Microreactor Engineering

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Microreactors Two-Phase Reactions
Production of Biodiesel in Microreactors

In Affiliation With:

MBI

Microproducts Breakthrough Institute

PTT - LOA

PTT - Laboratories Of America

Biodiesel Synthesis

Alcohol + **Oil** → **Biodiesel** + **Glycerol**

Cleaner-burning diesel substitute

Byproduct used in soaps and pharmaceuticals

Biodiesel Synthesis

Refined
Non-Refined

Liquid-Catalyst
Solid-Catalyst
NO-Catalyst

Alcohol + Oil → Biodiesel + Glycerol

Methyl
Ethyl
Butyl

Algal-oil
Soybean oil
Animal fat
Cotton seed oil
Mustard seed oil
Palm-oil
Rape-seed oil
Sunflower oil
Castrol oil
Canola oil
Fish oil

Room Temp. & Atm. Pressure
60 [^{o}C]. & 1.1 Atm.
Supercritical Conditions.

Biodiesel Synthesis

Liquid-Catalyst
Solid-Catalyst
NO-Catalyst

Refined
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Rape-seed oil
Sunflower oil
Castor oil
Canola oil
Fish oil

Room Temp. & Atm. Pressure
60 [^{o}C]. & 1.1 Atm.
Supercritical Conditions.

Biodiesel Synthesis - Reaction Steps

$$
\begin{array}{lcl}
CH_2\text{-}OOR_1 & & CH_2\text{-}OH \\
| & & | \\
CH\text{ - }OOR_2 & + & CH\text{-}OOR_2 \\
| & & | \\
CH_2\text{-}OOR_3 & & CH_2\text{-}OOR_3
\end{array}
\quad
\begin{array}{c}
K_1 \\ \leftrightarrow \\ K_2
\end{array}
\quad
\begin{array}{l}
CH_3CH_2\text{-}OOR_1 \\ \\ + \\ \\ \\
\end{array}
$$

Triglyceride + Ethanol = Diglyceride + Ethyl ester

$$
\begin{array}{lcl}
CH_2\text{-}OH & & CH_2\text{-}OH \\
| & & | \\
CH\text{ -}OOR_2 & + & CH\text{-}OOR_2 \\
| & & | \\
CH_2\text{-}OOR_3 & CH_3CH_2\text{-}OH & CH_2\text{-}OH
\end{array}
\quad
\begin{array}{c}
K_3 \\ \leftrightarrow \\ K_4
\end{array}
\quad
\begin{array}{l}
\\ \\ + \\ \\ CH_3CH_2\text{-}OOR_3
\end{array}
$$

Diglyceride Ethanol Monglyceride Ethyl ester

Biodiesel Synthesis - Reaction Steps

$$\begin{array}{l} CH_2\text{-}OH \\ | \\ CH\text{-}OOR_2 \\ | \\ CH_2\text{-}OH \end{array} + CH_3CH_2\text{-}OH \underset{K_6}{\overset{K_5}{\leftrightarrow}} \begin{array}{l} CH_2\text{-}OH \\ | \\ CH\text{-}\ OH \\ | \\ CH_2\text{-}OH \end{array} + CH_3CH_2OOR_2$$

Monglyceride **Ethanol** **Glycerol** **Ethyl ester**

Overall Reaction

$$\begin{array}{l} CH_2\text{-}OOR_1 \\ | \\ CH\ \text{-}OOR_2 \\ | \\ CH_2\text{-}OOR_3 \end{array} + 3\ CH_3CH_2\text{-}OH \underset{K_B}{\overset{K_A}{\leftrightarrow}} \begin{array}{l} CH_2\text{-}OH \\ | \\ CH\text{-}OH \\ | \\ CH_2\text{-}OH \end{array} + 3\ CH_3CH_2\text{-}OOR$$

Triglyceride **Ethanol** **Glycerol** **BIODIESEL**

Triglycerides

CH_2-OOC-R_1
|
CH-OOC-R_2
|
CH_2-OOC-R_3

Where R_1, R_2, R_3 are fatty acids

Saturated fatty acids Lauric Acid (12:00): [CH_3 $(CH_2)_{10}CO_2H$]

```
    H   H   H   H   H   H   H   H   H   H   H   O
    |   |   |   |   |   |   |   |   |   |   |   ||
H – C – C – C – C – C – C – C – C – C – C – C – C – OH
    |   |   |   |   |   |   |   |   |   |   |
    H   H   H   H   H   H   H   H   H   H   H
```

