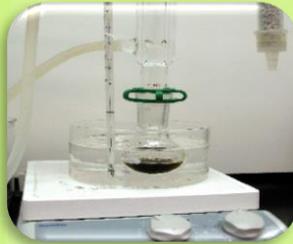
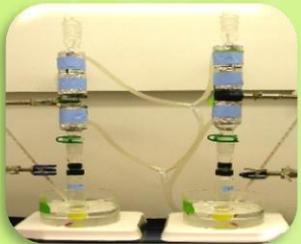
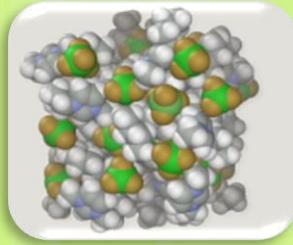




Co-Recovery of Lipids, Fermentable Sugars, and Protein from Bio-oil Bearing Biomass using Ionic Liquid co-Solvents

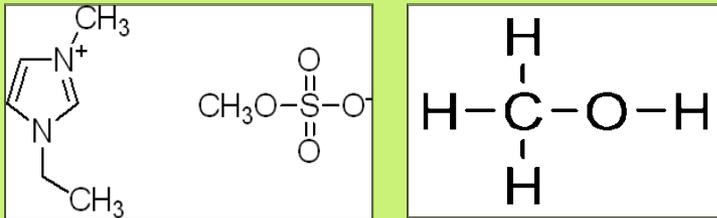


**Dr. Michael Cooney, &
Dr. Godwin Severa**

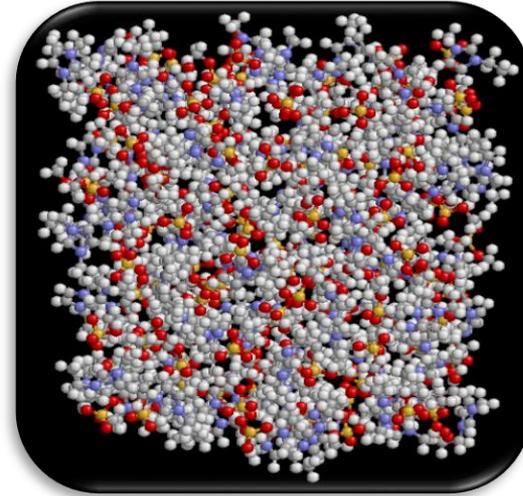
Hawaii Natural Energy Institute, University of
Hawaii at Manoa, Honolulu HI.



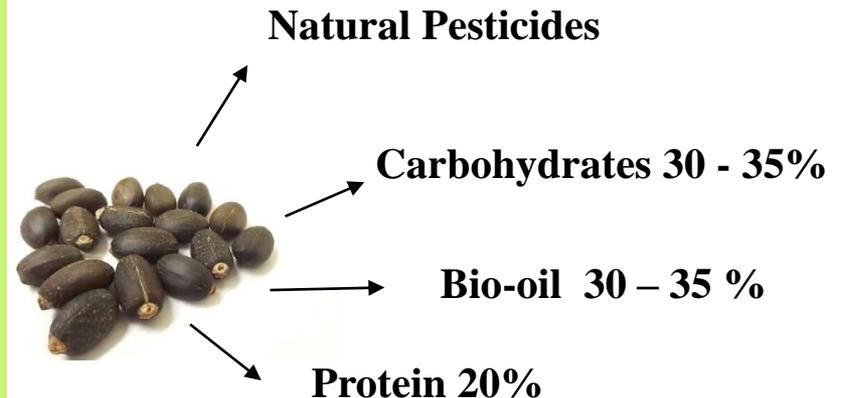
- IL co-solvents



- Characterized by heterogeneous distribution of charge and hydrophobic – hydrophilic regions at molecular scale
- Emerging solvent platform
- US Patent [US20090234146](#)



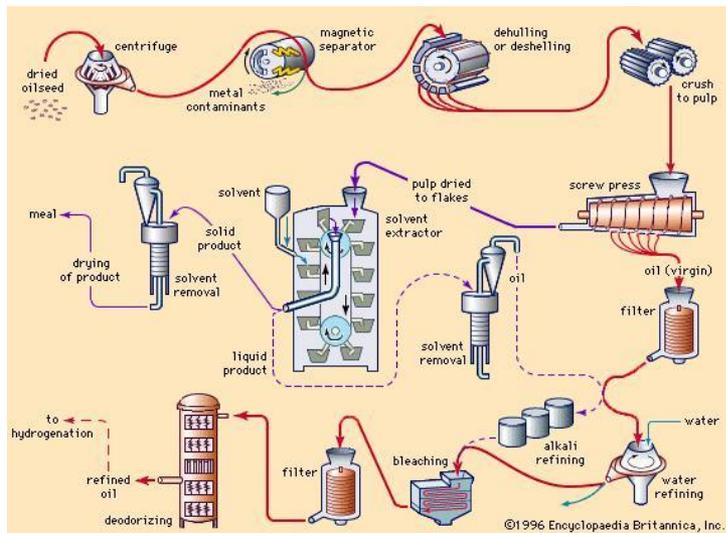
Application to Jatropha





- Mechanical pressing with a hydraulic or single expeller press¹.
- Generally achieves yields less than 80%. In the case of mechanical pressing the residual oil left in the oil cake may be anywhere from 6% to 14%
- The seedcake can be subjected to a different number of extractions through the expeller².
- The combination of these operations can produce oil extraction can yield up to 98% with residual oil content in cake meal of 0.5–1.5%³.
- There are problems, however. Screw presses induce friction, causing overheating, high energy consumption, and oil deterioration. Single-screw presses also provide insufficient crushing and mixing if they are not equipped with breaker bars, or other special equipment⁴.

