

Supporting Information for:

Sustainable Transesterification of Cellulose with high oleic sunflower oil in a DBU-CO₂ Switchable Solvent

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SI I: FT-IR Optimization studies using microcrystalline cellulose.

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SI VI: SEC traces (DMAc-LIBr) of lower DS (around 1.0) FACEs

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SI. I FT-IR Optimization study of transesterification reaction on microcrystalline cellulose (MCC)
using high oleic sunflower oil.

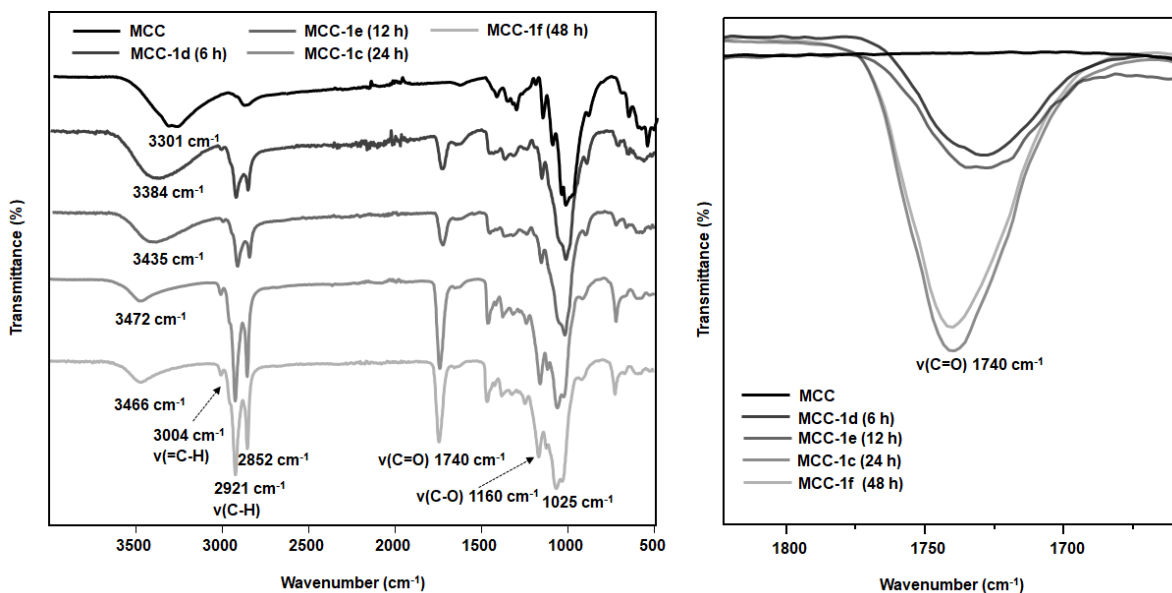


Figure S1: FT-IR spectra of FACES at various reaction time: MCC-1d (6 h), MCC-1e (12 h), MCC-1c (24 h), MCC-1f (48 h). (5 wt. (%) cellulose (MCC), 3 eq. high oleic sunflower oil/AGU cellulose, 115 °C).

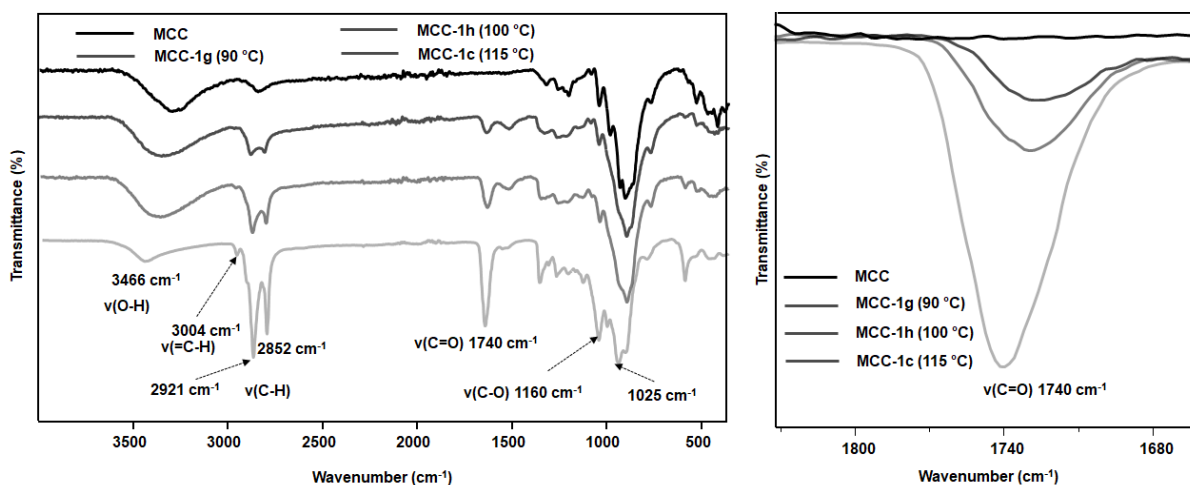


Figure S2: FT-IR spectra of FACES at various reaction temperature: MCC-1g (90 °C), MCC-1h (100 °C), MCC-1c (115 °C). (5 wt. (%) cellulose (MCC), 3eq. high oleic sunflower oil/AGU cellulose, 24 h).

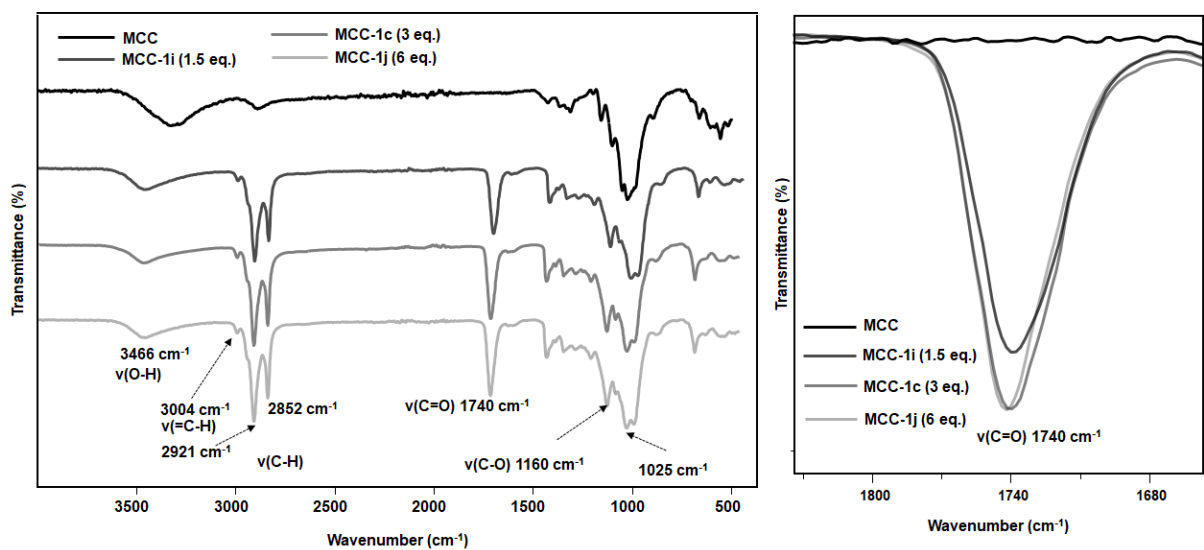


Figure S3: FT-IR spectra of FACES at various plant high oleic sunflower oil equivalents: MCC-1i (1.5 eq./AGU), MCC-1c (3 eq./AGU), MCC-1j (6 eq./AGU). (5 wt. (%) cellulose 115 °C, 24 h).