Triglycerides

Myristic Acid (14:00): [$CH_3\ (CH_2)_{12}CO_2H$]

```
    H   H   H   H   H   H   H   H   H   H   H   H   H     O
    |   |   |   |   |   |   |   |   |   |   |   |   |     ||
H – C – C – C – C – C – C – C – C – C – C – C – C – C –  C – OH
    |   |   |   |   |   |   |   |   |   |   |   |   |
    H   H   H   H   H   H   H   H   H   H   H   H   H
```

Palmitic Acid (16:00): [$CH_3\ (CH_2)_{14}CO_2H$]

```
    H   H   H   H   H   H   H   H   H   H   H   H   H   H   H   O
    |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   ||
H – C – C – C – C – C – C – C – C – C – C – C – C – C – C – C – C – OH
    |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
    H   H   H   H   H   H   H   H   H   H   H   H   H   H   H
```

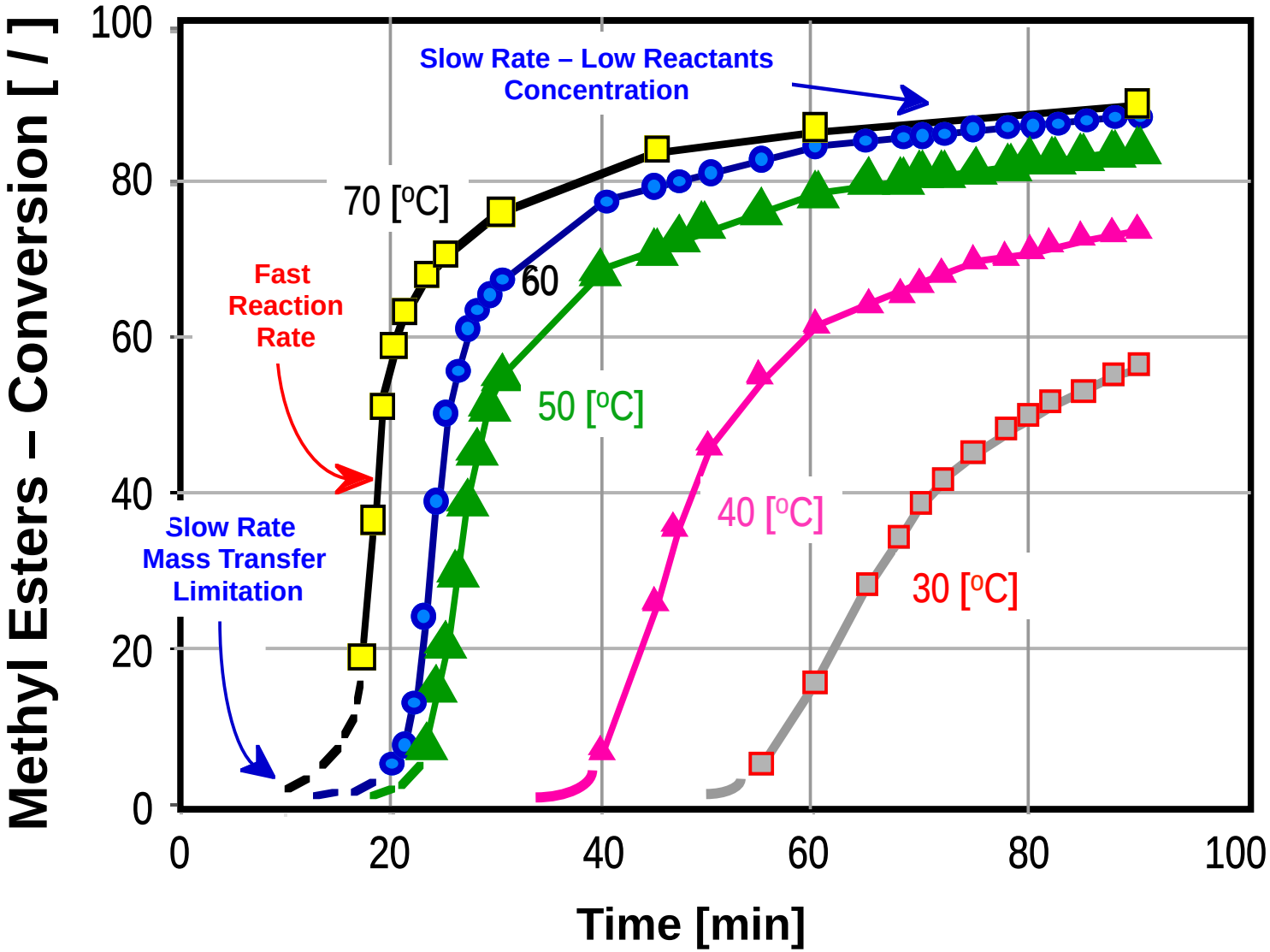
Triglycerides-Unsaturated Fatty Acids

Linoleic acid (18:02): [$CH_3(CH_2)_3(CH_2CH{=}CH)_2(CH_2)_7CO_2H$]

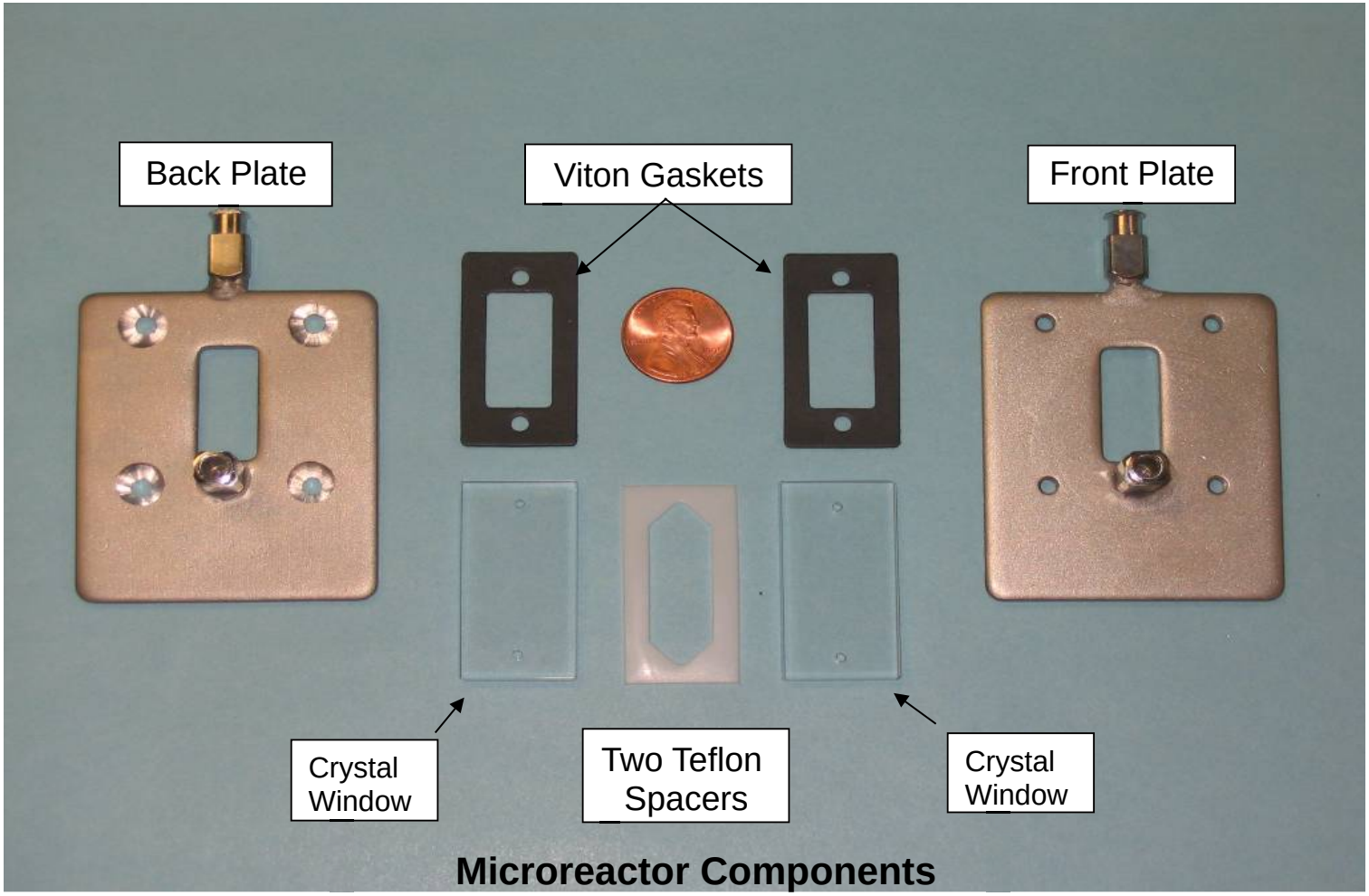
```
   H  H  H   H  H  H H  H  H   H H  H  H  H  H   H  H  O
   |  |  |   |  |  | |  |  |   | |  |  |  |  |   |  |  ||
H–C–C–C–C–C–C=C–C–C=C–C–C–C–C–C–C–C–C–OH
   |  |  |   |  |        |        | |  |  |  |  |  |  |
   H  H  H   H  H        H        H H  H  H  H  H  H  H
```

