Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information for

Compositional and structural feedstock requirements of a liquid phase cellulose-to-naphtha process in a carbon- and hydrogen-neutral biorefinery context

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A. Experimental details

Chemicals and materials

Microcrystalline Avicel PH-101 cellulose, Sigmacell Type 101 cellulose, Sigmacell Type 50 cellulose, Sigmacell Type 20 cellulose, α-cellulose, TSA hydrate, Ru/C (5 wt%) and *n*-decane were purchased from Sigma-Aldrich. Whatman filter 1, 4 and 5 were also purchased from Sigma-Aldrich. Vivapur cellulose was received from JRS Pharma. Wheat straw organosolv samples were received from the Energy research Centre of the Netherlands (ECN). Cotton was purchased from Kruidvat.

Avicel PH-101 cellulose was ball milled in a Retsch PM 100 planetary ball-mill for 0.5 h, 2 h and 6 h at 500 rpm (including 10 min cool down intervals after every hour of milling). Vivapur cellulose samples were sieved and the fraction lower and higher of 125 µm was used for reaction. Whatman filters were blended until a woolly cellulose substrate was obtained.

Thermogravimetric analysis, with a TGA Q500 from TA Instruments, under an inert N_2 atmosphere was used to determine the water content of all substrates. The weight of each component was corrected accordingly.

Light naphtha product analysis

GC analysis of the *n*-decane phase was performed on a Hewlett Packard 5890 GC equipped with an HP 7673 autosampler, a 60 m HP-1 column and a FID detector. HPLC analysis of the water phase was performed on an Agilent 1200 Series HPLC equipped with a Varian Metacarb 76 column and a RID detector. Neutralization of TSA with Cs_2CO_3 and filtration over a 0.45 µm filter was necessary to protect the HPLC column.

B. Characterization of different celluloses

Infrared (IR)

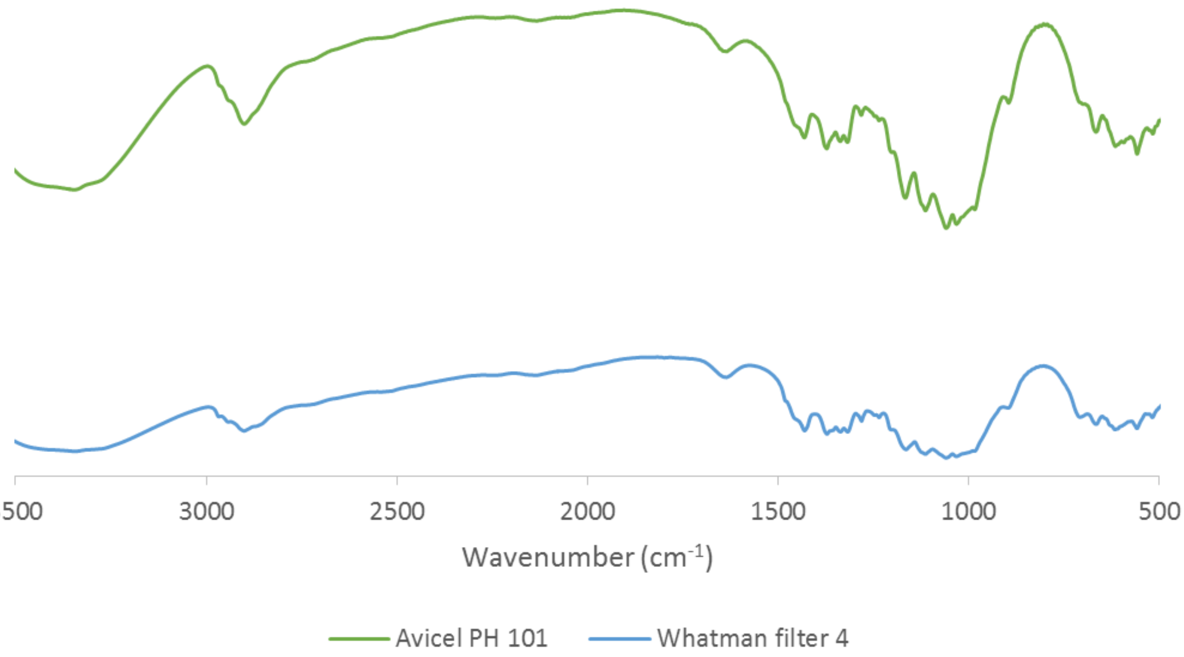
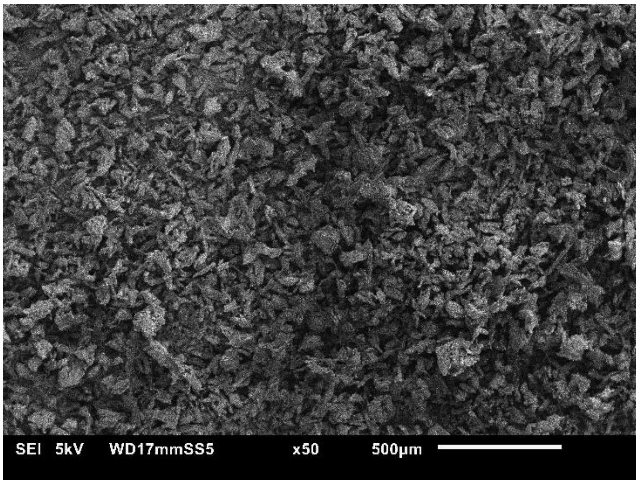
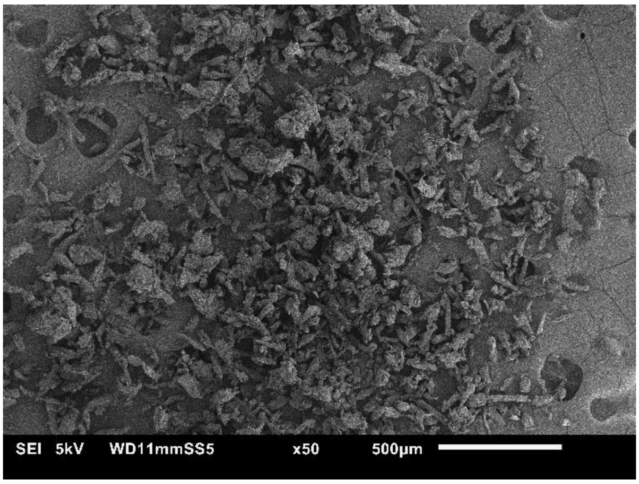


Figure S1 IR spectra of Avicel PH-101 and Whatman filter 4.

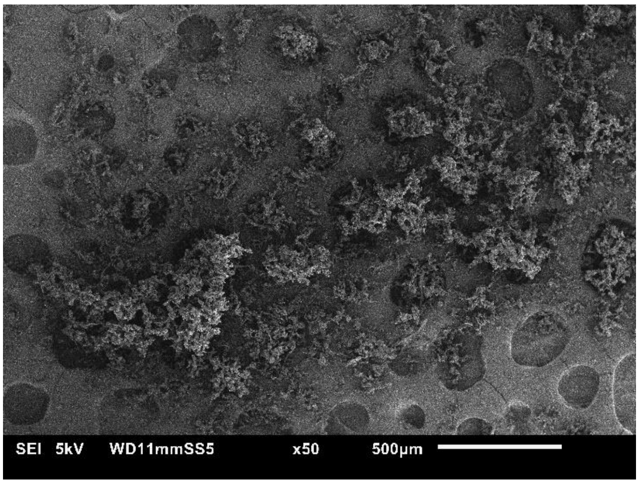
Scanning Electron Microscopy (SEM)



