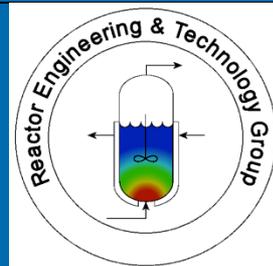




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Process Intensification for Advanced Biodiesel Production from Residual Oils

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Biodiesel

- ✦ Australia is dependent on crude oil for 97% of its transport fuels.
- ✦ Biodiesel (BD) can be used as a substitute for, or blended with petrodiesel.
- ✦ Offers several advantages:
 - ✦ Renewable – produced from plant oils
 - ✦ 80% lower net CO₂ emissions
 - ✦ Provides market for waste/inedible oils
- ✦ BD uptake hampered by high feedstock and production costs



Biodiesel

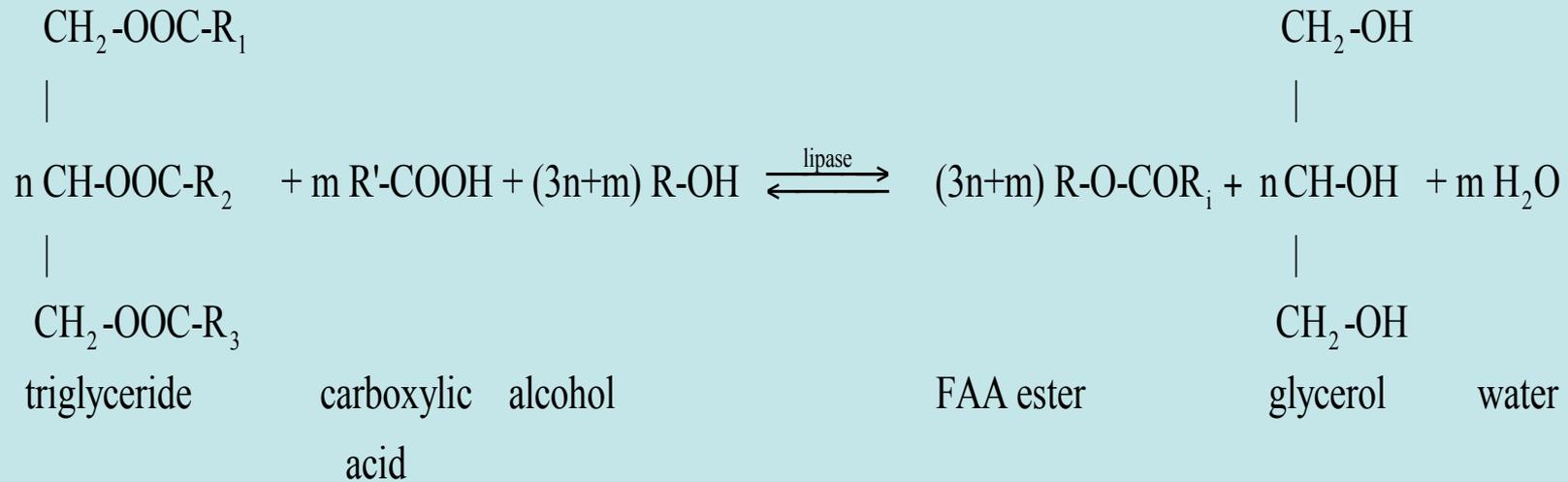
- ✦ Food-energy security issues necessitates the use of alternative oleaginous feedstock for BD production.
- ✦ The 4 types of non-edible oil feedstock are:
 - ✦ Animal fats
 - ✦ Brown & yellow greases
 - ✦ Microalgae lipids
 - ✦ Waste cooking oils

Oils contain – glycerides (MG, DG, TG) + FFAs + non-saponifiables

Enzymatic Biodiesel Production

- ✿ Lipase immobilised on solid support.
- ✿ 100% selectivity to biodiesel – esterification and transesterification, no soap formation.
- ✿ Can cope with low quality (high FFA) feedstocks, e.g. waste cooking oil, without pre-treatment.
- ✿ Low temperature, low alcohol to oil ratio.
- ✿ Disadvantages
 - ✿ High cost of enzyme.
 - ✿ Slow reaction relative to inorganic catalysts.

The lipasic alcoholysis of oils may be written:



Process Intensification

- ✿ Both transesterification and esterification involved in BD production are equilibrium-limited.
- ✿ BD synthesis rate may be mass transfer-controlled since oils and alcohols are essentially immiscible. Products are also distributed across both aqueous and organic phases.
- ✿ Many commercial processes are carried out in batch mode but continuous processing will improve production economics.

Process Intensification

- ☀ Challenges may be addressed via PI
- ☀ PI = any chemical engineering development that leads to a substantially smaller, cleaner and more energy-efficient technology¹.

In the present system, the following benefits accrue:

- ☀ Reduction in capital and operating costs thro' continuous reactor operation.
- ☀ Reduction in downstream purification steps – reaction and separation combined in a single unit.
- ☀ Use of crude bioethanol (~15%v/v EtOH) as solvent.

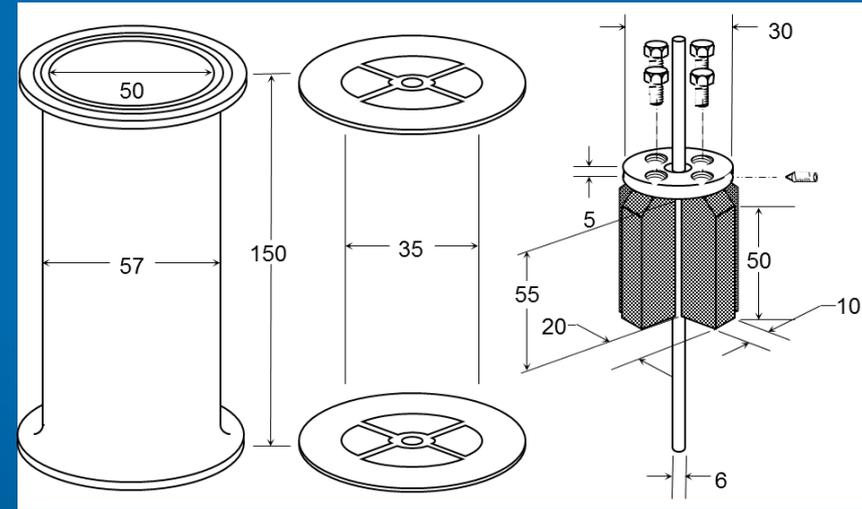
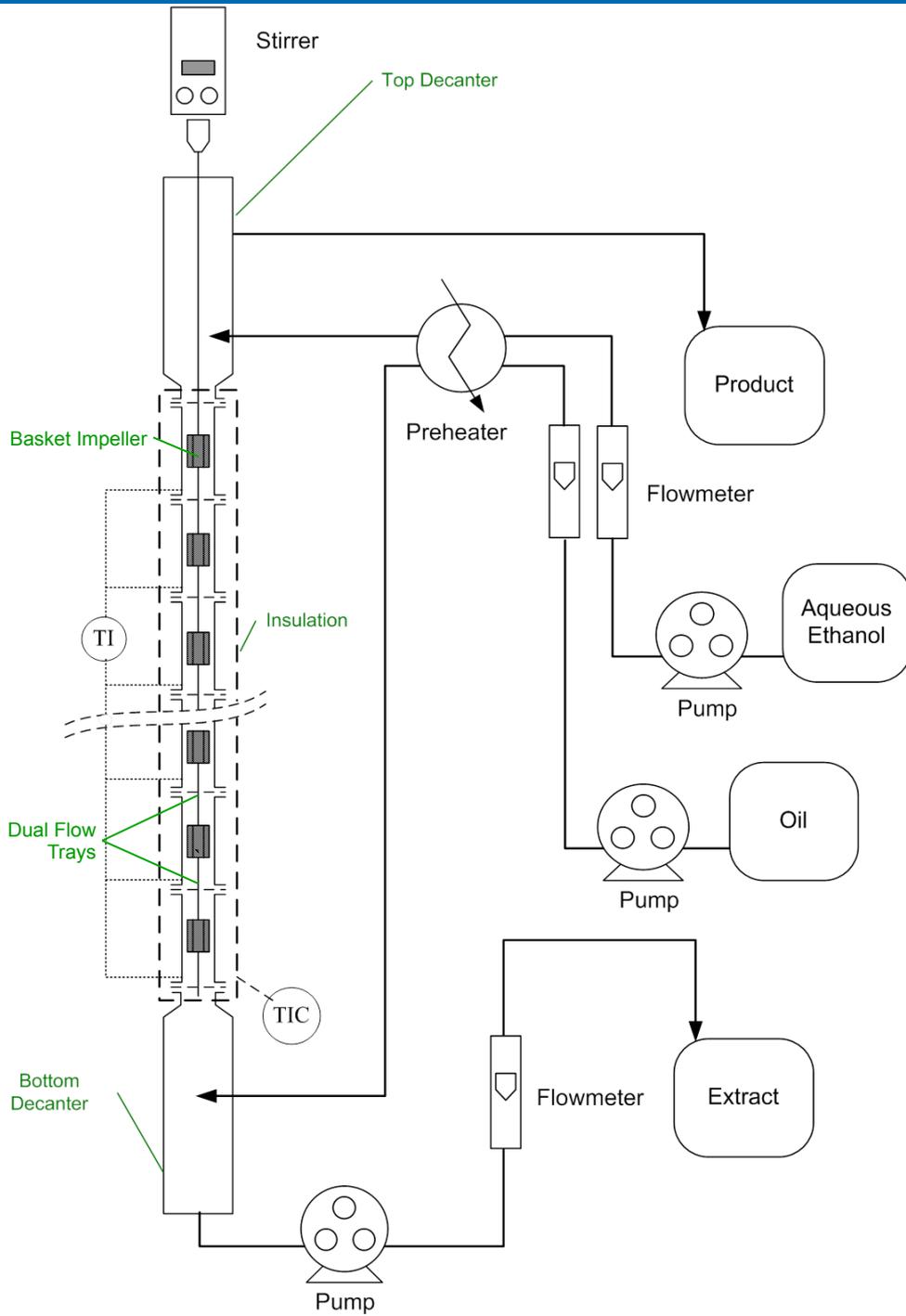
1. Ponce-Ortega, JM, Al-Thubaiti, MM & El-Hawagi, MM, Chem. Eng. Proc. PI, 53 (2012) 63.

Extractive Reaction

- ✿ Liquid-liquid extractive reactor could improve commercial feasibility via:
 - ✿ Enhanced biodiesel yield – by-product glycerol is removed into extract phase.
 - ✿ Faster reaction rate – water improves lipase activity.
 - ✿ Heterogeneous catalyst contained in basket impellers permits the realization of the advantages of both packed bed and slurry reactor operation – solid-liquid separation and superior interphase mass transfer.



Basket Impeller Column (BIC)



Adesina, AA,
Mahmud, MS,
Safinski TS,
Australian
Provisional Patent,
No.2011901903,
2012

Study objectives

- ✦ Biphasic (organic-aqueous) equilibrium studies to delineate regions for enhanced product recovery.
- ✦ Kinetics of lipolytic ethanolysis of spent cooking oil.
- ✦ Steady-state modelling of the extractive reactor system.
- ✦ Experimental verification and optimization.

