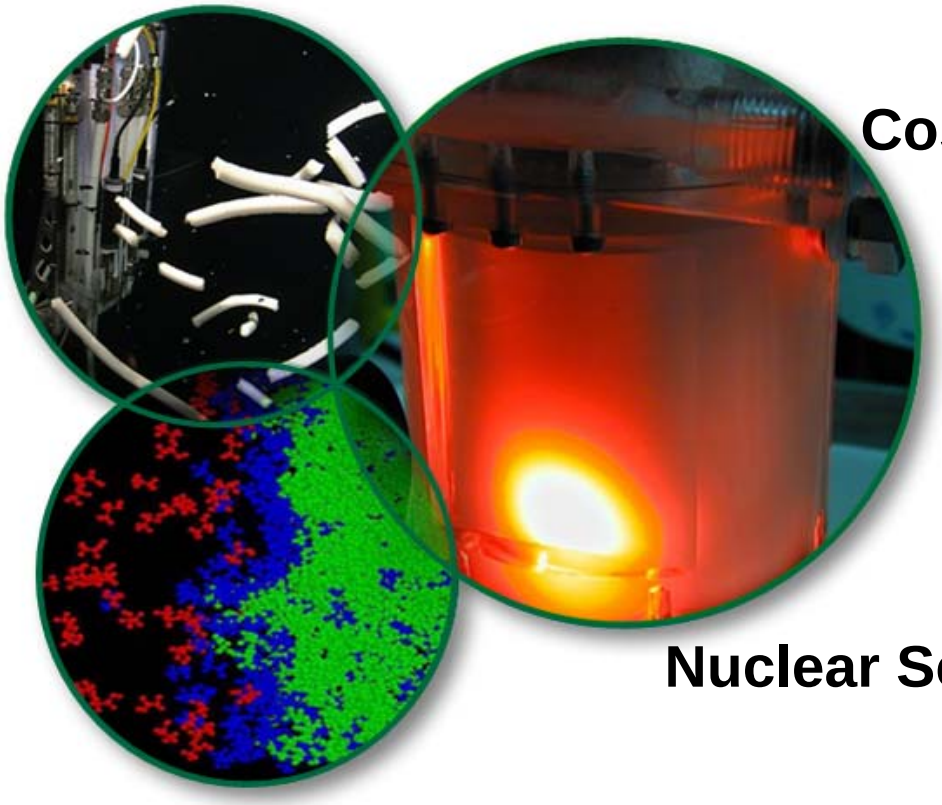
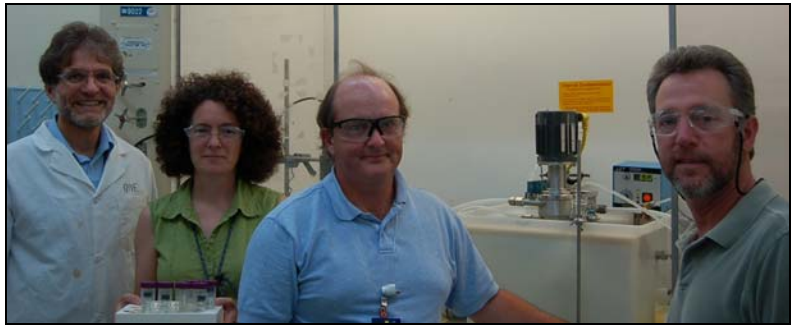
Continuous Production of Biodiesel via an Intensified Reactive/Extraction Process



Costas Tsouris, Joanna McFarlane

Joe Birdwell, and Hal Jennings



Nuclear Science and Technology Division

Oak Ridge National Laboratory

Collaborator: Nu Energie, LLC

Background

- **ORNL project - 2006**
  - **Goal: demonstrate a continuous process for biodiesel production**

- **Motivation**
  - **Commercial processes are slow**
  - **Reaction is fast**
  - **Limiting step is product separation**
- **The right tool for combined reaction/separation**
  - **Centrifugal contactor: used for solvent extraction and phase separation**
  - **Allows short residence time to avoid radiolysis and hydrolysis of solvent**

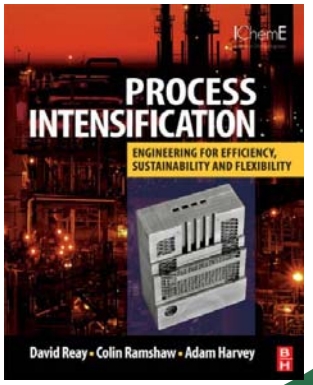
Centrifugal contactor: A two-phase (bio)catalytic reactor/separator

The Role of Centrifugal Contactors as Chemical-Bio-Catalytic Reactors is Being Recognized

- **Applications for liquid-liquid systems**
- **Emphasis on "Process Intensification"**
- **Recent example:**
  - **"Two-Phase (Bio)Catalytic Reactions in a Table-Top Centrifugal Contactor"** Gerald N. Kraai, Floris van Zwol, Boelo Schuur, Hero J. Heeres, and Johannes G. de Vries, *Angew. Chem. Int. Ed. 2*008, 47, 3905-3908 (in *Process Intensification* section)
- **<u>Questions addressed in this presentation:</u>**
  - **What is "Process Intensification?"**
  - **Is the current commercial version of centrifugal contactors adequate for chemical reactions? How it can be improved?**
  - **What are the limitations of the centrifugal contactor/reactor?**
  - **How can centrifugal contactors be used in biodiesel production?**

What Is Process Intensification (PI)?

- **Engineering strategy of making dramatic reductions in the size of unit operations in order to reduce capital cost, footprint, inventory, energy needed, and raw materials (Stankiewicz and Moulijn, I&EC Res., 2002)**
  - **Integration of unit operations**
    - **Eastman technology for esterification of methanol to methyl acetate combines reaction and distillation (Kingsport, TN)**
    - **Static mixers enable delivery and mixing of fluids in pipes**
  - **Process integration leads to reduction of capital cost**
    - **Reactors, heat exchangers, separators (20% of total)**
    - **Pipes, structural support and other civil engineering (80% of total)**
- **Enhanced safety and effectiveness**
  - **Reduced inventory of hazardous materials**
  - **Reduced volume of expensive solvent**



http://pig.ncl.ac.uk/

What Are the Current Drivers for PI?

- **Novel or enhanced products**
  - **Not optimal by other means because of highly exothermic reactions, or the reactants are too hazardous**
- **Improved chemistry**
  - **Leading to improved chemical yields and purity through precise control**
- **Enhanced safety**
  - **Reduced inventory of hazardous materials**
- **Improved processing**
  - **Opportunities in pharmaceutical industry with batch reactors**
- **Energy and environmental benefits**
  - **Reduced energy and operating cost with reduced emissions**
- **Capital cost reduction**
- **Enhanced corporate image**
  - **"Lower emissions", "doing more with less", "safest available", "sustainable, intensified chemical processing"**
- **Diversified units – just-in-time philosophy (adjustable to market demands)**
  - **Lower inventories**