SI II: ^{31}P NMR for DS determination of FACES from microcrystalline cellulose (MCC)

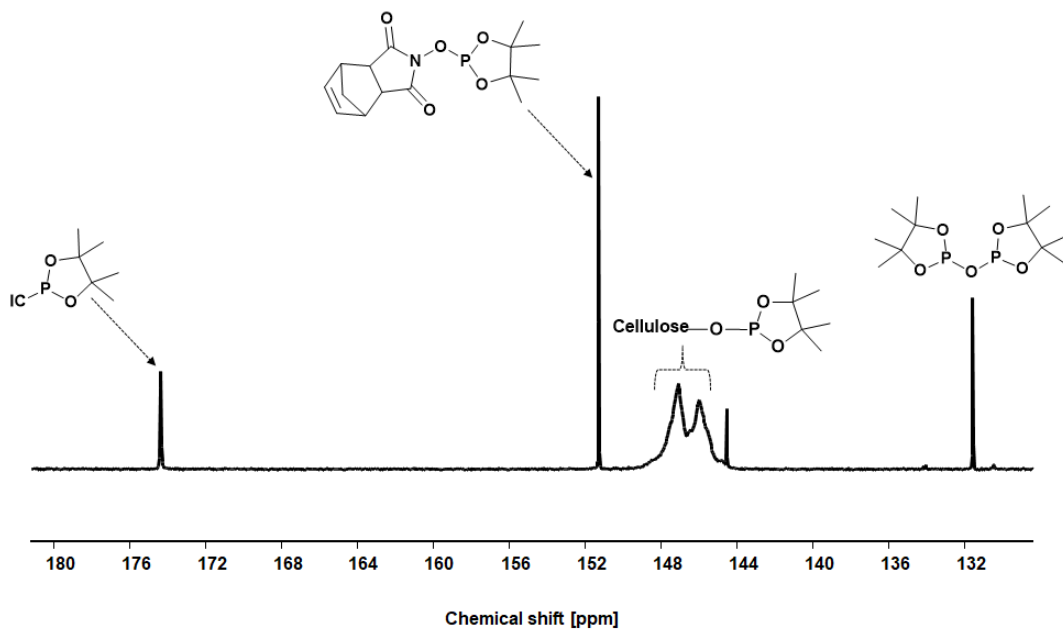


Figure S4: ^{31}P NMR (CDCl_3), 400 MHz, 1024 scans: Determination of degree of substitution (DS) of FACE (MCC-1d). (5 wt. (%) MCC, 3 eq. high oleic sunflower oil/AGU, 115 °C, 6 h).

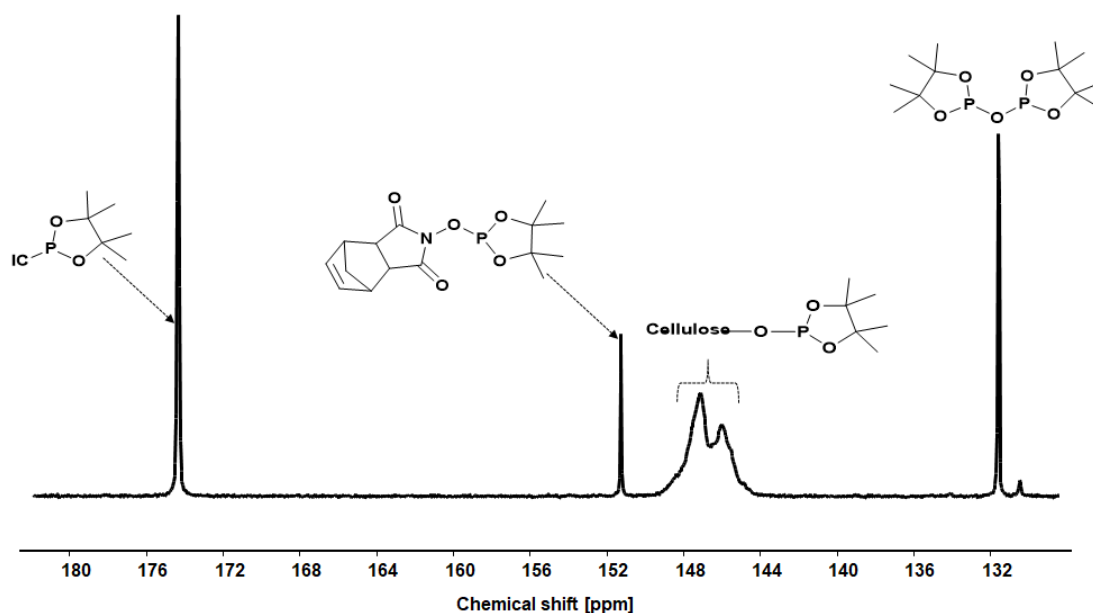


Figure S5: ^{31}P NMR (CDCl_3), 400 MHz, 1024 scans: Determination of degree of substitution (DS) of FACE (MCC-1e). (5 wt. (%) MCC, 3 eq. high oleic sunflower oil/AGU, 115 °C, 12 h).

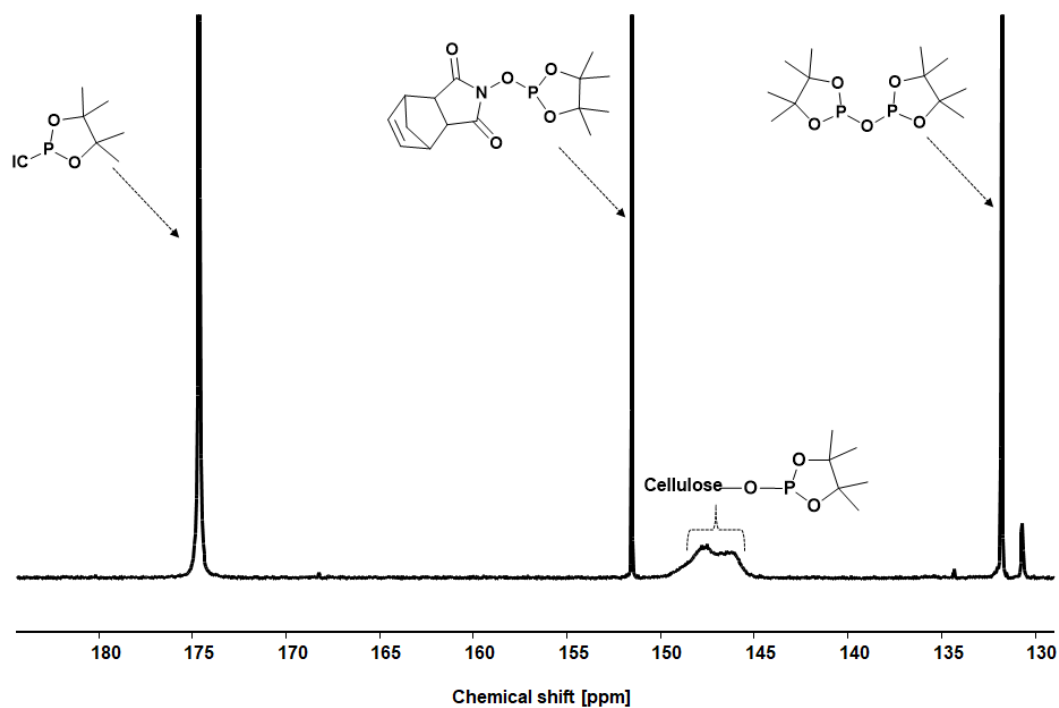


Figure S6: ^{31}P NMR (CDCl_3), 400 MHz, 1024 scans: Determination of degree of substitution (DS) of FACE (MCC-1c). (5 wt. (%) MCC, 3 eq. high oleic sunflower oil/AGU, 115 °C, 24 h).

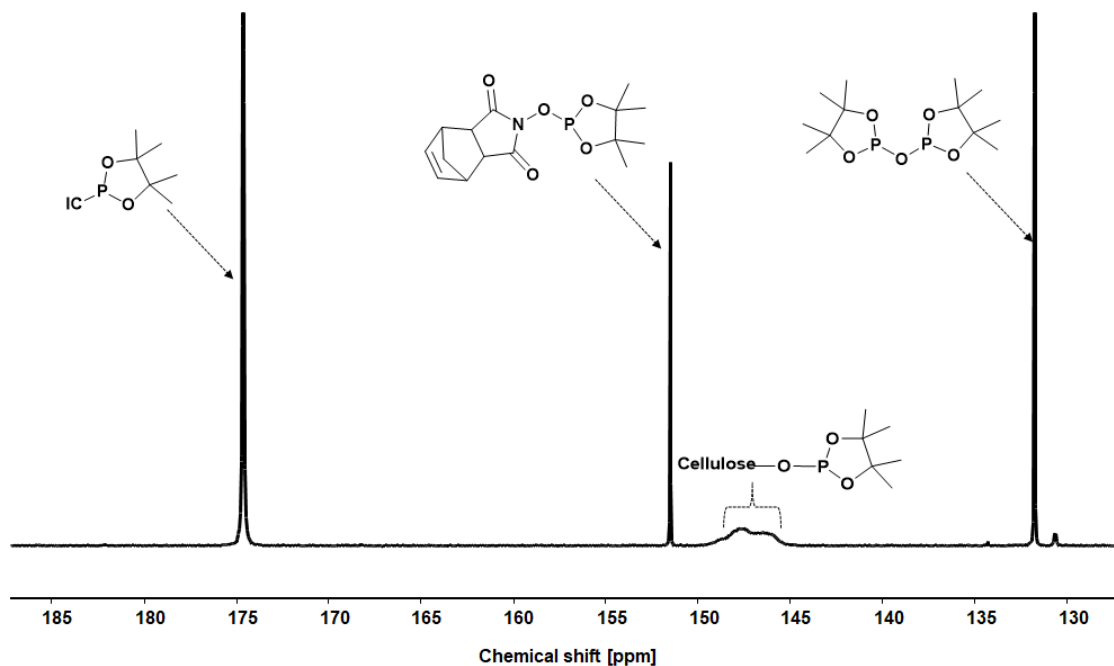


Figure S7: ^{31}P NMR (CDCl_3), 400 MHz, 1024 scans: Determination of degree of substitution (DS) of FACE (MCC-1c). (5 wt. (%) MCC, 3 eq. high oleic sunflower oil/AGU, 115 °C, 48 h).

