Supplementary Information

Substituting fossil-based with bio-based chemicals: The case of limonene as a greener pore expander for micellar templated silica

Umair Sultan[a,b], Katrin Städtke[a], Andreas Göpfert[a], Daniel Lemmen[a], Ezzeldin Metwali[c], Santanu Maiti[c], Carola Schlumberger[d], Tadahiro Yokosawa[e], Benjamin Apeleo Zubiri[e], Erdmann Spiecker[e], Nicolas Vogel[b], Tobias Unruh[c], Matthias Thommes[d], Alexandra Inayat[a]

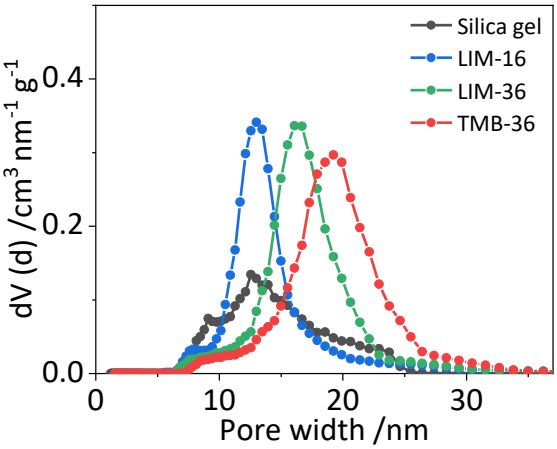

Figure S1. Comparison of the pore size distributions of templated silica (LIM-16, LIM-36 and TMB-36) and commercial silica gel to visualise the need for template and expander to obtain high pore volumes and narrower pore size distribution in the size range of 10 to 25 nm.