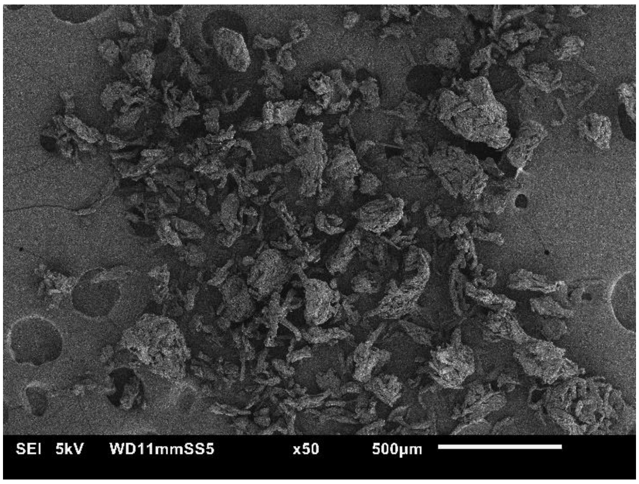
Avicel PH-101



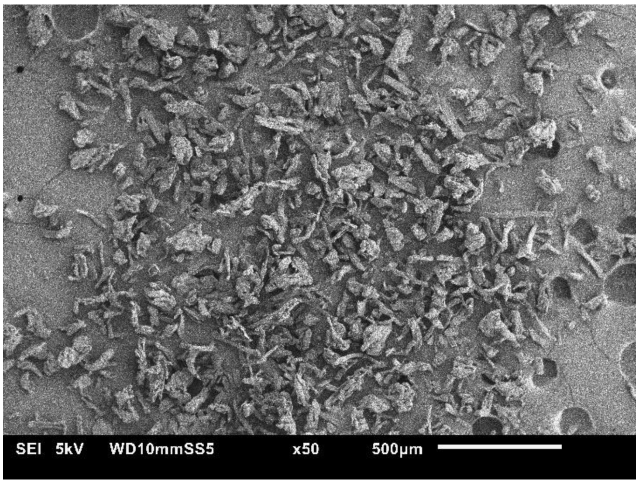
Sigmacell Type 50



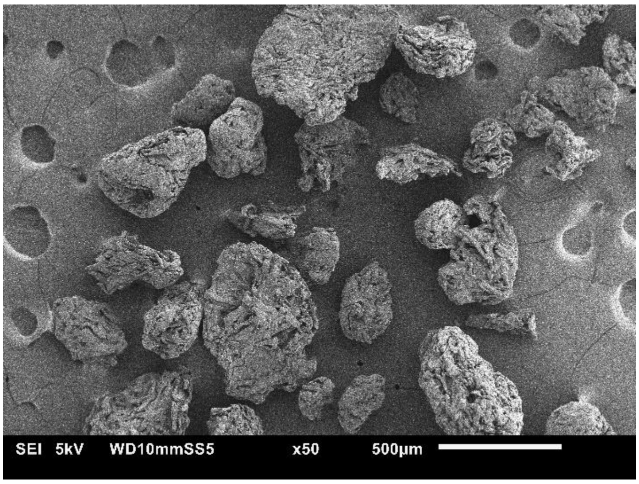
Sigmacell Type 101



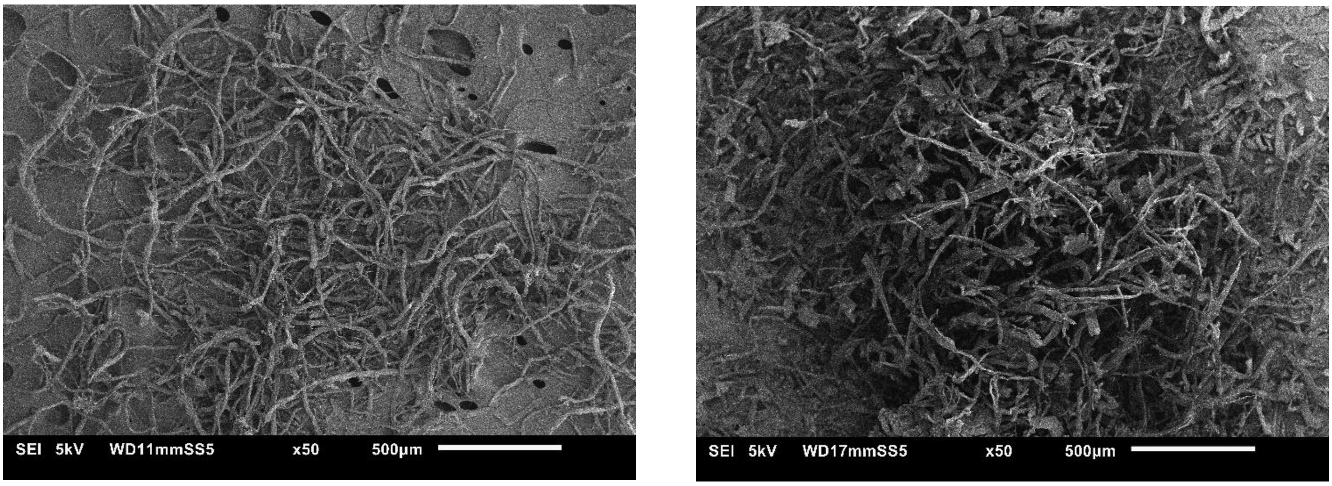
Vivapur



Vivapur (Sieving: < 125 µm)

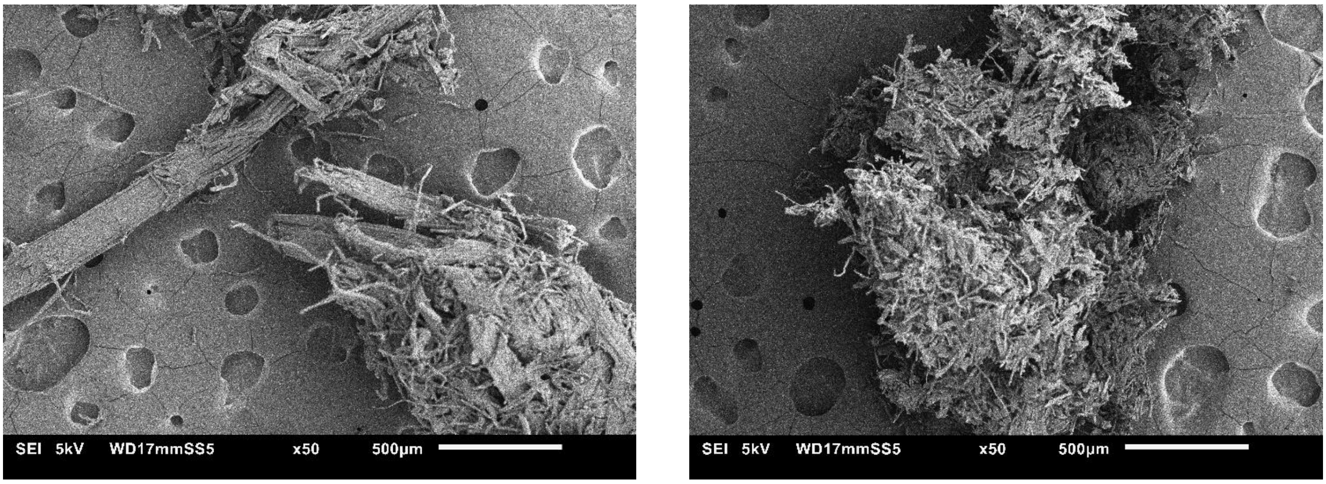


Vivapur (Sieving: > 125 µm)



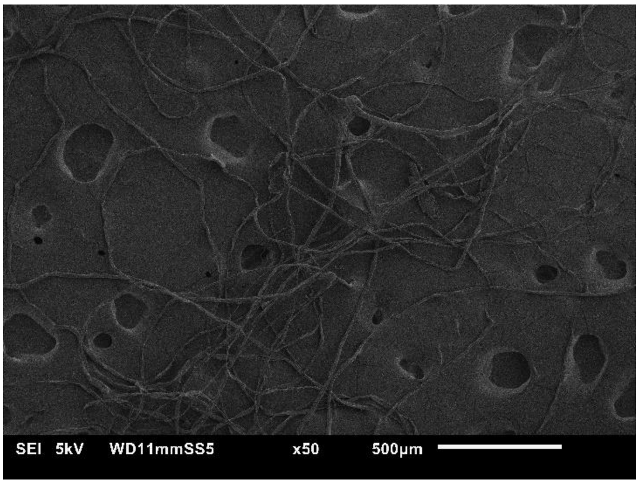
Whatman filter 4

α-cellulose



Wheat straw organosolv

Wheat straw organosolv - bleached



Cotton

Figure S2 SEM pictures of the different cellulose substrates.