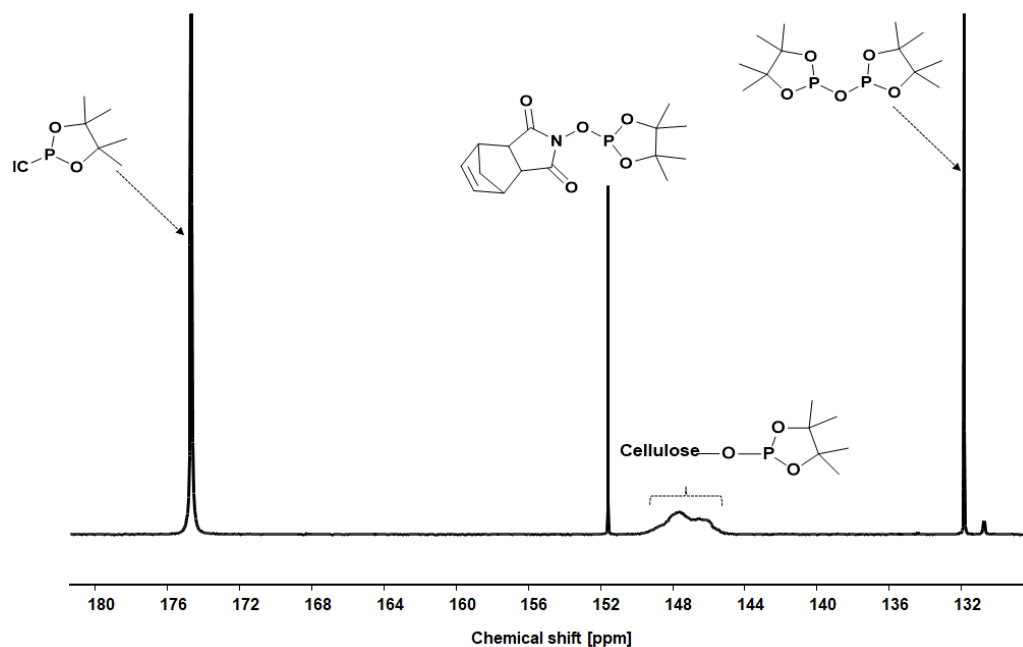


Figure S8: ^{31}P NMR (CDCl_3), 400 MHz, 1024 scans: Determination of degree of substitution (DS) of FACE (MCC-1i). (5 wt. (%) MCC, 1.5 eq. high oleic sunflower oil/AGU, 115 °C, 24 h)

Table S1: Control of degree of substitution (DS) of FACE with reaction time.

Sample	Reaction time	DS
MCC-1d	6 h	0.34
MCC-1e	12 h	0.50
MCC-1c	24 h	1.59
MCC-1f	48 h	1.44

Reaction conditions: 3 eq. high oleic sunflower oil per AGU cellulose (MCC), 5 wt. % MCC, 115 °C (DS calculated from ^{31}P NMR).

SI III: FT-IR spectra of FACEs from cellulose filter paper (FP) and cellulose pulp (CP)

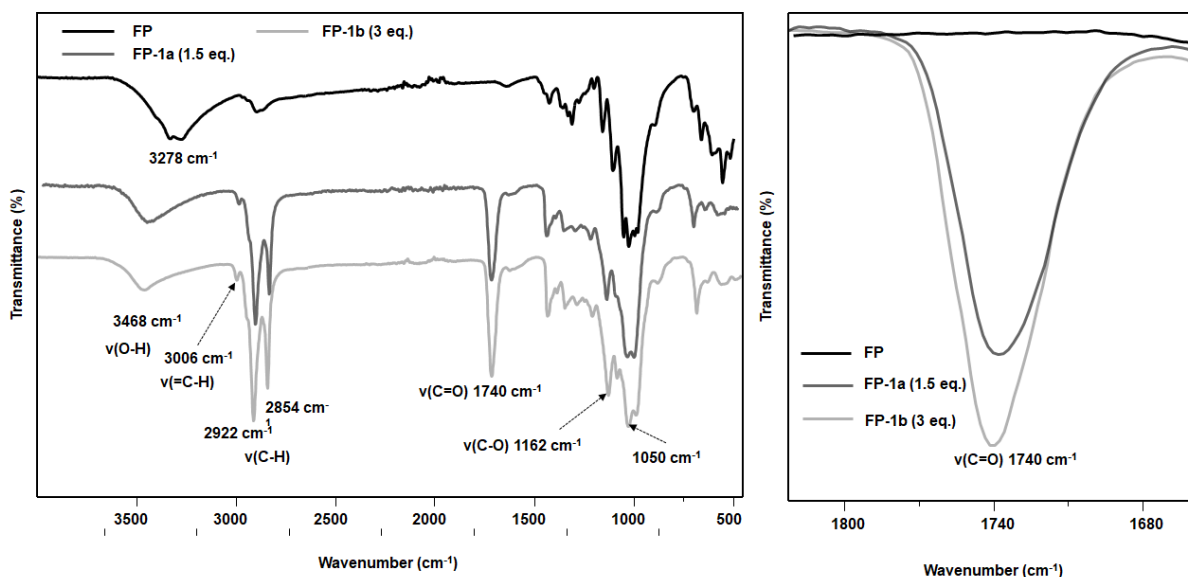


Figure S9: FT-IR spectra of FACEs at various plant high oleic sunflower oil equivalents: FP-1a (1.5 eq./AGU), FP-1b (3 eq./AGU, 5 wt. (%) cellulose Whatman™ filter paper No. 5, 115 °C, 24 h).

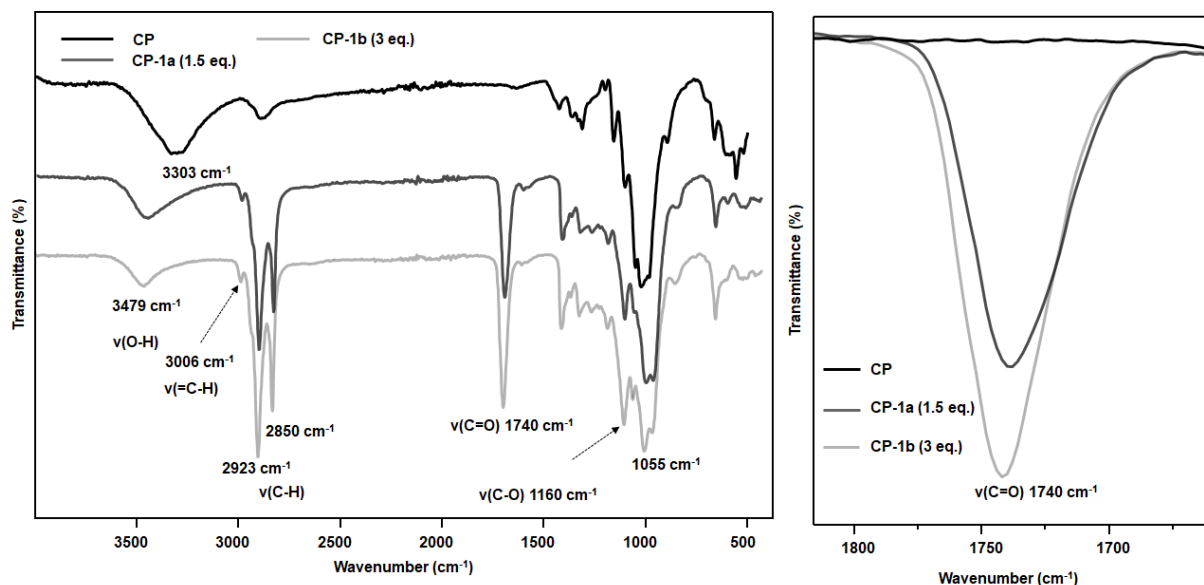


Figure S10: FT-IR spectra of FACES at various plant high oleic sunflower oil equivalents: CP-1a (1.5 eq./AGU), CP-1b (3 eq./AGU, 5 wt. (%) cellulose pulp, 115 °C, 24 h)