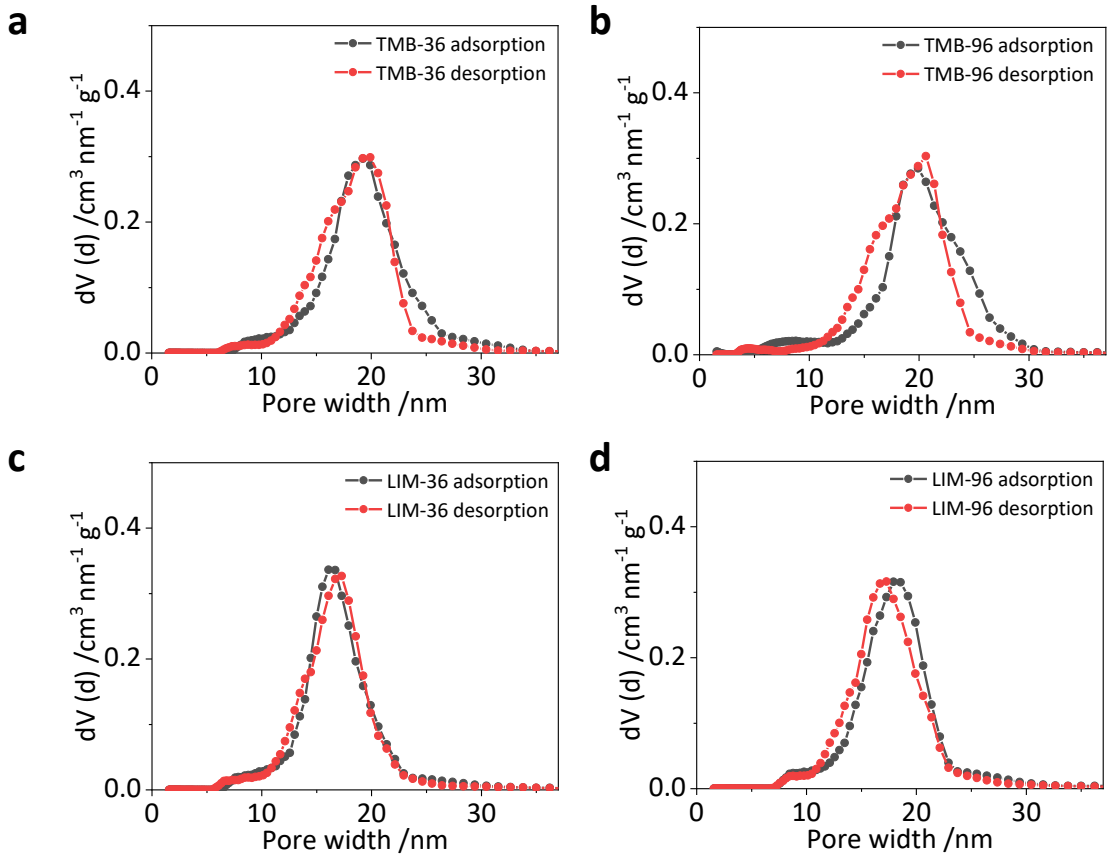

Figure S2. Pore size distributions from nitrogen physisorption for samples synthesised with low (36) and high (96) expander/P123 molar ratio using TMB (top row) and limonene (LIM, bottom row). The comparison of pore size distributions calculated from the adsorption and desorption branches of the isotherms shows very similar mode pore diameters. This indicates that the majority of the pores are not restricted by narrower pore openings and are freely accessible.

Table S1. Micropore volumes (from t-plot) for all the mesoporous silica samples

Sample	Micropore volume ($cm^3\ g^{-1}$)
silica gel	0.001
SBA-15	0.008
TMB-4	0.008
TMB-16	0.060
TMB-36	0.020
TMB 56	0.003
TMB-76	0.010
TMB-96	0.030
LIM-4	0.040
LIM-16	0.007
LIM-36	0.020
LIM-56	0.030
LIM-76	0.020
LIM-96	0.020