Linolenic acid (18:03): [$CH_3(CH_2CH{=}CH)_3(CH_2)_7CO_2H$]

```
   H  H  H  H  H  H  H  H  H  H  H  H  H  H  H  H  H  O
   |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  ||
H–C–C–C–C–C–C=C–C–C=C–C=C–C–C–C–C–C–C–OH
   |  |  |  |  |        |              |  |  |  |  |
   H  H  H  H  H        H              H  H  H  H  H
```

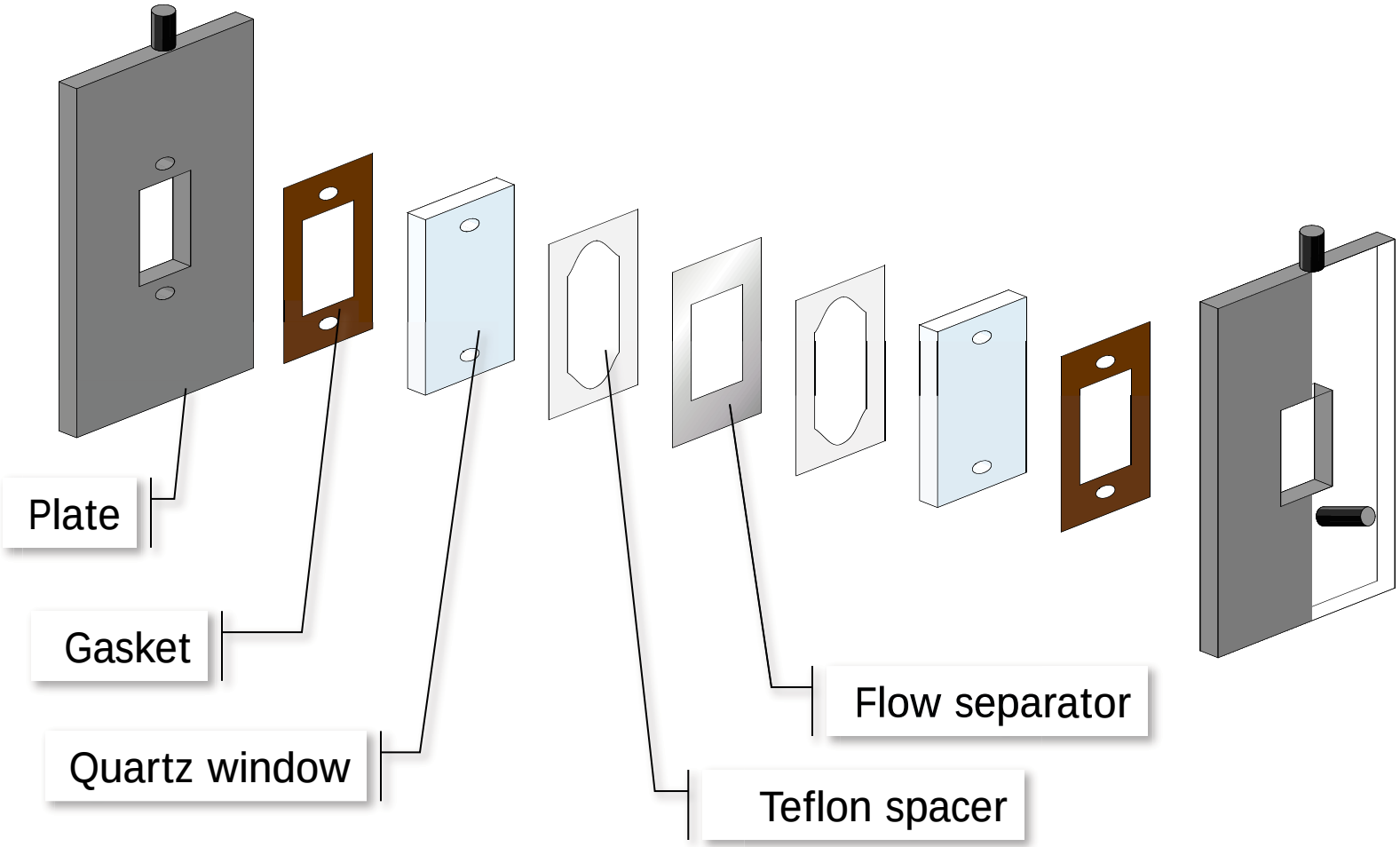

Methyl Esters – Conversion [/]
Time [min]
0
20
40
60
80
100
Slow Rate – Low Reactants Concentration
Fast Reaction Rate
Slow Rate Mass Transfer Limitation
70 [ºC]
60
50 [ºC]
40 [ºC]
30 [ºC]