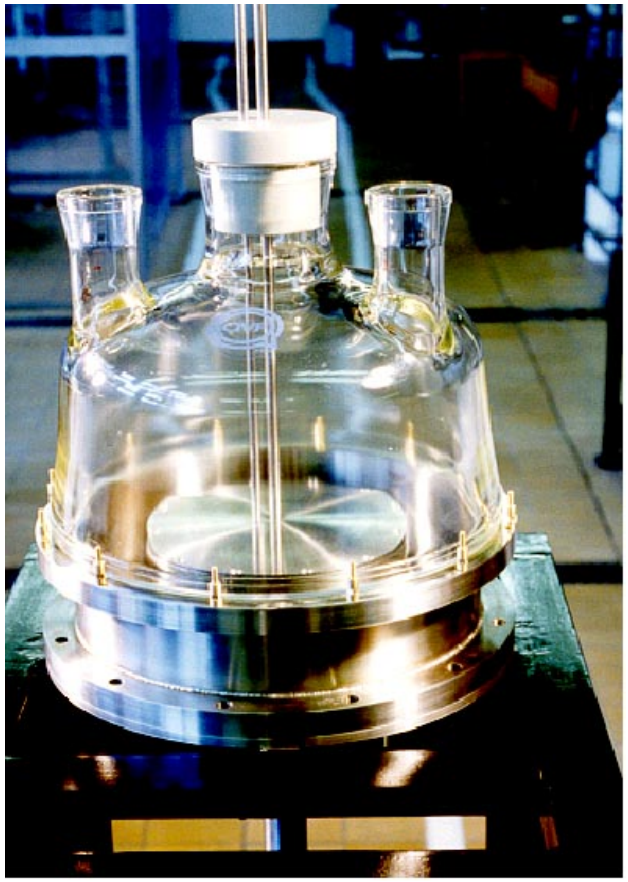
Tsouris & Porcelli, *Chem. Eng. Prog.*, 99(10), 50-55 (2003)

Examples of Process Intensification

- **Reactive distillation**
- **Static mixers**
- **High-G reactors/separators**
  - **Spinning disc**
  - **Centrifugal contactor**
- **Membrane catalytic reactors**
- **Heat-exchanger reactors**
- **Microreactors**
- **Oscillatory flow reactors**
- **Reactors/separators driven by external fields (electric, magnetic, sound, gravity, microwaves)**

Tsouris & Porcelli, *Chem. Eng. Prog.*, 99(10), 50-55 (2003)

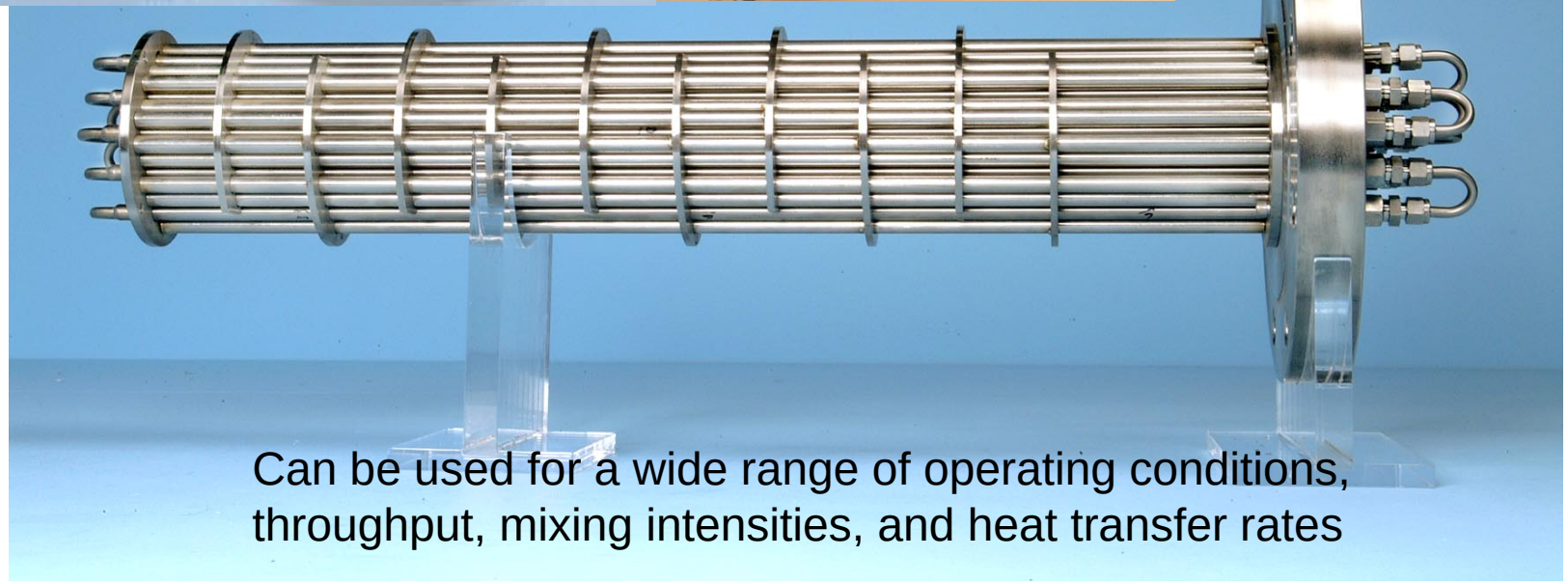
Spinning Disc Reactor



- **The multi-purpose reactor developed by Colin Ramshaw, University of Newcastle.**
- **It can be used for separations (via absorption or extraction), and polymerization processes.**

http://pig.ncl.ac.uk/

Flex Reactor

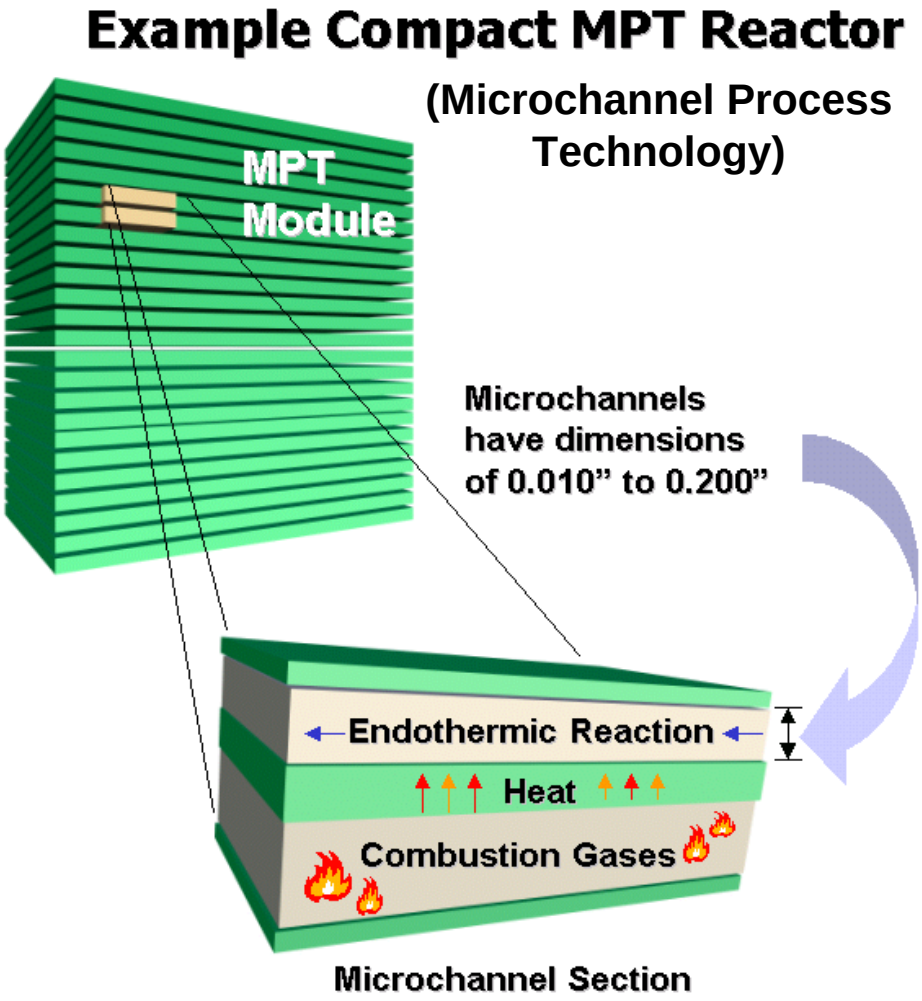


Can be used for a wide range of operating conditions, throughput, mixing intensities, and heat transfer rates