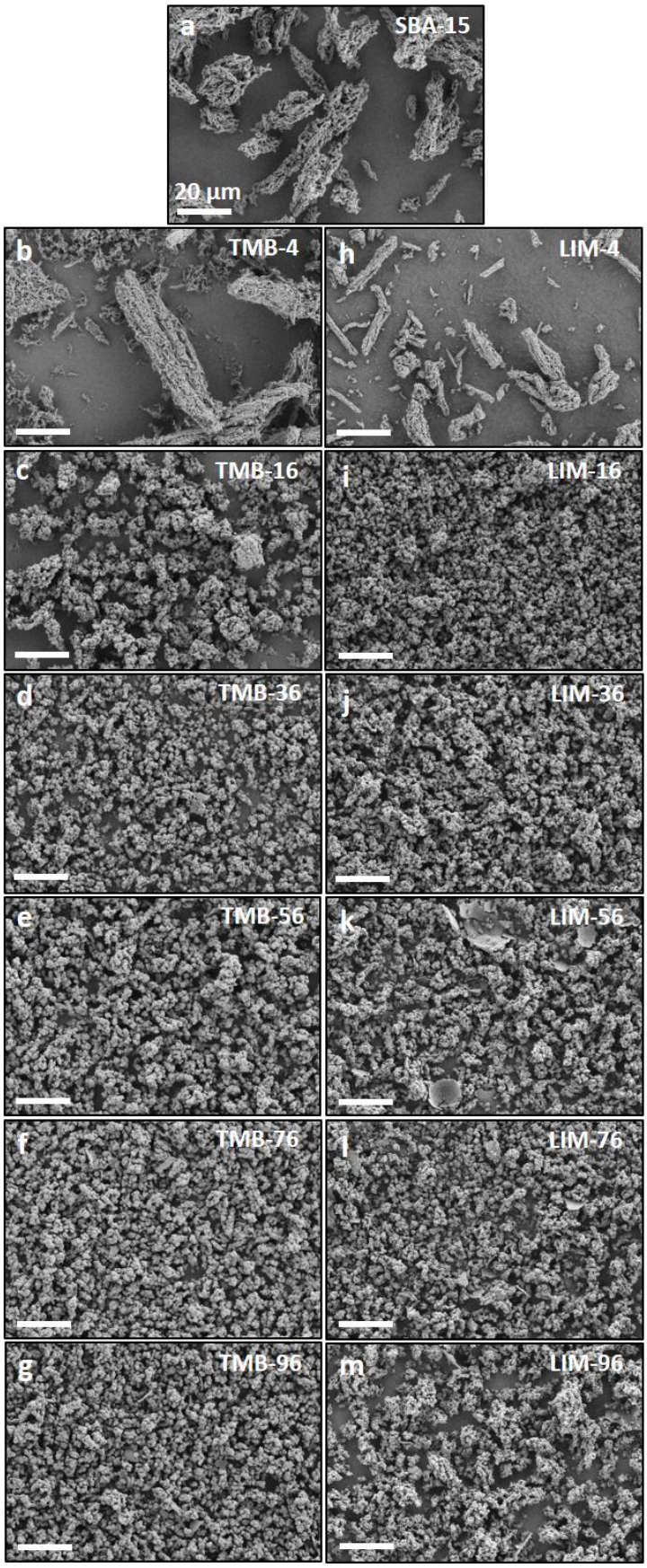

Figure S3. Low magnification overview SEM images of mesoporous silica materials with increasing expander to P123 molar ratio using TMB (left column) and limonene (right column) as expander molecule. All scale bars are 20 µm.

Table S2. Elementary or process flows, calculated quantities for the production of 1 t expander molecule and specification of the input data taken from the ecoinvent database.

Elementary or process flow	Quantity for the production of 1t expander molecule	Ecoinvent process / category
Inputs Route TMB		
Self-condensation (implemented data(from simulation))		
Acetone, liquid*	3076.2 kg	phenol production, from cumene | acetone, liquid | Cutoff, U - RER
Silica sand (Nb cut-off)	38.7 kg	silica sand production | silica sand | Cutoff, U - DE
Electricity, medium voltage scenario: gate-gate renewable energy	25163.2 MJ	electricity voltage transformation from high to medium voltage | electricity, medium voltage | Cutoff, U –DE market for electricity, medium voltage, label-certified | electricity, medium voltage, label-certified | Cutoff, U - CH
transport of 1.5 t crude oil from Russia to Germany (1224 km pipeline)	1836 t*km	transport, pipeline, offshore, petroleum
transport of 2 t hard coal from Russia to Germany (1300 km)	2600 t*km	transport, freight train (for hard coal)
Outputs Route TMB		
TMB	1000.0 kg	None (new implemented)
Acetic acid	2.1 kg	Elementary flow> Emission to air/ unspecified
Hydrocarbons, aliphatic, alkenes, C12, internal	11.7 kg	Elementary flow> Emission to air/ unspecified
Isobutene	11.2 kg	Elementary flow> Emission to air/ high population density
Trimethylbenzene	16.2 kg	Elementary flow> Emission to air/ high population density
Acetone (recycling)	585. kg	Elementary flow> Emission to air/ unspecified
Catalyst (ideal recycling)	35.0 kg	none
Waste water, average	687.5 kg	Water supply> Sewerage
Inputs Route Limonene		
Orange juice production		
Orange, fresh grade	571.9 t	orange production, fresh grade | orange, fresh grade | Cutoff, U - ES
Nitric acid	0.2 kg	nitric acid production, product in 50% solution state | nitric acid, without water, in 50% solution state | Cutoff, U - RER w/o RU

Soda ash, dense	6.0 kg	market for soda ash, dense | soda ash, dense | Cutoff, U - GLO
heat, district or industrial, natural gas electricity, medium voltage	11.9 MJ 115.1 MWh	heat and power co-generation, natural gas, 1MW electrical, lean burn | heat, district or industrial, natural gas | Cutoff, U - Europe without Switzerland electricity voltage transformation from high to medium voltage | electricity, medium voltage | Cutoff, U - ES
Steam distillation		
Orange peel	192.3 t	Orangepeel_Allo5
Water, deionised	14.8 t	water production, deionised | water, deionised | Cutoff, U - Europe without Switzerland
electricity, medium voltage scenario: gate-gate renewable energy	35944.4 MJ	electricity voltage transformation from high to medium voltage | electricity, medium voltage | Cutoff, U –DE market for electricity, medium voltage, label-certified | electricity, medium voltage, label-certified | Cutoff, U - CH
transport of 192 t dry orange peel from Spain to Germany by lorry (1300 km)	249600 t*km	transport, freight, lorry EURO5
Outputs Route Limonene		
Orange juice production		
Orange peel	192.3 t	none
Orange juice (allocation)	611.0 t	none
Waste water (orange juice production)	723.1 t	Water supply> Sewerage
Steam distillation (implemented data from simulation)		
Limonene	1000.0 kg	none
By-products	20.0 t	Manufacturing> Manufacture of sugar
Compost	171.3 t	Agriculture, forestry and fishing>Support activities for crop production
Waste water	148 t	Water supply> Sewerage