Conventional



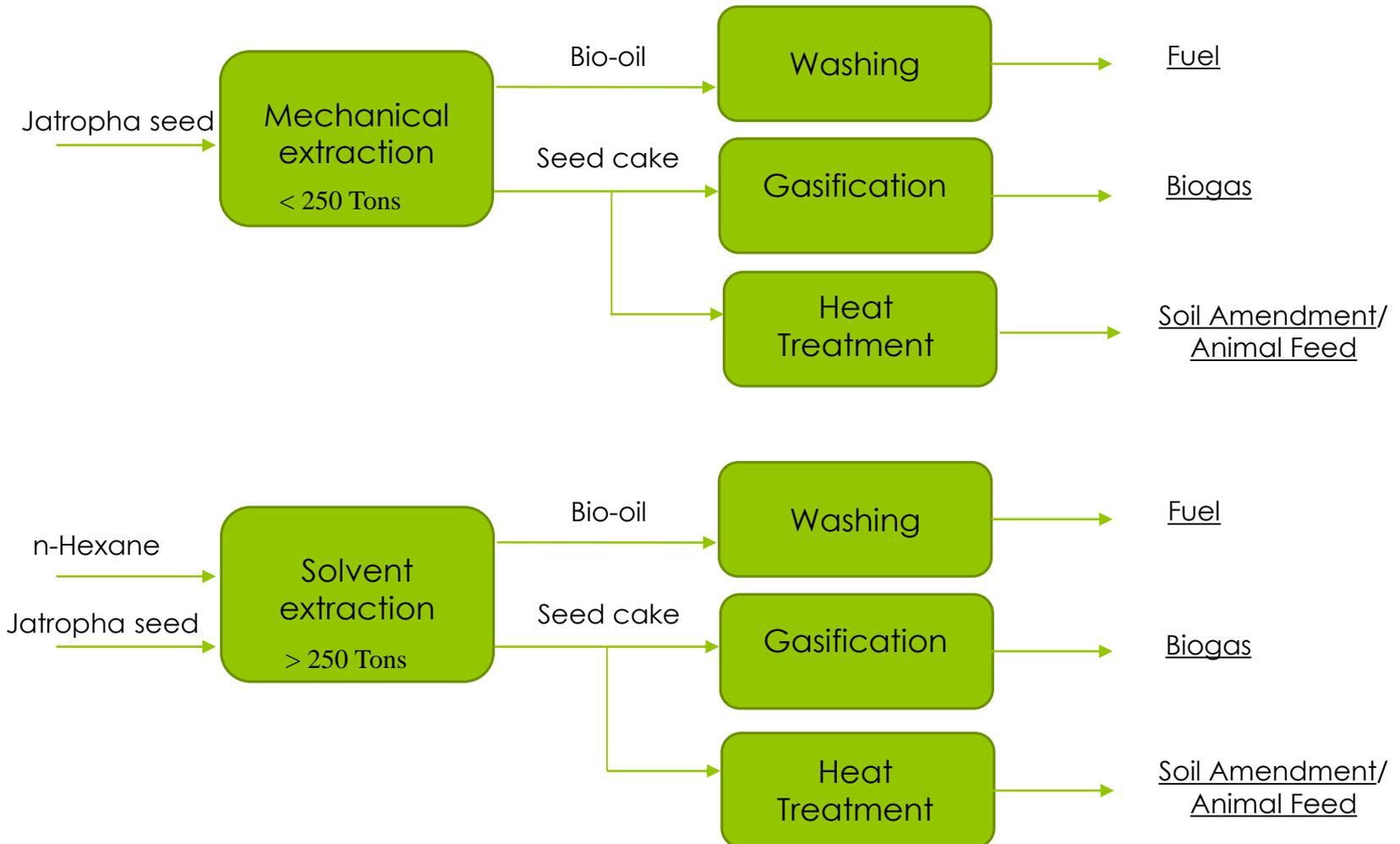
- The solvent extraction most commonly used today is percolation extraction with a countercurrent flow using hexane as a solvent⁵.
- The solvent extraction method recovers almost all the oils and leaves behind only 0.5% to 0.7% residual oil in the raw material.
- Solvent extraction is only economical at a large-scale production of more than 50 t bio-diesel per day.
- *n*-hexane solvent extraction possesses negative environmental impacts (generation of waste water, higher specific energy consumption and higher emissions of volatile organic compounds) and human health impacts (working with hazardous and inflammable chemicals)⁶.