The FlexReactor (Flexible intensified reactor) developed by BHR Group.

http://bhrgroup.co.uk/pi/flexreactor.htm

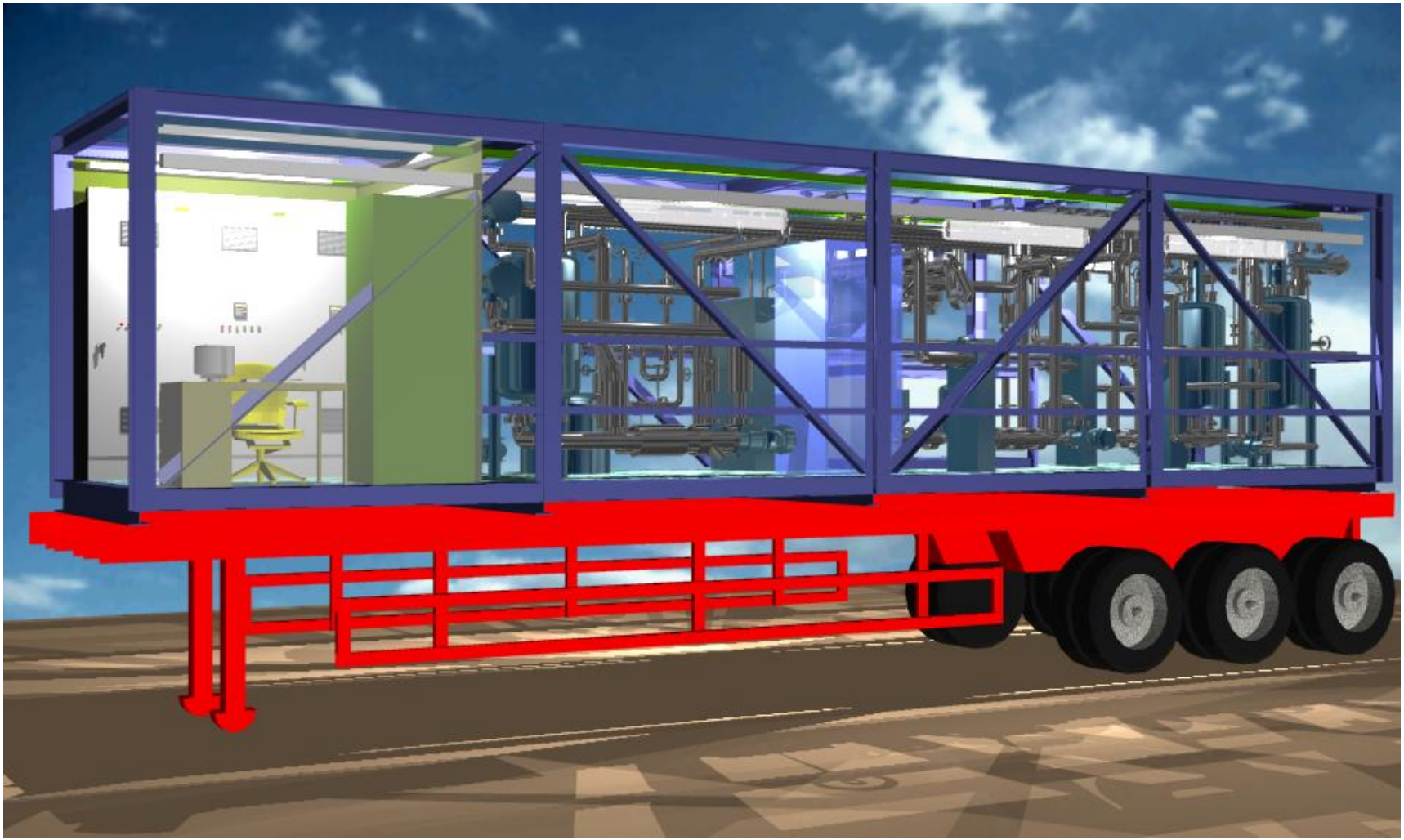
Microreactors



Velocys has developed manufacturing techniques to scale-up microreactors to industrial capacities.