Properties of waste cooking oil used

Physicochemical Properties

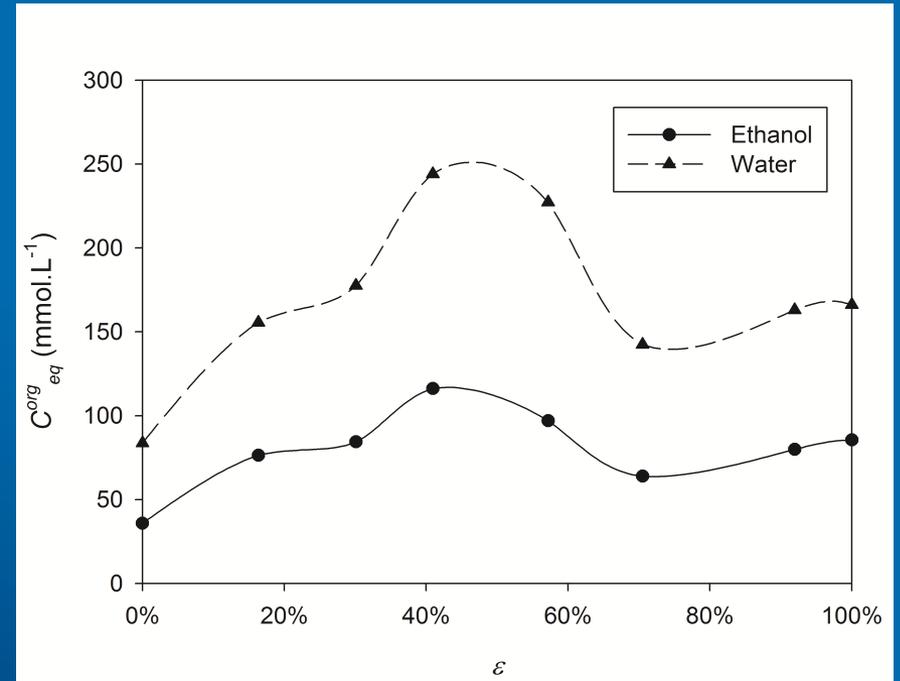
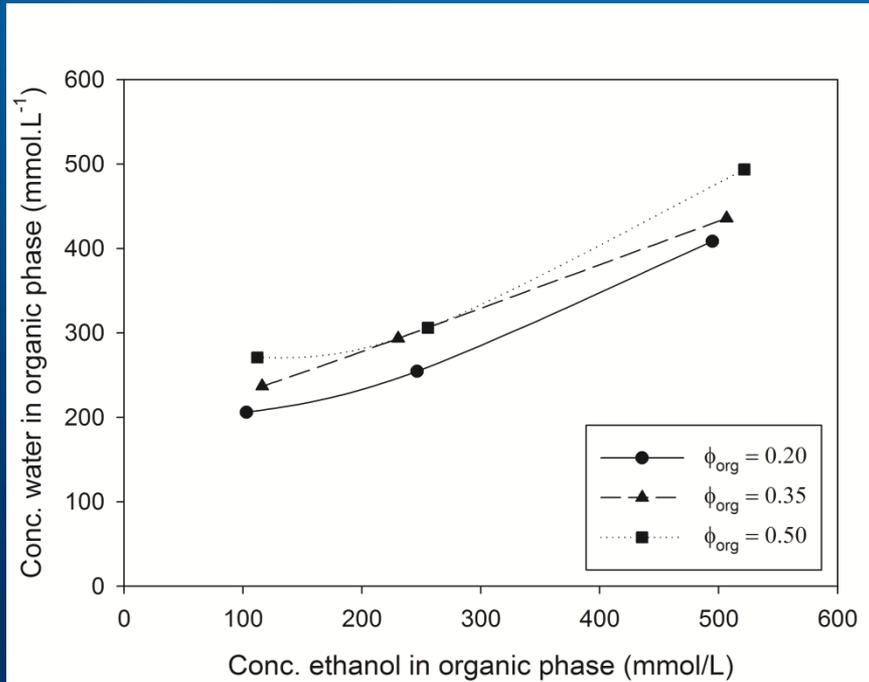
Specific gravity ($\text{kg}\cdot\text{m}^{-3}$ at 293 K)	936
Kinematic Viscosity ($\text{mm}^2\cdot\text{s}^{-1}$ at 318 K)	37.2
Acid Value ($\text{mg}_{\text{KOH}}\cdot\text{g}^{-1}$)	1.10
Saponification Value ($\text{mg}_{\text{KOH}}\cdot\text{g}^{-1}$)	198
Water Content (wt%)	0.0504
Molecular Weight ($\text{g}\cdot\text{mol}^{-1}$)	858

Fatty acid composition (mol%)

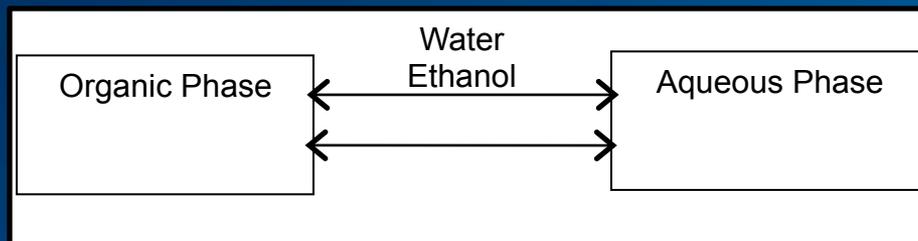
Myristic (C14:0)	0.9
Palmitic (C16:0)	26.9
Stearic (C18:0)	2.1
Oleic (C18:1)	16.4
Linoleic (C18:2)	53.5
Linolenic (C18:3)	0.2

Phase equilibrium

Ethanol and water in the organic phase

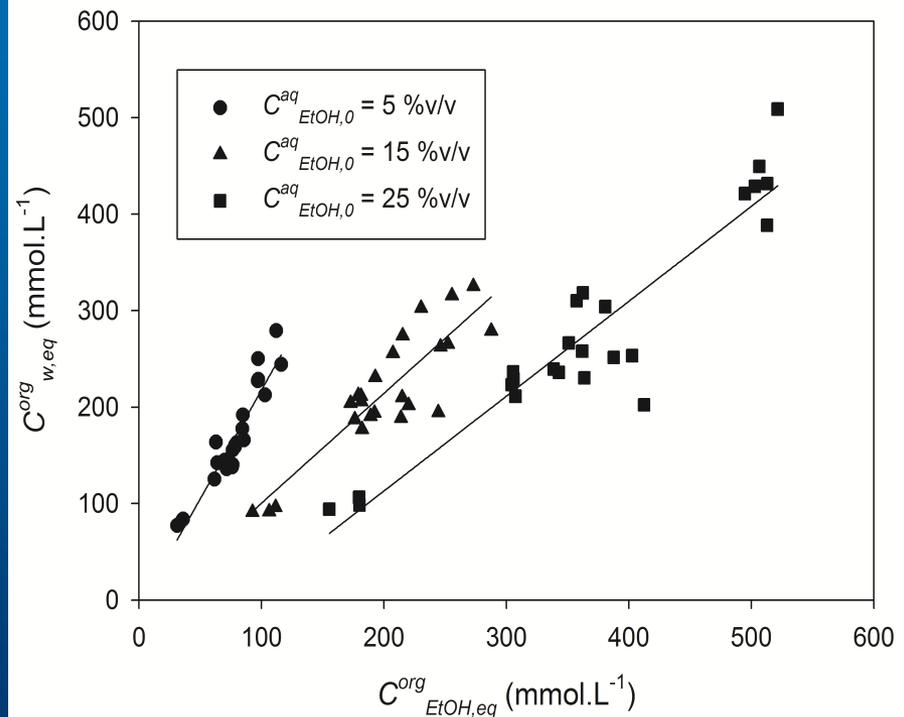
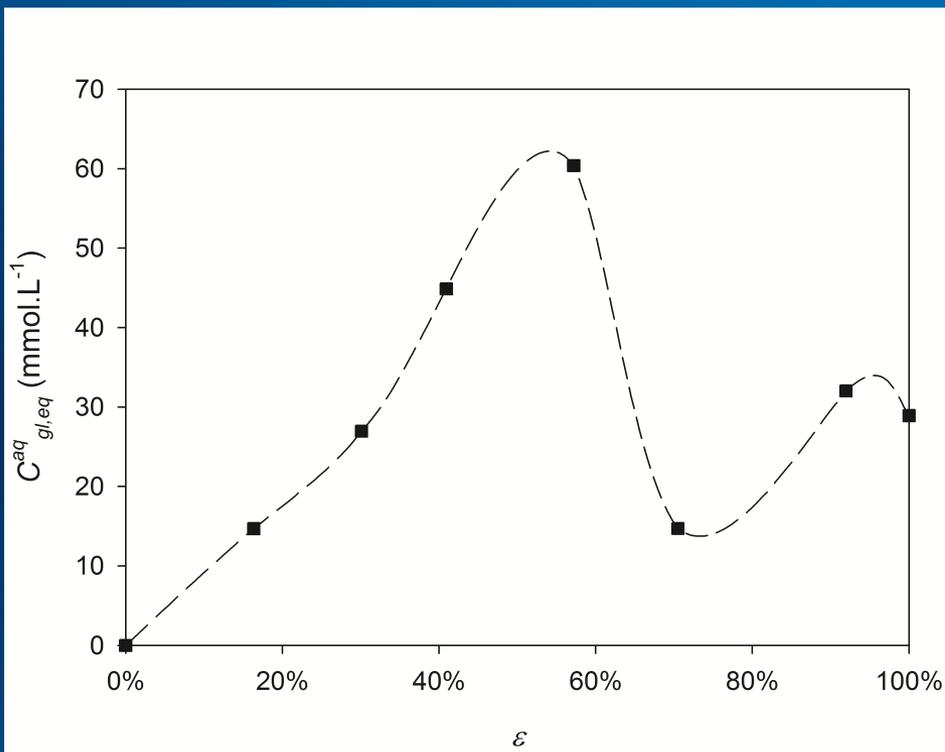


Simplified model for biphasic interaction



Phase equilibrium

(a). Glycerol conc the organic phase and (b) the relationship between ethanol & water conc.



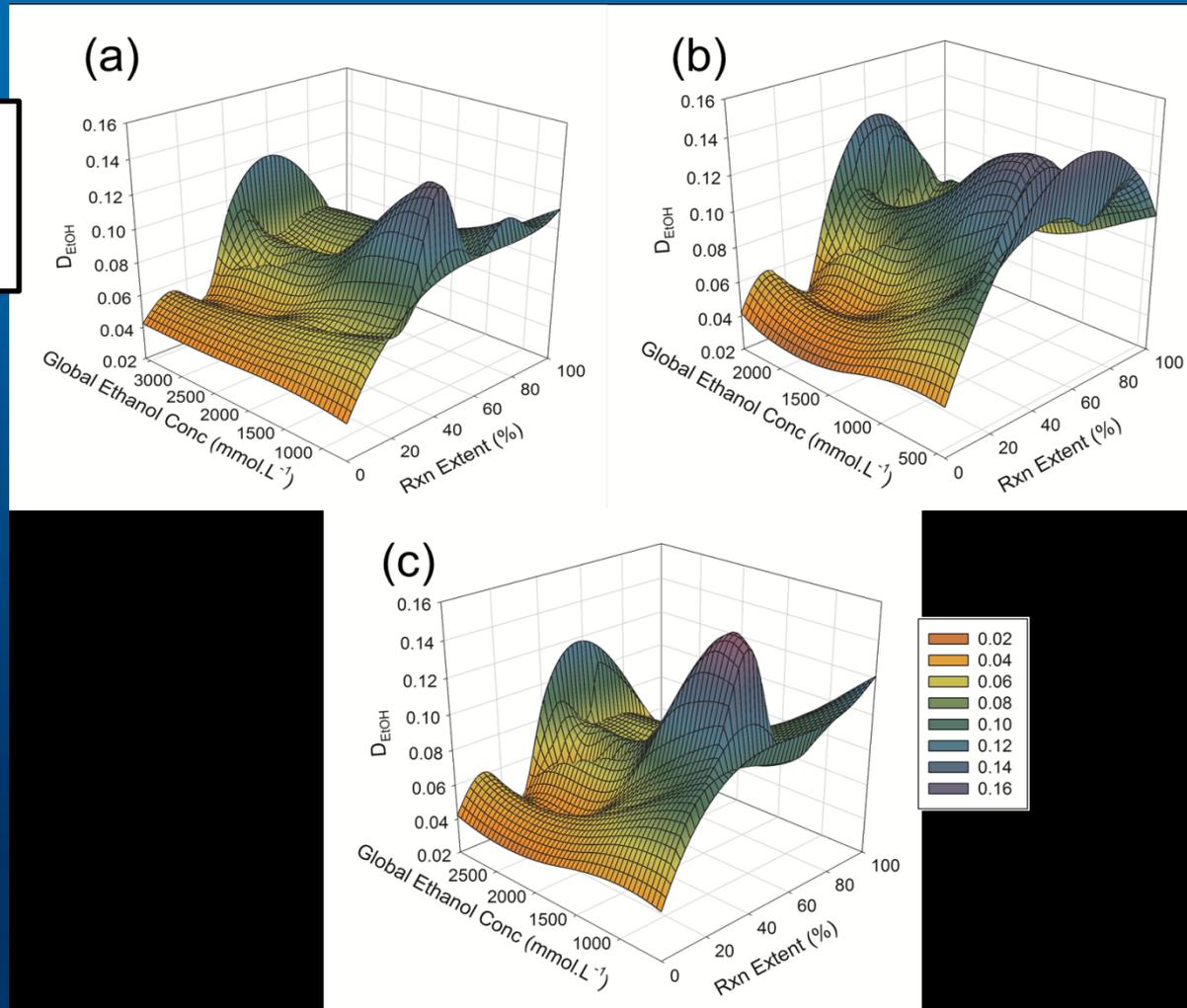
Observations

- ✦ Water concn in the organic phase increased with increased ethanol concn. in the organic phase at any given organic phase volume fraction.
- ✦ Both ethanol and water concns rose from a minimum in the unreacted oil to a peak when the extent of reaction, ε , is 40-50%.
- ✦ $\varepsilon = 40\%$ corresponds to maximum in mono- and di-glycerides conc in palm oil². High concs of MG & DG would increase the amphiphilic nature of the organic phase making it more polar and hence, higher uptake of water and ethanol.