SI IV: ^1H and ^{13}C NMR of FACES

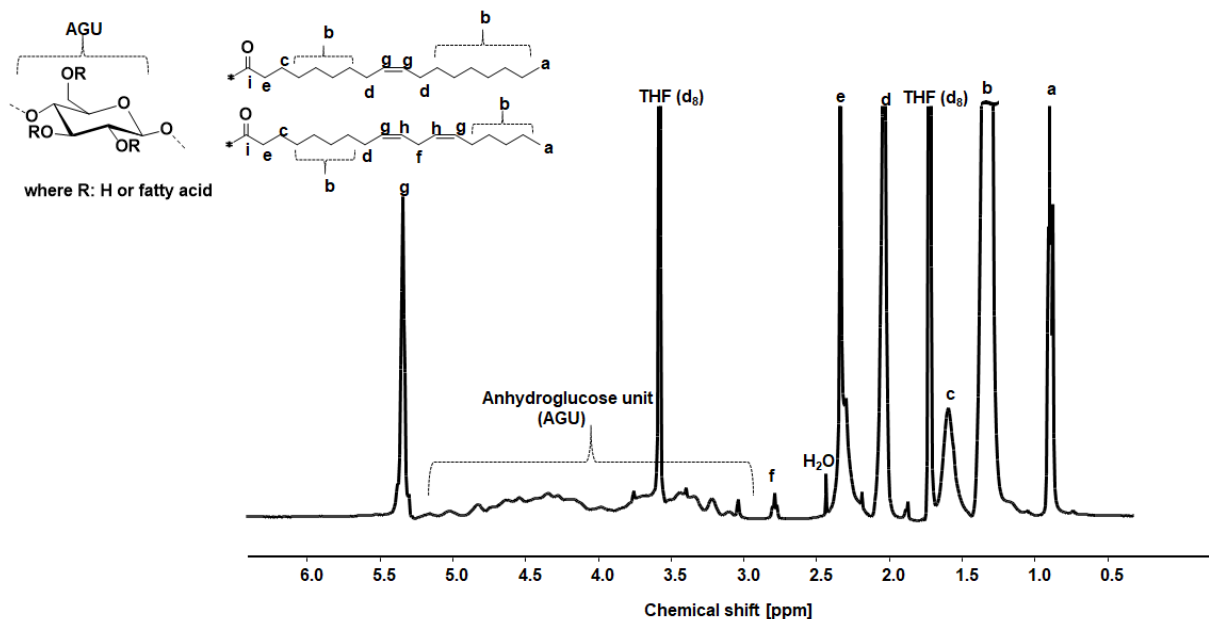


Figure S11a: ^1H NMR (THF, d_8), 400 MHz, 1024 scans at 50 °C for FACE: MCC-1c. (5 wt. (%) MCC, 3 eq. high oleic sunflower oil/AGU, 115 °C, 24 h).

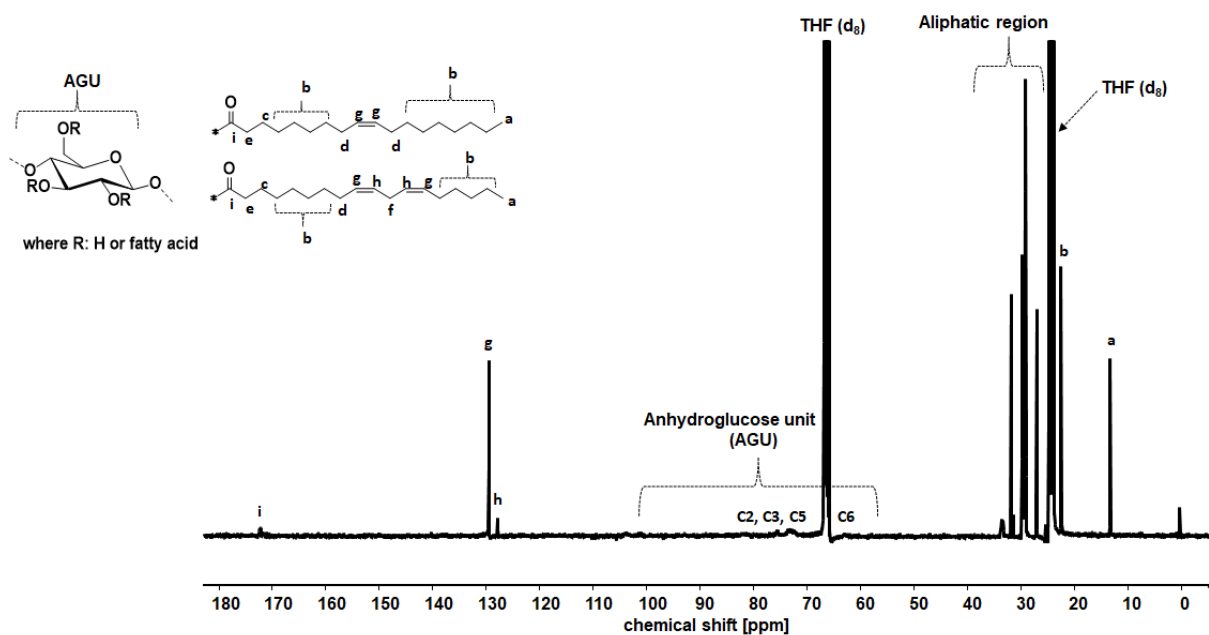


Figure S11b: ^{13}C NMR (THF, d₈), 100 MHz, 6000 scans at 50 °C for FACE: MCC-1c. (5 wt. (%) MCC, 3 eq. high oleic sunflower oil/AGU, 115 °C, 24 h).

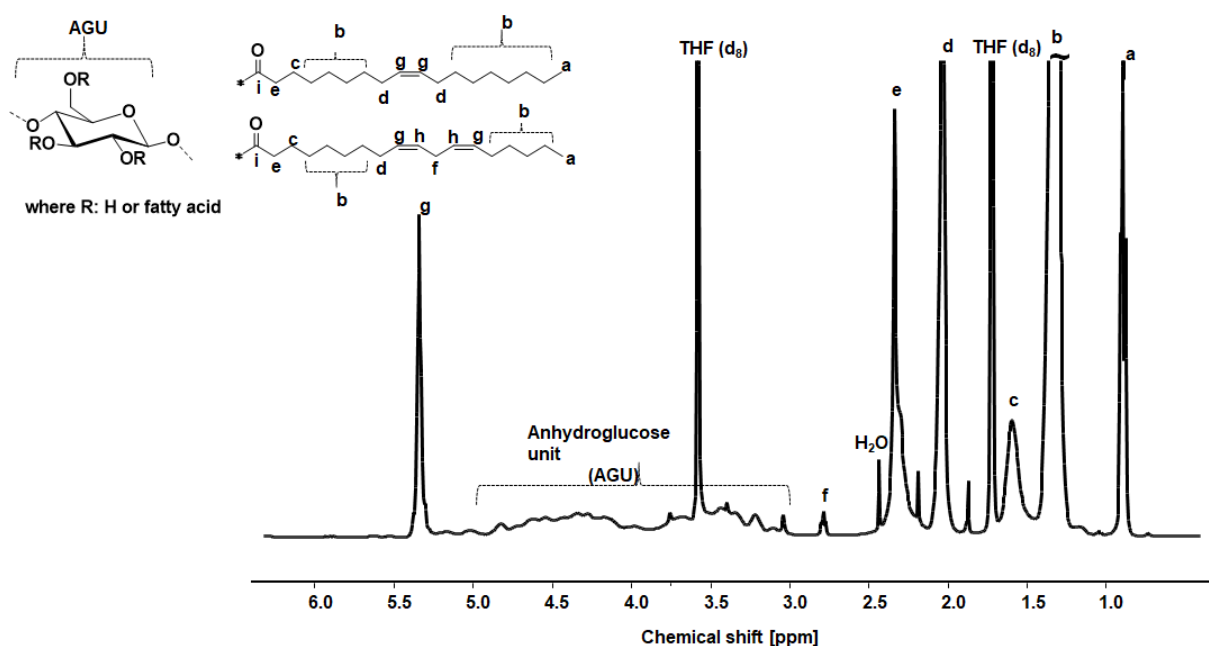


Figure S12a: ^1H NMR (THF, d₈), 400 MHz, 1024 scans at 50 °C for FACE: FP-1b. (5 wt. (%) cellulose Whatman™ filter paper No. 5 (FP), 3 eq. high oleic sunflower oil/AGU, 115 °C, 24 h).