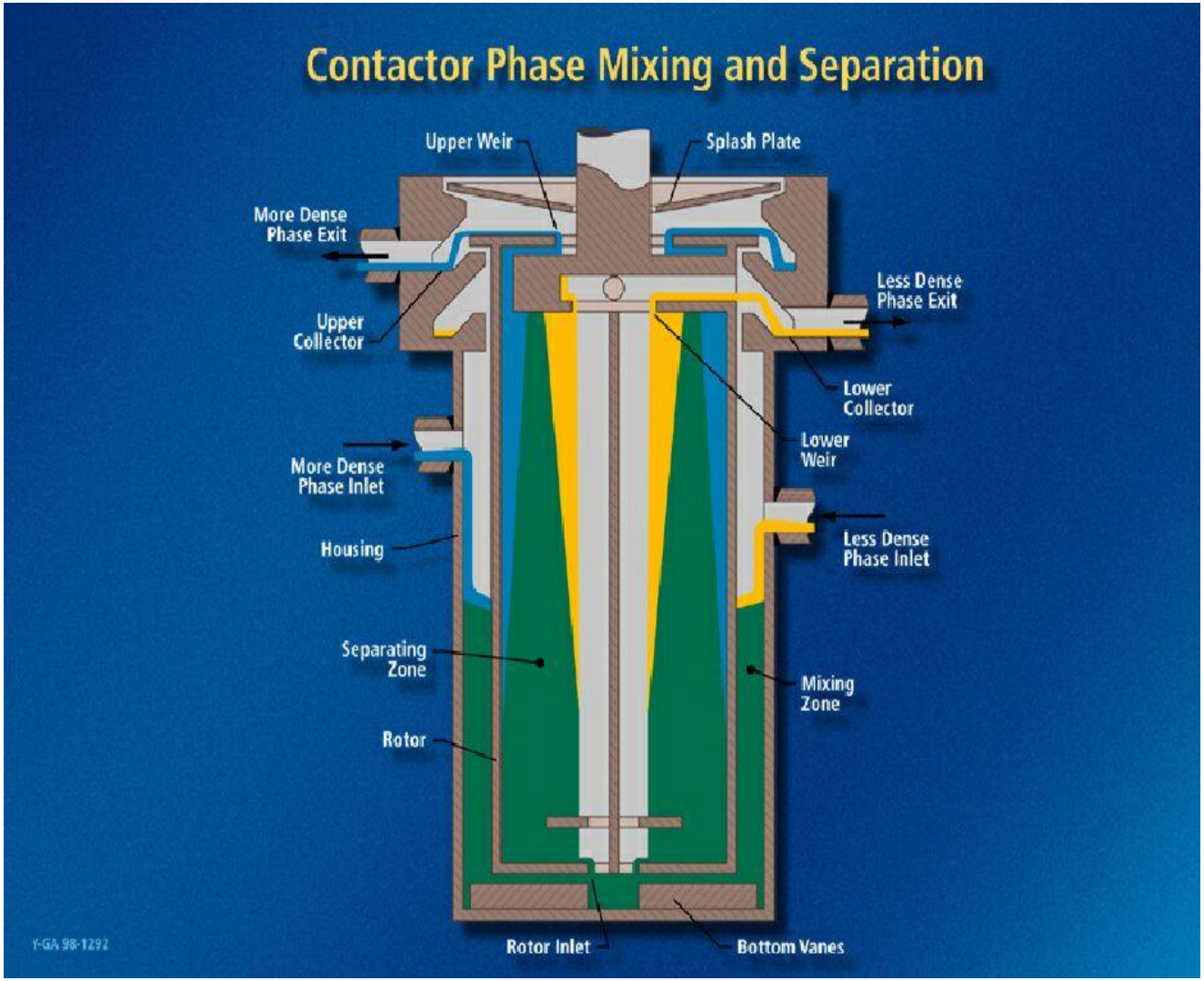
http://www.velocys.com/technology/

On-Site Process Intensification



On Site Process Intensification (OSPRI) plant: mobile PI plant designed by BHR Group to enable fine/specialty chemical companies to prove feasibility of PI processes at their sites.

Centrifugal Contactor



Developed for solvent extraction at DOE laboratories over 30 years ago and evolved from the mixer-settlers.

How Does the Centrifugal Contactor Help Process Intensification?

- **Reduces unit operations by integrating reaction and separation**
  - **Reduction of unit operations leads to simpler plant with fewer tanks and pipes**
- **Allows high throughput (acts as a pump) or low residence time (order of seconds)**
- **Provides intense mixing in the mixing zone and high G in the phase separation zone**
  - **Effective for mass transfer, reaction, and phase separation**
- **Centrifugal contactors can be used in a series of a multistage operation**
  - **Effective process control**
  - **Scalable**

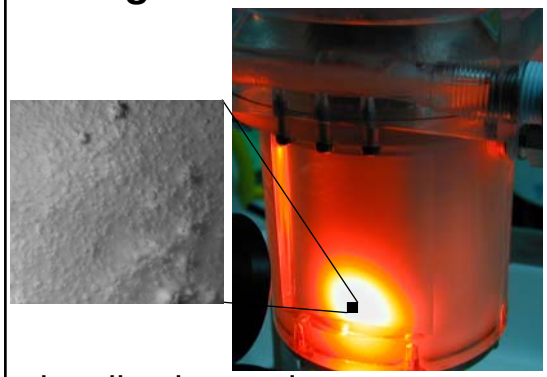
OAK RIDGE National Laboratory

Application Guided by Basic Studies*

- ***A coupled effort is undertaken to provide realistic simulation of centrifugal contactors aimed at scale-up and novel designs***

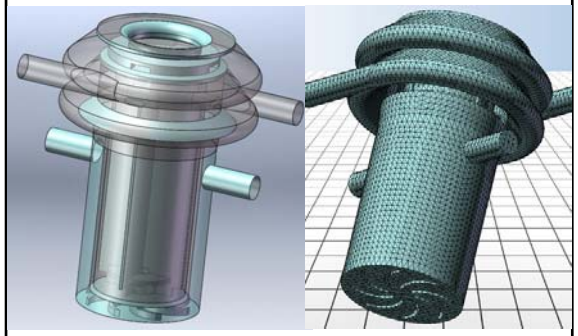
FLUID FLOW

Experimental study for insight and calibration



visualization and measurement

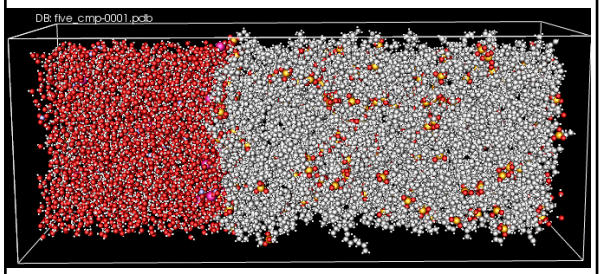
Advanced Modeling and Simulation



- Multiphase 3D fluid flow
- Reactive multispecies

CHEMICAL TRANSPORT

Sub-scale molecular modeling



insight and transport parameters

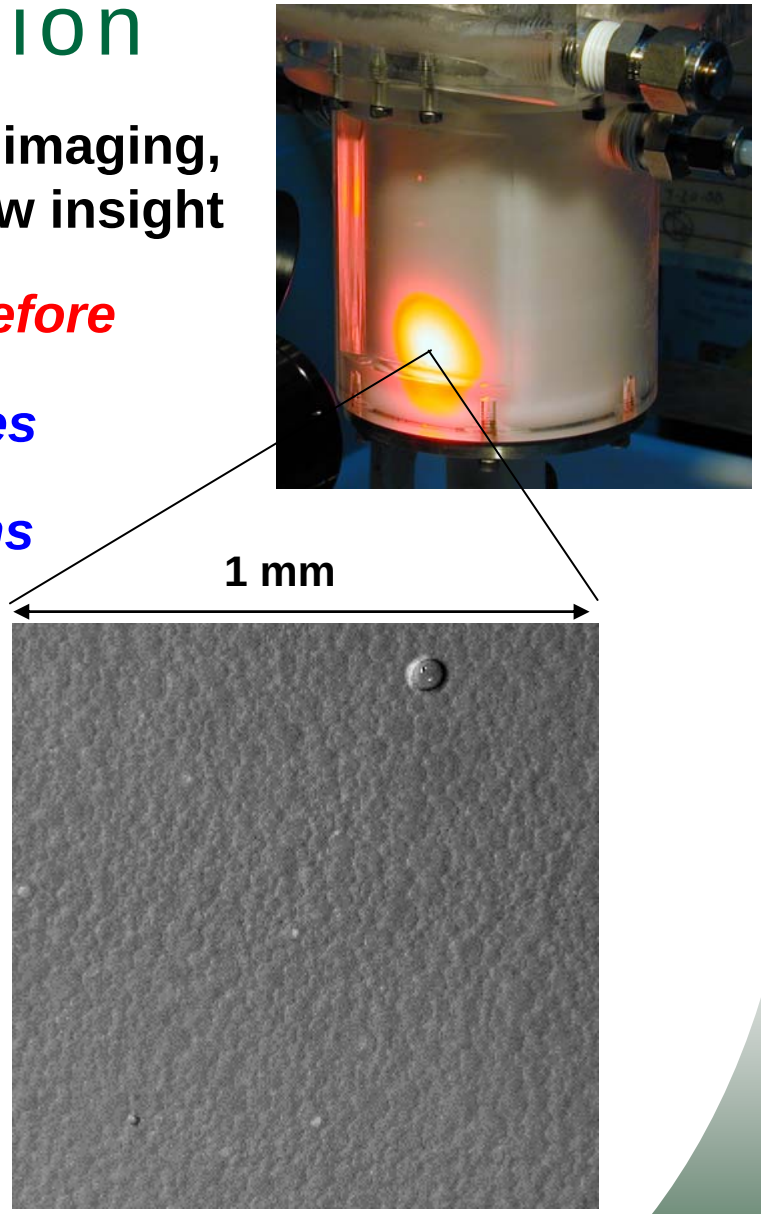
- ***We are developing non-equilibrium, multi-scale, space-time modeling and simulation approaches to predict the separation efficiency of contactors***