Conventional

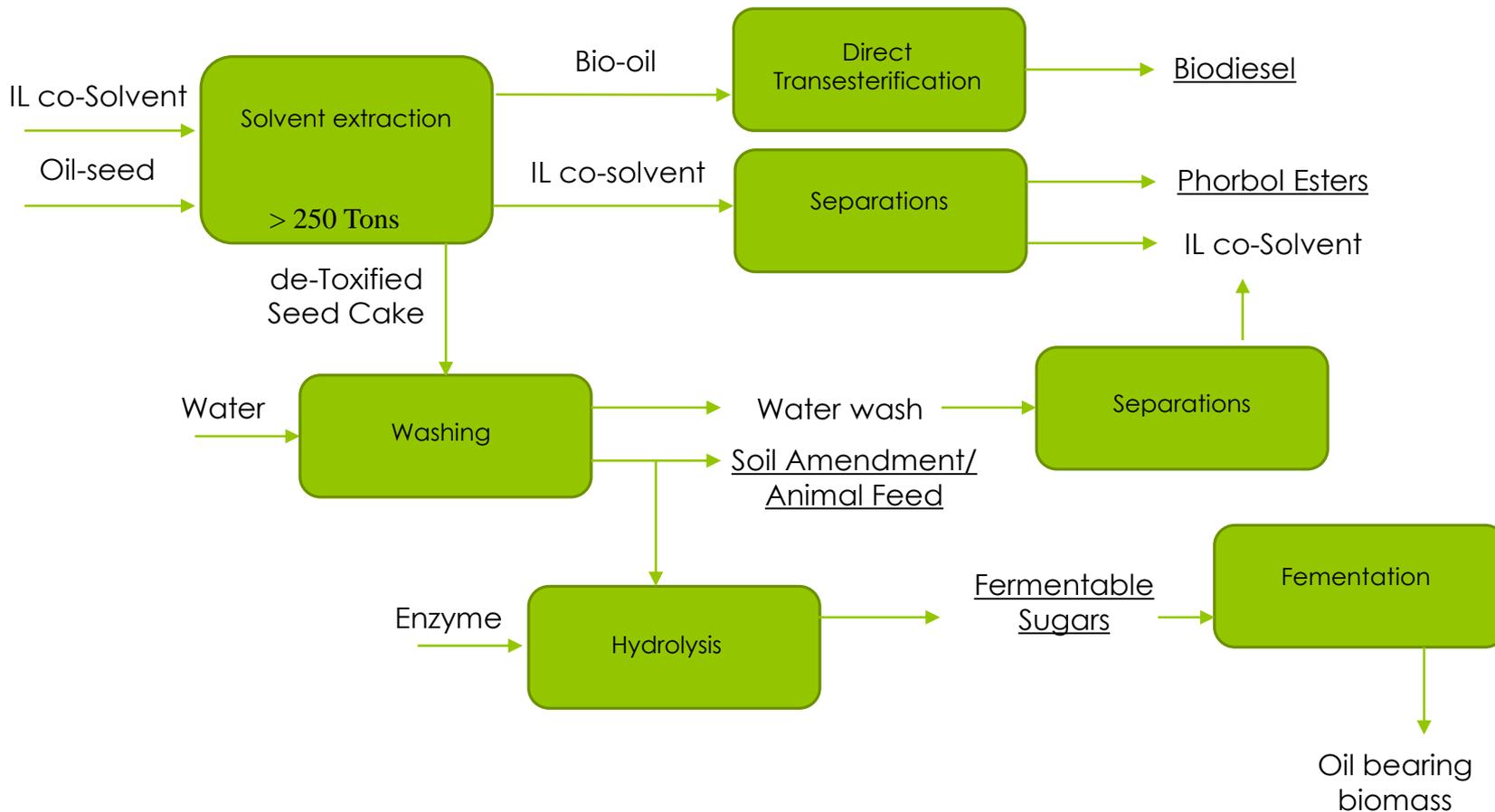
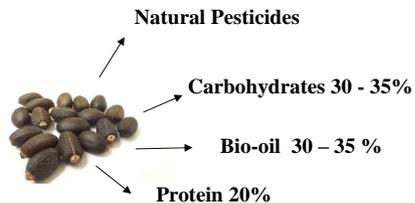


- New generation *n*-hexane extraction units are very efficient and produce far less environmental burdens than the older units,
- *n*-hexane extraction does not detoxify the seedcake, however.
- Due to its toxic nature, the seed cake must be used for animal feeding nor can be used in agricultural farming⁷.
- Seed cake can be used for energy production - 93.8% total solid (TS) out of which 92.5% is volatile solid (VS). The cake is high in organic matter and has good potential for biogas generation⁸.