Experimental Setup



Microreactor Components

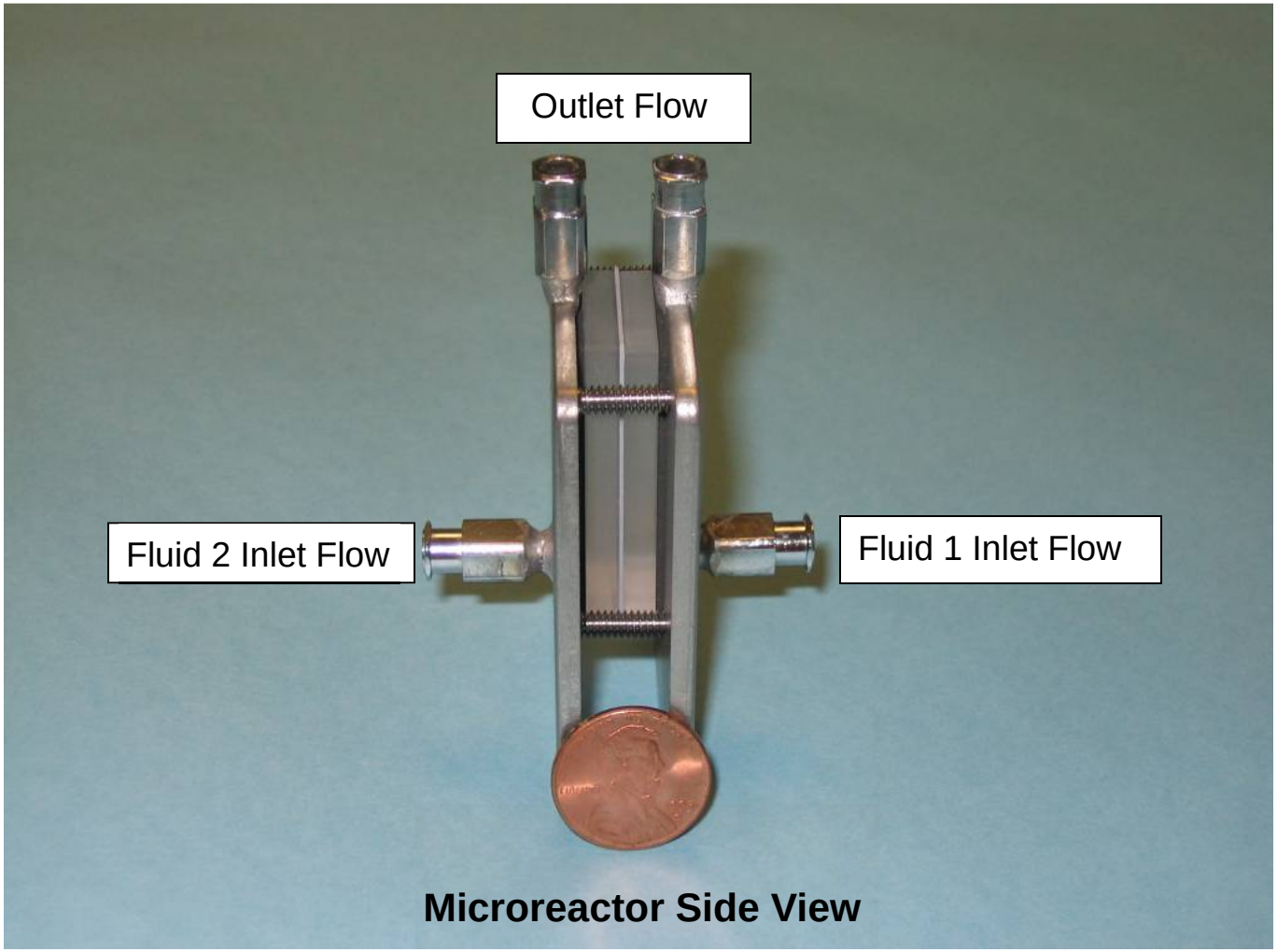
Experimental Setup