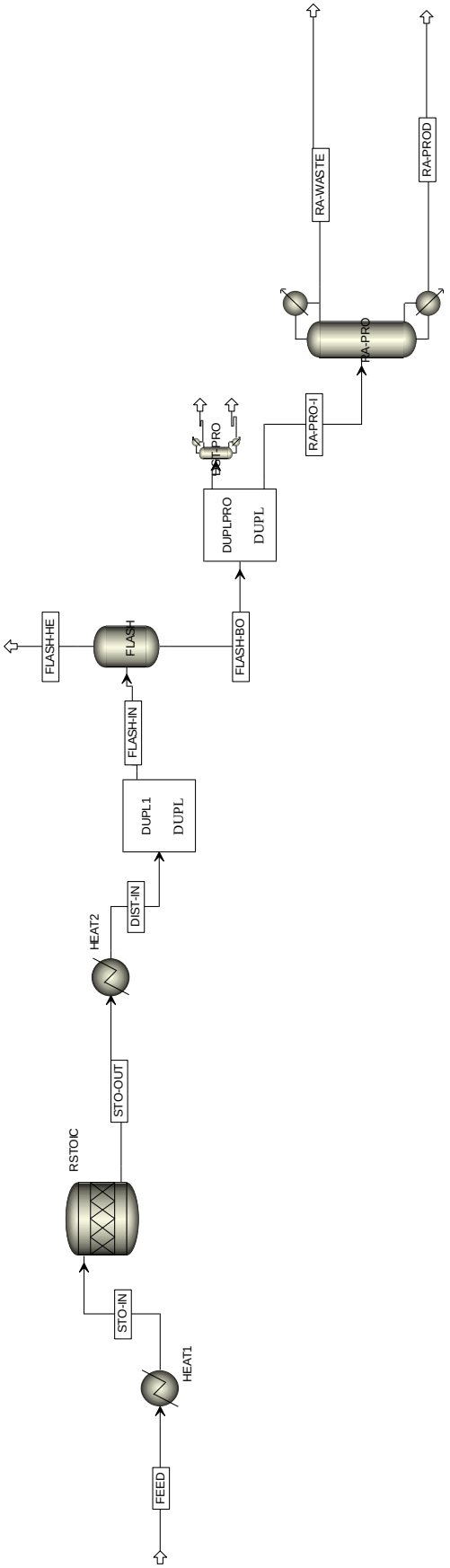

Figure S4. Process of TMB production via self-condensation of acetone: AspenPlus flow sheet of the simulation using the NRTL model.