***V. de Almeida, C. Tsouris, J. Birdwell, D. DePaoli, R. Archibald, S. Cui, B. Khomami, "Modeling and Simulation of Solvent Extraction in Centrifugal Contactors," 15th Symposium on SS&T, Gatlinburg, TN, October, 2007**

Flow Regime Visualization

- **State-of-the-art high-speed, digital video imaging, solid-state light, and optics providing flow insight**
- ***Sub-millimeter flow regime never seen before***
- ***Reveals significant time and length scales***
- ***Realistic system and operating conditions used in nuclear applications***
  - **Contactor rotation: 2500 rpm**
  - **Aqueous flow rate:** 300 ml/min
  - **Organic flow rate:** 300 ml/min
  - **Organic:** 30% by volume TBP in Dodecane
  - **Aqueous:** 1 *M* HNO_3

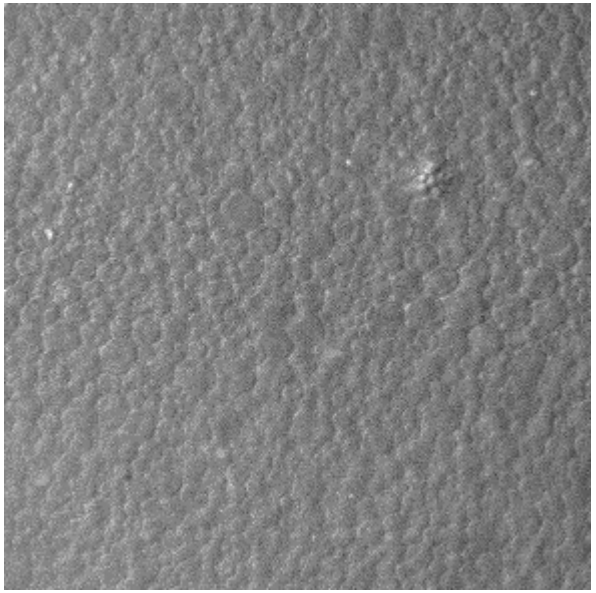
  - **Framing:** 5400 fps (185 μs between frames)
  - **Exposure:** 24 μs
  - **Field of view:** ~3.5 mm
  - **Spatial resolution:** ~7 μm
  - **Elapsed time:** 37 ms (200 frames)



Flow Regime Samples

- **1:5 O/A flow ratio**

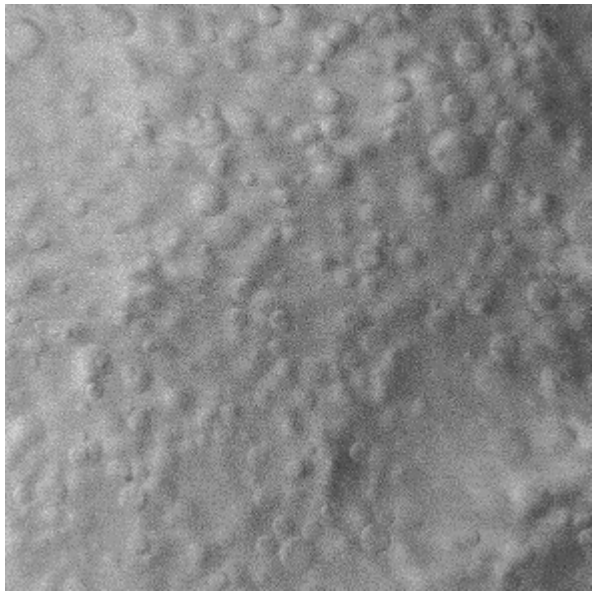
1 mm



- **Elapsed time:** 37 ms (200 frames)

- **5:1 O/A flow ratio**

1 mm



- **Elapsed time:** 18.5 ms (100 frames)

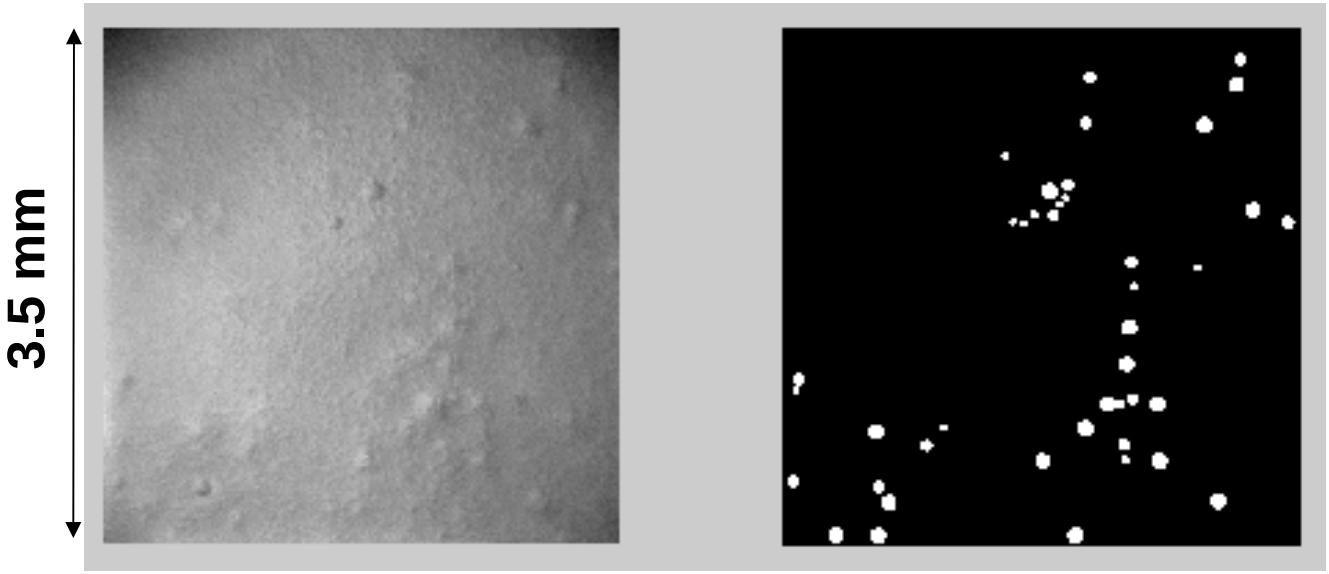
- ***Organic-rich flow regimes entrain more air***

- ***Identified significant air entrainment in realistic operation for most corresponding flow rate ratios***