Experimental Setup

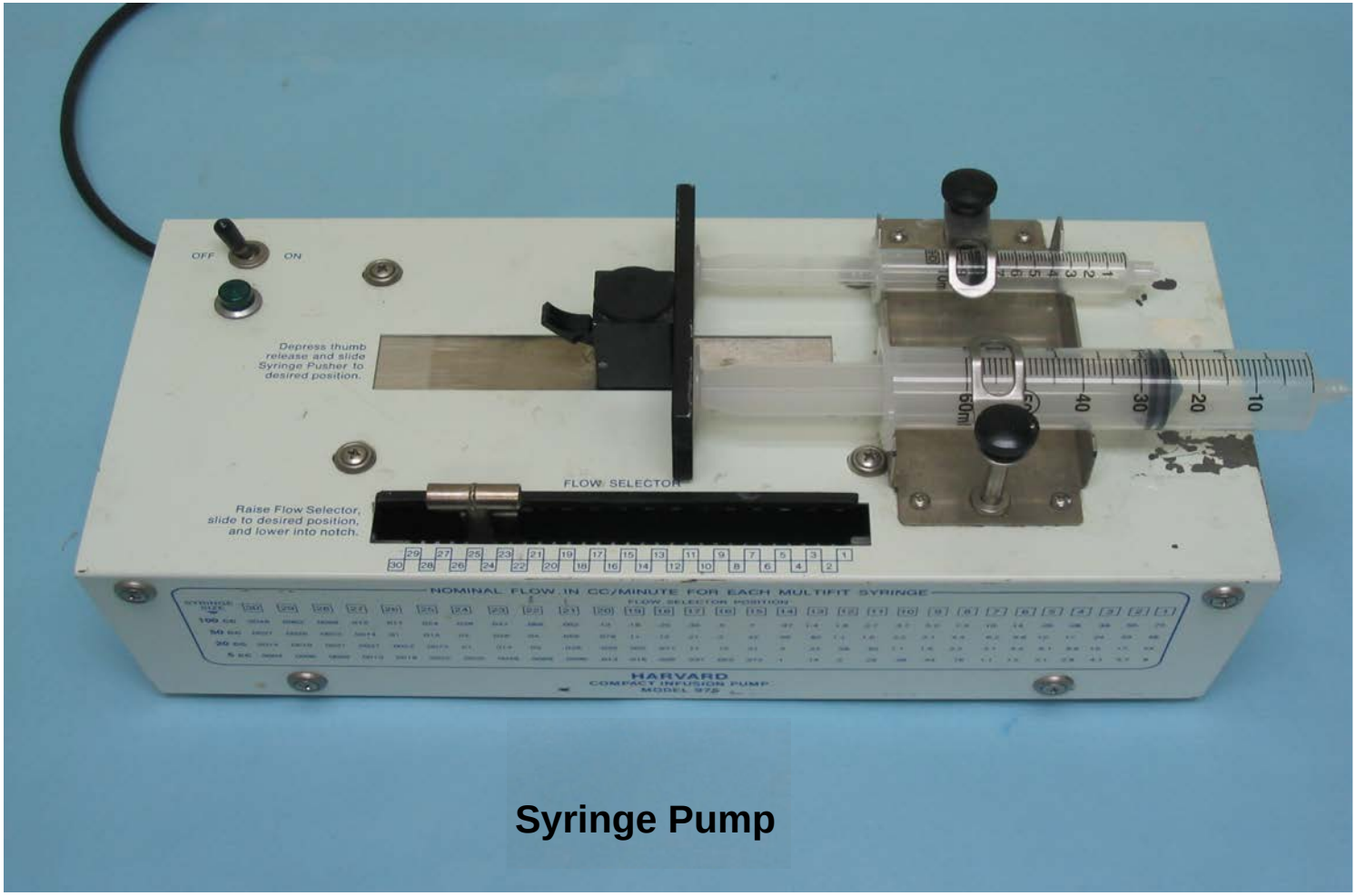
Microreactor Assembled without Back Plate