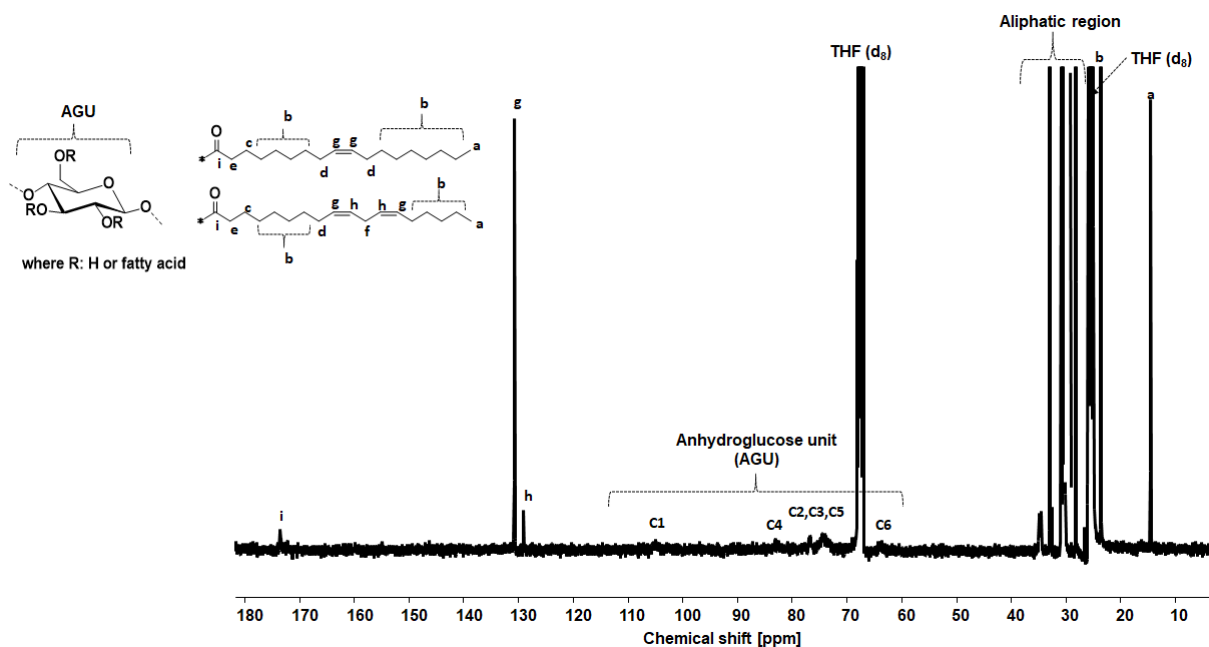


Figure S12b: ^{13}C NMR (THF, d_8), 100 MHz, 6000 scans at 50 °C for FACE: FP-1b. (5 wt. (%) cellulose WhatmanTM filter paper No. 5 (FP), 3 eq. high oleic sunflower oil/AGU, 115 °C, 24 h).

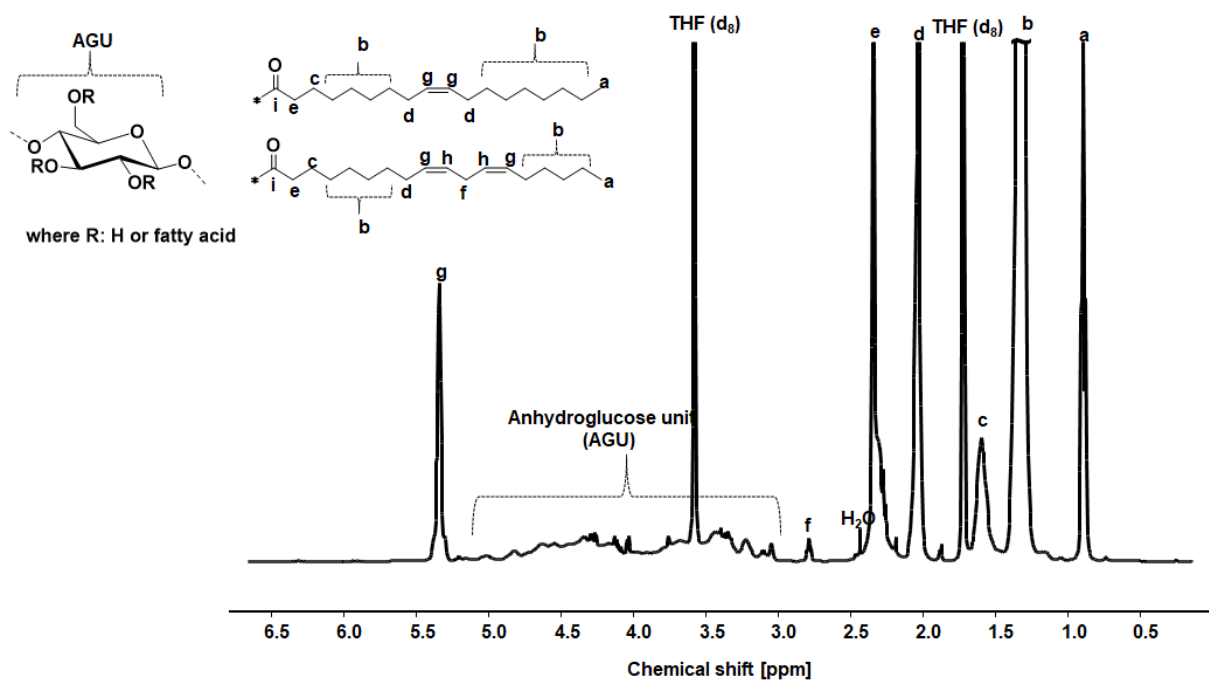


Figure S13a: ^1H NMR (THF, d_8), 400 MHz, 1024 scans at 50 °C for FACE: CP-1b. (5 wt. (%) cellulose pulp (CP), 3 eq. high oleic sunflower oil/AGU, 115 °C, 24 h).

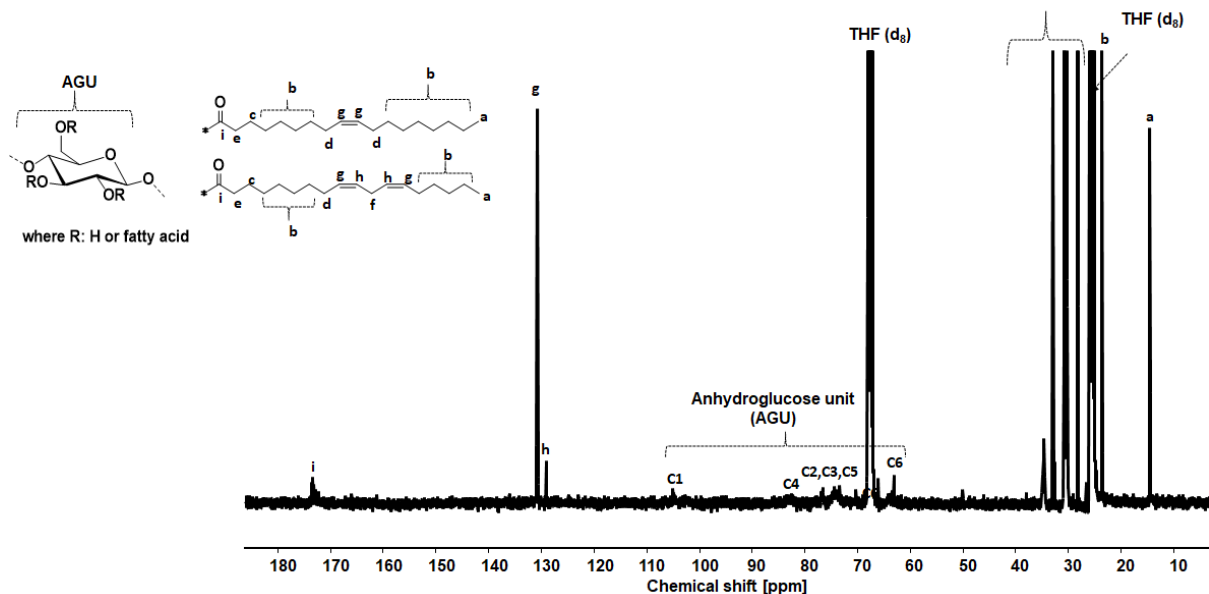


Figure S13b: ^1H NMR (THF, d_8), 100 MHz, 6000 scans at 50 °C for FACES. (5 wt. (%) cellulose pulp (CP), 3 eq. high oleic sunflower oil/AGU, 115 °C, 24 h).