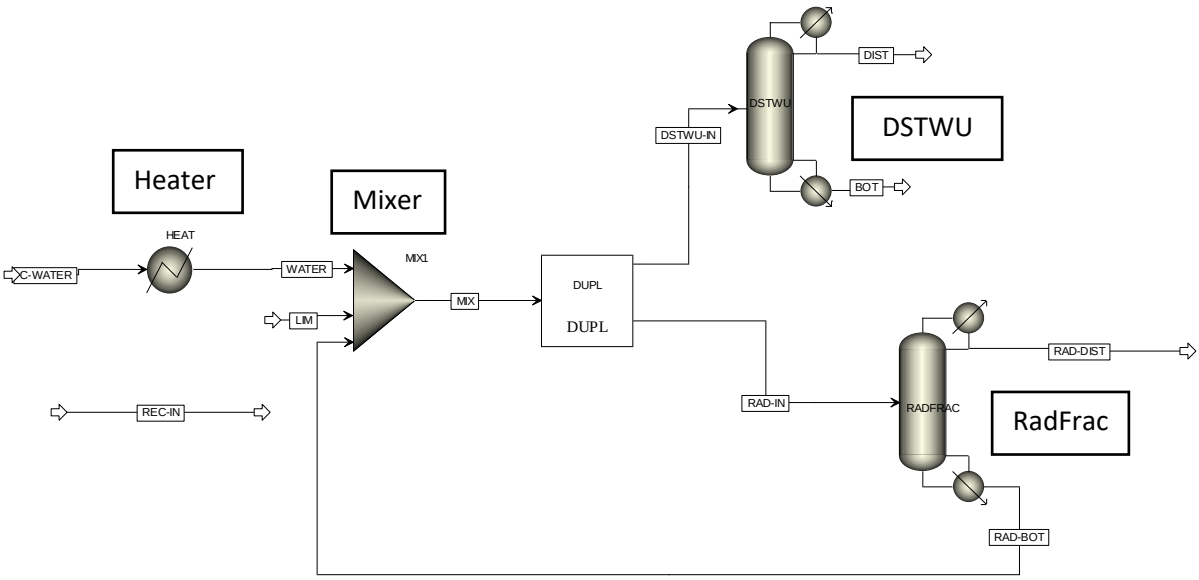

Figure S5. Process of limonene production from orange peels: AspenPlus flow sheet of the simulation using the NRTL model.

Table S3: Inputs for the self-condensation of acetone (production of TMB) and steam distillation of orange peels (production of limonene) for the AspenPlus simulation.

INPUTS TMB				
		T / °C	p / bar	Comment
PROPERTY METHOD	NRTL			
FEED-Stream	Acetone	25	1	0.068 $kmol.h^{-1}$
HEAT1 (HEATER)		350	1	
RSTOIC	2 ACE → MO + H_2O (X=0.6) ACE + MO → TMB +H_2O (X=0.7)	350	1	MO represented for all by-products
HEAT2 (HEATER)		110	1	cooling
FLASH		85	1	Separation gas-liquid
RADFRAC	Stages: 34 Feed-stage: 15 Distillate-to-feed: 0.291 Reflux ratio: 1.928			Estimation DSTWU → 99.99 mol% TMB
INPUTS LIM				
PROPERTY METHOD	NRTL			
FEED-Streams	Water	20	1	324.310 $kmol{\cdot}h^{-1}$
	Limonene	20	1	31.162 $kmol{\cdot}h^{-1}$
HEAT (HEATER)		100	1	Steam generation
MIX1 (MIXER)				Mixing of water, Limonene, recycled Limonene from orange peel
RADFRAC	Stages: 5 Feed-stage: 5 Distillate-to-feed: 0.829 Reflux ratio: 0.232			Estimation DSTWU

Table S4: Absolute values of the LCA ecological impact indicators for the cradle-to-gate production of 1 t limonene.

Limonene	Ammonium Nitrate production	Irrigation	Pesticides	Energy for steam distillation	Cultivation of orange plantation	Transport	**total impact (sum)**
Fossil resource scarcity/ kg oil eq	176	63	105	468	136	201	**1148**
Freshwater eutrophication/ kg P eq	0.02	0.04	0.05	2.57	0.42	0.34	**3.40**
Global warming potential/ kg CO_2 eq	590	182	423	1904	1441	426	**4965**
Human carcinogenic toxicity/ kg 1.4-DCB	1	3	2	123	5	184	**318**
Land use/ m^2a crop eq	0	1	8	17	3784	62	**3872**
Terrestrial acidification/ kg SO_2 eq	20	6	2	4	20	2	**36**
Water depletion potential/ m^3	9	2235	6	11	-619	4	**1646**

Table S5: Absolute values of the LCA ecological impact indicators for the cradle-to-gate production of 1 t 1,3,5-trimethyl benzene.

TMB	Benzene	Propene	Energy self condensation	Process water (cooling)	Transport	**total impact (sum)**
Fossil resource scarcity/ kg oil eq	1962	1012	195	0	87	**3256**
Freshwater eutrophication/ kg P eq	0.82	0	1.65	0.02	0.10	**2.57**
Global warming potential/ kg CO_2 eq	2567	1079	1316	903	407	**6272**
Human carcinogenic toxicity/ kg 1,4-DCB	49	0	73	8	25	**326**
Land use/ m^2a crop eq	13	0	1	0	0	**14**
Terrestrial acidification/ kg SO_2 eq	8	2	2	0	0	**12**
Water depletion potential/ m^3	35	8	9	25	11	**88**