Laser diffraction

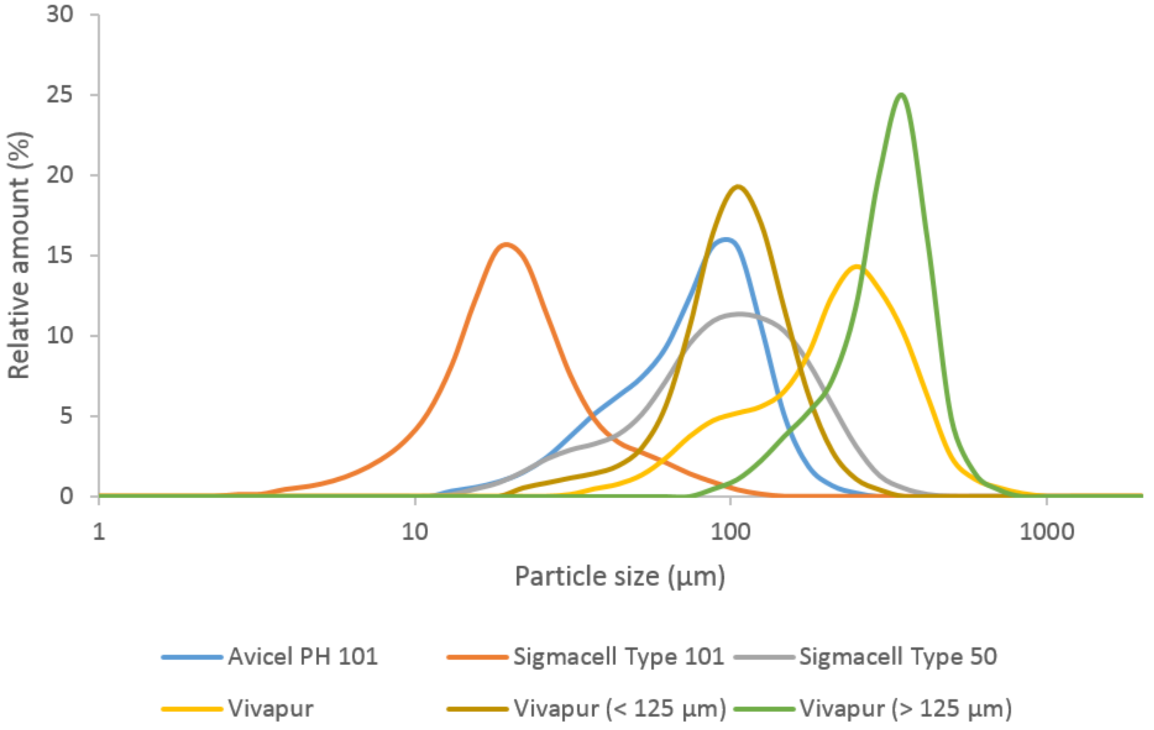


Figure S3a Particle size distributions of different pure cellulose substrates. Particle size distribution of the Whatman filters could not be determined reliably with laser diffraction.

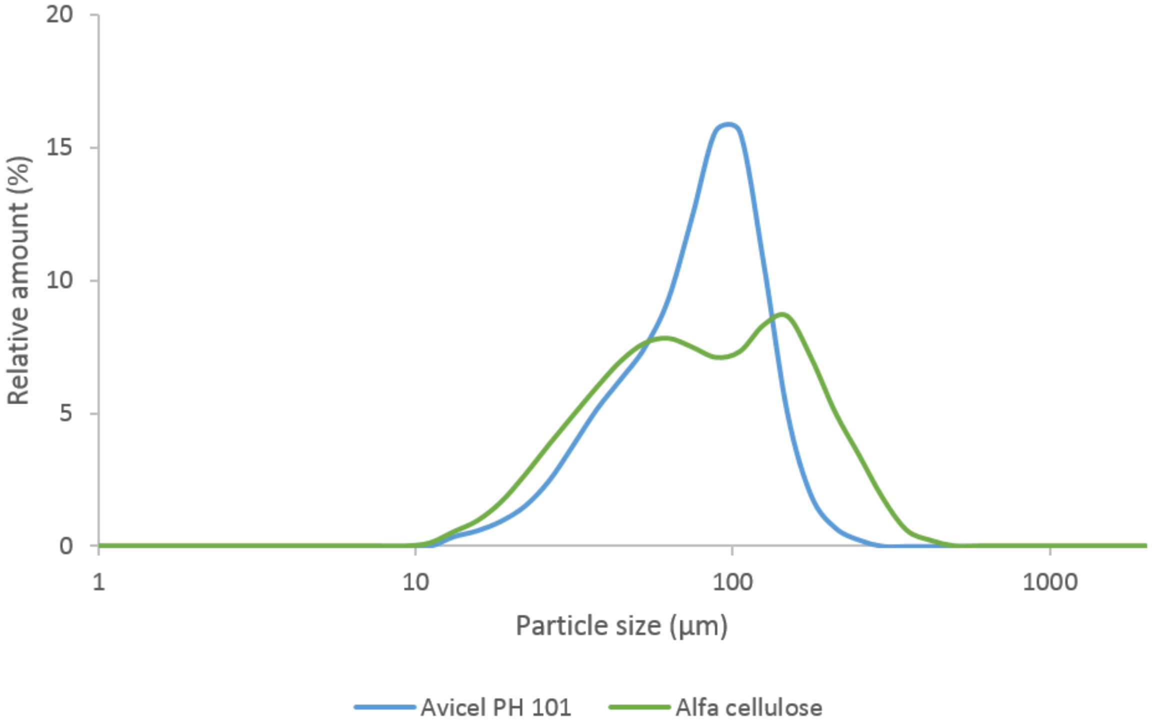
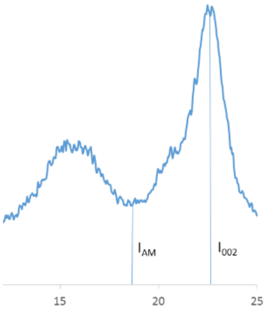


Figure S3b Particle size distributions of cellulose substrates with impurities. Particle size distribution of the organosolv wheat straw substrates could not be determined reliably with laser diffraction.