Relationship between distribution coefficient of water, and ϵ is oscillatory as seen below³

$$D_w = \frac{X_w^{org}}{X_w^{aq}}$$

- (a). $\phi_{org} = 0.2$
 (b). $\phi_{org} = 0.35$
 (c). $\phi_{org} = 0.5$



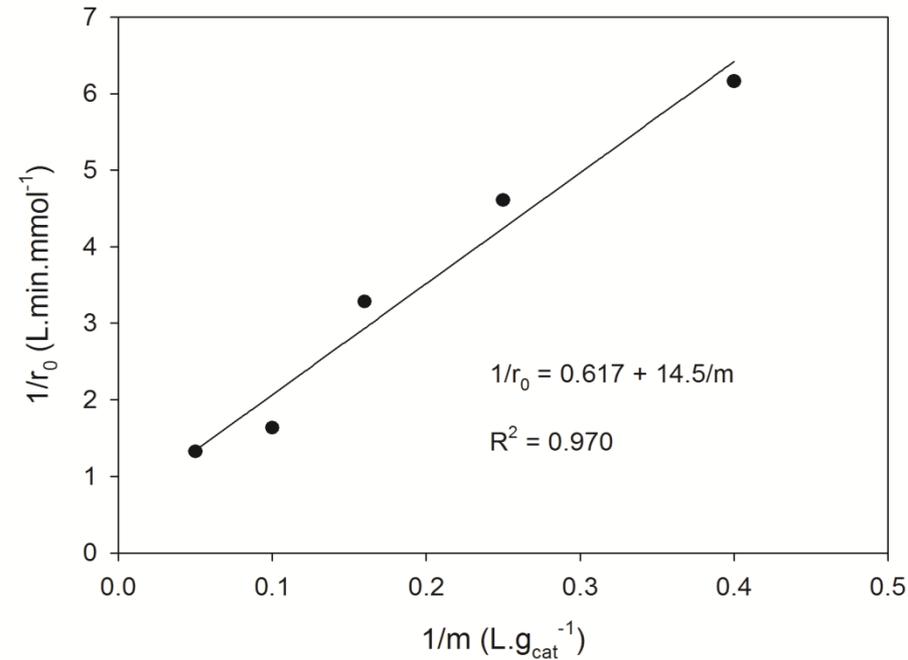
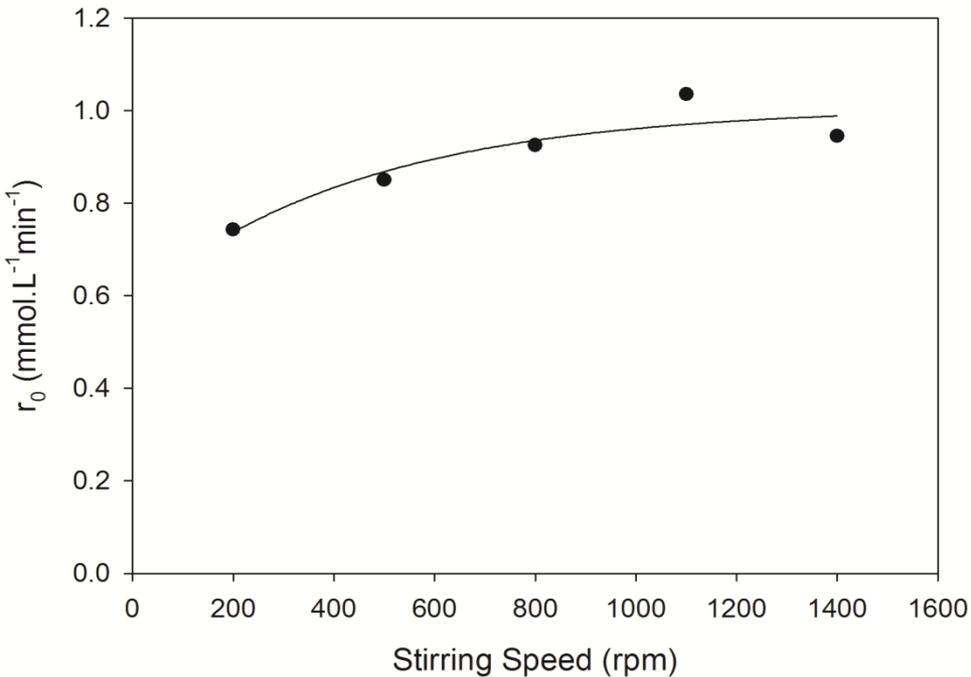
Model for the distribution coefficient is an underdamped second order decay expression

$$D_w = K \left\{ A - \exp\left(-\frac{\xi \varepsilon}{\tau}\right) \left[\cos\left(\frac{\sqrt{1-\xi^2}}{\tau} \varepsilon\right) + \frac{\xi}{\sqrt{1-\xi^2}} \sin\left(\frac{\sqrt{1-\xi^2}}{\tau} \varepsilon\right) \right] \right\}$$

ϕ_{org}	$C_{EtOH,0}^{aq}$ (%v/v)	K	A	ξ	τ	R^2
0.2	5	1.92E-03	1.79	0.208	0.141	0.860
	15	2.61E-03	1.83	0.226	0.135	0.949
	25	4.57E-03	1.52	0.118	0.140	0.947
0.35	5	1.96E-03	1.90	0.178	0.133	0.854
	15	3.02E-03	1.75	0.210	0.133	0.977
	25	5.11E-03	1.51	0.149	0.142	0.918
0.5	5	2.12E-03	1.81	0.073	0.137	0.892
	15	3.44E-03	1.61	0.180	0.137	0.949
	25	5.67E-03	1.40	0.133	0.141	0.903



Biodiesel synthesis kinetics

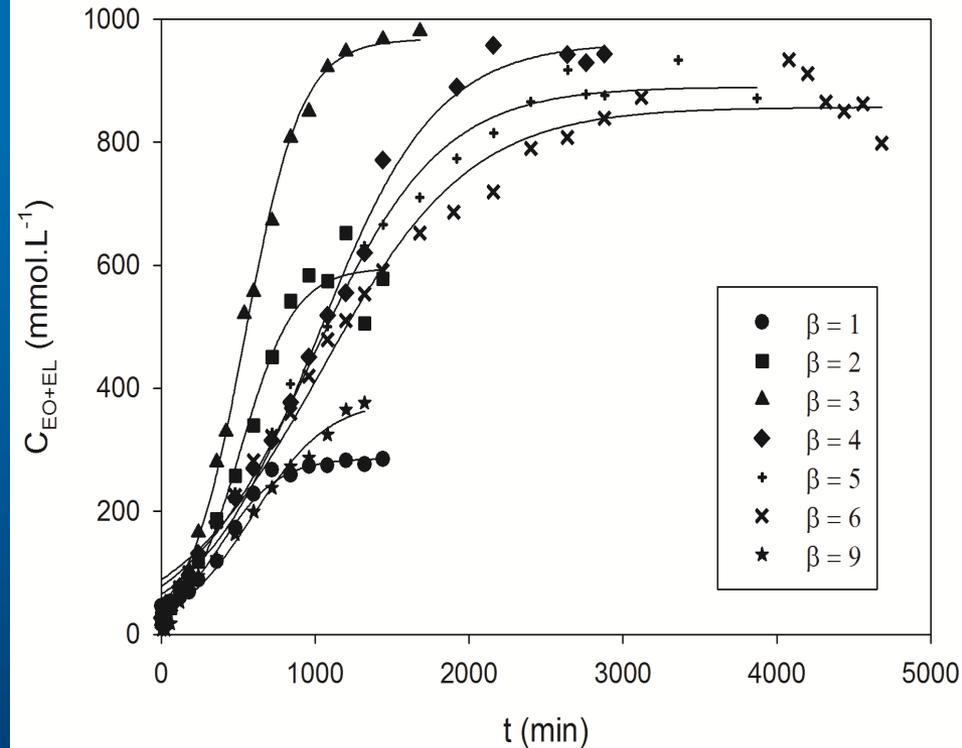
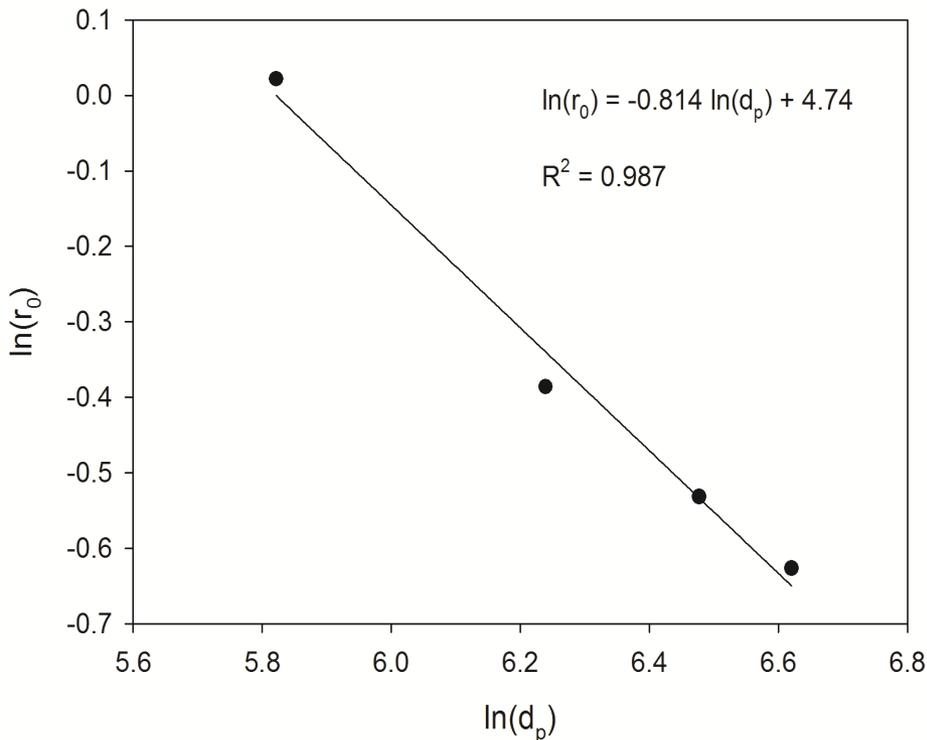


$T = 318$ K, ethanol:oil ratio, $\beta = 3$,
FAEE = Ethyl oleate + ethyl linoleate

Biodiesel synthesis kinetics

T= 318 K, ethanol:oil ratio, $\beta=3$, FAEE = Ethyl oleate + ethyl linoleate ; m = 6.25 g L⁻¹

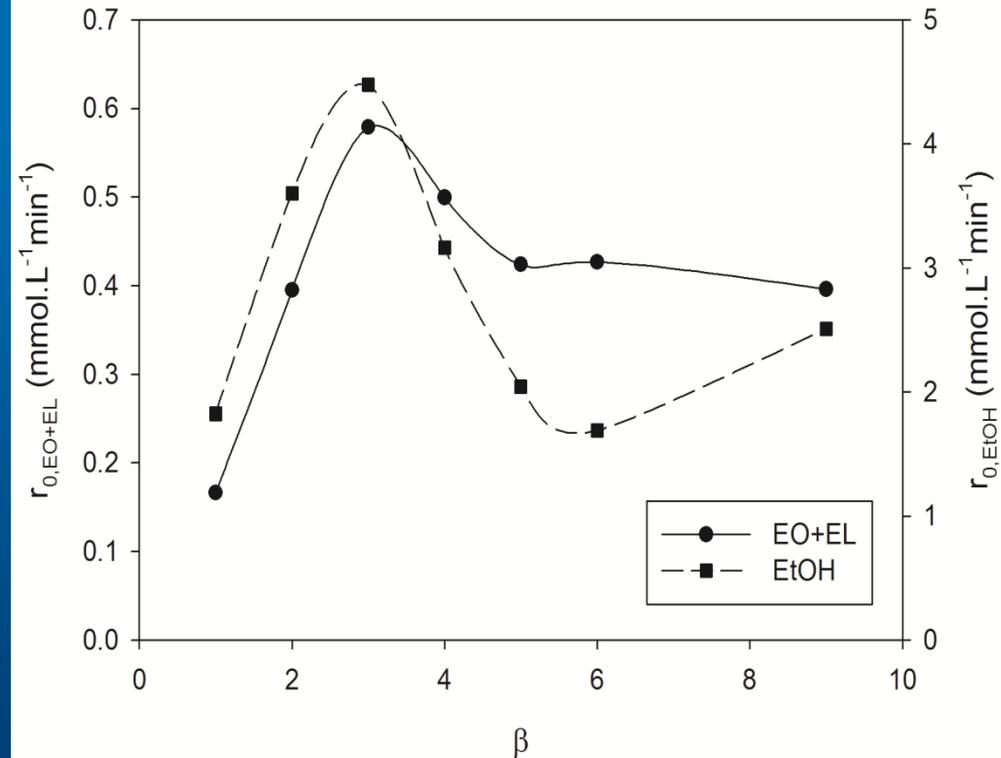
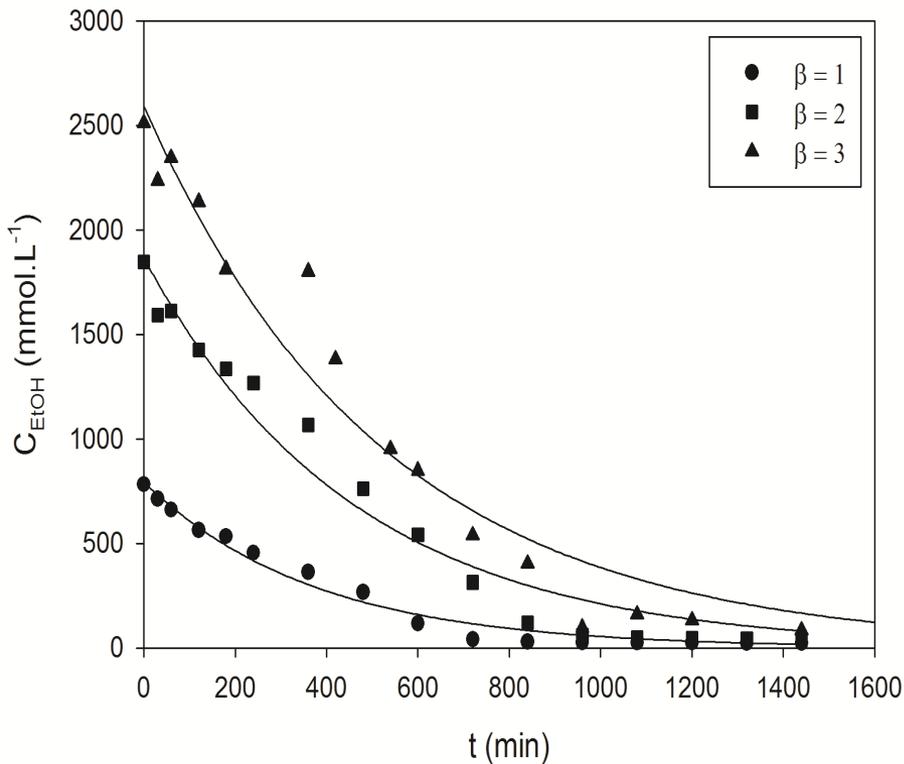
$$\text{Model: } C_{EO} = C_{EO,SS} [1 - \exp(-\lambda t)]$$



