abundance (%) |
|----------|--------|------------------------|
| ![Compound 1](image1.png) | 110+ H⁺= 111 | 27 |
| ![Compound 2](image2.png) | 126+ H⁺= 127 | 15 |
| ![Compound 3](image3.png) | 138+ H⁺= 139 | 100 |
| ![Compound 4](image4.png) | 156+ H⁺= 157 | 15 |
| ![Compound 5](image5.png) | 180+ H⁺= 181 | 29 |
| ![Compound 6](image6.png) | 224+ H⁺=225 | 31 |
ESI (+) full scan spectrum of Bio-oil recovered after overnight time at 155 °C.

Full scan 0-500

| Compound | m/z+H⁺ | Relative abundance (%) |
|----------|-------|------------------------|
| ![Chemical Structure](image) | 224+ H⁺=225 | 32 |
8. ESI (+) MS/MS spectra

Peak = 127.27
Peak = 111.18
Peak = 139.21
Peak = 225
9. FT-IR spectra of the Bio-oil recovered after different reaction times.

FT-IR spectrum of the Bio-oil recovered after 30 minutes of reaction time at 155 °C.

FT-IR spectrum of the Bio-oil recovered after 1 hour at 155 °C.
FT-IR spectrum of the Bio-oil recovered after 2 hours at 155 °C.

FT-IR spectrum of the Bio-oil recovered after 3 hours at 155 °C.
FT-IR spectrum of the Bio-oil recovered after 5 hours at 155 °C.

FT-IR spectrum of the Bio-oil recovered after overnight time at 155 °C.
10. Determination of pH, hydroxyl group content and total acid number of Bio-oil.

The corresponding pH of all the bio-oils were measured using a pH-meter, dissolving 100 mg of the samples in 10 ml of distilled water, each measure was repeated three times and the final value expressed as a mean value. The total acid content was obtained by a potentiometric titration following the standard method ASTM D664. 100 mg of the corresponding bio-oil were dissolved in 50 ml of distilled water. Acetone was used as the titration solvent, NaOH was used as alkaline titrant and 0.1 mol/L of HCl in water as standard solution. Each experiment was repeated three times and the value expressed as a mean value. Hydroxyl content was calculated using the standard method ASTM D4274-16, by esterification of bio-oil using phthalic anhydride. Phthalic anhydride (112 g) and imidazole (17 g) was mixed in pyridine (700 mL) to prepare phtalation reagent. A mixture of polyol (1 g) and phthalation reagent (25 mL) was heated at 100 °C for 15 min and then cooled to room temperature. Then, pyridine (50 mL) and ultrapure water (10 mL) was added. The mixture was titrated with KOH (0.5 M) solution to its equivalence.

2 Oasmaa A, Elliott DC, Korhonen J. Acidity of biomass fast pyrolysis bio-oils. Energy Fuels. 2010, 24, 6548–54.
3 Amran U A, Zakaria S., Chia C.H., Roslan R., Jaafar S. N. S. J., Salleh k. M. Cellulose. 2019, 26, 3231–3246.

11. FT-IR spectrum of complete esterification of the Bio-oil by phthalic anhydride.
### 12. Elemental analysis of cellulose, Bio-oil and cellulose citrate

| Sample            | Reaction time | % C  | % H  | % O  |
|-------------------|---------------|------|------|------|
| Cellulose         | /             | 42.37| 6.43 | 51.20|
| Bio-oil           | 30 min        | 35.64| 3.96 | 60.40|
| Bio-oil           | 1 h           | 35.22| 3.96 | 60.82|
| Bio-oil           | 2 h           | 33.69| 3.91 | 62.40|
| Bio-oil           | 3 h           | 39.63| 4.91 | 55.46|
| Bio-oil           | 5 h           | 43.59| 4.71 | 51.70|
| Cellulose citrate | 30 min        | 43.59| 4.71 | 51.70|
| Cellulose citrate | 1 h           | 42.25| 5.97 | 51.78|
| Cellulose citrate | 2 h           | 41.79| 6.04 | 52.17|
| Cellulose citrate | 3 h           | 42.35| 5.96 | 51.69|
| Cellulose citrate | 5 h           | 42.05| 5.97 | 51.98|

*Each analysis was duplicated and the value expressed as a mean value. Oxygen percentage was calculated by the difference from the total of carbon and hydrogen percentages.*
13. Free energy profile describing the esterification of cellobiose in presence of CA by condensation when the hydroxyl group at C2 is involved. Relative energies are in kcal mol$^{-1}$ and calculated with respect to the zero reference energy of separated reactants.