Powder X-ray diffraction (PXRD)



Crystallinity indices were calculated using the XRD peak height method according to Segal *et al.*. The maximum intensity of the (002) plane reflection in the cellulose sample is represented with I_{002} (2θ between 22° and 24°). The minimum intensity is represented with I_{AM}, intensity of the amorphous reflection (2θ of about 18°).[1] A background signal without cellulose was subtracted from all patterns and intensities were normalized with respect to the highest intensity.

$$\mathrm{CrI}(\%) = \frac{(I_{002} - I_{AM})}{I_{002}} \times 100$$

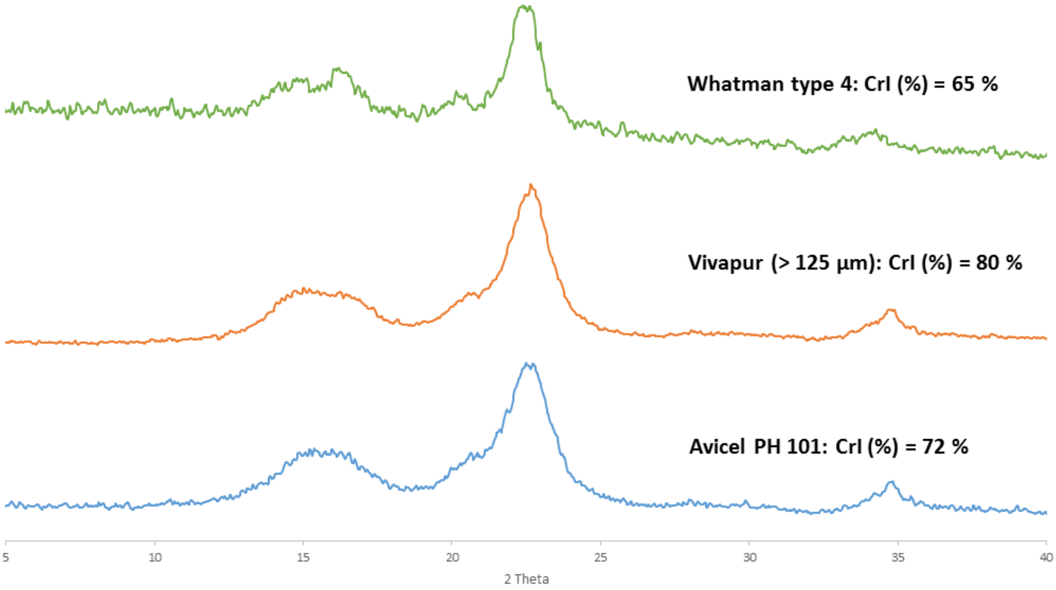


Figure S4a XRD patterns of pure cellulose substrates with the highest yield of light naphtha alkanes (Whatman filter 4 and Vivapur > 125 µm). XRD pattern of Avicel PH-101 is given as reference.

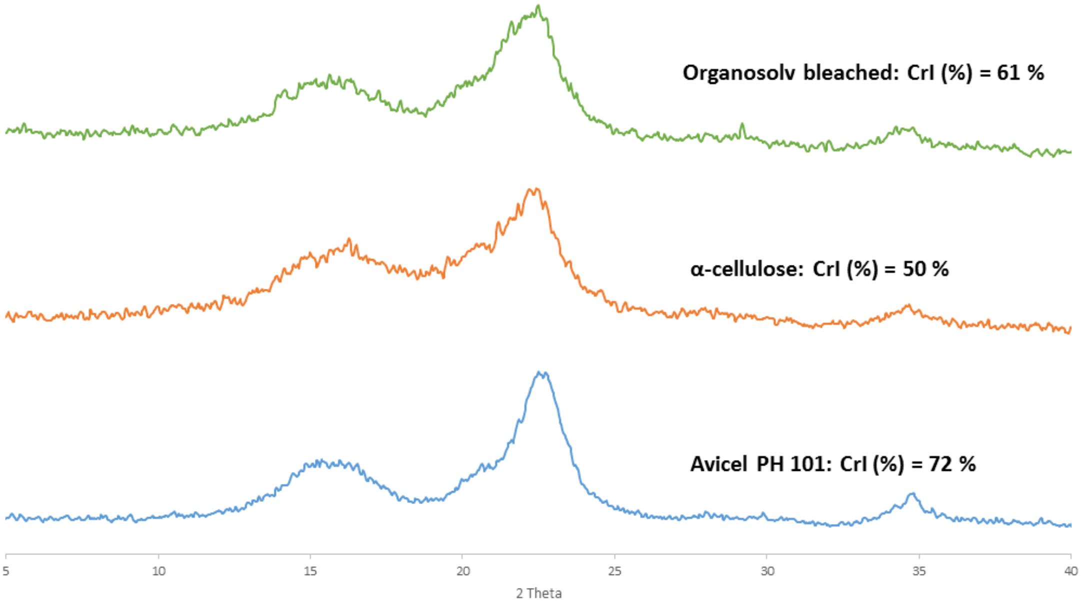


Figure S4b XRD patterns of cellulose substrates with impurities (organosolv bleached and α-cellulose). XRD pattern of Avicel PH-101 is given as reference.

C. Representation of cellulose as a sphere

Volume of a sphere: $V = \frac{4}{3}\pi r^3$

Surface area of a sphere: $A = 4\pi r^2$

⇨ $V = \frac{A}{3} r = 1.33\ cm^3$ (2 g cellulose with a characteristic density of 1.5 g/cm³)

⇨ $A = \frac{3.99}{r}$

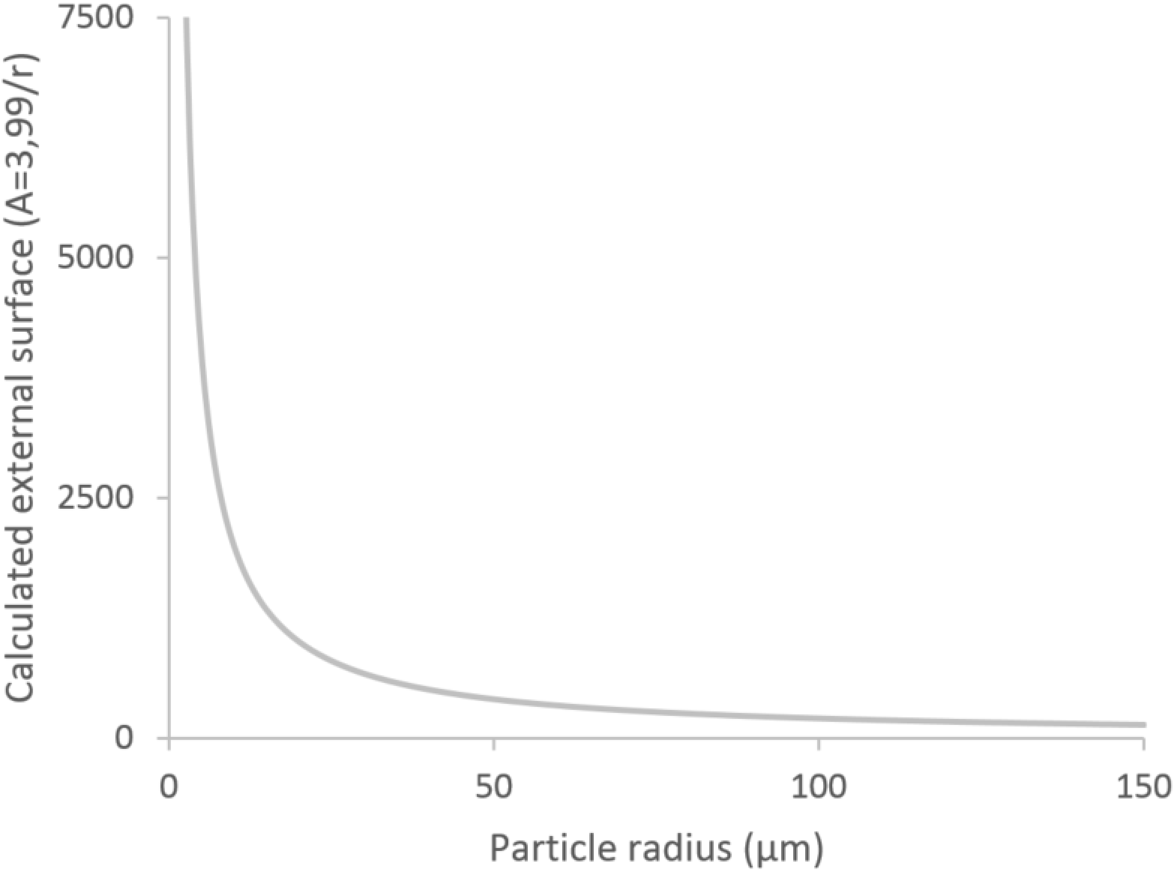


Figure S5 External surface of cellulose particles: reciprocal function of the particle radius.