4. Chesterfield, DM, Rogers, PL, Al-Zaini, EO & Adesina, A.A., Chem. Eng. J., 208 (2012) 701

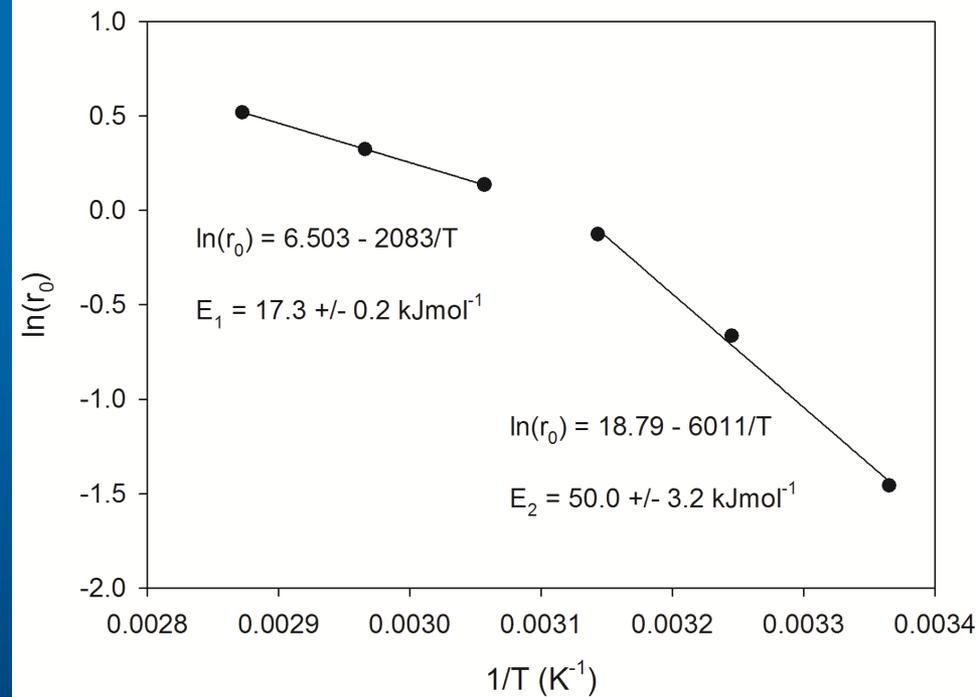
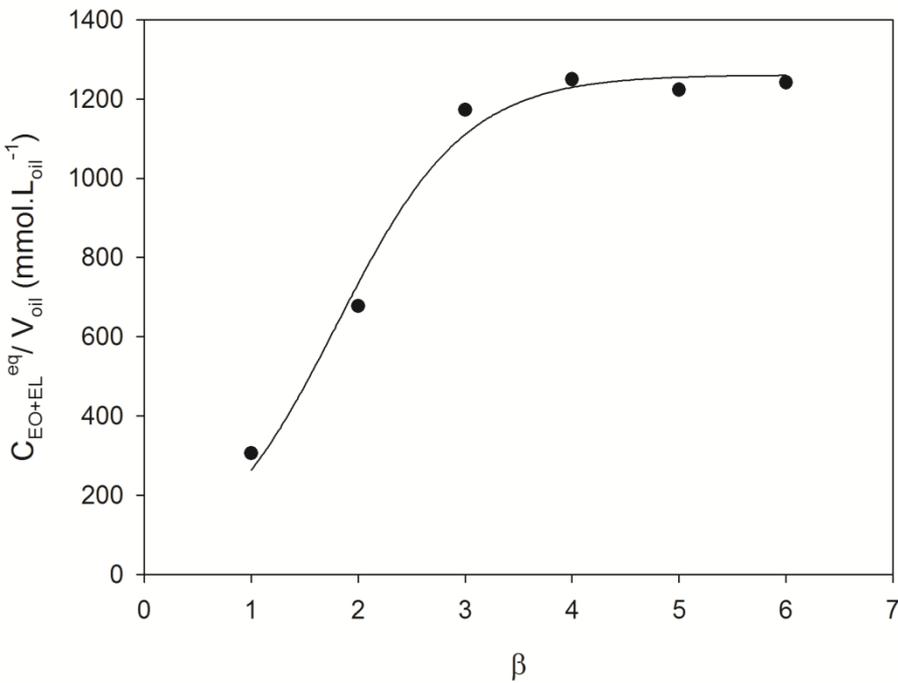
Biodiesel synthesis kinetics

T= 318 K, ethanol:oil ratio, $\beta=3$, FAEE = Ethyl oleate + ethyl linoleate ; m = 6.25 g L⁻¹



The drop in rate for $\beta > 3$ is indicative of ethanol inhibition in FAEE synthesis. However, additional increase in EtOH consumption may be due to side-rxns e.g. ethanol dimerization to ethyl ether since there was no corresponding increase in FAEE production.

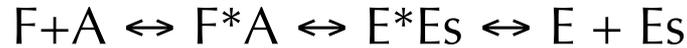
Arrhenius plot reveals two E_A values of $E_1 = 50 \text{ kJ mol}^{-1}$ ($T < 320 \text{ K}$) and $E_2 = 17.3 \text{ kJ mol}^{-1}$ ($T > 320 \text{ K}$). Behavior is due to thermal destruction of active sites not intraparticle resistance. Lipase denaturation occurred at $T > 323 \text{ K}$. The std. heat of denaturation for lipase was estimated as 32.7 kJ mol^{-1} ($E_1 - E_2$).



Ratio of ester equilibrium concn, C_{EO+EL}^{eq} to the initial oil volume, V_{oil} is an indicator of BD yield and has a sigmoidal relationship to β given by:

$$\frac{C_{EO,EL}^{eq}}{V_{oil}} = \frac{a}{\left[1 + \exp\left(\frac{\beta_0 - \beta}{b}\right)\right]}$$

Reaction mechanism



S = glyceride substrate; E = lipase native site

F = acylated form of the enzyme

P = glyceride product with 1 fewer acyl group than S

A = acyl acceptor (ethanol in this case)

Es = FAEE product

Competitive inhibition by ethanol is captured by;



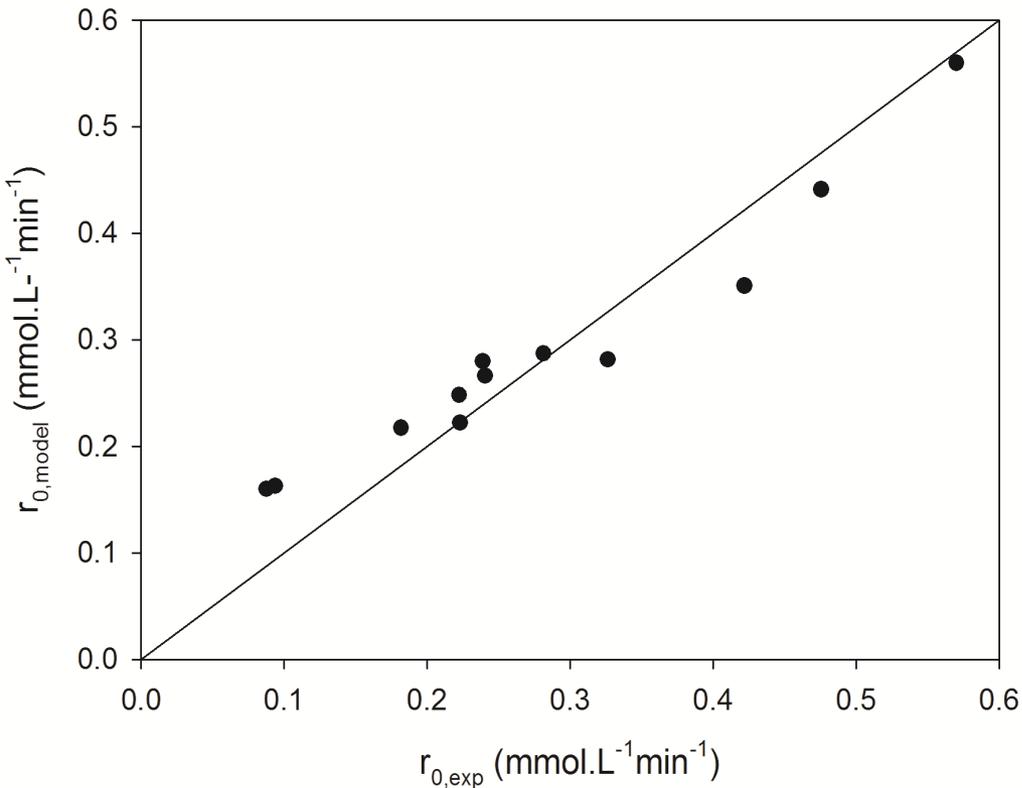
$$\frac{-r_{0,\text{exp}}}{X_{(TO+TL),\text{oil}}} = \frac{V'_{\text{max}}}{\left[1 + \frac{K_{I,\text{EtOH}}}{C_{\text{EtOH},0}} \left(1 + \frac{C_{\text{TG},0}}{K_{M,\text{TG}}} \right) + \frac{K_{I,\text{TG}}}{C_{\text{TG},0}} \left(1 + \frac{C_{\text{EtOH},0}}{K_{M,\text{EtOH}}} \right) \right]}$$

where $X_{(TO+TL),\text{oil}}$ = combined mole fraction of triolein and trilinolein in the oil; TO+TL = TG;

$$C_{\text{EtOH},0} = \beta C_{\text{TG},0} ;$$

$$C_{\text{TG},0} = \frac{\rho_{\text{EtOH}} \rho_{\text{oil}}}{\rho_{\text{EtOH}} M_{\text{oil}} + \beta \rho_{\text{oil}} M_{\text{EtOH}}}$$