SI V: ^{31}P NMR for DS determination of FACES of cellulose filter paper (FP) and cellulose pulp (CP)

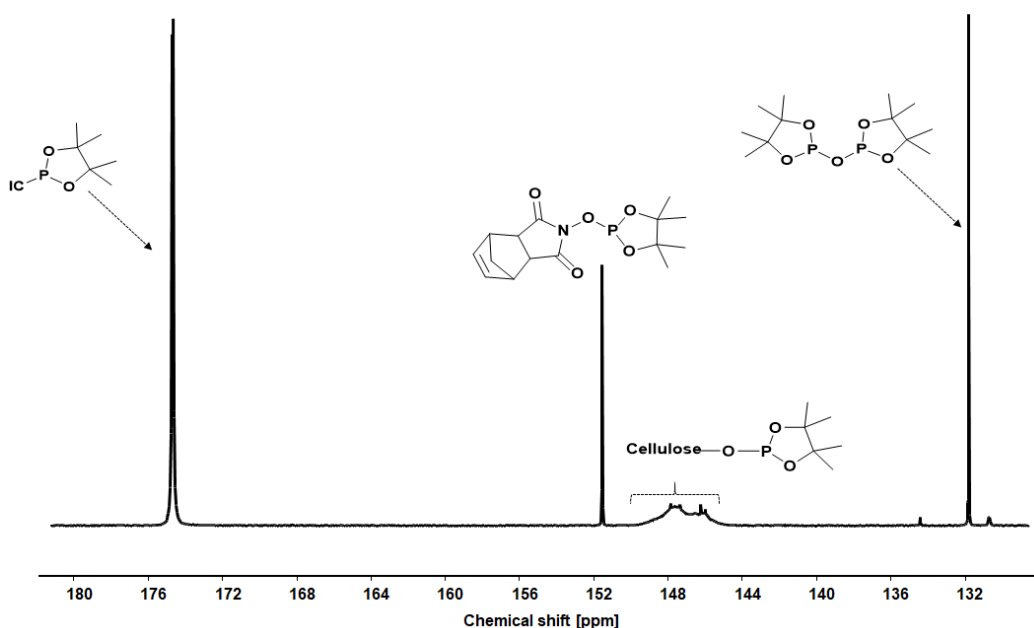


Figure S14: ^{31}P NMR (CDCl_3), 400 MHz, 1024 scans determination of degree of substitution (DS) of fatty acid cellulose esters (FACE): FP-1a. (5 wt. (%) cellulose Whatman™ filter paper No. 5 (FP) 1.5 eq. high oleic sunflower oil/AGU, 115 °C, 24 h).

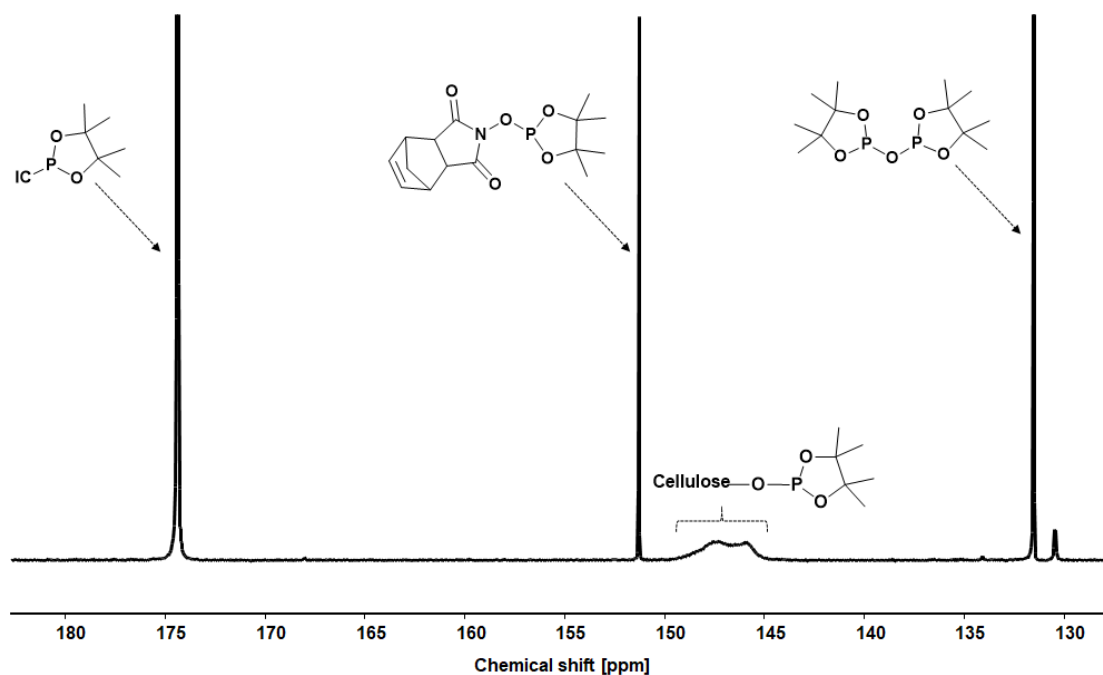


Figure S15: ^{31}P NMR (CDCl_3), 400 MHz, 1024 scans determination of degree of substitution (DS) of FACE: FP-1b. (5 wt. (%) cellulose WhatmanTM filter paper No. 5 (FP) 3 eq. high oleic sunflower oil/AGU, 115 °C, 24 h).

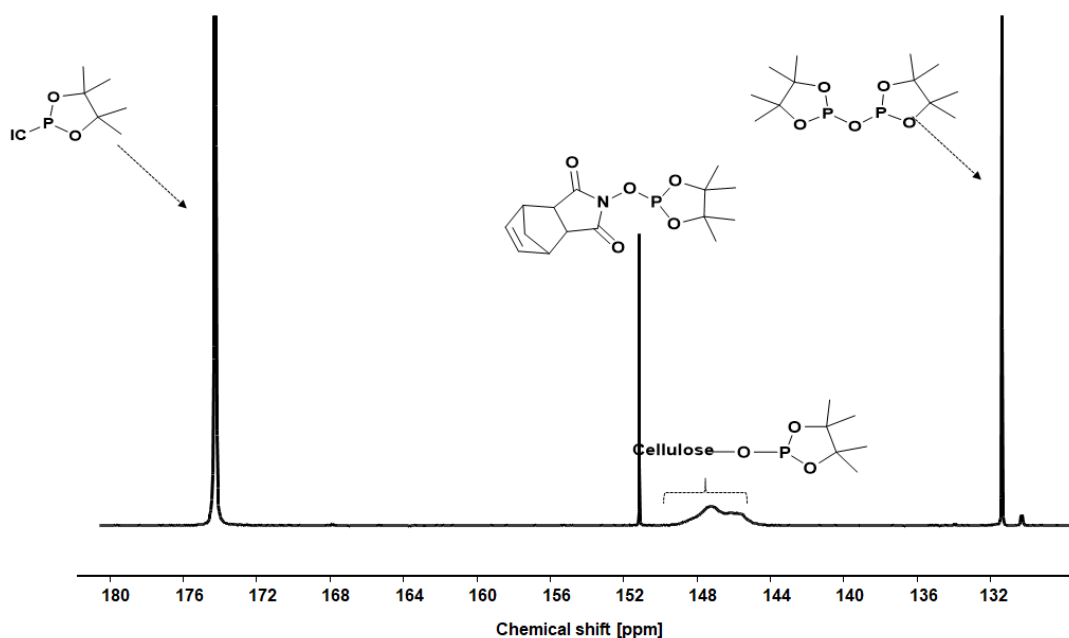


Figure S16: ^{31}P NMR (CDCl_3), 400 MHz, 1024 scans determination of degree of substitution (DS) of FACE: CP-1a. (5 wt. (%) cellulose pulp, (CP) 1.5 eq. high oleic sunflower oil/AGU, 115 °C, 24 h).