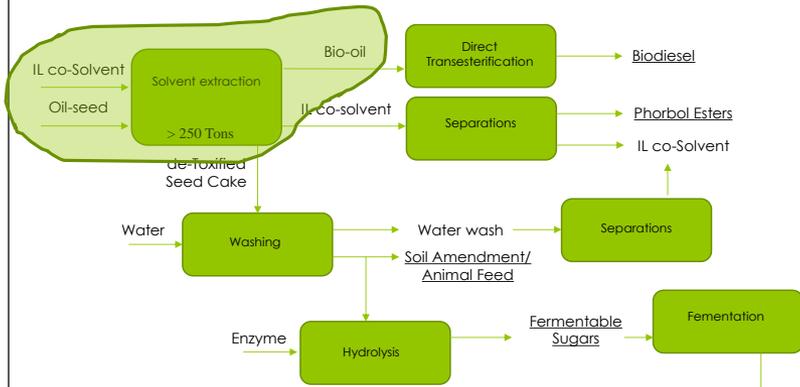
Conventional



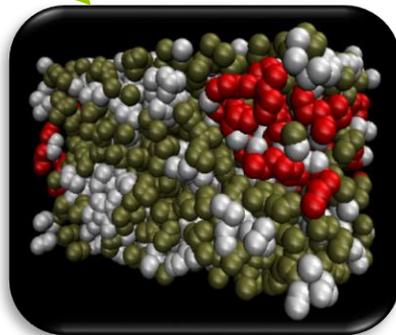
IL solvent pathway



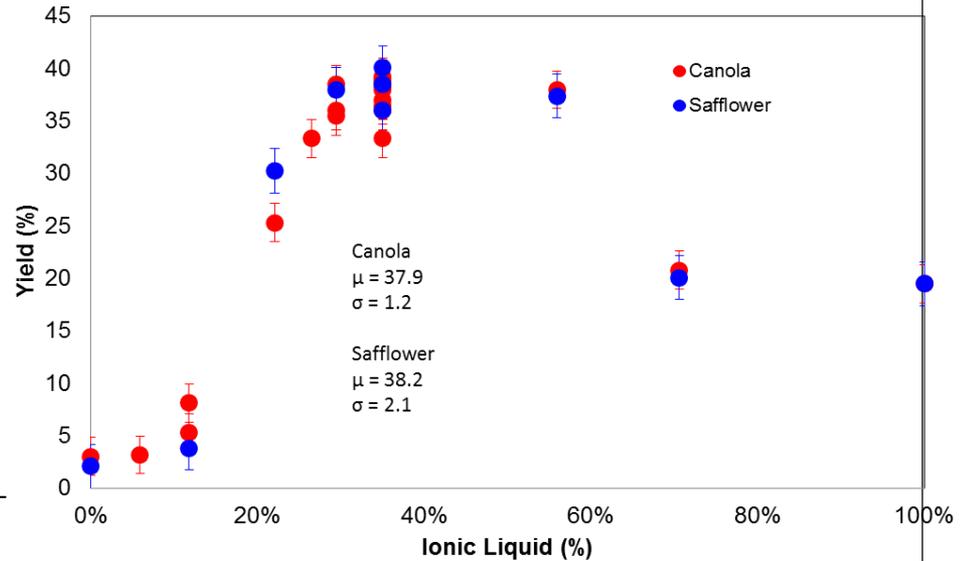
Bio-oil extraction



Visualization of macro-scale lipid aggregate formed in [EMIN] [MeSO₄]-methanol mixture.



Visualization of molecular-scale lipid aggregate formed in [EMIN] [MeSO₄]-methanol mixture.



Yield of bio-oil from oil seeds as a function of IL/co-solvent ratio

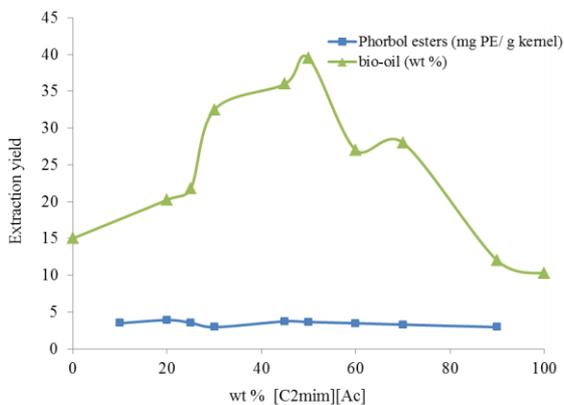
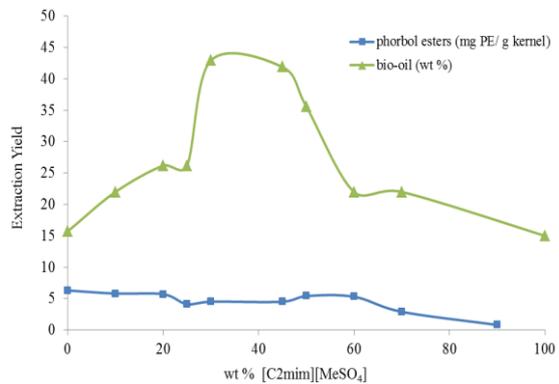
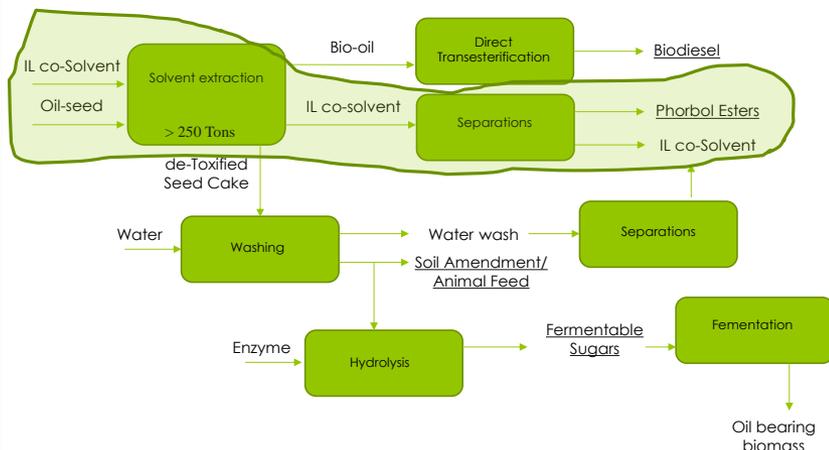
Table 2. The effect of PCM on extraction

PCM	Yield (wt %)*	Comments
Dimethyl sulfoxide	6.0	Low yield, highly viscous product
Acetic Acid	5.6	Low yield, highly viscous product
Methanol	7.9	Baseline PCM
Acetone	9.2	High yield, with a solid precipitate
Chloroform	8.4	High yield, with a solid precipitate
Isopropyl Alcohol	8.5	Product very similar to methanol

*The biomass used in this study, *Dunaliella* microalgae, had a lipid content of approximately 8-11% (wt %).