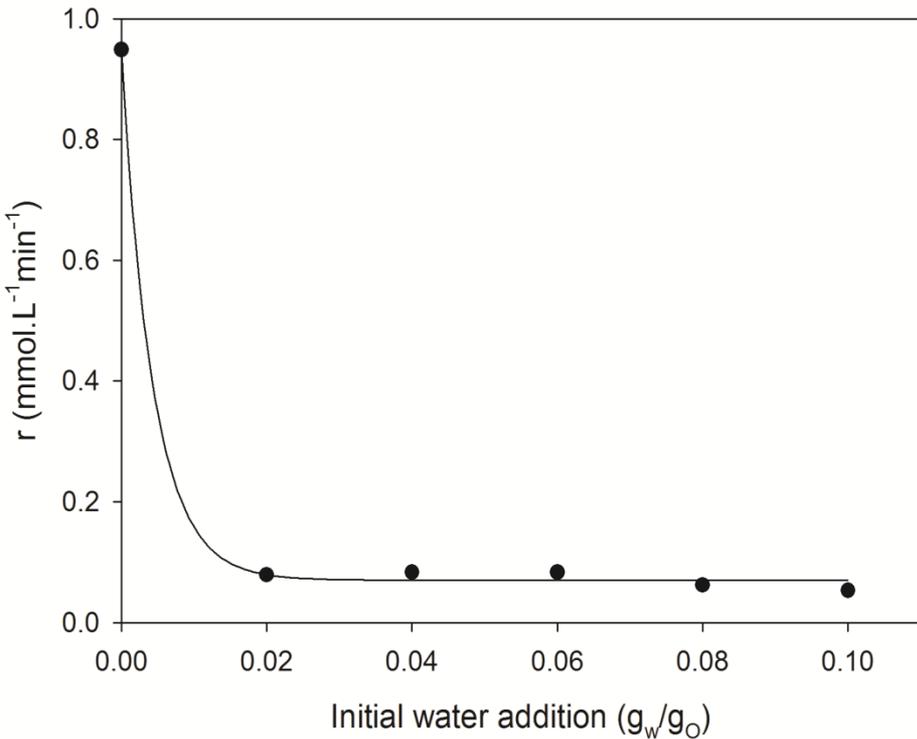
Parity plot



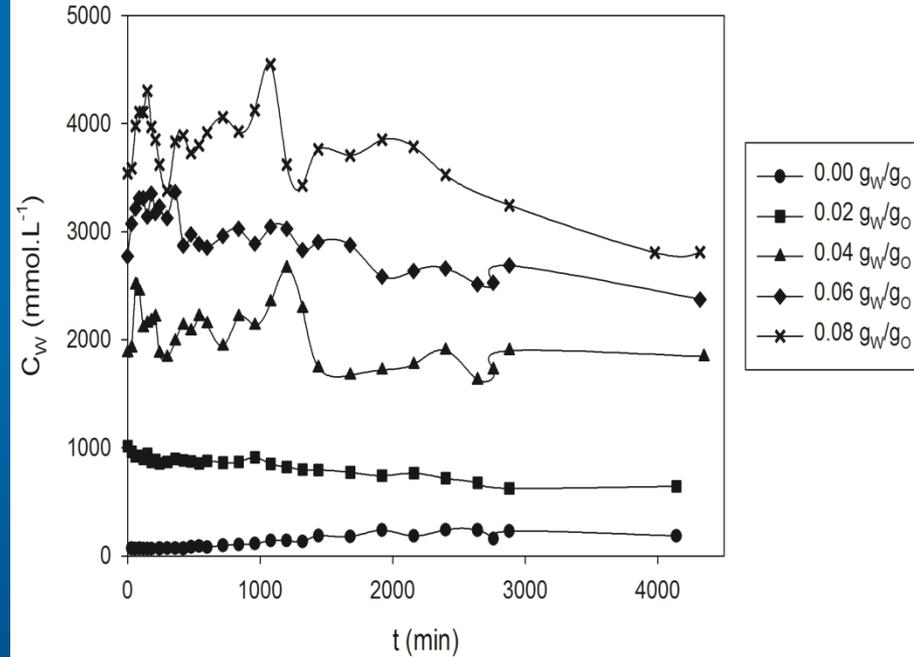
Parameter Estimates for data at
 $T=297\text{-}348\text{ K}$ and $m = 6.25\text{ g}_{\text{cat}}\text{L}^{-1}$

Parameter	Regressed Value
$V'_{max,0}$ ($\text{mmol.L}^{-1}\text{.min}^{-1}$)	3260
$K_{M,TG,0}$ (mmol.L^{-1})	29.0
$K_{M,EtOH,0}$ (mmol.L^{-1})	948
$K_{I,TG,0}$ (mmol.L^{-1})	219
$K_{I,EtOH,0}$ (mmol.L^{-1})	83.0
E_{Vm} (kJ.mol^{-1})	19.5
$\Delta H_{I,EtOH}$ (kJ.mol^{-1})	-1.16
$\Delta H_{M,TG}$ (kJ.mol^{-1})	1.16

Effect of water in the reaction system



Influence of water addition on FAEE rate



Transient water profile for runs with different levels of water addition at $\beta = 3$

Modeling of the novel extractive reactor

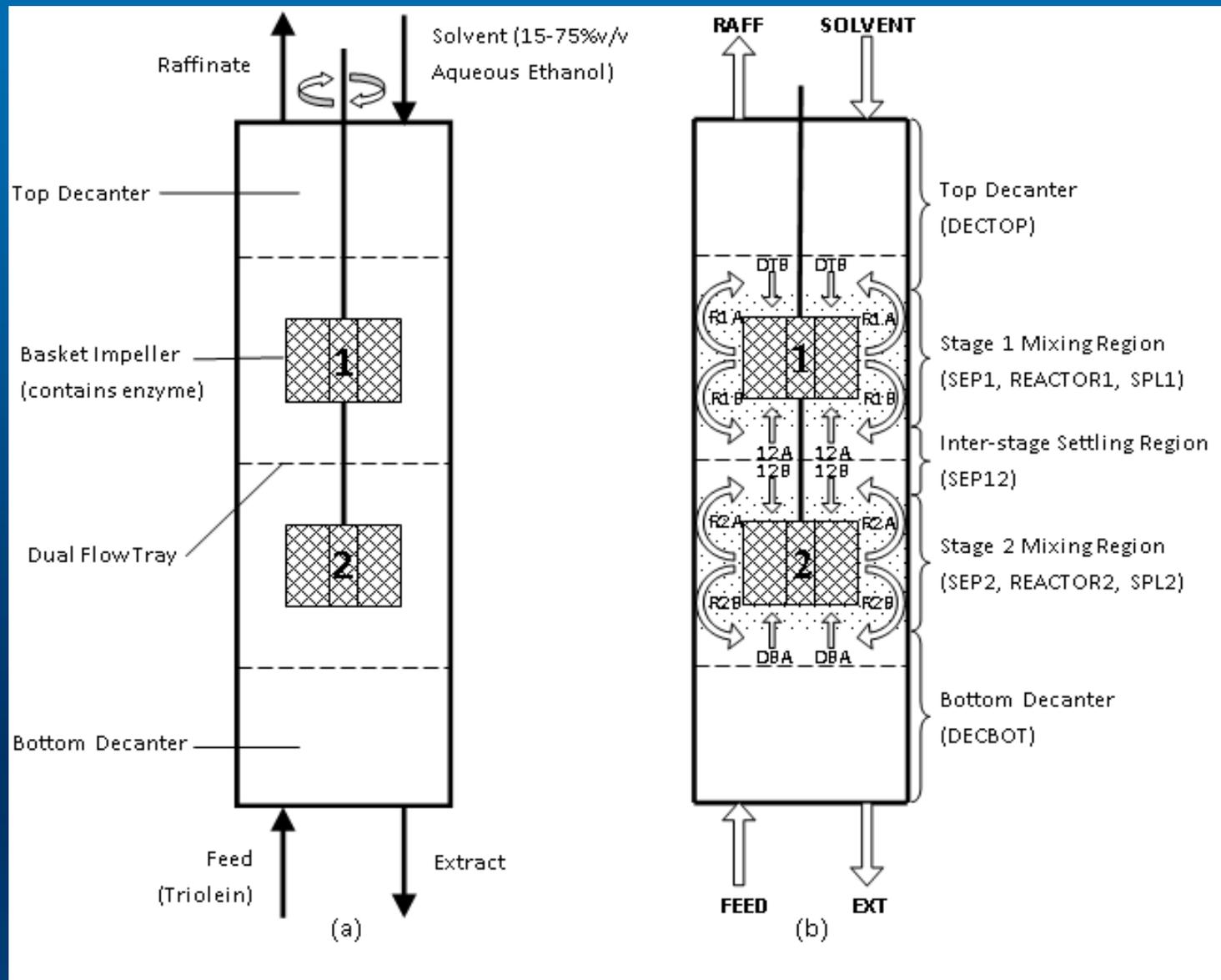
- ✦ Develop a basic steady-state model of the BIC for lipasic biodiesel production from vegetable oil and crude bioethanol.
- ✦ Use model to investigate parameters including:
 - ✦ Stirring speed
 - ✦ Number of stages
 - ✦ Solvent to feed ratio
 - ✦ Solvent composition
 - ✦ Recycle ratio

Model Assumptions

1. Isothermal operation at 45°C.
2. Oil composed only of glycerides – triolein/trilinolein.
3. Organic phase is dispersed.
4. Reaction only in organic phase
5. Ideal mixing (hydrodynamics neglected)
6. Instantaneous interfacial mass transfer of reactants and products (i.e. reaction is rate-limiting).

Modeling Approach

- ✦ Modeled multistage mixer-settler counter-current extractive reactors with 1-32 stages.
- ✦ Aspen Plus
- ✦ Each stage conceptualised as a CSTR + flow splitter.
- ✦ Stage boundaries as decanters.
- ✦ Utilised Ping Pong Bi Bi rate model
- ✦ Dortmund-modified UNIFAC for phase equilibrium calculations.

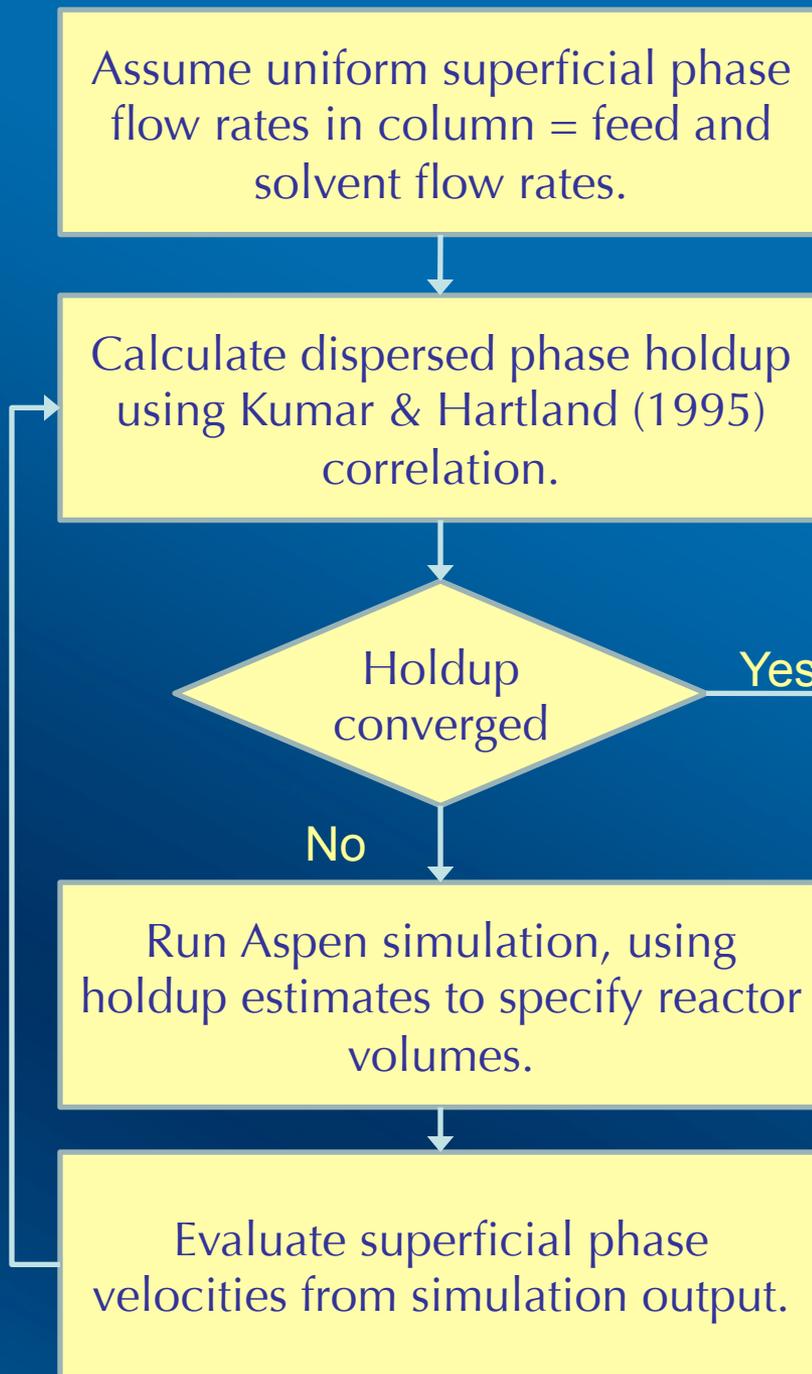


Organic Phase Holdup

Kumar & Hartland's (1995) generalised correlation for dispersed phase holdup in a liquid-liquid extraction column:

$$\phi = \left[0.27 + \left\{ \frac{\epsilon}{g} \left(\frac{\rho_c}{g\gamma} \right)^{1/4} \right\}^{0.78} \right] \left[V_d \left(\frac{\rho_c}{g\gamma} \right)^{1/4} \right]^{0.87} \times$$
$$\exp \left[3.34 V_c \left(\frac{\rho_c}{g\gamma} \right)^{1/4} \right] \left(\frac{\Delta\rho}{\rho_c} \right)^{-0.58} \left(\frac{\mu_d}{\mu_w} \right)^{0.18} C_{\Gamma} e^{n_6} \left[l \left(\frac{\rho_c g}{\gamma} \right)^{1/2} \right]^{-0.39}$$

Based on empirical data from various agitated, packed and pulsed LLE columns.



- Holdup estimate requires a priori knowledge of phase flow rates at each stage.