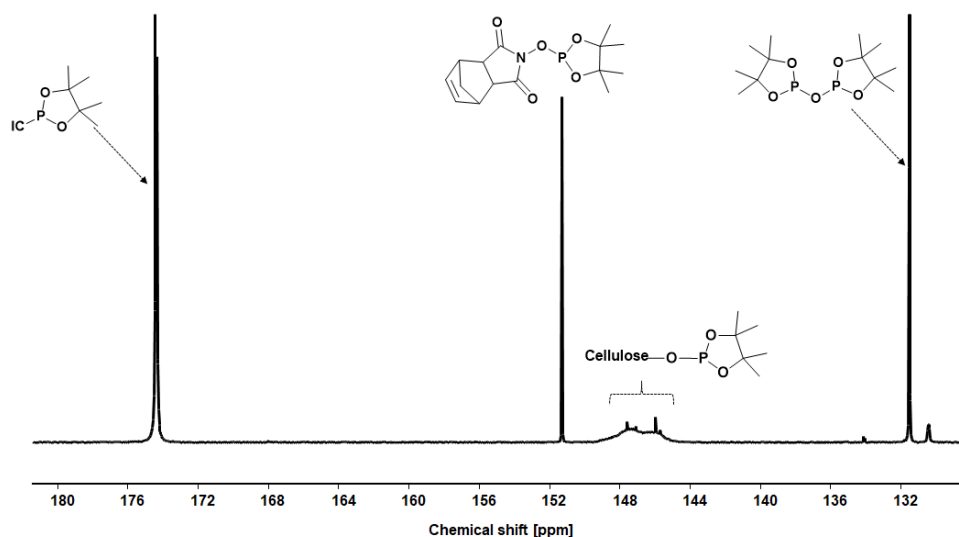


Figure S17: ^{31}P NMR (CDCl_3), 400 MHz, 1024 scans determination of degree of substitution (DS) of FACE: CP-1b. (5 wt. (%) cellulose pulp, (CP) 3 eq. high oleic sunflower oil/AGU, 115 °C, 24 h).

SI VI: SEC traces (DMAc-LiBr) of lower DS (around 1.0) FACES

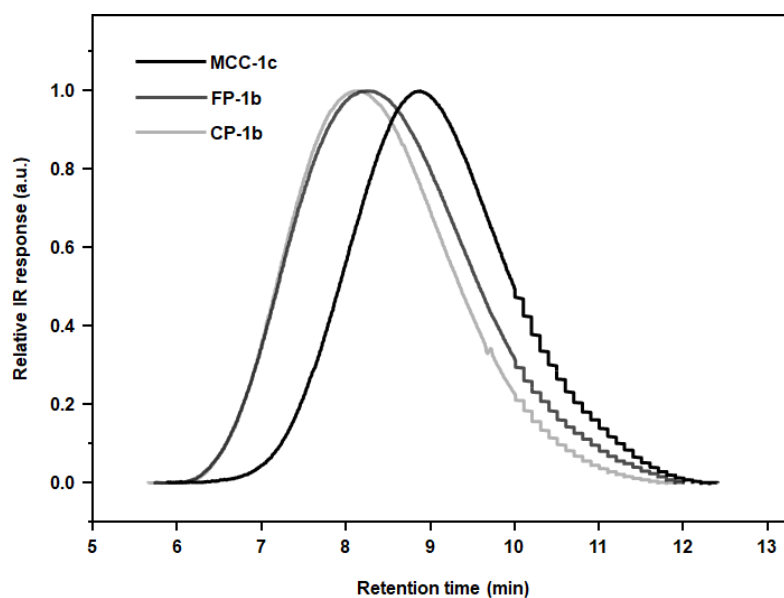


Figure S18: SEC traces (DMAc-LiBr) comparison of FACES from microcrystalline cellulose (MCC-1i; DS 1.06), Whatman™ filter paper No. 5 (FP-1a; DS 1.02) and cellulose pulp (CP-1a; DS 1.08).

SI VII: XRD patterns of FACES of cellulose filter paper (FP) and cellulose pulp (CP)

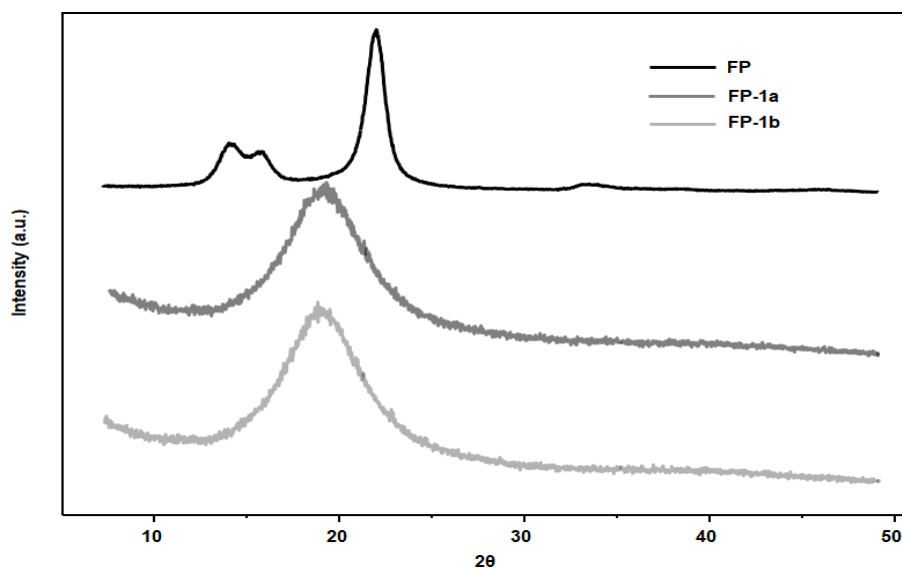


Figure S19: X-ray diffraction pattern of cellulose Whatman™ filter paper No. 5 (FP) and resulting FACES from FP (FP-1a, FP-1b) (5 wt. (%) cellulose, 24 h, 115 °C).

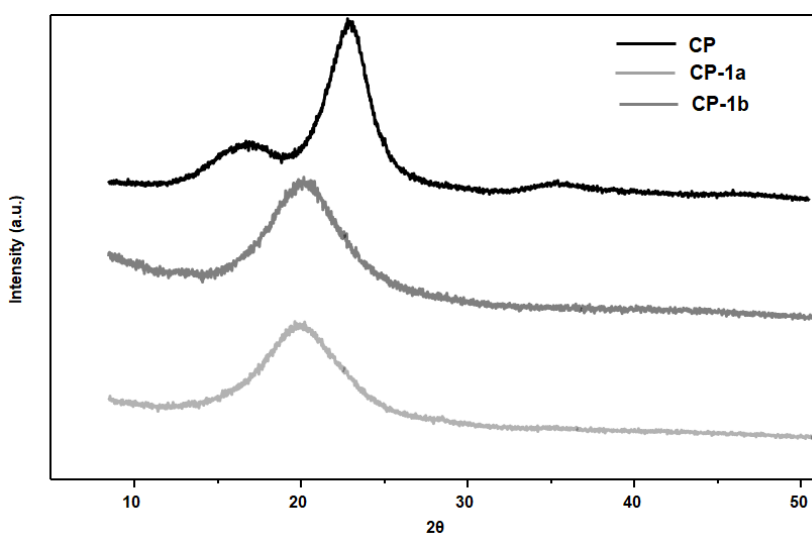


Figure S20: X-ray diffraction pattern of cellulose pulp (CP) and resulting FACES from cellulose pulp (CP-1a, CP-1b) (5 wt. (%) cellulose, 24 h, 115 °C).