D. Case study of the capacity of the process: the route towards styrene

Focusing on the market of benzene (50 million metric tons by 2018), three major aromatic end applications are aniline, cumene and styrene production.[2,3] Whereas aniline- and cumene-derived molecules may better be targeted starting from the phenolic lignin components[4–7], styrene is not immediately related to biomass building blocks today. However, this paper shows the opportunity to synthesize sustainable styrene by coupling bio-benzene with bio-ethylene, both originating from cellulose feedstock (see Figure 1).

The size of the styrene market is approximately 30 million metric tons in total.[8] Incorporating 10% sustainable carbon and hydrogen will ask a total production of 3 million metric tons renewable styrene. Assuming that a typical biorefinery can convert 2 000 tons/day in an economical feasible way[9], a biorefinery of 730 000 tons/year needs to be constructed. Taking into account the amount of weight loss as a result of: *(i)* moisture, *(ii)* other streams within the lignocellulose (hemicellulose and lignin) and *(iii)* defunctionalisation through reaction; the production of approximately 150 000 ton styrene/year is possible in one biorefinery. In the end, 20 biorefineries are needed worldwide to produce 10% renewable styrene, which is not unrealistic regarding the fact that in the U.S. alone more than 200 ethanol refineries (with a total capacity of 480 million metric ton in total) are running today.[10] Moreover, this case study does not even mention the valorization of for instance lignin in the synthesis of phenolic-derived compounds, which are related to cumene and aniline end applications.[4–7]

E. Closed energy and mass streams: 2 scenarios approached by 4 different concepts

Theoretical reaction with 100 mol% C of n-hexane yield – Steam-reforming:

Type	Reaction equation
HDO of glucose	$19\ C_6H_{12}O_6 + 133\ H_2 \rightleftarrows 19\ C_6H_{14} + 114\ H_2O$
Steam-reforming of *n*-hexane + WGS reaction	$7\ C_6H_{14} + 84\ H_2O \rightleftarrows 42\ CO_2 + 133\ H_2$
Burning of *n*-hexane	$12\ C_6H_{14} + 114\ O_2 \rightleftarrows 72\ CO_2 + 84\ H_2O$
Photosynthesis	$114\ H_2O + 114\ CO_2 \rightleftarrows 19\ C_6H_{12}O_6 + 114\ O_2$

In case of 100 mol% C *n*-hexane yield, there is the net formation of 12 molecules of *n*-hexane starting from 19 molecules of glucose. These 12 molecules can be used for chemicals, materials and (as additive) for fuels, while the other 7 molecules of *n*-hexane are used to recover H_2 via steam reforming.

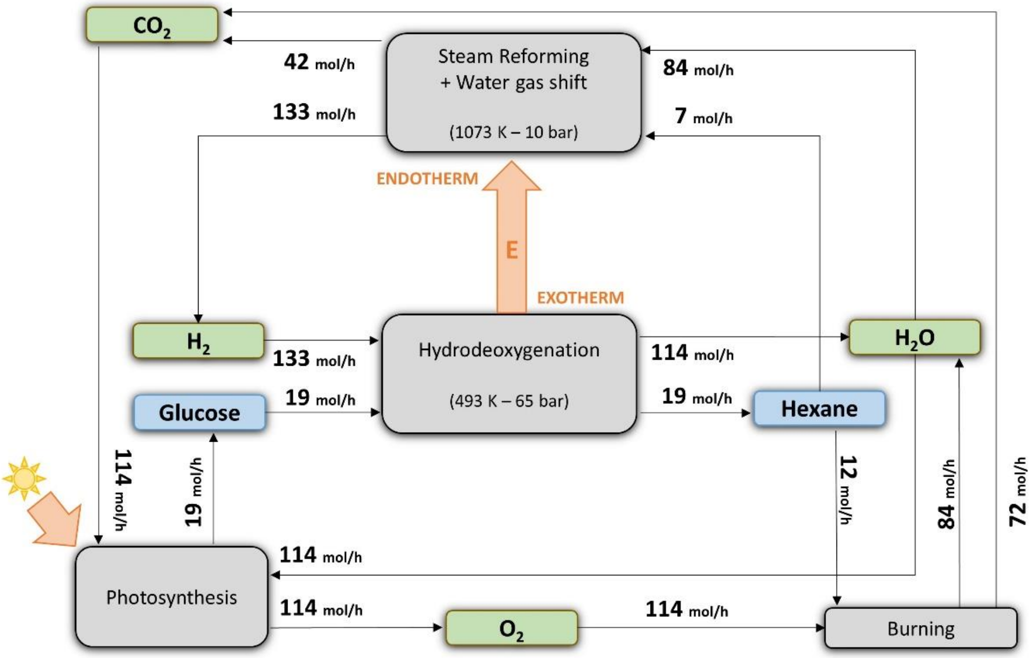


Figure S6a Theoretical process scheme assuming 100 mol% C of *n*-hexane yield (of which 7/19 is steam-reformed for H_2-recuperation).

% carbon used for H_2 recovery = $\frac{7}{19}$ = **36.8%**

The stoichiometry of the chemical reaction equations is entered as input (mol/h) to calculate the thermodynamic equilibrium for the HDO of glucose and the steam-reforming (+ WGS) of *n*-hexane. The results at the advisable conditions of each reaction are given in Table S1.

Table S1 Calculated streams (thermodynamic equilibrium) of combined HDO of glucose and steam-reforming (+ WGS) of *n*-hexane

Component	HDO of glucose [a]			Steam-reforming (+ WGS) of *n*-hexane [b]		
	Mixed [c]	Vapor [d]	Liquid [d]	Vapor [c]	Vapor [d]	Liquid [d]
$C_6H_{12}O_6$ (mol/h)	19.0	$3.7 . 10^{-6}$	$3.3 . 10^{-1}$	0	0	0
H_2 (mol/h)	133.0	2.3	$3.2 . 10^{-2}$	0	127.5	0
C_6H_{14} (mol/h)	0	18.6	$6.9 . 10^{-2}$	7.0	0.3	0
H_2O (mol/h)	0	11.5	100.5	84.0	3.5	0
CO_2 (mol/h)	0	0	0	0	40.3	0
Total (mol/h)	152.0	32.4	101.0	91.0	171.5	0
Molar H (kJ/mol)	$-1.4 . 10^{2}$	$-1.6 . 10^{2}$	$-2.7 . 10^{2}$	$-1.9 . 10^{2}$	$-7.1 . 10^{1}$	/
Molar S (kJ/mol K)	$-1.3 . 10^{-1}$	$-3.1 . 10^{-1}$	$-1.2 . 10^{-1}$	$-3.4 . 10^{-2}$	$2.9 . 10^{-2}$	/
ΔH (kJ/h)		-10 971.2			5 477.9	

[a] Conditions: T = 493 K; p = 65 bar. [b] Conditions: T = 1073 K; p = 10 bar. [c] Starting mixture and input in AspenTech software. [d] End streams.

Theoretical reaction with 100 mol% C of benzene yield – Steam reforming:

Type	Reaction equation
HDO of glucose	$5\ C_6H_{12}O_6 + 35\ H_2 \rightleftarrows 5\ C_6H_{14} + 30\ H_2O$
Dehydrocyclisation of *n*-hexane	$4\ C_6H_{14} \rightleftarrows 4\ C_6H_6 + 16\ H_2$
Steam-reforming of *n*-hexane + WGS reaction	$C_6H_{14} + 12\ H_2O \rightleftarrows 6\ CO_2 + 19\ H_2$
Burning of benzene	$4\ C_6H_6 + 30\ O_2 \rightleftarrows 24\ CO_2 + 12\ H_2O$
Photosynthesis	$30\ H_2O + 30\ CO_2 \rightleftarrows 5\ C_6H_{12}O_6 + 30\ O_2$

See Table 3 and Figure 4 in article.