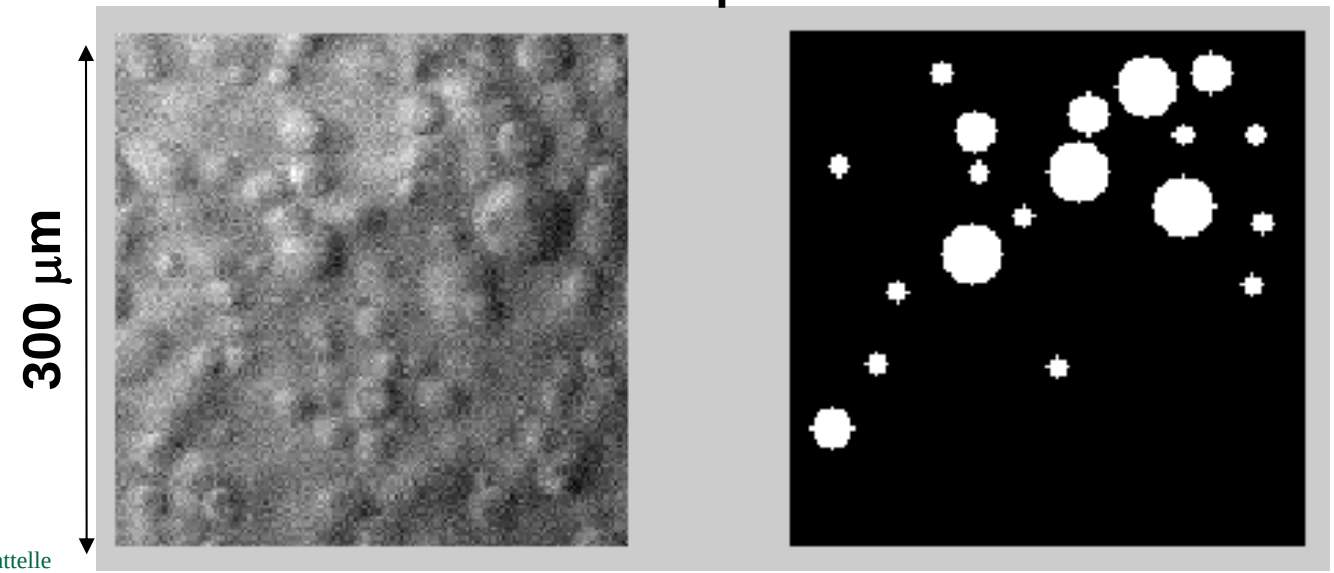
Computer-Aided Image Analysis

- **5:1 O/A flow ratio**

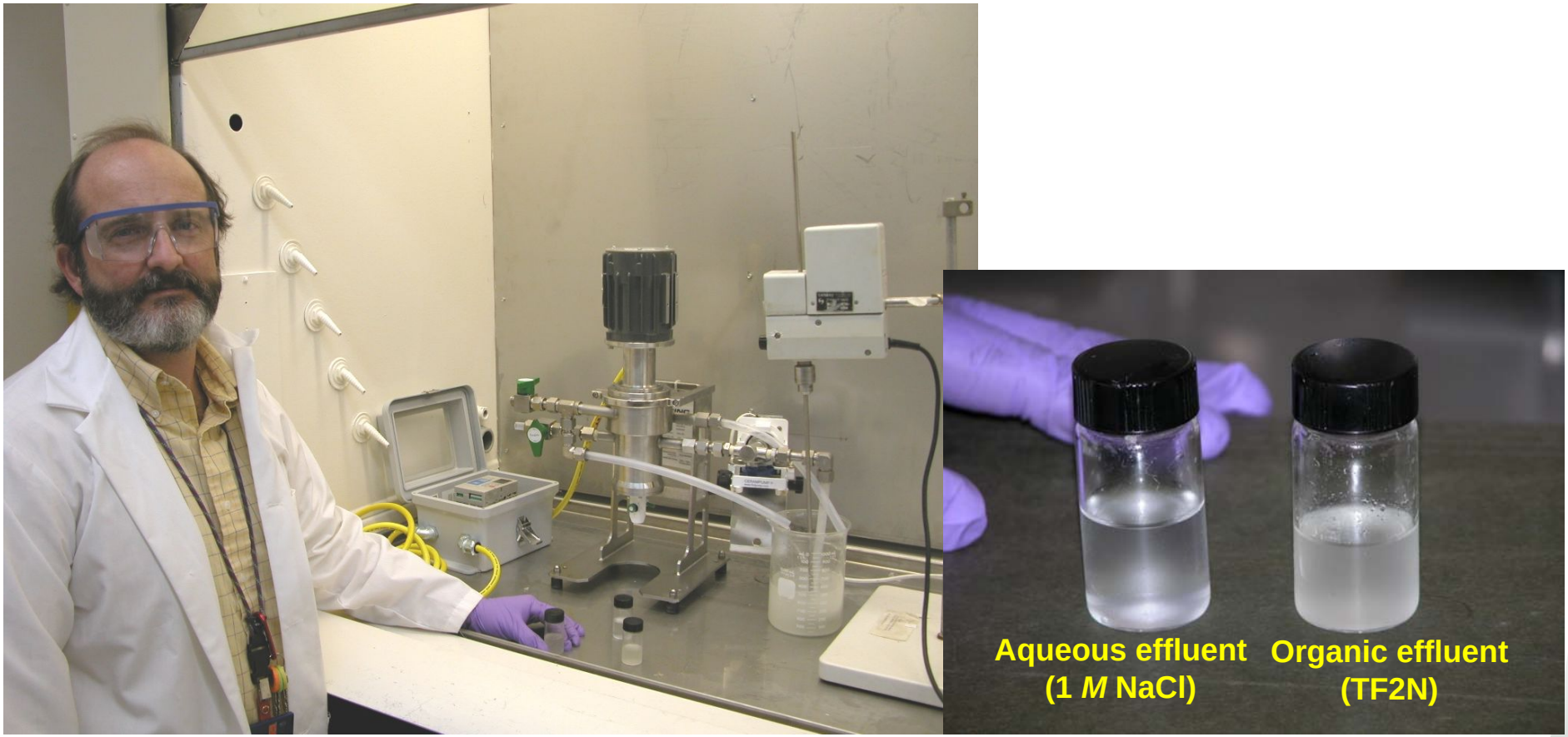
bubbles



drops



Centrifugal Contactor for Phase Separation



Contactor test results show promise for separating ionic liquids, even in cases in which the two phases have nearly equal densities and the organic phase has high viscosity (Birdwell, J.F., J. McFarlane, D.L. Schuh, R.D. Hunt, H. Luo, D.W. DePaoli, S. Dai, "Separation of Ionic Liquid Dispersions in Centrifugal Solvent Extraction Contactors," *Sep. Sci. Technol* 41, 2205-2223, 2006).

Is the current commercial version of centrifugal contactors adequate for reactive systems?

- **Advantages of centrifugal contactor**
  - **High-shear region for good mixing and mass transfer in liquid-liquid systems**
  - **High inter-phase mass-transfer rates**
  - **High G region for phase separation**
  - **High volumetric throughput because the high G separates the phases effectively**
  - **Low residence time (typically ~ 10 s)**
  - **Excellent performance over wide range of physical properties**
- **Fundamental limitations**
  - **Makes sense <u>for liquid-liquid systems</u>**
  - **Because of the pumping action of the rotor, <u>very little control over residence time</u> is allowed**
  - **Due to the high G, <u>solids are trapped</u> and accumulate in the contactor**

Not recommended when solids are involved

How Can the Centrifugal Contactor Effectively Function as a Multiphase Reactor?