SI VIII: TGA analysis of FACEs of microcrystalline cellulose (MCC), filter paper (FP) and cellulose pulp (CP)

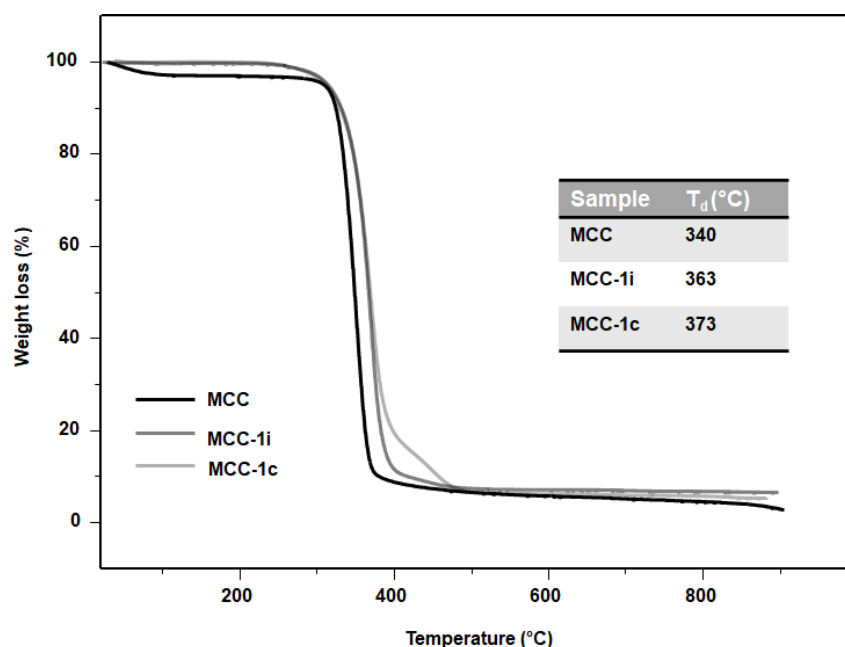


Figure S21: Thermogravimetric analysis (TGA) of microcrystalline cellulose (MCC) and resulting FACEs from MCC (MCC-1c, MCC-1i) (5 wt. (%) cellulose, 24 h, 115 °C).

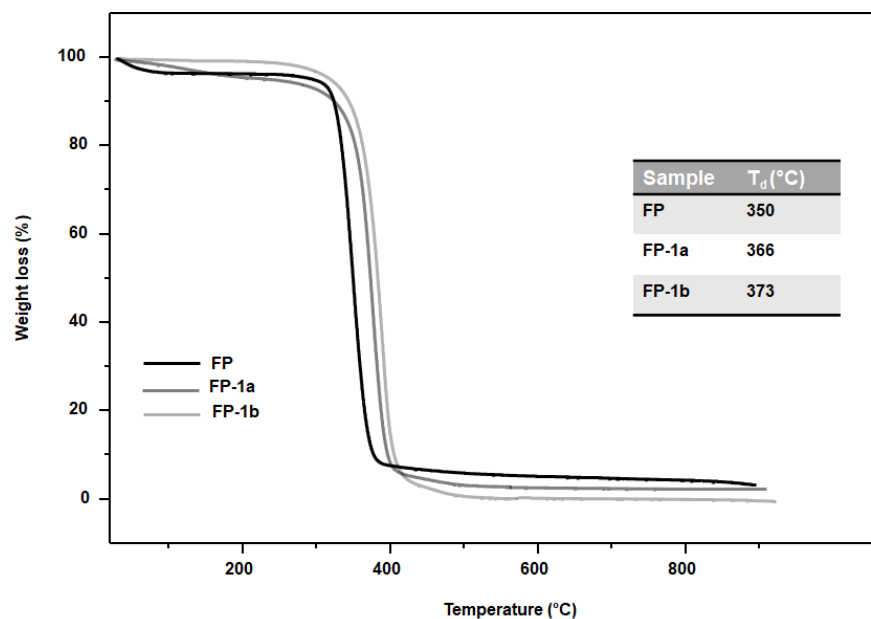


Figure S22: Thermogravimetric analysis (TGA) of cellulose Whatman™ filter paper No. 5 (FP) and resulting FACEs from FP (FP-1a, FP-1b) (5 wt. (%) cellulose, 24 h, 115 °C).

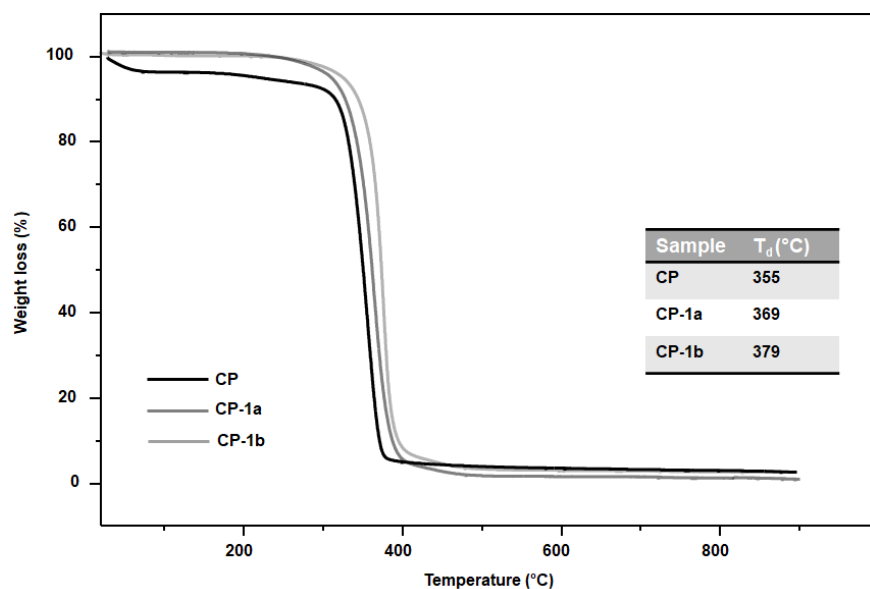


Figure S23: Thermogravimetric analysis (TGA) of cellulose pulp (CP) and resulting FACES from CP (CP-1a, CP-1b) (5 wt. (%) cellulose, 24 h, 115 °C).

SI IX: TGA analysis of FACES films

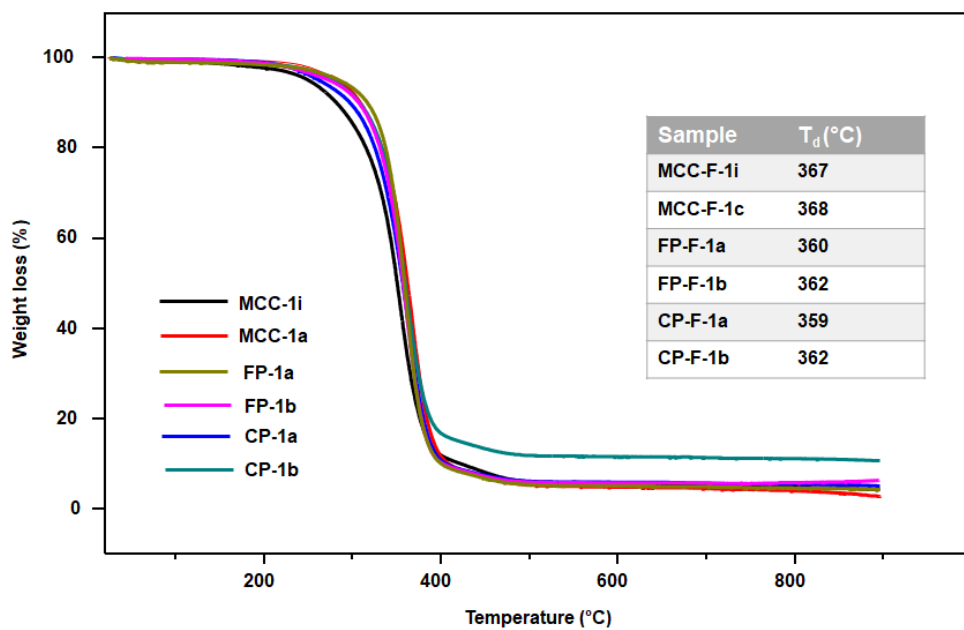


Figure S24: Thermogravimetric analysis (TGA) of FACES films (MCC-F-1i, MCC-F-1c, FP-F-1a, FP-F-1b, CP-F-1a, CP-F-1b).