Electronic Supplementary Material (ESI) for Green Chemistry.

Sensitivity Analysis – life cycle assumptions

Solvent	Process details	LCA system	Data source
Ethyl Acetate	Production of EtOAc from the reaction of ethanol and acetic acid	From raw materials to final product. Manufacture of acetic acid and fossil-ethanol from Gabi database; and **1 kg ethyl acetate** modelled from ethanol in Europe	EcoInvent Combined GaBi engineering database (ethanol, acetic acid); Ecoinvent-European plant (EtOAc)
	Process[a] for producing ethyl acetate by ***dehydrogenation of ethanol*** using a homogenous catalyst system	Production of **1 kg ethyl acetate** (81% yield) according to process[a]; with ethanol production modeled from GaBi datasets. LCA modelling of catalyst not included	Combined GaBi engineering database (fossil-ethanol); and Nielsen et al. 2013 (patent) [a]
2-MeTHF	Corn stover	From US corn field to harvesting, generation of straw, collection of stover and bio-chemical prod. of levulinic acid as intermediate followed by the synthesis of **1 kg** of **2-MeTHF**; transportation not included	LCA models described in Khoo et al. 2015[b]
	Sugarcane bagasse	From Brazillian sugarcane plantation to milling process and generation of bagasse, bio-chemical prod. of levulinic acid as intermediate followed by the synthesis of **1 kg** of **2-MeTHF**; transportation not included	
	Rice straw (RS)	From China rice paddy field to harvesting, generation of straw, collection of straw and bio-chemical prod. of levulinic acid as intermediate followed by the synthesis of **1 kg** of **2-MeTHF**; transportation not included	
Fossil-CPME	Synthesized from cyclopentene and fossil-methanol	From refinery co-products; cyclopentene produced from pyrolysis gasoline. Synthesis of **1 kg CPME** from fossil-MeOH and cyclopentene with 89% yield	Ecoinvent
Bio-CPME	Synthesized from cyclopentene and RS-methanol	Streamlined LCA, from farm cultivation of rice, harvesting and straw as by-product to RS-Methanol; cyclopentene produced from pyrolysis gasoline. Synthesis of **1 kg CPME** from RS-MeOH and cyclopentene with 89% yield	US NREL (RS) RS-MeOH from Xiao et al.[c] ; GaBi life cycle database (fossil-resources)
	Synthesized from "bio"-cyclopentene (from cyclopentanol derived from stover) and RS-methanol	Streamlined LCA, from farm cultivation of rice, harvesting and straw as by-product to RS-Methanol; cyclopentene produced from cyclopentanol which is produced from hydrogenation of furfural. It was estimated that 9.06 kg stover is needed per kg furfural[d]. Synthesis of **1 kg CPME** from RS-MeOH and cyclopentene with 89% yield; energy requirements for bio-processes involved in converting stover to cyclopentanol not included.	US NREL (RS and stover); RS-MeOH from Xiao et al.[c] ; GaBi life cycle database (fossil-resources)

[a] Nielsen, M., Kammer, A., Junge, H., Beller, M. (2013) *A process for producing ethyl acetate by dehydrogenation of ethanol using a homogenous catalyst system* (Patent WO 2013079659 A1), http://www.google.com/patents/WO2013079659A1?cl=en

[b] Khoo, H.H., Wong, L.L., Tan, J., Isoni, V., Sharratt, P. (2015) Synthesis of 2-Methyl tetrahydrofuran from various lignocellulosic feedstocks: sustainability assessment via LCA. *Res. Conserv. Rec.* 95: 174 – 182.

[c] Xiao, J., Shen, L., Zhang, Y., Gu, J. (2009) Integrated Analysis of Energy, Economic, and Environmental Performance of Biomethanol from Rice Straw in China, *Ind. Eng. Chem. Res.* 48, 9999 – 10007.

[d] Zhou, M., Zhu, H., Niu, L., Xiao, G., Xiao, R. (2014) Catalytic Hydroprocessing of Furfural to Cyclopentanol Over Ni/CNTs Catalysts: Model Reaction for Upgrading of Bio-oil, *Catal Lett.* 144, 235 – 241.

Uncertainty Analysis – one table

Changes		10% Increase		10% Reduce	
		Yield/ Bio-Conversion	Energy efficiency	Yield/ Bio-Conversion	Energy efficiency
Estimated effects in life cycle impacts					
EtOAc (fossil)	GWP	8% reduce	2% reduce	7.5% increase	1.6% increase
	Energy	4% reduce	13% reduce	4% increase	12.3% increase
2MeTHF (bio)	GWP	10% reduce	1.3% reduce	9.9% increase	1.6% increase
	Energy	9.9% reduce	7.2% reduce	10% increase	7.2% increase
CPME (mix bio + fossil)	GWP	11% reduce	3% reduce	11% increase	2.6% increase
	Energy	10% reduce	1% reduce	9.05% increase	1% increase