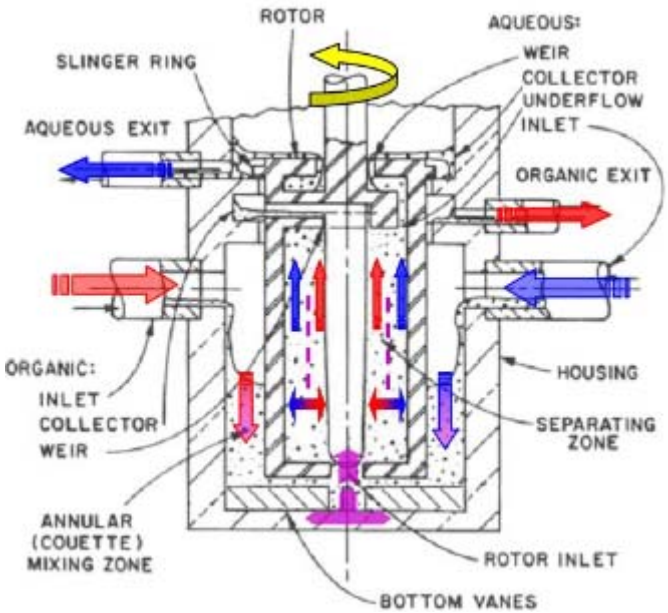
- **Need to control residence time in mixing region**
  - **It is desirable to be able to select the residence time from a wide range of values to match with the reaction kinetics**
  - **Not possible with the commercial version of centrifugal contactor**
- **Need to control temperature**
  - **The reaction temperature is important not only for the kinetics, but also for the quality of the products**
  - **Temperature control can be done with commercial system**
- **Scaleup should be possible**
  - **The ability to scale up the reactor without any effects on product quality is always important**
  - **Profitability highly depends on scaleup**
  - **Scaleup is possible with commercial contactors, but predictive tools do not exist; scaleup requires experimental verification**

Equipment modification needed to control residence time

OAK RIDGE National Laboratory

Integrated Reactor and Centrifugal Separator (patent pending)

- **A modified centrifugal contactor to allow control of the fluid residence time in the mixing zone**
- **The integrated reactor/separator can handle reactions that need up to 1-2 minutes for completion**
- **Suitable for liquid-liquid reactive systems at temperatures up to 100°C or higher**
- **Allows addition of a reactive or inert gas**
- **Cannot handle solids denser than the dense liquid phase**
- **Can be used for continuous production of biodiesel**



Residence-time control is achievable

Continuous Production of Biodiesel

- **Experimental setup allows for temperature control**
- **Base-catalyzed pathway is being utilized**
- **Cooperative research into biobased fuels between ORNL and Nu Energie, LLC (biodiesel production company) has been established**

- **Base-catalyzed reaction is used**

$$\begin{array}{l} H_2C\text{-}OCOR' \\ | \\ HC\text{-}OCOR'' \\ | \\ H_2C\text{-}OCOR''' \end{array} + 3\,CH_3OH \xrightarrow{KOH} \begin{array}{l} CH_3OCOR' \\ + \\ CH_3OCOR'' \\ + \\ CH_3OCOR'''\text{‘} \end{array} + \begin{array}{l} H_2C\text{-}OH \\ | \\ HC\text{-}OH \\ | \\ H_2C\text{-}OH \end{array}$$

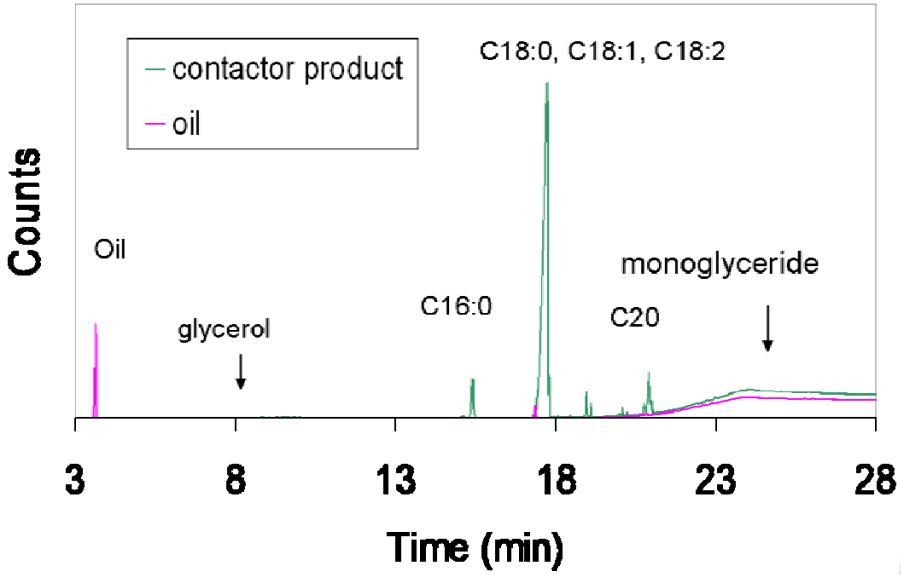
$$\text{Triglyceride + Methanol} \xrightarrow{\text{Catalyst}} \text{Methyl Esters + Glycerol}$$

Known chemistry for biodiesel synthesis is used

Gas Chromatography: FID Used to Analyze Reagents and Products

- **ASTM D6854**
- **2-5 mL samples**
- **Reactions halted with addition of acid**
- **Batch reaction sampled, light (ester) and heavy (glycerol) phase**
- **>99% conversion**
- **No entrained glycerol**

Equilibrium results



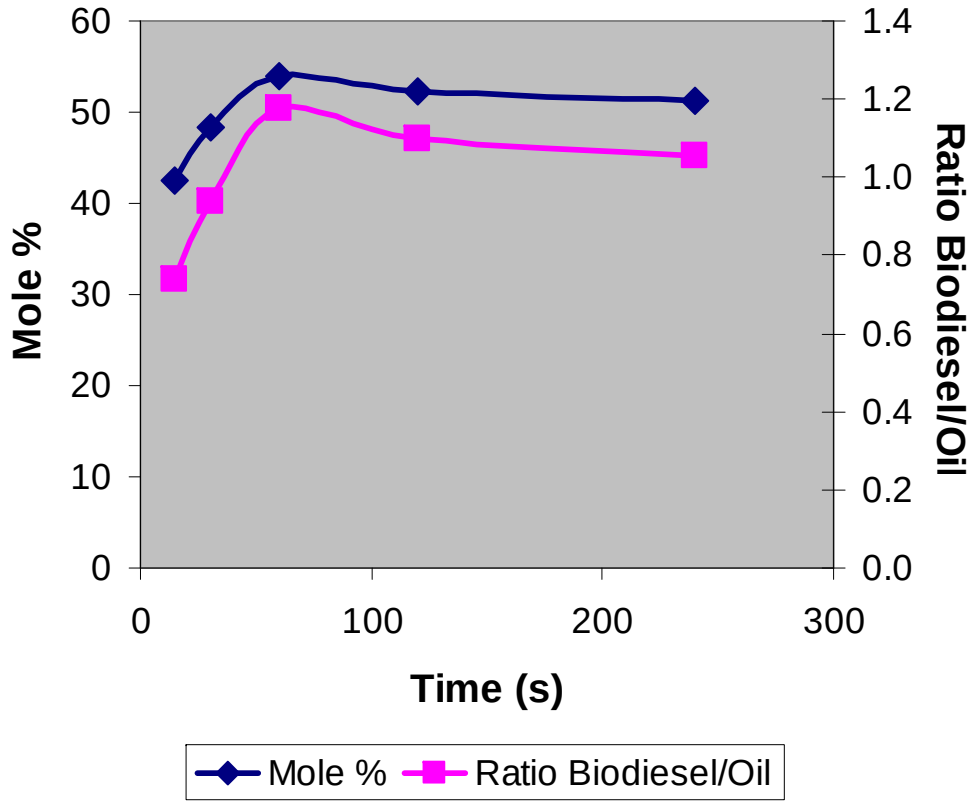
Superposition of two chromatograms for the reagent oil (pink) before reaction and the product methyl esters (green)

Established standard techniques are used for product analysis.
Near complete conversion observed at equilibrium

Kinetic Study Showed Rapid Production of Biodiesel

- **Reagents at 5:1 phase ratio (oil:methoxide) mixed in high speed homogenizer**
- **Samples taken at 15s, 30s, 1min, 2 min, 4 min**
- **Analysis by GC-FID shows both oil and products peaks to be present**
- **Reaction does not proceed further after 1 min**