Theoretical reaction with 100 mol% C of n-hexane yield – Aqueous Phase Reforming (APR):

Type	**Reaction equation**
HDO of glucose	$12\ C_6H_{12}O_6 + 84\ H_2 \rightleftarrows 12\ C_6H_{14} + 72\ H_2O$
Production of ethylene glycol from glucose	$7\ C_6H_{12}O_6 + 21\ H_2 \rightleftarrows 21\ C_2H_6O_2$
APR + WGS reaction	$21\ C_2H_6O_2 + 42\ H_2O \rightleftarrows 42\ CO_2 + 105\ H_2$
Burning of *n*-hexane	$12\ C_6H_{14} + 114\ O_2 \rightleftarrows 72\ CO_2 + 84\ H_2O$
Photosynthesis	$114\ H_2O + 114\ CO_2 \rightleftarrows 19\ C_6H_{12}O_6 + 114\ O_2$

In case of 100 mol% C *n*-hexane yield, there is the consumption of 12 molecules of glucose starting from 19 molecules of glucose. These 12 molecules of *n*-hexane can be used for chemicals, materials and as (additive) for fuels, while the other 7 molecules of glucose are used to recover H_2 via APR.

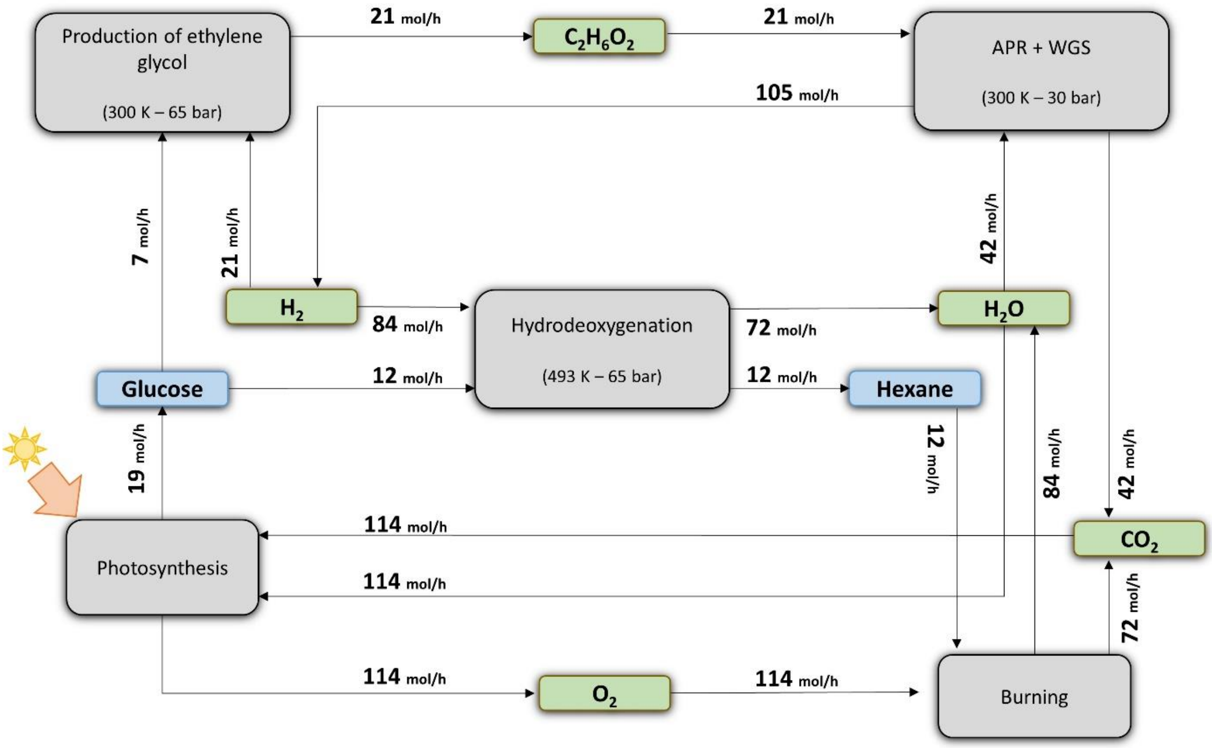


Figure S6b Theoretical process scheme assuming 63.2 mol% C of *n*-hexane yield (7/19 of the total carbon is aqueous-phase reformed for H_2-recuperation).

$$\boxed{\%\ \text{carbon used for } H_2 \text{ recovery} = \frac{7}{19} = \mathbf{36.8\%}}$$

The stoichiometry of the chemical reaction equations is entered as input (mol/h) to calculate the thermodynamic equilibrium for the HDO of glucose and production of ethylene glycol. The APR of ethylene glycol (+ WGS) is calculated with an excess of water (5 wt% ethylene glycol in water). The results at the advisable conditions of each reaction are given in Table S2.

Table S2 Calculated streams (thermodynamic equilibrium) of combined HDO of glucose, production of ethylene glycol from glucose and APR of ethylene glycol with WGS reaction

Component	HDO of glucose [a]			Production of ethylene glycol from glucose [b]		APR of ethylene glycol + WGS [c]	
	Mixed [d]	Vapor [e]	Liquid [e]	Vapor [d]	Liquid [e]	Vapor [d]	Vapor [e]
$C_6H_{12}O_6$ (mol/h)	12.0	$8.5 . 10^{-7}$	$8.3 . 10^{-2}$	7.0	$2.0 . 10^{-2}$	0	0
H_2 (mol/h)	84.0	$5.7 . 10^{-1}$	$8.8 . 10^{-3}$	21.0	$6.1 . 10^{-2}$	0	105.0
C_6H_{14} (mol/h)	0	11.9	$4.5 . 10^{-2}$	0	0	0	0
H_2O (mol/h)	0	6.9	64.6	0	0	1 447.0	1 405.0
$C_2H_6O_2$ (mol/h)	0	0	0	0	20.9	21.0	$6.3 .10^{-13}$
CO_2 (mol/h)	0	0	0	0	0	0	42.0
Total (mol/h)	96.0	19.3	64.8	28.0	21.0	1 468.0	1 552.0
Molar H (kJ/mol)	$-1.4 . 10^{2}$	$-1.6 . 10^{2}$	$-2.7 . 10^{2}$	$-2.9 . 10^{2}$	$-4.2 . 10^{2}$	$-2.4 . 10^{2}$	$-2.2 . 10^{2}$
Molar S (kj/mol K)	$-1.3 . 10^{-1}$	$-3.3 . 10^{-1}$	$-1.2 . 10^{-1}$	$-2.3 . 10^{-1}$	$-3.6 . 10^{-1}$	$-5.6 . 10^{-2}$	$-4.6. 10^{-2}$
ΔH (kJ/h)	-7 018.3			-812.2		2 180.8	

[a] Conditions: T = 493 K; p = 65 bar. [b] Conditions: T = 518 K; p = 65 bar. [c] Conditions: T = 523 K; p = 30 bar; excess of H_2O and feed concentration of 5 wt% . [d] Starting mixture and input in AspenTech software. [e] End streams.

Theoretical reaction with 100 mol% C of benzene yield – Aqueous Phase Reforming (APR):

Type	**Reaction equation**
HDO of glucose	$4\ C_6H_{12}O_6 + 28\ H_2 \rightleftarrows 4\ C_6H_{14} + 24\ H_2O$
Dehydrocyclisation of *n*-hexane	$4\ C_6H_{14} \rightleftarrows 4\ C_6H_6 + 16\ H_2$
Production of ethylene glycol from glucose	$1\ C_6H_{12}O_6 + 3\ H_2 \rightleftarrows 3\ C_2H_6O_2$
APR+ WGS reaction	$3\ C_2H_6O_2 + 6\ H_2O \rightleftarrows 6\ CO_2 + 15\ H_2$
Burning of hexane	$4\ C_6H_6 + 30\ O_2 \rightleftarrows 24\ CO_2 + 12\ H_2O$
Photosynthesis	$30\ H_2O + 30\ CO_2 \rightleftarrows 5\ C_6H_{12}O_6 + 30\ O_2$

In case of 100 mol% C benzene yield, there is the formation of 4 molecules of benzene starting from 5 molecules of glucose. These 4 molecules can be used for chemicals and materials, while the other molecule of glucose is used to recover H_2 via APR.