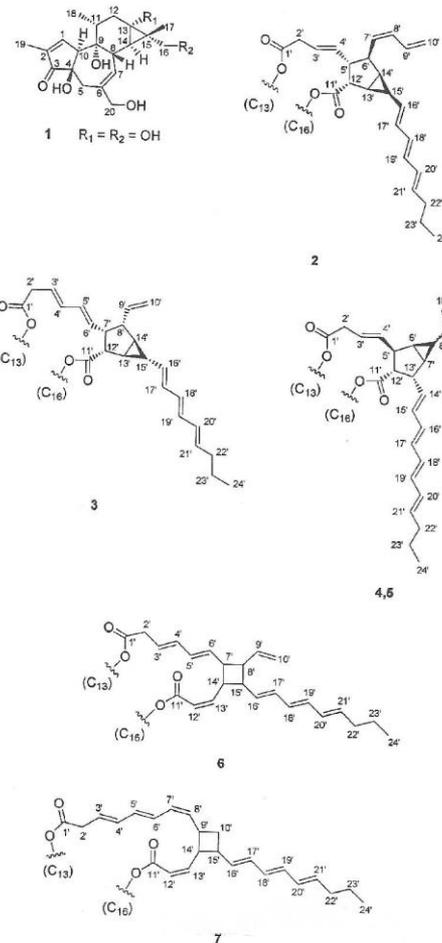
Red = Lipid Green = Methanol White = IL

Phorbol Esters

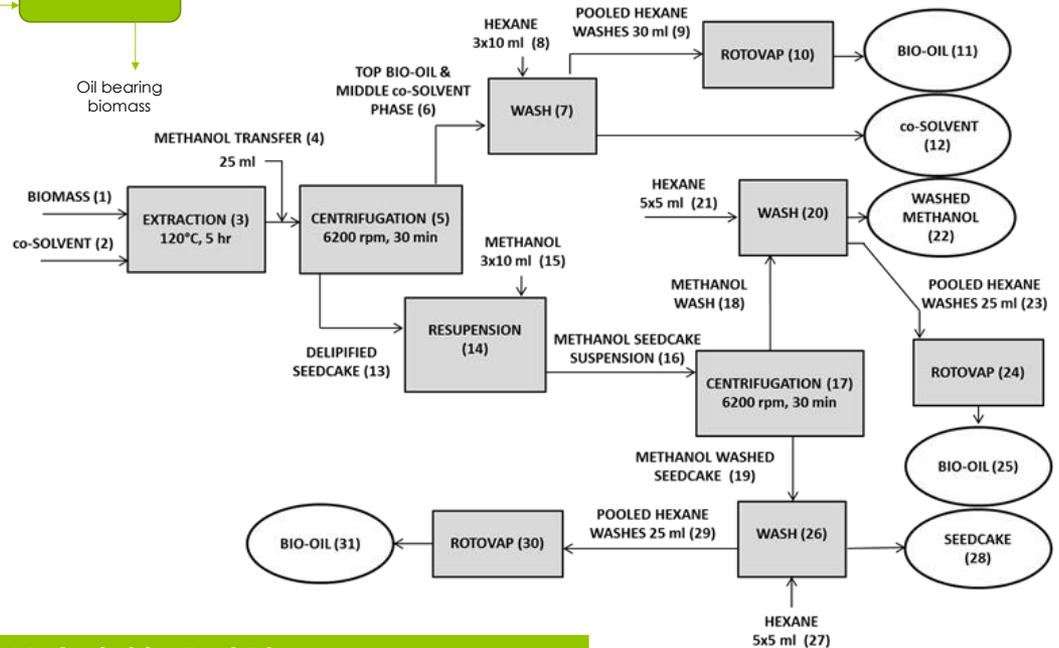
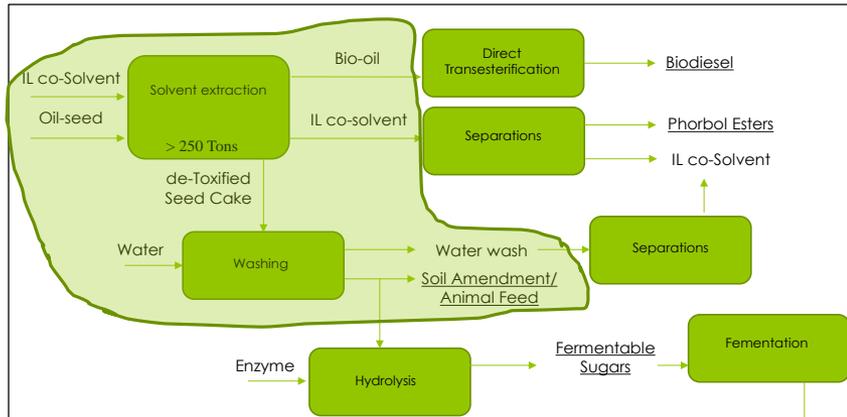


Yields of extracted phorbol esters and bio-oil as a function of [C2mim][MeSO₄] weight %.

Yields of extracted phorbol esters and bio-oil as a function of [C2mim][Ac] weight %.