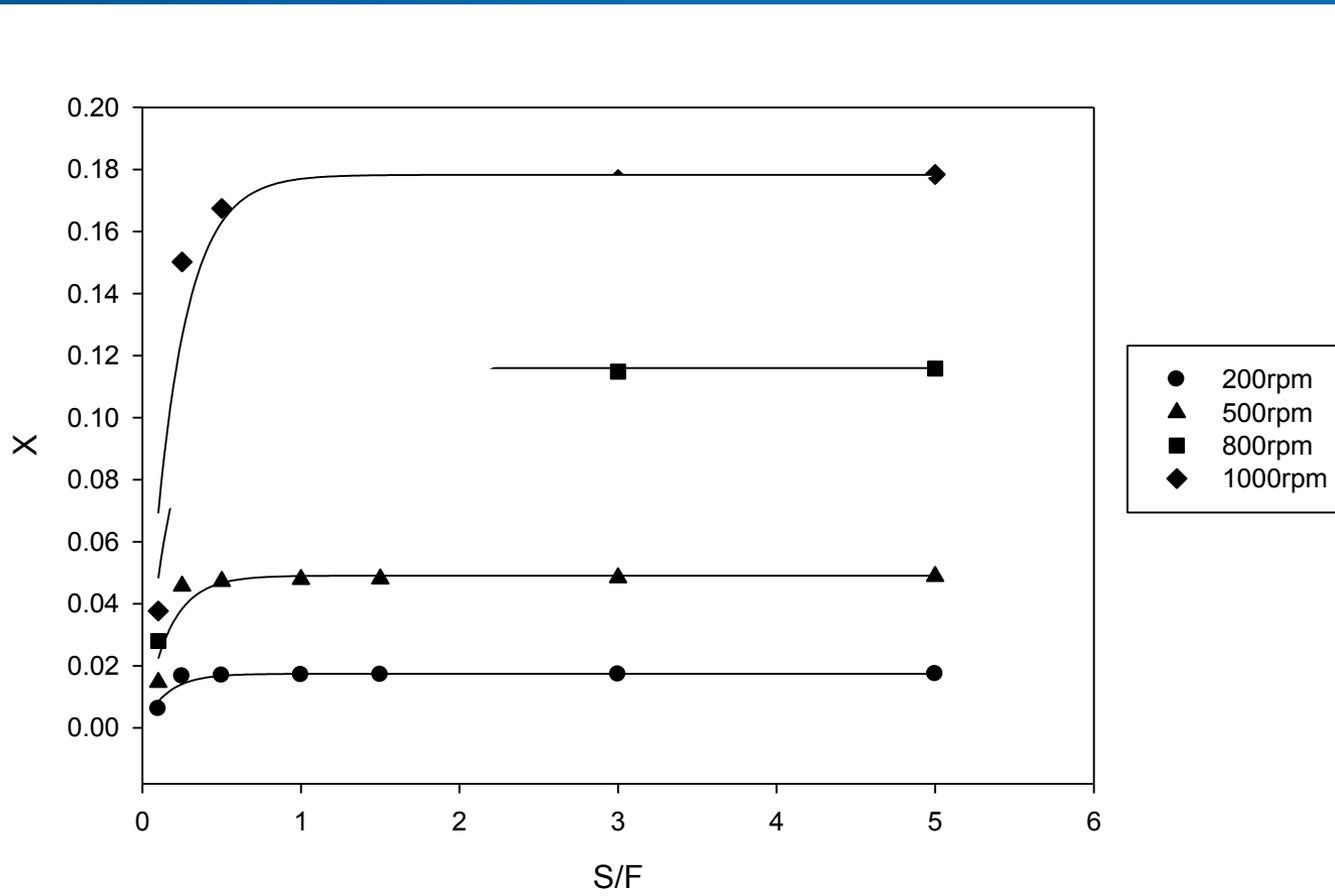
Simulation results accepted.

- Start with assumption of uniform phase flows.

- Iterative approach

Solvent to Feed Ratio (S/F)

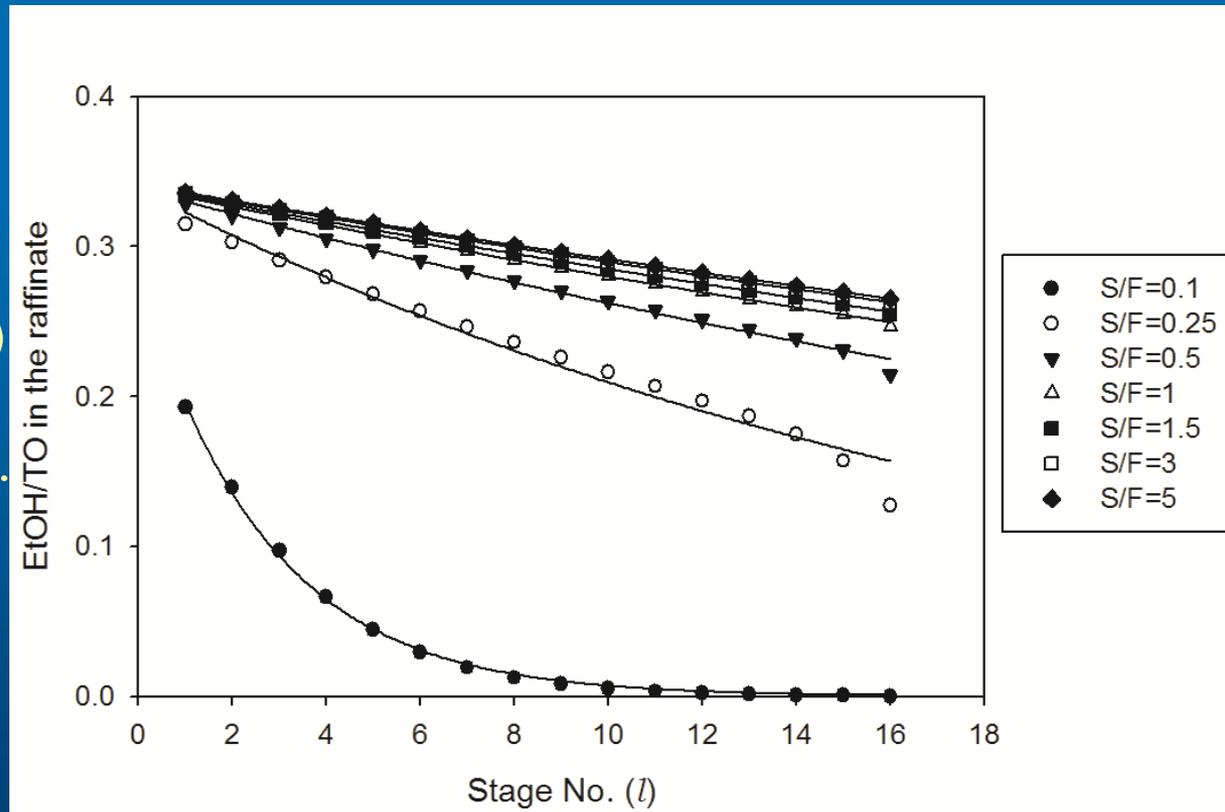
- Triolein conversion \uparrow as S/F at low values of S/F.
- Above stoichiometric ratio of EtOH:TO at S/F=1.2, conversion \rightarrow as S/F \uparrow .



Conversion of triolein as a function of solvent to feed ratio (N=16 stages).

Solvent to Feed Ratio (S/F)

- At $S/F=0.1$, EtOH fully consumed by midpoint of reactor.
- Below $S/F=1$, EtOH content in organic (reactive) phase \uparrow with S/F . Hence improvement in X observed.
- At $S/F \geq 1$, molar ratio of EtOH:TO in organic phase throughout column unaffected by S/F , hence X stable.
- Suggests organic phase reached EtOH saturation at $S/F \approx 1$.



Molar ratio of ethanol to triolein in the organic phase throughout the extractive reactor at various S/F ratios ($N=16$ stages, $\omega=1000$ rpm)

Stirring Speed

In excess EtOH, conversion varies with square of stirring speed as

$$X = \alpha + \beta N_s^2$$

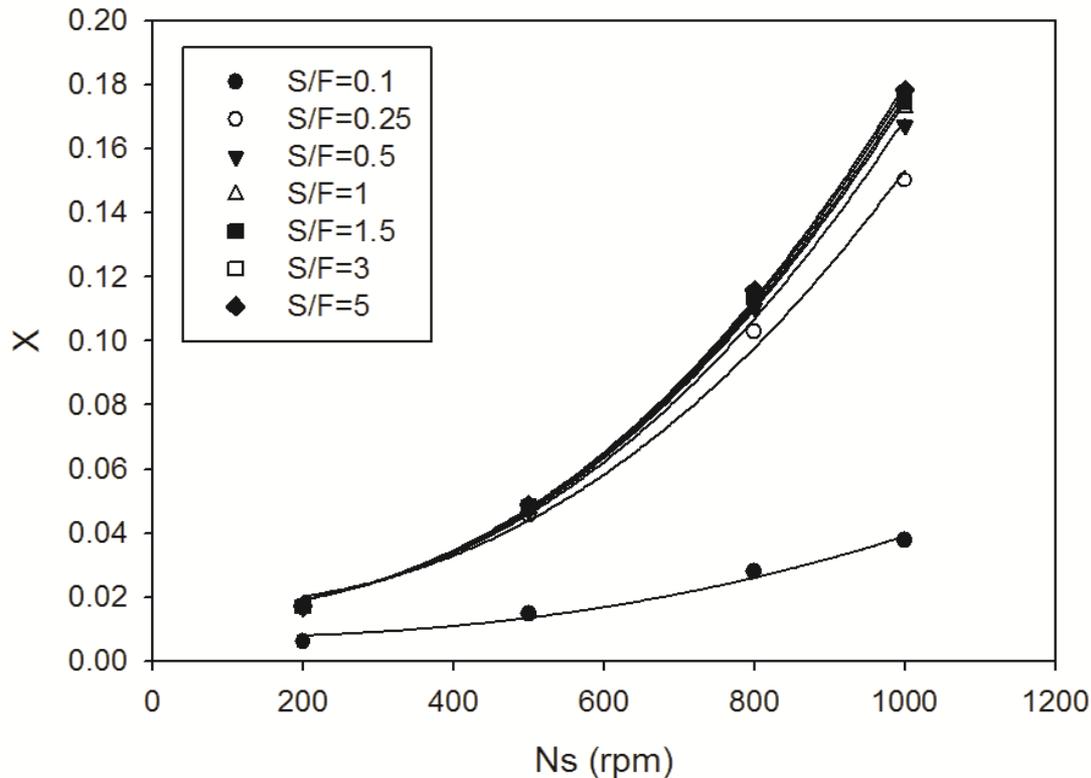
where α is conversion in static extractive reactor, βN_s^2 is contribution of stirring to conversion.

Substituting impeller Froude number,

$$Fr_I = \frac{\left(\frac{N_s}{60}\right)^2 D_I}{g}$$

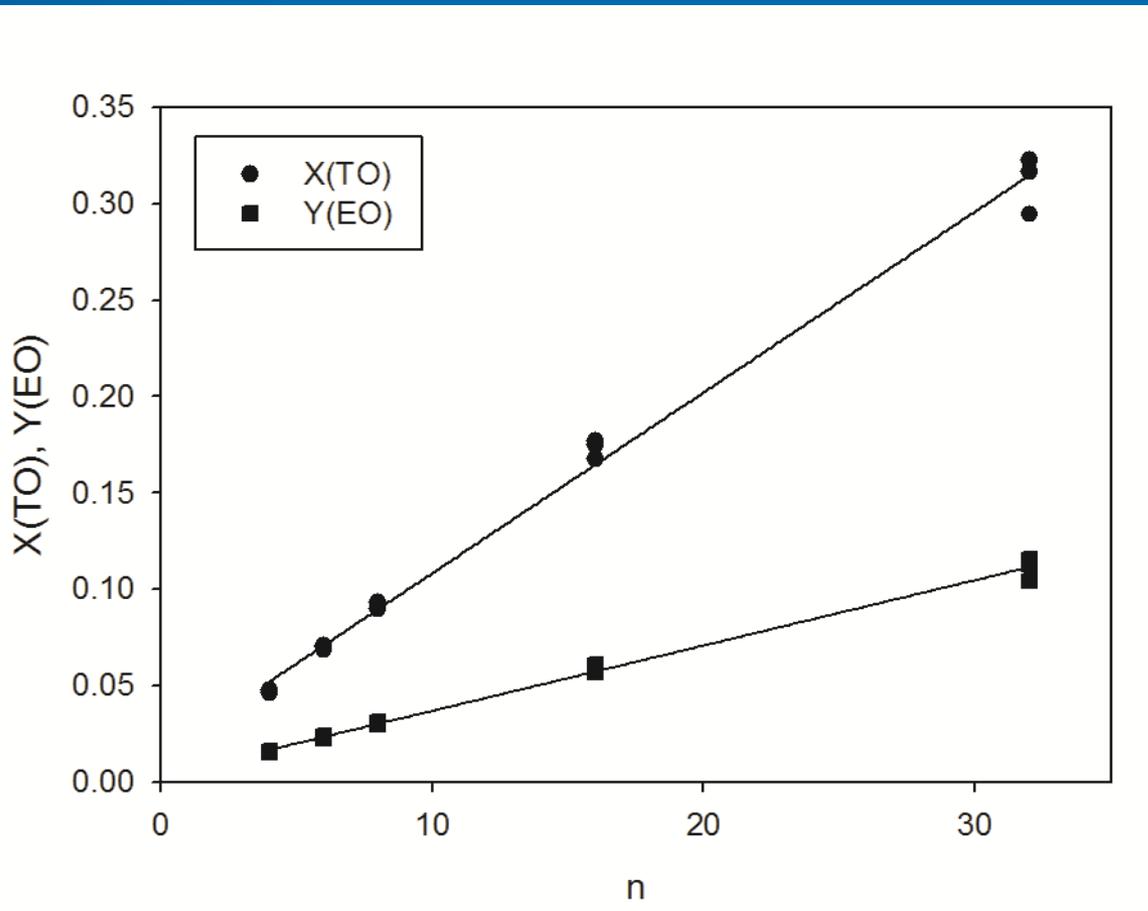
we get

$$X = \psi_1 + \psi_2 Fr_I$$



Conversion of triolein as a function of stirring speed (N=16 stages).

