Electronic Supporting Information

Bio-based Solvents as entrainers for Extractive Distillation in Aromatic/Aliphatic and Olefin/Paraffin Separation

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This supporting information document contains four sections.

1. Materials

Table S1: All used chemicals with their purity and vendor specified

Chemical	Purity	Vendor
Methylcylohexane	Reagent Grade. 99%	Honeywell
Toluene	ACS, Reag.Ph.Eur.	VWR
Sulfolane™	99%	Sigma Aldrich
Acetone	LiChrosolv®	Merck
Cyrene™	99.3%	Circa Group
Propylene Glycol	≥ 99.5%	Sigma Aldrich
Ethylene Glycol	Emsure®, Reag.Ph.Eur	Merck
Propionic acid	≥ 99.5%	Sigma Aldrich
γ-Valerolactone	98%	Acros Organics
Methyl salicylate	>99%	Sigma Aldrich
Ethylene Carbonate	98%	Sigma Aldrich
Isophorone	97%	Sigma Aldrich
Guaiacol	≥ 99%	Sigma Aldrich
Phenol	≥ 99%	Sigma Aldrich
Furfural	99%	Sigma Aldrich
Levulinic acid	98+%	Acros Organics
Acetophenone	99%	Sigma Aldrich
Triacetin	99%	Acros Organics
Tributyl phosphate	99+%	Acros Organics
n-Heptane	99%	Alfa Aesar
1-Heptene	97%	Sigma Aldrich
D-chloroform	99.5%	Cambridge Isotope Laboratories, Inc.
N-methylpyrrolidone	99.5%	Sigma Aldrich

2. Additional xy- and Txy-diagrams of Methylcyclohexane-Toluene-Solvent

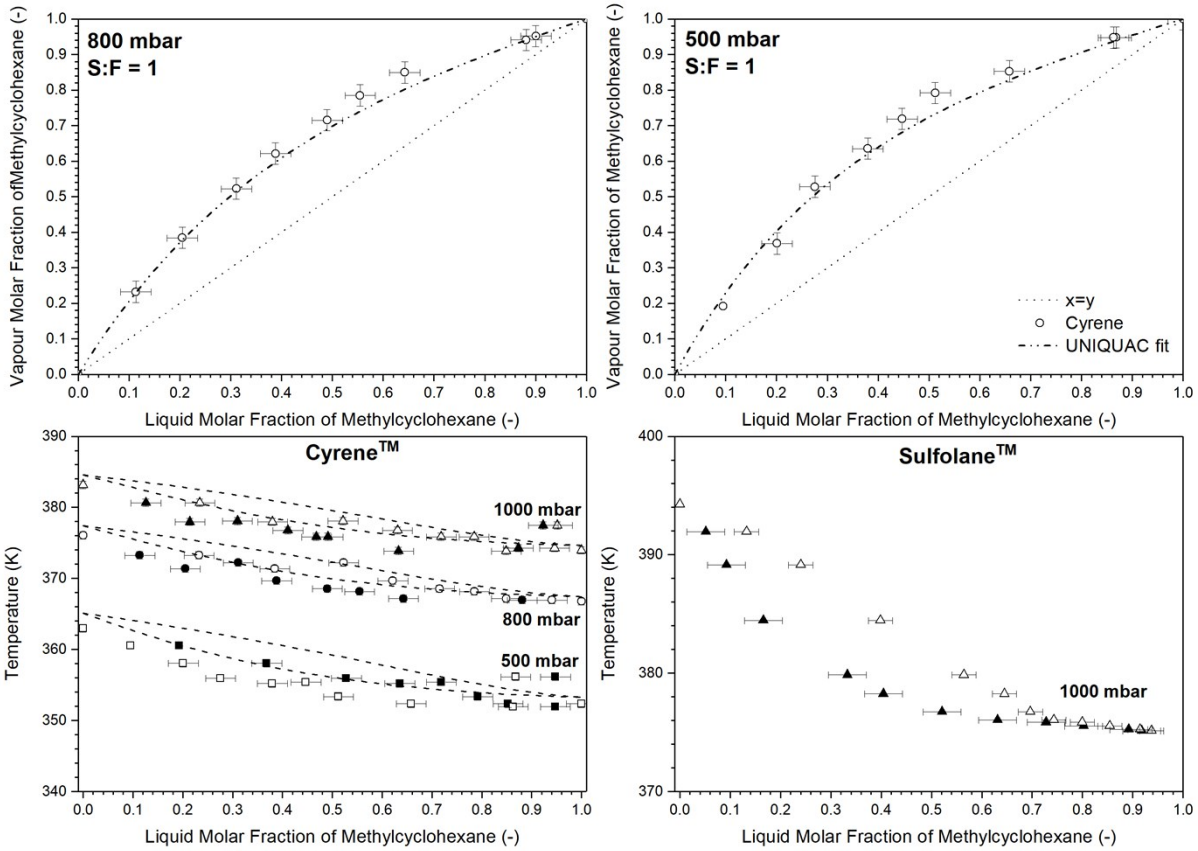

Figure S1: (upper) The xy-diagram of methylcyclohexane and toluene in a solvent to feed (mass basis) of 1 with Cyrene™ at 800 mbar and 500 mbar. (lower) Also the temperature profile of methylcyclexane and toluene in a solvent to feed (mass basis) of 1 with Cyrene™ at 1000 mbar, 800 mbar and 500 mbar and Sulfolane™ at 1000 mbar. The open symbols indicate gas composition, while the closed symbols indicate liquid composition.