Nitrogen Tracking

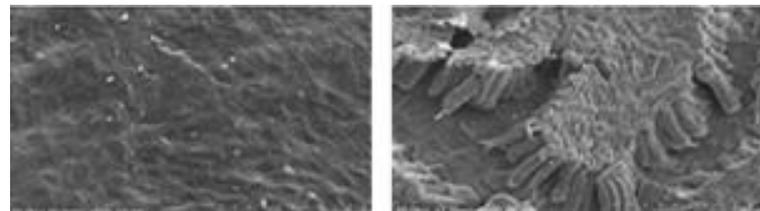
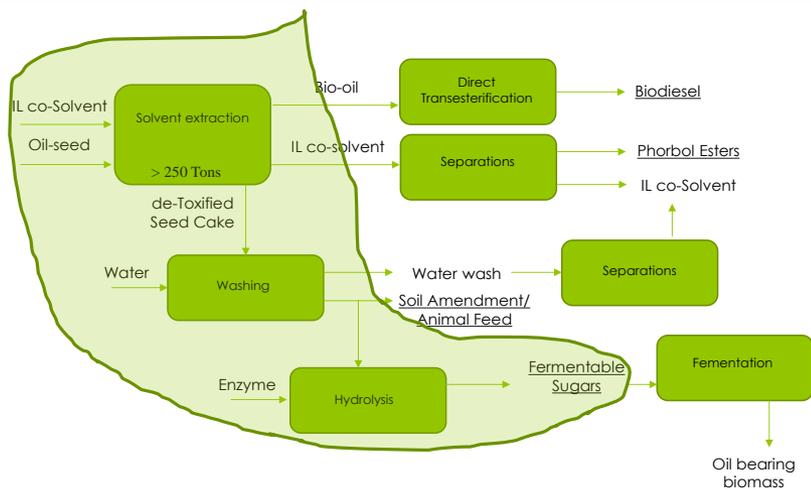


Treatment Pathway for nitrogen tracking

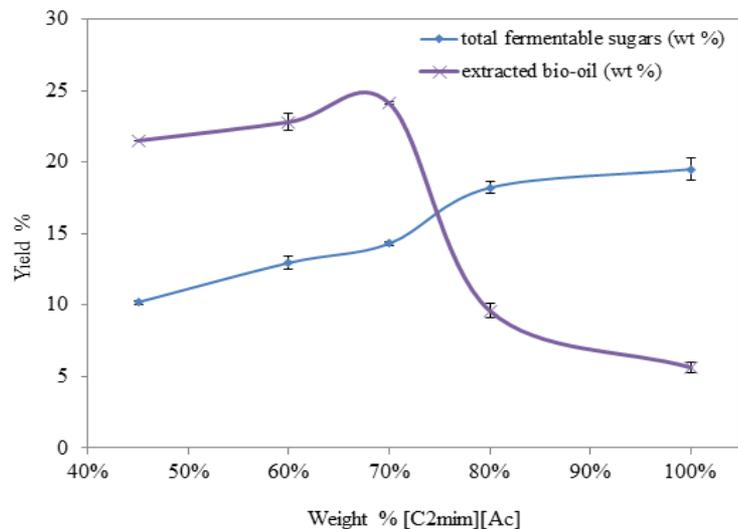
Table 1. Percent of Starting Material in End Phases

	Bio-oil (11)	Co-solvent (12)	Washed Methanol (22)	Bio-oil (25)	Bio-oil (31)	Seed Cake (28)	Total
Protein (BM) (%)¹:	0	12	1.3	0	0.004	86.6	99.9
Lipid (BM) (%)²:	55	0	0	14.9	20.6	0	90.5
Ionic liquid (CS) (%)³:	0.04	59.4	9.4	0.04	0	31	99.88