Number of Stages



- Increasing number of stages increased reactive phase volume, hence conversion.

- Linear relationship typical of systems with low Da ($Da < 0.1$).

- Intuitively, X(TO) and Y(EO) would approach asymptotic values at large n.

Triolein conversion and ethyl oleate yield vs. number of stages ($N_s = 1000\text{rpm}$).

Conversion Correlation

Multivariate nonlinear regression model for the influence of S/F , Fr_I , and n on triolein conversion:

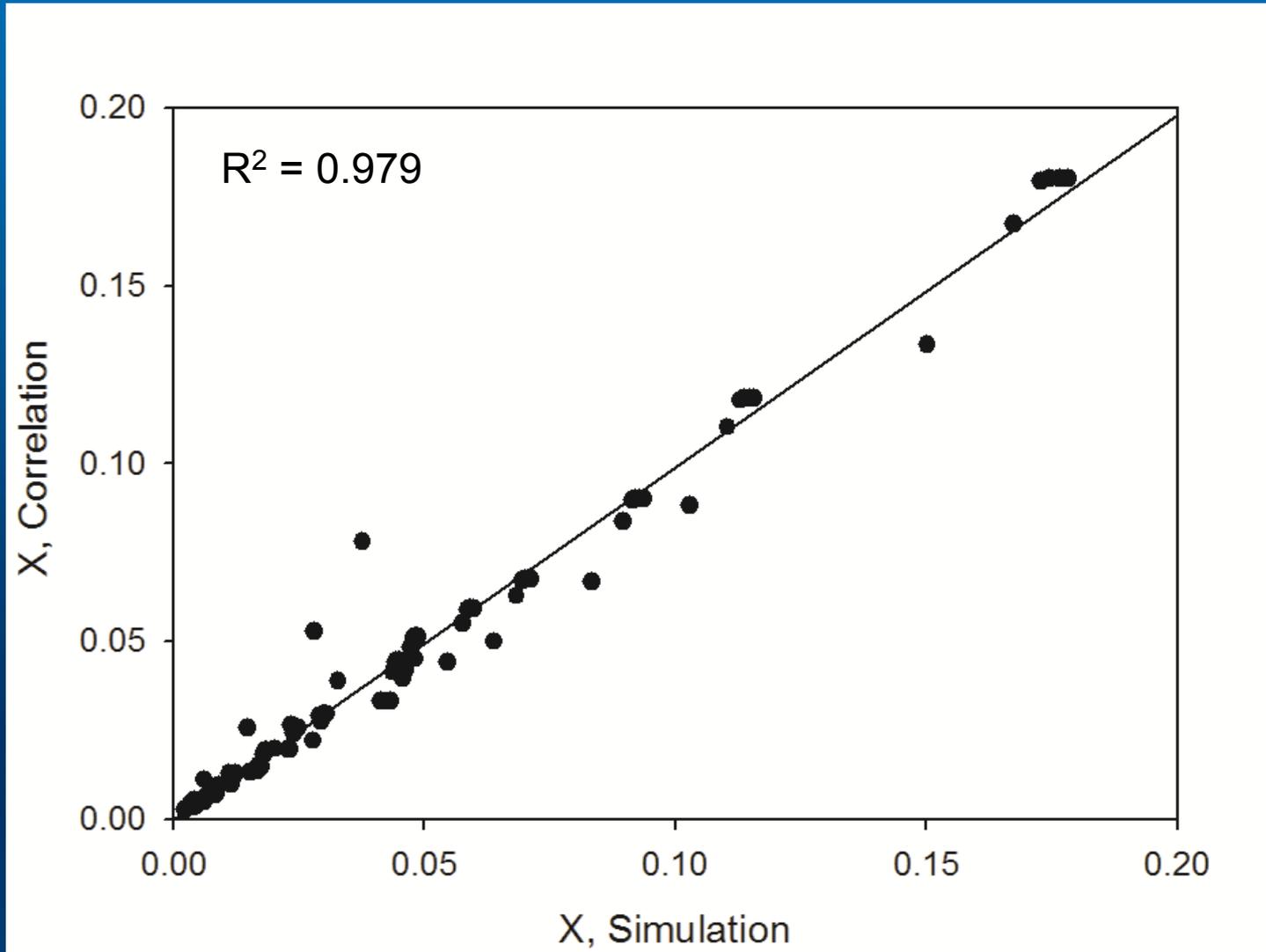
$$X = \psi_1 + \psi_2 Fr_I$$

where

$$\begin{aligned}\psi_1 &= \psi_1(n, S/F) \\ &= 5.25 \times 10^{-4} n \left\{ \exp \left(-1.19 \times 10^{-3} \left(\frac{S}{F} \right) \right) - 8.58 \times 10^{-4} \left[1 - \exp \left(8.61 \times 10^{-7} \left(\frac{S}{F} \right) \right) \right] \right\}\end{aligned}$$

$$\begin{aligned}\psi_2 &= \psi_2(n, S/F) \\ &= 9.49 \times 10^{-3} n \left\{ 1 - \exp \left(-5.19 \left(\frac{S}{F} \right) \right) \right\}\end{aligned}$$

Parity Plot of Conversion Data



Ethanol Content in Solvent

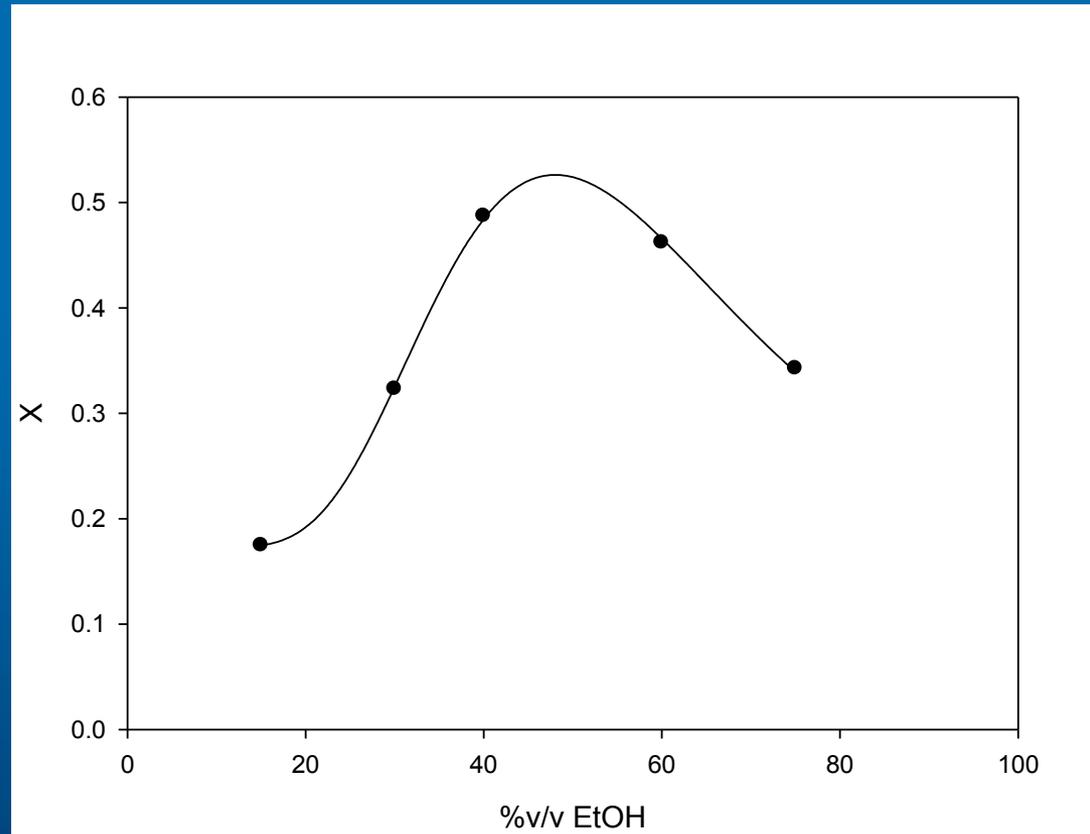
Triolein conversion \uparrow with ethanol concentration in solvent, to a maximum at $\sim 46\%v/v$, before decreasing.

Two effects of EtOH content on model:

1. Reaction rate \uparrow with c_{EtOH} .
2. As $c_{\text{EtOH}} \rightarrow 46\%v/v$, phase density difference, $\Delta \rho \rightarrow 0$. Low $\Delta \rho$ encourages high ϕ , - dispersed phase vol. fraction -(but leads to flooding).

Above optimum EtOH, reaction rate will continue to rise, while $\phi \downarrow$, reducing reactive phase volume.

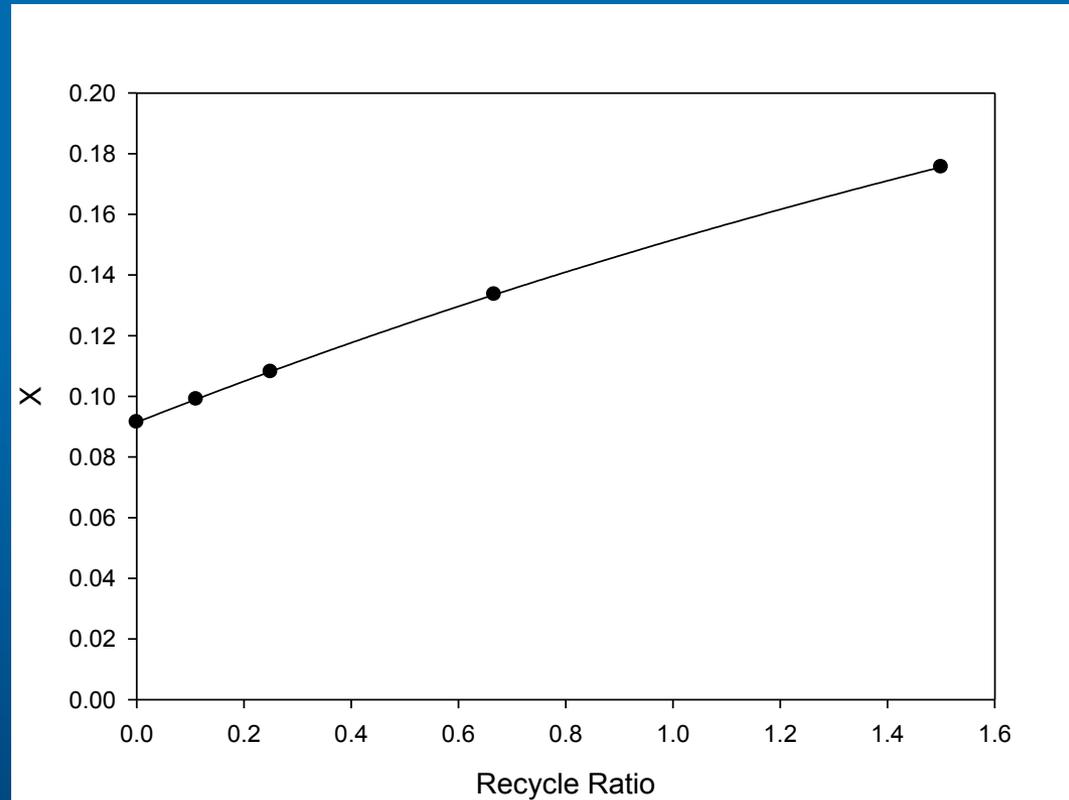
Net reduction in conversion.



Triolein conversion as a function of ethanol content in solvent (N=16 stages, S/F=1.5, $\omega=1000\text{rpm}$).