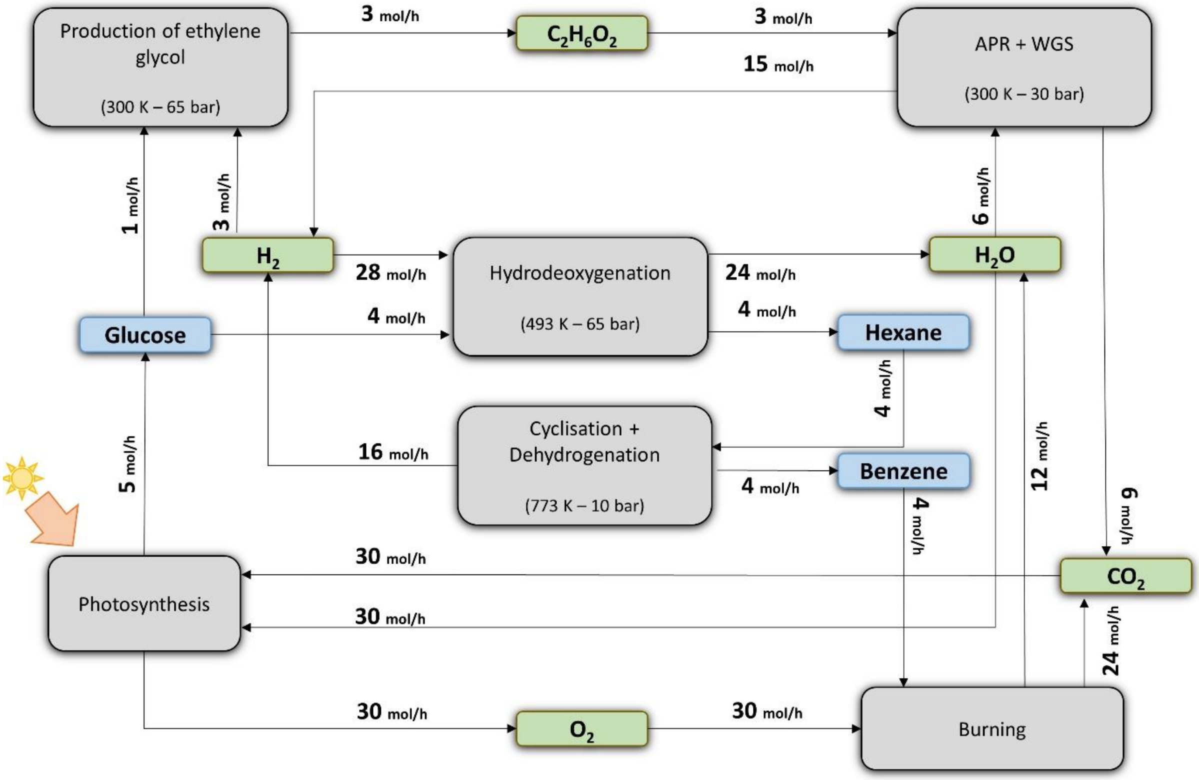


Figure S6c Theoretical process scheme assuming 80 mol% C of benzene yield (1/5 of the total carbon is aqueous-phase reformed for H_2-recuperation).

% carbon used for H_2 recovery = $\frac{1}{5}$ = **20.0%**

The stoichiometry of the chemical reaction equations is entered as input (mol/h) to calculate the thermodynamic equilibrium for the HDO of glucose, dehydrocyclisation of *n*-hexane to benzene and production of ethylene glycol from glucose. APR of ethylene glycol (+ WGS) is calculated with an excess of water (5 wt% ethylene glycol in water). The results at the advisable conditions of each reaction are given in Table S3.

Table S3a Calculated streams (thermodynamic equilibrium) of combined HDO of glucose and dehydrocyclisation of *n*-hexane

Component	HDO of glucose [a]			dehydrocyclisation of hexane [b]		
	Mixed [c]	Vapor [d]	Liquid [d]	Vapor [c]	Vapor [d]	Liquid [d]
$C_6H_{12}O_6$ (mol/h)	4.0	$2.2 . 10^{-9}$	$2.2 . 10^{-4}$	0	0	0
H_2 (mol/h)	28.0	$1.5 . 10^{-3}$	$2.5 . 10^{-5}$	0	12.4	0
C_6H_{14} (mol/h)	0	4.0	$1.5 . 10^{-2}$	4.0	1.0	0
H_2O (mol/h)	0	2.2	21.8	0	0	0
C_6H_6 (mol/h)	0	0	0	0	3.1	0
Total (mol/h)	32.0	6.2	21.8	4.0	16.5	0
Molar H (kJ/mol)	$-1.4 . 10^{2}$	$-1.7 . 10^{2}$	$-2.7 . 10^{2}$	$-6.0 . 10^{1}$	$3.5 . 10^{1}$	0
Molar S (kJ/mol K)	$-1.3 . 10^{-1}$	$-3.4 . 10^{-1}$	$-1.2 . 10^{-1}$	$-3.8 . 10^{-1}$	$-2.0 . 10^{-2}$	0
ΔH (kJ/h)		-2 358.9			815.6	

[a] Conditions: T = 493 K; p = 65 bar. [b] Conditions: T = 773 K; p = 10 bar. [c] Starting mixture and input in AspenTech software. [d] End streams.

Table S3b Calculated streams (thermodynamic equilibrium) of combined production of ethylene glycol from glucose and APR of ethylene glycol with WGS reaction

Component	Production of ethylene glycol from glucose [a]			APR of ethylene glycol + WGS [b]		
	Mixed [c]	Vapor [d]	Liquid [d]	Vapor [c]	Vapor [d]	Liquid [d]
$C_6H_{12}O_6$ (mol/h)	1.0	0	$2.9 . 10^{-3}$	0	0	0
H_2 (mol/h)	3.0	0	$8.7 . 10^{-3}$	0	15.0	0
$C_2H_6O_2$ (mol/h)	0	0	3.0	3.0	$8.9 . 10^{-14}$	0
H_2O (mol/h)	0	0	0	207.0	201.0	0
CO_2 (mol/h)	0	0	0	0	6.0	0
Total (mol/h)	4.0	0	3.0	210.0	222.0	0
Molar H (kJ/mol)	$-2.9 . 10^{2}$	0	$-4.2 . 10^{2}$	$-2.4 . 10^{2}$	$-2.2 . 10^{2}$	0
Molar S (kJ/mol K)	$-2.3 . 10^{-1}$	0	$-3.6 . 10^{-1}$	$-5.6 . 10^{-2}$	$-4.6 . 10^{-2}$	0
ΔH (kJ/h)		-116.0			309.1	

[a] Conditions: T = 518 K; p = 65 bar. [b] Conditions: T = 523 K; p = 30 bar; excess of H_2O and feed concentration of 5 wt%. [c] Starting mixture and input in AspenTech software. [d] End streams.