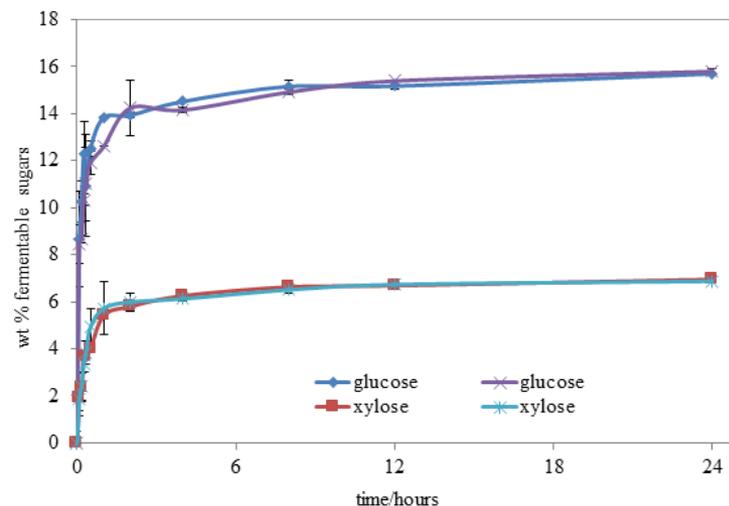
Carbohydrate Hydrolysis



Jatropha shell before and after IL co-solvent treatment

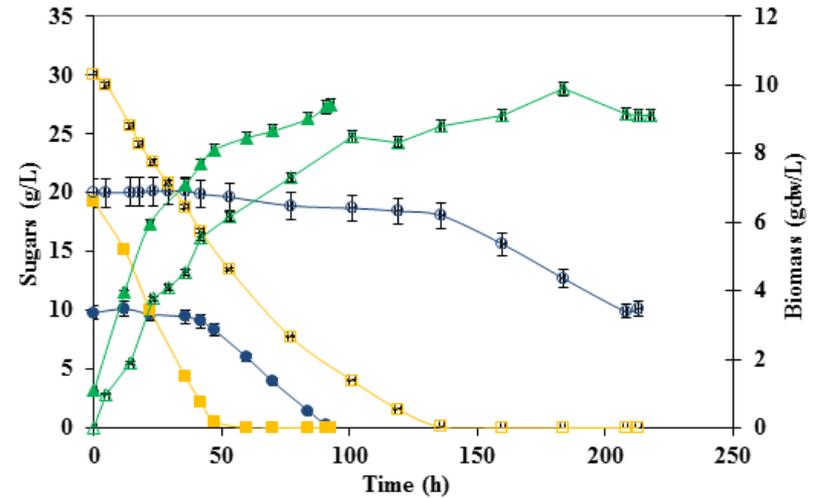
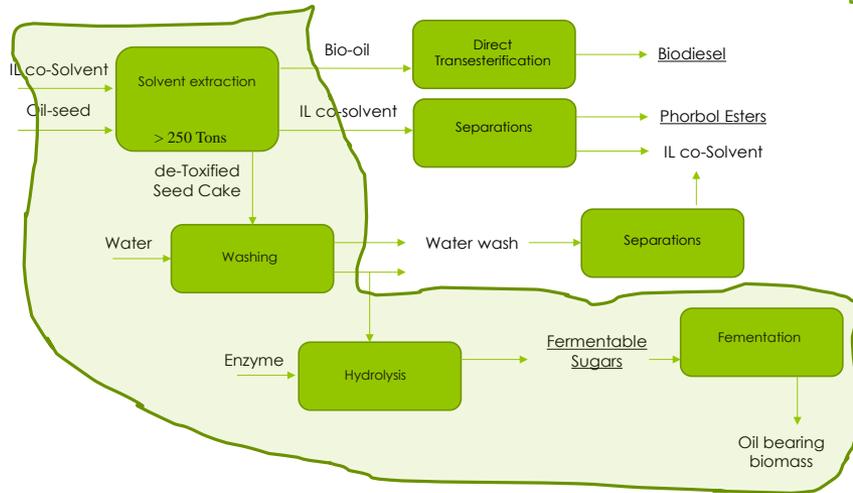


Total fermentable sugars and bio-oil yields relative to weight of whole seed obtained from pretreated *jatropha* whole seed (kernel plus shell) at different concentrations of [C2mim][Ac].



Effect of ionic liquid concentration on hydrolysis kinetics of *safflower* whole seed, using pure and 70 wt% [C2mim][Ac] at 120°C.

Fermentable sugars recycle



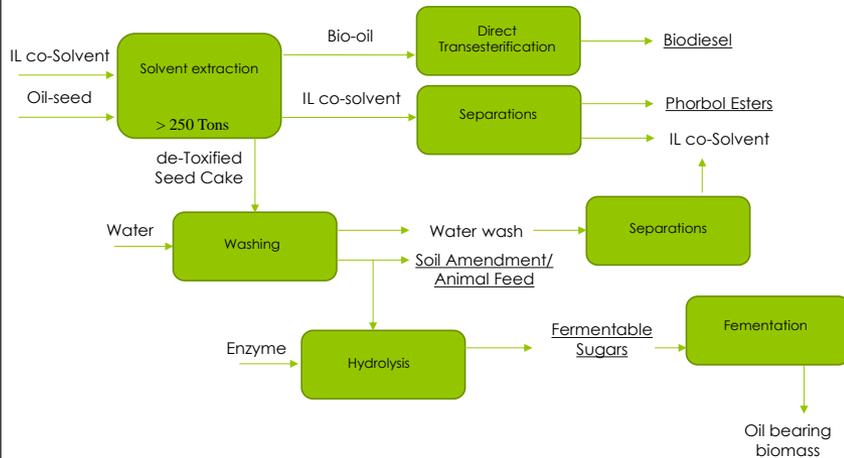
Biomass production and carbohydrate consumption by *R. toruloides*: batch one (open symbols) and batch two (closed symbols). Circles: xylose; Squares: glucose; triangles: cell mass.



Batch fermentation data

Batch	Cell mass	Cell mass fermentable sugars		Cell mass to lipid yield ($Y_{P/X}$)	Substrate to lipid yield ($Y_{P/S}$)
	(gdw/L)	Glucose % (w/w) ¹	Mannose % (w/w) ¹	% (w/w) ¹	(g/g)
1	9.1 (±0.2)	8.6 (±0.2)	0.9 (±0.1)	60.5 (±1.5)	0.12 (±0.07)
2	9.4 (±0.2)	9.8 (±0.2)	1.4 (±0.1)	57.4 (±0.3)	0.16 (±0.07) ²