Raffinate Recycle

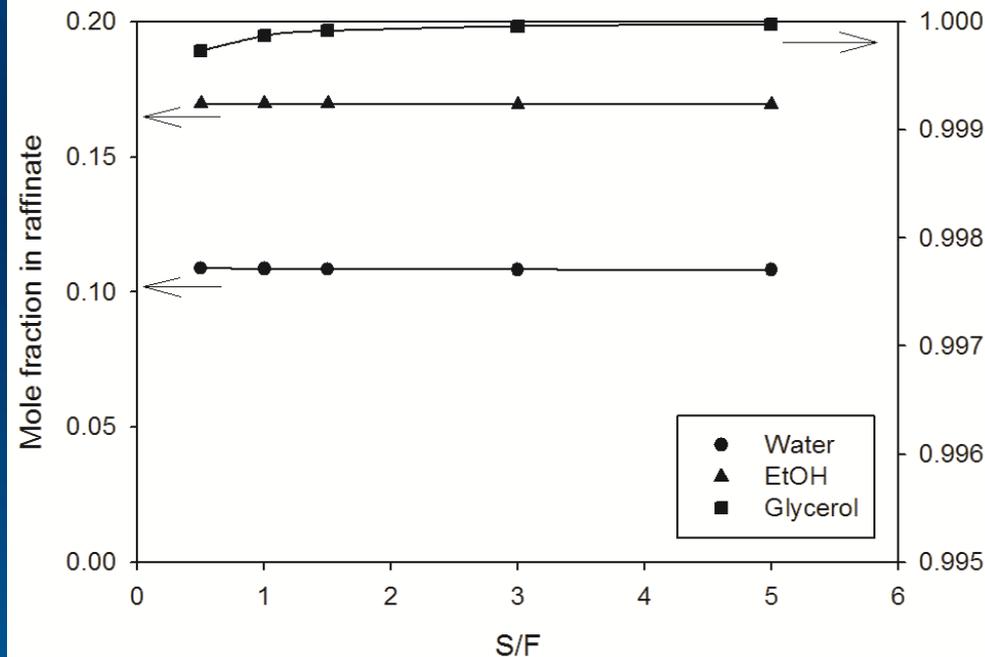
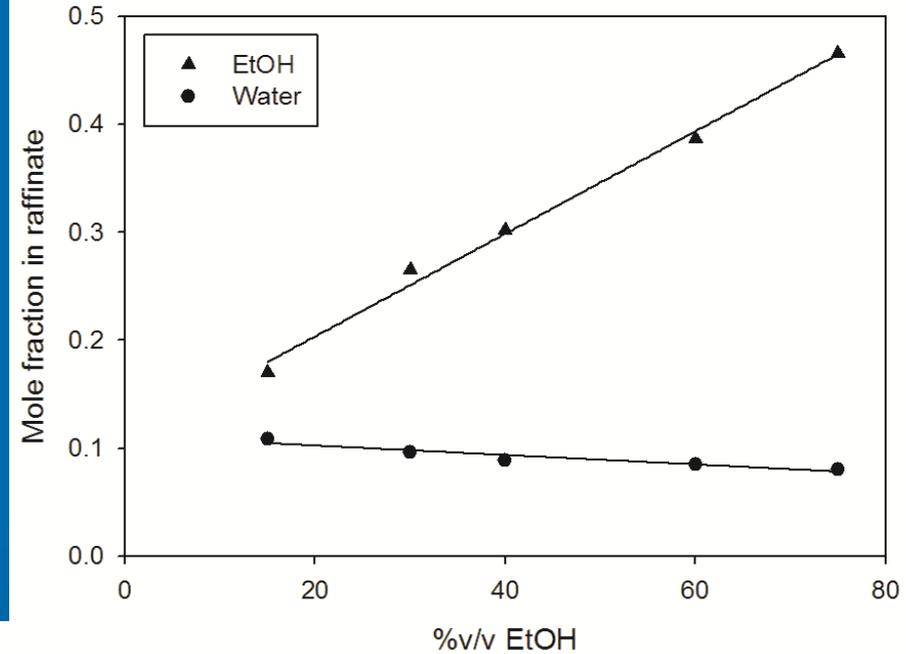
- Recycling raffinate improved conversion, as expected.
- At a recycle ratio of 1.5, conversion in 8 stage reactor > 16-stage reactor with no recycle.
- Physical limitation on recycle ratio, due to occurrence of flooding.



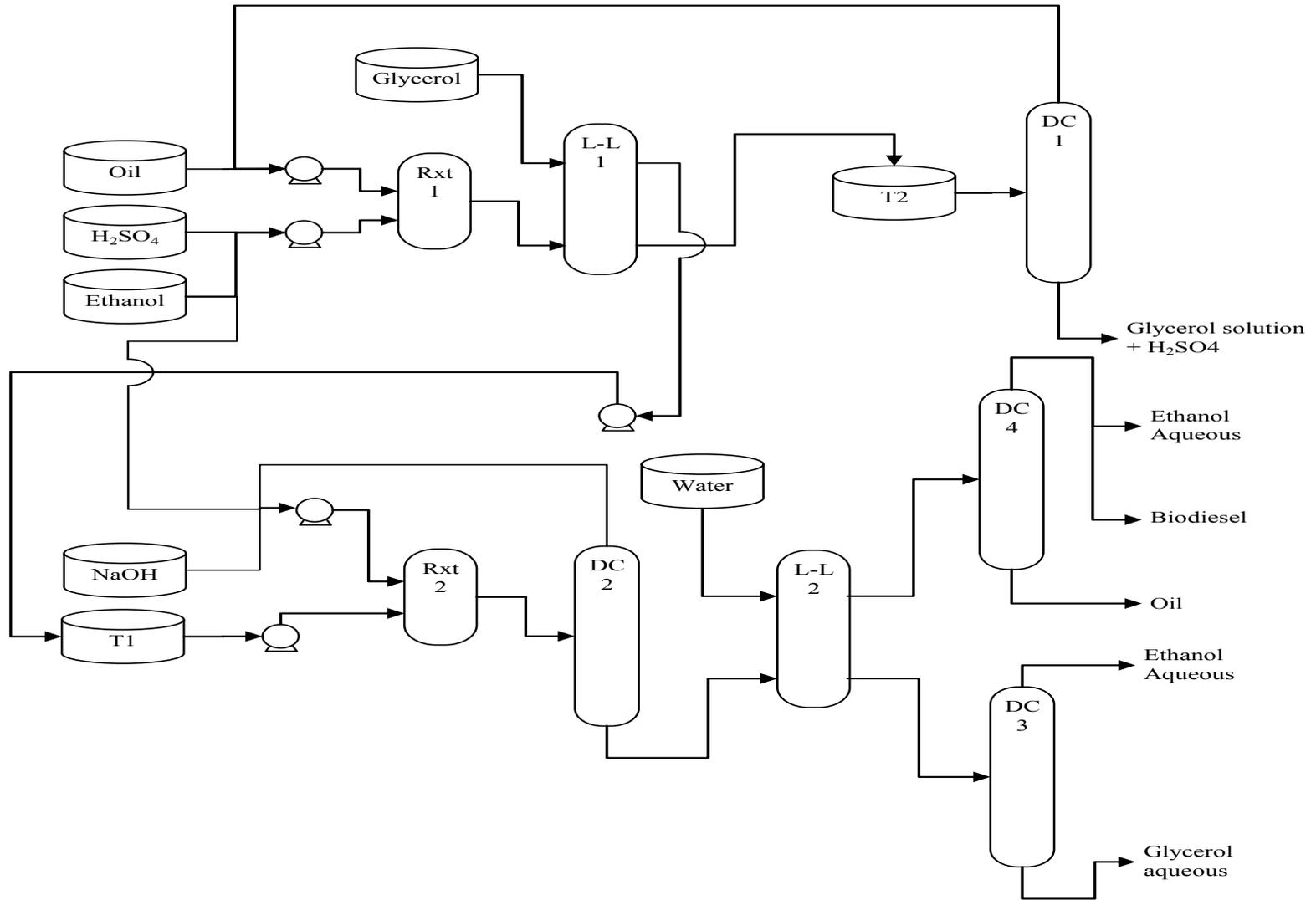
Effect of recycle ratio on triolein conversion (N=8 stages, $\omega=1000\text{rpm}$, $S/F=1$).

Phase Separation

- Higher EtOH concentration \rightarrow lower purity raffinate.
- Further incentive to use inexpensive crude bioethanol as solvent.

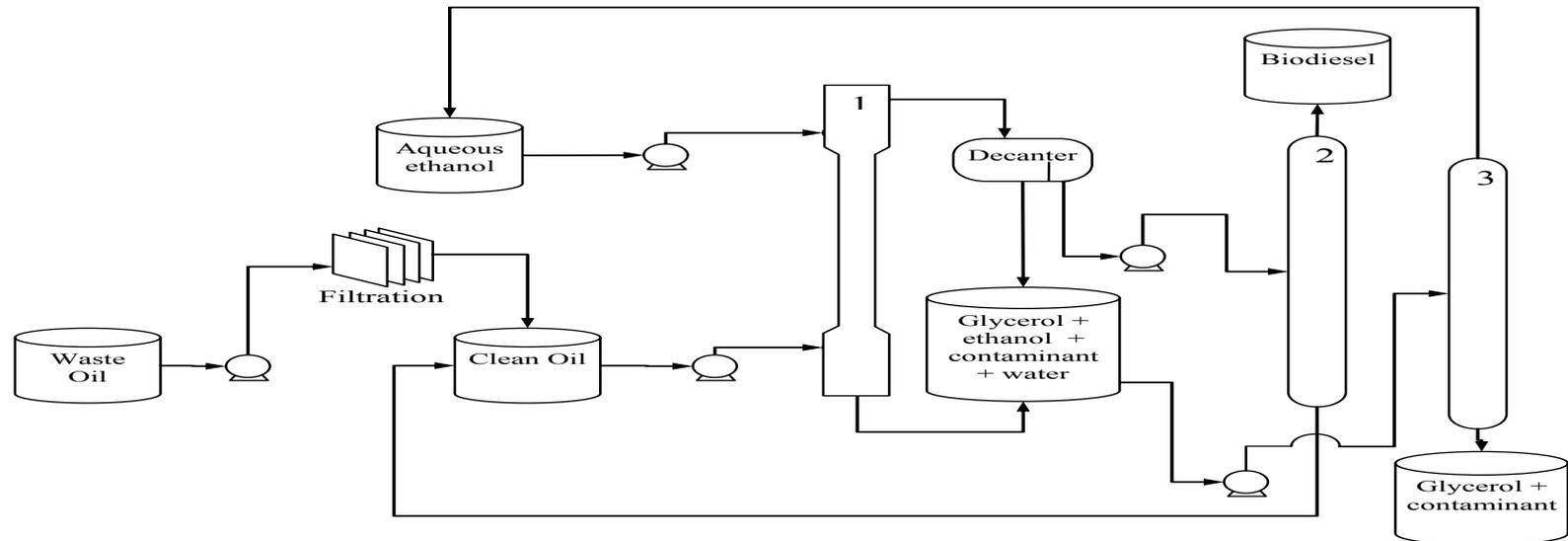


- S/F has negligible effect on raffinate purity and glycerol recovery in extract.
- Glycerol recovery $>99.9\%$ under all simulation conditions



Simplified Continuous Plant Design Using Conventional Catalysts Equipped with (Rxt1) Esterification and (Rxt2) Transesterification Reactors, (L-L1) Glycerol and (L-L2) Water Washing Tower, (T1) Treated Oil and (T2) Extract Tanks and (DC1) Extract, (DC2 and DC3) Ethanol Recovery and (DC4) Product Purification Columns

Process Economics



Process Flow Diagram for The Extractive Reaction Process of Biodiesel Production with (1) L-L Extractor, (2) Biodiesel Purification and (3) Ethanol Recovery Column

Comparison between the UNSW Invention and Conventional Continuous System of Biodiesel Production (Zhang et al., 2003) based on 8000 tonnes/year and Fixed Capital Cost for 2010

Unit of Operation	This system		Conventional system	
	No. of unit	Cost	No. of unit	Cost
Reactors	1	35,951	3	391,000
Distil Columns	2	687,170	6	1,768,007
Heat Exchangers	0	0	11	25,716
Pumps	5	72,328	8	115,724
Gravity Separator	1	30,000	1	91,615
Filter (Plate & Frame)	1	2,323	0	0
Tanks	6	610,640	13	1,323,053
Catalyst	Lipase 513 kg x 2 1,715,472		Including Solvent 2,266,264	
	Total Cost (USD) = 3,153,884		5,981,379	

Conclusions

- ✦ $X \uparrow$ as S/F for $S/F < \text{stoichiometric}$.
- ✦ $X \propto N_s^2$ over the range 200-1000rpm.
- ✦ $X \propto n$ over the range 4-32 stages.
- ✦ Correlation developed for prediction of X in terms of dimensionless parameters.
- ✦ Optimum EtOH conc. in solvent of 46%v/v.
- ✦ X was doubled at a recycle ratio of 1.5.
- ✦ Glycerol recovery in extract $>99.9\%$.

Future Work

- ✦ Investigate real performance, with non-equilibrium stages.
- ✦ Identify physical limitations, e.g. flooding conditions.
- ✦ Extend model to account for dispersed phase drop behaviour, mass transfer processes.
- ✦ Optimise BIC performance.



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