3. UNIQUAC Fit Parameters

The UNIQUAC model required the Van der Waals area (r_i) and volume (q_i) of each component. These parameters are known for methylcyclohexane and toluene, however not of Cyrene™. The unknown parameters are estimated with Density Functional Theory with a B3LYP 6-311+G** parameterization in combination with the methodology of Banerjee et al.[1]

Table S2: Van der Waals area (r_i) and volume (q_i) of each component for the UNIQUAC correlation

Component	r_i	q_i	(ref)
Methylcyclohexane	5,174	4,396	[2]
Toluene	3,920	2,970	[3]
CyreneTM	4,843	3,322	-

The fitting of both models resulted in the following parameters.

Table S3: The parameters associated with the UNIQUAC fitting procedure

UNIQUAC							
I	**J**	a_{ij}	a_{ji}	b_{ij}	b_{ji}	c_{ij}	c_{jj}
Methylcyclohexane	**Cyrene™**	-7.904	15.97	533.5	-418.1	1.022	-2.592
Toluene	**Cyrene™**	76.88	-13.22	815.3	-799.8	-13.59	2.666
Methylcyclohexane	**Toluene**	$1.983 \cdot 10^{-1}$	$-4.047 \cdot 10^{-2}$	-93.56	5.613	(-)	(-)

* The pure component vapor pressure of Cyrene™ has been used from. [4]

4. Stability Test using 1H-NMR of Cyrene™

The stability of Cyrene™ was evaluated by comparing fresh Cyrene™ with Cyrene™ which has been reclaimed after experimentation and purified via rotary evaporation. Additionally, the reclaimed Cyrene™ was stored for over 9 months. The results of the 1H-NMR spectrum, the samples were diluted in D-chloroform, are shown in Figure S2.

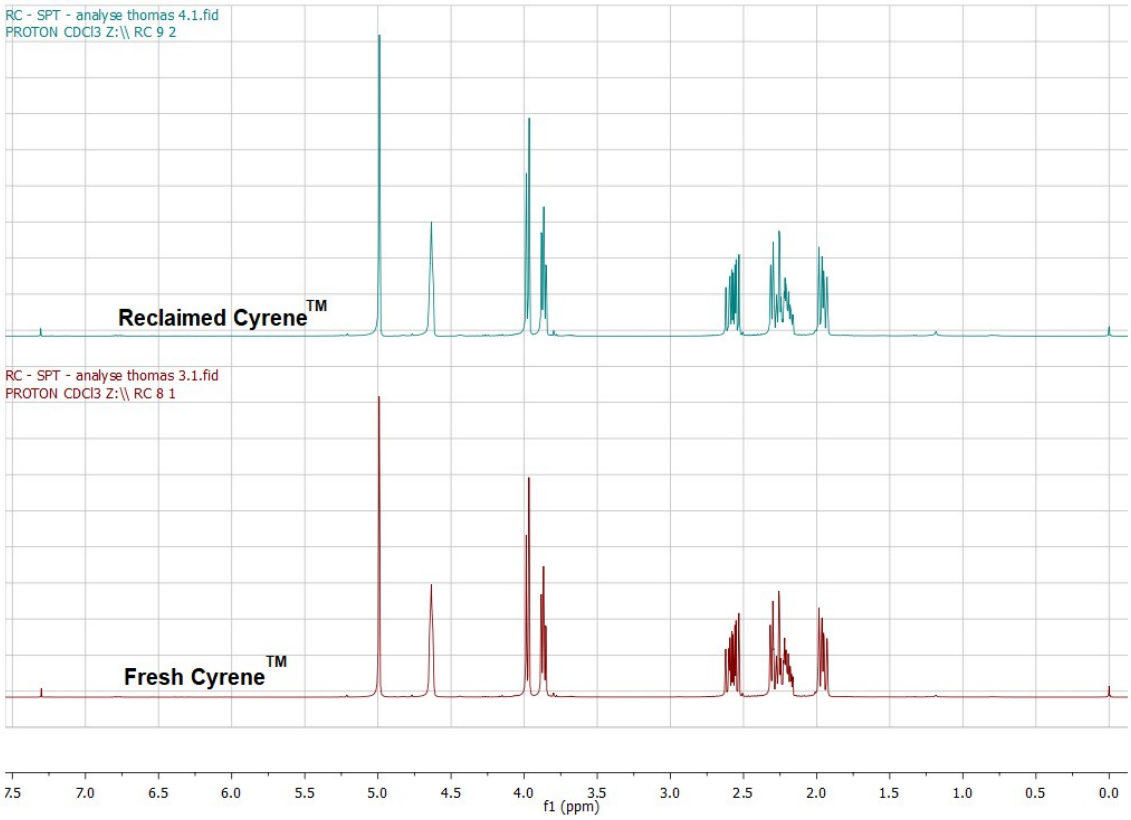

Figure S2: The ^{1}H-NMR spectra of fresh (below) and reclaimed (upper) Cyrene™ diluted in d-chloroform.

5. References

1. Banerjee, T., et al., *Volume, surface and UNIQUAC interaction parameters for imidazolium based ionic liquids via polarizable continuum model.* Fluid Phase Equilibria, 2005. **234**(1-2): p. 64-76.
2. Chen, D., H. Ye, and H. Wu, *Liquid–liquid equilibria of methylcyclohexane–benzene–N-formylmorpholine at several temperatures.* Fluid phase equilibria, 2007. **255**(2): p. 115-120.
3. Gupta, S., et al., *Isobaric vapour—liquid equilibria of the systems: Benzene—triethylene glycol, toluene—triethylene glycol and benzene—N-methylpyrrolidone.* Fluid phase equilibria, 1989. **46**(1): p. 95-102.
4. Baird, Z., et al., *Vapor pressures, densities, and PC-SAFT parameters for 11 bio-compounds.* 2019.