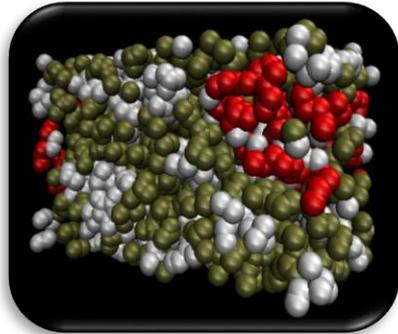
Summary



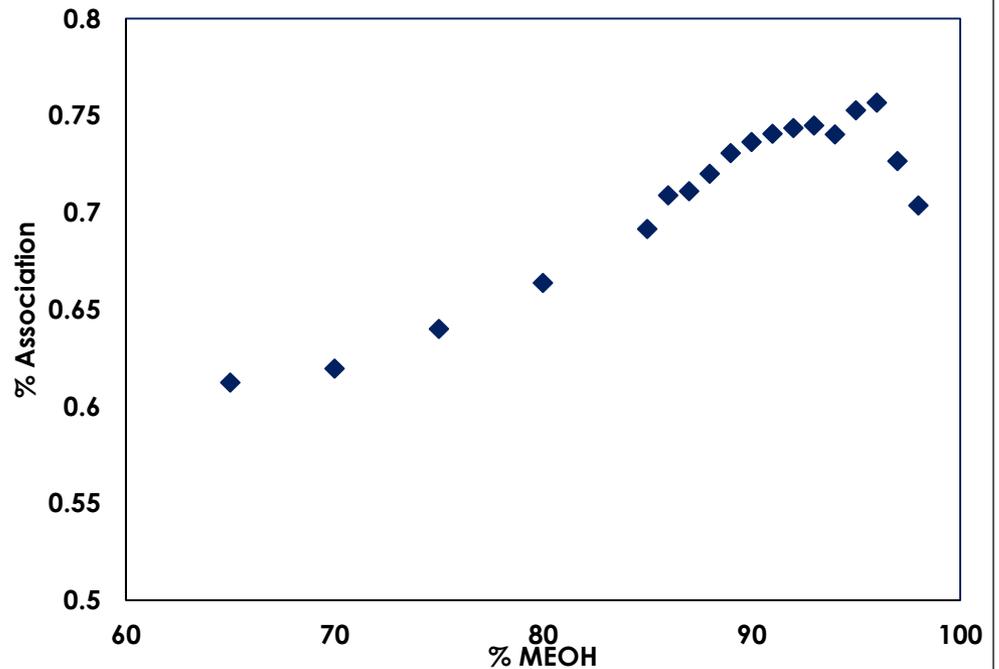
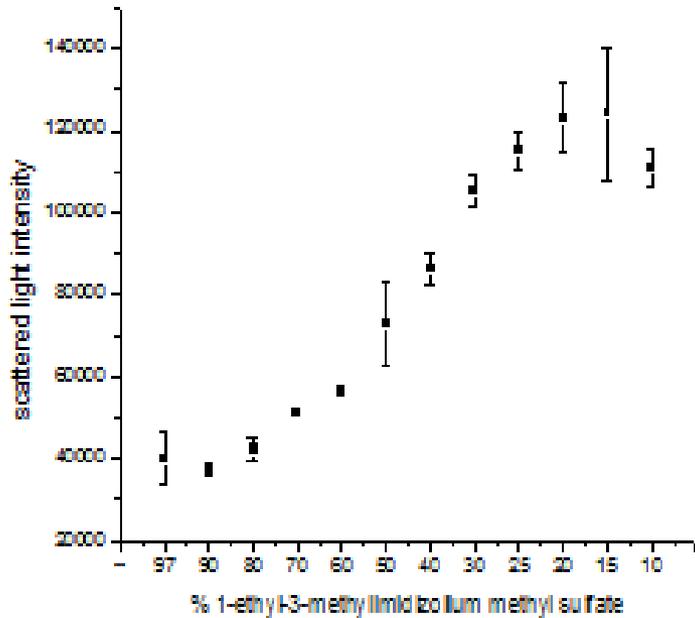
- IL co-solvents offer unique opportunities to expand treatment of bio-oil seeds.
- Co-solvents expand the number of solvent properties achieved at the molecular scale.
- By changing the nature of the polar co-solvent molecule, or the identify of the cation or anion, co-solvent systems can be tailored for uniuqe applications.

- The combination of methanol and hydrophilic IL's with a strong hydrogen bond disrupter provide a unique combination to extract and separate bio-oil as well as to pretreat biomass.
- The heterogeneous distribution of charge and hydrophobic/hydrophilic regions within the micro-scale solvent structure offers ability to extract and absorb polar molecules.
- IL co-solvents permit a novel platform to expand upon the products available from bio-oil bearing biomass

Related work



Red = Lipid
Green = Methanol
White = IL ions



(Left) scattered light intensity as function of concentration of MEOH,
(right) clustering analysis of the same

Courtesy: Ken Benjamin SDSM&T

Funding:

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Collaborators:

Greg Young, Guneet Kumar, Franz Nippgen, Sebastian Titterbrand, Melisa Imbrahovic.

Presentation

- ¹Amalia Kartika et al, 2010. Twin-screw extruder for oil processing of sunflower seeds: Thermo-mechanical pressing and solvent extraction in a single step. *Industrial Crops and Products* 32 (2010) 297–304.
- ²Acthen et al, 2008. *Jatropha* bio-diesel production and use. *Biomass and Bioenergy*. 33(12):1063-1084.
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- ⁵Hu, W, Wells, J.H., Tai-Shun Shin, Godber, J.S., 1996. Comparison of isopropanol and hexane for extraction of vitamin E and oryzanols from stabilized rice bran. *J. Am. Oil Chem. Soc.* 73, 1653–1656.
- ⁶T. Adriaans, 2006. Suitability of solvent extraction for *Jatropha curcas*. Eindhoven: FACT Foundation, 9.
- ⁷Pant et al, 2015. Utilization of biodiesel by-products for mosquito control. *Journal of Bioscience and Bioengineering*. In Press.
- ⁸Singh et al, 2008. SPRERI experience on holistic approach to utilize all parts of *Jatropha curcas* fruit for energy. *Renewable Energy* 33 (2008) 1868–1873.

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- Severa, G., G. Kumar, and M. J. Cooney[✉]. **2014**. Co-Recovery of lipids and fermentable sugars from *Rhodospiridium toruloides* using ionic liquid co-solvents: Application of recycle in batch fermentation. *Journal of Biotechnology Progress*. DOI: 10.1002/btpr.1952.
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- Young, G., Nippgen, F., Titterbrandt, S., and M. J. Cooney[✉]. **2010**. *Lipid extraction from biomass using co-solvent mixtures of ionic liquids and polar covalent molecules*. *Separation and Purification Technology*. 72(1): 118-121.

QUESTIONS?