Overview:

Type	**Net reaction equation**
1. Hexane with H_2 via steam-reforming	$19\ C_6H_{12}O_6 \rightleftarrows 12\ C_6H_{14} + 30\ H_2O + 42\ CO_2$
2. Benzene with H_2 via steam-reforming	$5\ C_6H_{12}O_6 \rightleftarrows 4\ C_6H_6 + 18\ H_2O + 6\ CO_2$
3. Hexane with H_2 via APR	$19\ C_6H_{12}O_6 \rightleftarrows 12\ C_6H_{14} + 30\ H_2O + 42\ CO_2$
4. Benzene with H_2 via APR	$5\ C_6H_{12}O_6 \rightleftarrows 4\ C_6H_6 + 18\ H_2O + 6\ CO_2$

Table S4 Overview of 4 theoretical reactions for 100% renewable carbon and hydrogen

Reaction	End product	# mol end product	# mol glucose consumed	H_2 needed total	H_2 recuperated from benzene	# mol H_2 from water (%)	# mol H_2 from carbon source (%)
1	*n*-hexane	12	19	133	/	84 (63)	49 (37)
2	benzene	12	15	105	48	36 (63)	21 (37)
3	*n*-hexane	12	19	105	/	42 (40)	63 (60)
4	benzene	12	15	93	48	18 (40)	27 (60)

F. Closed energy and mass streams: calculation Vivapur (sieving: > 125 µm)

HDO of glucose:

This subsection shows the number of consumed H_2 (mol), going from glucose to the corresponding alkanes by hydrodeoxygenation.

Alkane	Reaction	# mol H_2 consumed
***n*-Butane**	$C_6H_{12}O_6 + 9\ H_2 \rightleftarrows C_4H_{10} + 6\ H_2O + 2\ CH_4$	**9**
***n*-Pentane**	$C_6H_{12}O_6 + 8\ H_2 \rightleftarrows C_5H_{12} + 6\ H_2O + CH_4$	**8**
***n*-Hexane**	$C_6H_{12}O_6 + 7\ H_2 \rightleftarrows C_6H_{14} + 6\ H_2O$	**7**
Cyclic C_6 alkane	$C_6H_{12}O_6 + 6\ H_2 \rightleftarrows C_6H_{12} + 6\ H_2O$	**6**

Steam-reforming of C_{1-6} alkanes:

This subsection shows the number of produced H_2 (mol) by steam-reforming of the alkanes. In addition, it is important to notice the additional production of H_2 by WGS of CO.

Alkane	Reaction	# mol H_2 produced
Methane	$CH_4 + H_2O \rightleftarrows CO + 3\ H_2$	**4** (3+1)
***n*-Butane**	$C_4H_{10} + 4\ H_2O \rightleftarrows 4\ CO + 9\ H_2$	**13** (9+4)
***n*-Pentane**	$C_5H_{12} + 5\ H_2O \rightleftarrows 5\ CO + 11\ H_2$	**16** (11+5)
***n*-Hexane**	$C_6H_{14} + 6\ H_2O \rightleftarrows 6\ CO + 13\ H_2$	**19** (13+6)

+ water gas-shift | $CO + H_2O \rightleftarrows CO_2 + H_2$

H_2 balance:

In the previous subsections we mentioned the consumption and production of H_2 by hydrodeoxygenation and steam-reforming respectively. With respect to these reactions, the amount of consumed H_2 (mol) is calculated for the best actual cellulose reaction (Vivapur cellulose, sieving: > 125 µm) below. The amount of alkanes (# mol) is received by GC-analysis of the *n*-decane phase after hydrodeoxygenation of Vivapur cellulose (> 125 µm). The amount of consumed H_2 by calculation via the products for this reaction is 0.0605 mol, which is more or less equal to the actual consumption calculated by using the ideal gas law and the measured pressure drop (20 bar) after reaction (or ca. 0.0565 mol of H_2).

Alkane	# mol alkanes	# mol H_2 consumed/alkane	# mol H_2 consumption	# mol n-Methane	# mol n-Butane	# mol H_2O produced
***n*-Butane**	0.0002	9	0.0018	0.0004	0.0002	0.0012
***n*-Pentane**	0.0015	8	0.0120	0.0015	/	0.0090
***n*-Hexane**	0.0059	7	0.0413	/	/	0.0354
Cyclic C_6 alkane	0.0009	6	0.0054	/	/	0.0054
Total	/	/	**0.0605**	**0.0019**	**0.0002**	0.0510

Further calculations are made by using the most conservative (largest) consumption of H_2, being 0.0605 mol. In a first step H_2 is recovered by steam-reforming (+ WGS) of methane and *n*-butane which results in a H_2 recuperation of 16.9%. The additional steam-reforming (+ WGS) of *n*-pentane gives a H_2 recuperation of 56.5% in total.

Alkane	# mol alkane	# mol H_2 produced/alkane	# mol H_2 produced	# mol H_2O consumed
Methane	0.0019	4	0.0076	0.0038
***n*-Butane**	0.0002	13	0.0026	0.0016
Total	/	/	**0.0102**	0.0054

$$H_2 \text{ recuperation}_{\text{ gaseous products}} = \frac{Production\ steam\ reforming}{Consumption} = \frac{0.0102}{0.0605} \cdot 100 = \mathbf{16.9\%}$$

Alkane	# mol alkane	# mol H_2 produced/alkane	# mol H_2 produced	# mol H_2O consumed
Methane	0.0019	4	0.0076	0.0038
***n*-Butane**	0.0002	13	0.0026	0.0016
***n*-Pentane**	0.0015	16	0.0240	0.0150
Total	/	/	**0.0342**	0.0204

$$H_2 \text{ recuperation}_{\text{ gasesous products + n-pentane}} = \frac{Production\ steam\ reforming}{Consumption} = \frac{0.0342}{0.0605} \cdot 100 = \mathbf{56.5\%}$$

To obtain 100% renewable hydrogen, an additional recovery of 43.5% (or 0.0263 mol H_2) is needed. A first strategy is the APR of hexitols or hexitol-derived dehydration products ("hexitols") actual formed in the reaction (mainly isosorbide and sorbitan isomers). Stoichiometrically, there is the net formation of 12 molecules of H_2 from isosorbide via APR. In the end, 0.0022 mol (or 0.0132 mol C) of isosorbide, or analogous molecules, needs to be available in the polar phase. By consequence, the yield of "hexitols" is not sufficient for this hydrodeoxygenation reaction with Vivapur (> 125 µm) cellulose.

Type	Reaction	# mol H_2 consumed/produced
Formation of isosorbide	$C_6H_{12}O_6 + H_2 \rightleftarrows C_6H_{10}O_4 + 2\ H_2O$	**1**
APR + WGS	$C_6H_{10}O_4 + 8\ H_2O \rightleftarrows 6\ CO_2 + 13\ H_2$	**13**
Net reaction	$C_6H_{12}O_6 + 6\ H_2O \rightleftarrows 6\ CO_2 + 12\ H_2$	**12**

Another solution to produce the remaining amount of hydrogen is the recuperation of H_2 during the cyclisation and dehydrogenation of *n*-hexane and cyclic C_6 alkanes to benzene. In the case of the formation of benzene, just enough H_2 is produced to have 59 mol% C benzene yield with a 100% renewable carbon and 100% renewable hydrogen. In this case, the hexitols do not need to be used to recover H_2.

Type	Reaction	# mol H_2 produced
Formation of benzene from *n*-hexane	$C_6H_{14} \rightleftarrows C_6H_6 + 4\ H_2$	**4**
Formation of benzene from cyclic C_6 alkanes	$C_6H_{12} \rightleftarrows C_6H_6 + 3\ H_2$	**3**

Alkane	# mol alkane	# mol H_2 produced/alkane	# mol H_2 produced	# mol benzene produced
***n*-hexane**	0.0059	4	0.0236	0.0059
Cyclic C_6 alkane	0.0009	3	0.0027	0.0009
Total	0.0068	/	**0.0263**	**0.0068**

The total H_2 recovery, after steam-reforming of C_1-C_5 alkanes and dehydrocyclisation of C_6 alkanes, is 86.3% and 88.6% for Sigmacell cellulose Type 101 and Avicel cellulose PH-101 respectively. These lower values compared to Vivapur cellulose were caused by a lower ratio of C_1-C_5 alkanes to C_6 alkanes after hydrodeoxygenation. Ideally, this ratio resembles the carbon efficiency (1:4) of the theoretical route B,C in Figure 3 of the article.

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