Kinetic results from homogenizer

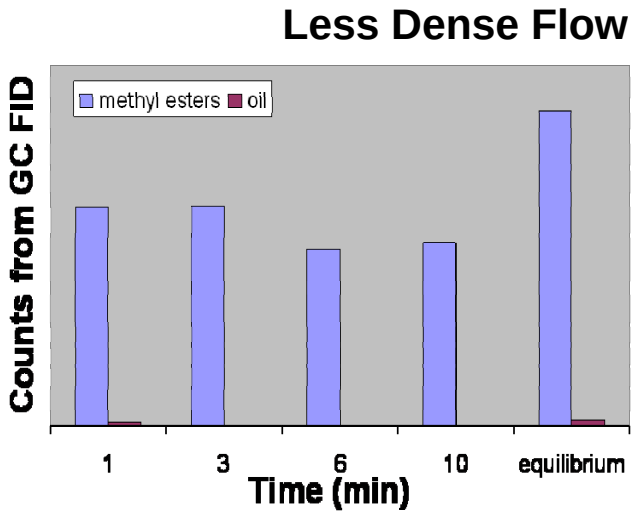


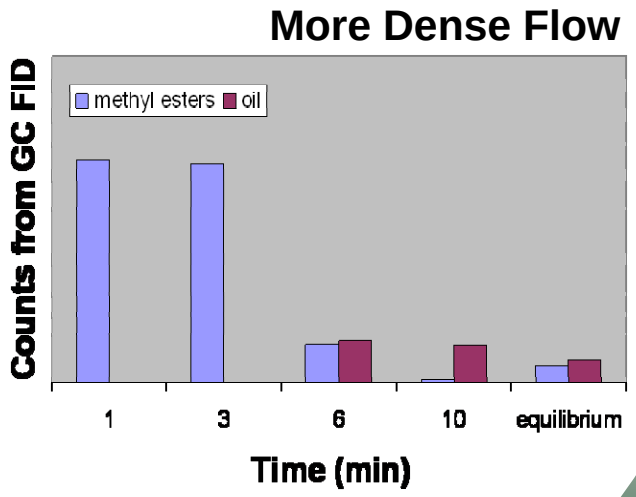
Mole % = methyl ester GC signal x100/ (methyl ester + oil signals)

Kinetic data show that the reaction is completed within 1 min

Continuous Production of Biodiesel Achieved by the Centrifugal Contactor

- **Reagents preheated**
- **Continuous feed into reactor**
- **Product streams separated and sampled at outlet of reactor**
- **Timing started at start of mixing. Took 3 minutes to establish steady state**
- **Low-density flow from reactor was methyl ester**
- **High-density flow from reactor at steady state was glycerol**





Project successfully demonstrated continuous biodiesel production

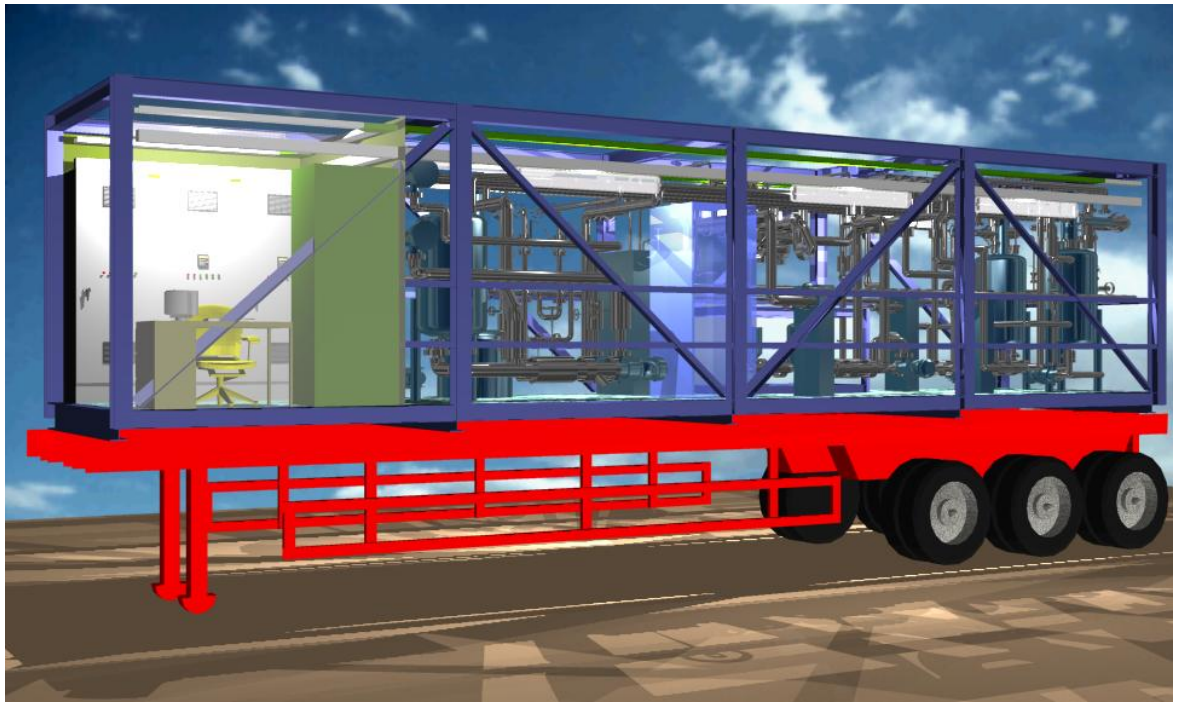
Project Successfully Demonstrated Application of Process Intensification to Biodiesel Production

- **One-step, base-catalyzed reaction/separation**
- **Innovation in contactor technology to control residence time**
- **Demonstration of fast chemical kinetics**
- **Rapid separation of product flows**
- **Principles of process intensification satisfied**
  - Process combines reaction and phase separation
  - Allows high throughput
  - Provides intensive multiphase mixing
  - Allows short residence time
  - Requires small footprint
  - Can be a mobile process (special applications)
  - Series of centrifugal contactors can be used in various steps of biodiesel production: **reaction, phase separation, purification**

Continuous, compact, fast, scalable…

The Future of Biodiesel Production

- **Variety of feedstocks**
  - **seed oils**
  - **waste fat oil and grease**
  - **animal products**
- **Compact, movable, versatile plants of different sizes**
  - **For varying feedstocks and throughput**



OSPRI plant designed by BHR Group

Ideal for small operations

Summary

- **Process intensification offers several advantages to biodiesel production:**
- **Reduces size and number of unit operations by integrating units (e.g., reaction & separation)**
- **Leads to faster operations with less footprint and lower chemical inventories**
- **A compact unit operation, with on-line analysis and control, has the potential to handle variations in the quality of the feedstocks**
- **Pre-treatment/post-treatment components can be added to handle wide variety of feedstocks**
- **Small, versatile operations are possible, reducing the transportation cost of feedstocks**

Acknowledgments

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- **Special thanks to Brian Hullette and Joel Day of Nu-Energie for their interest to commercialize the ORNL technology, to Valmor de Almeida for providing slides on basic studies of centrifugal contactors, and to David DePaoli for his valuable comments and support.**

- **Special thanks to Ian Henderson, Protensive Ltd.; Gul Ozcan-Taskin and Andrew Green, BHR Group; and Laura Silva, Velocys, Inc., for providing pictures.**

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