Experimental Setup



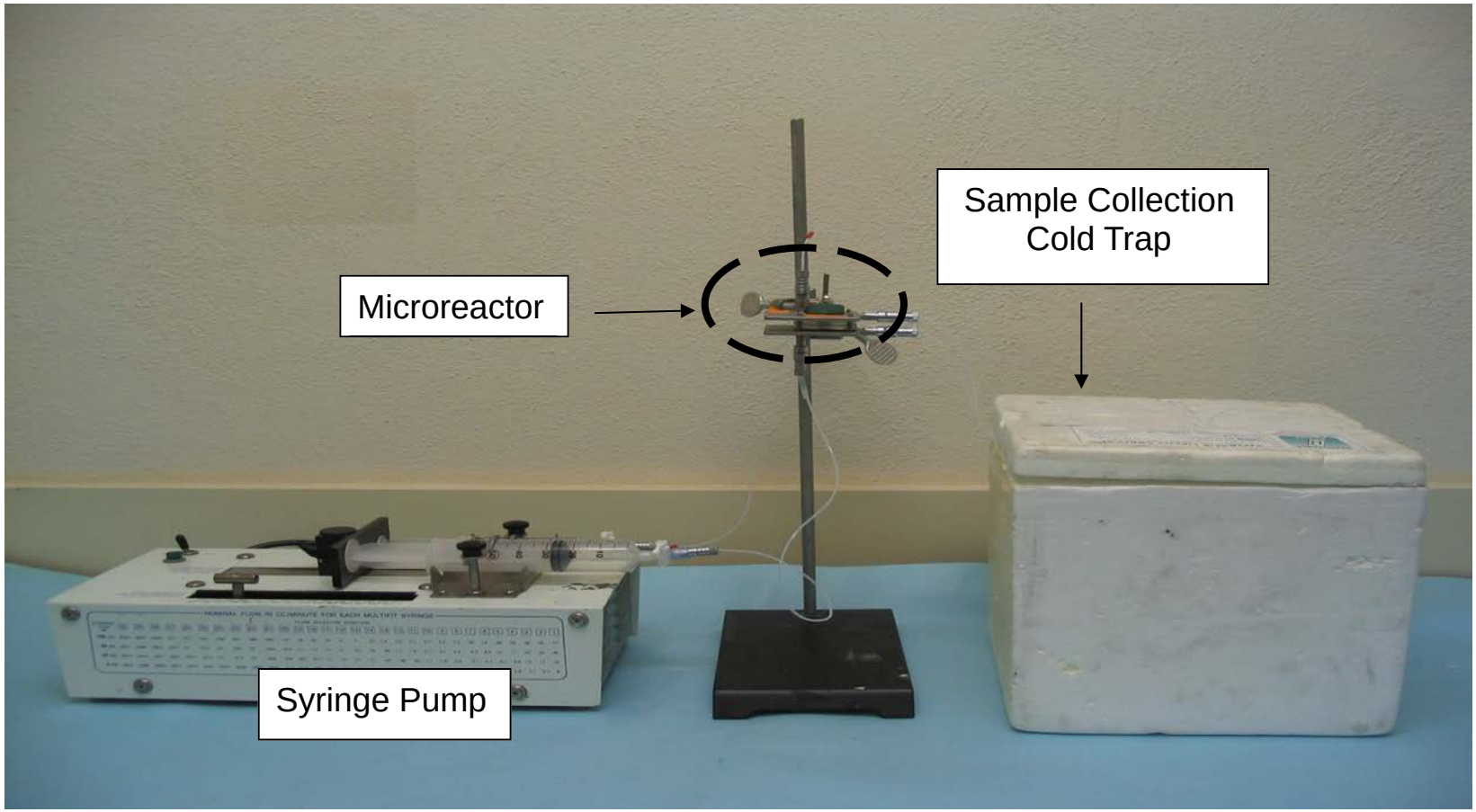
Microreactor Side View

Experimental Setup

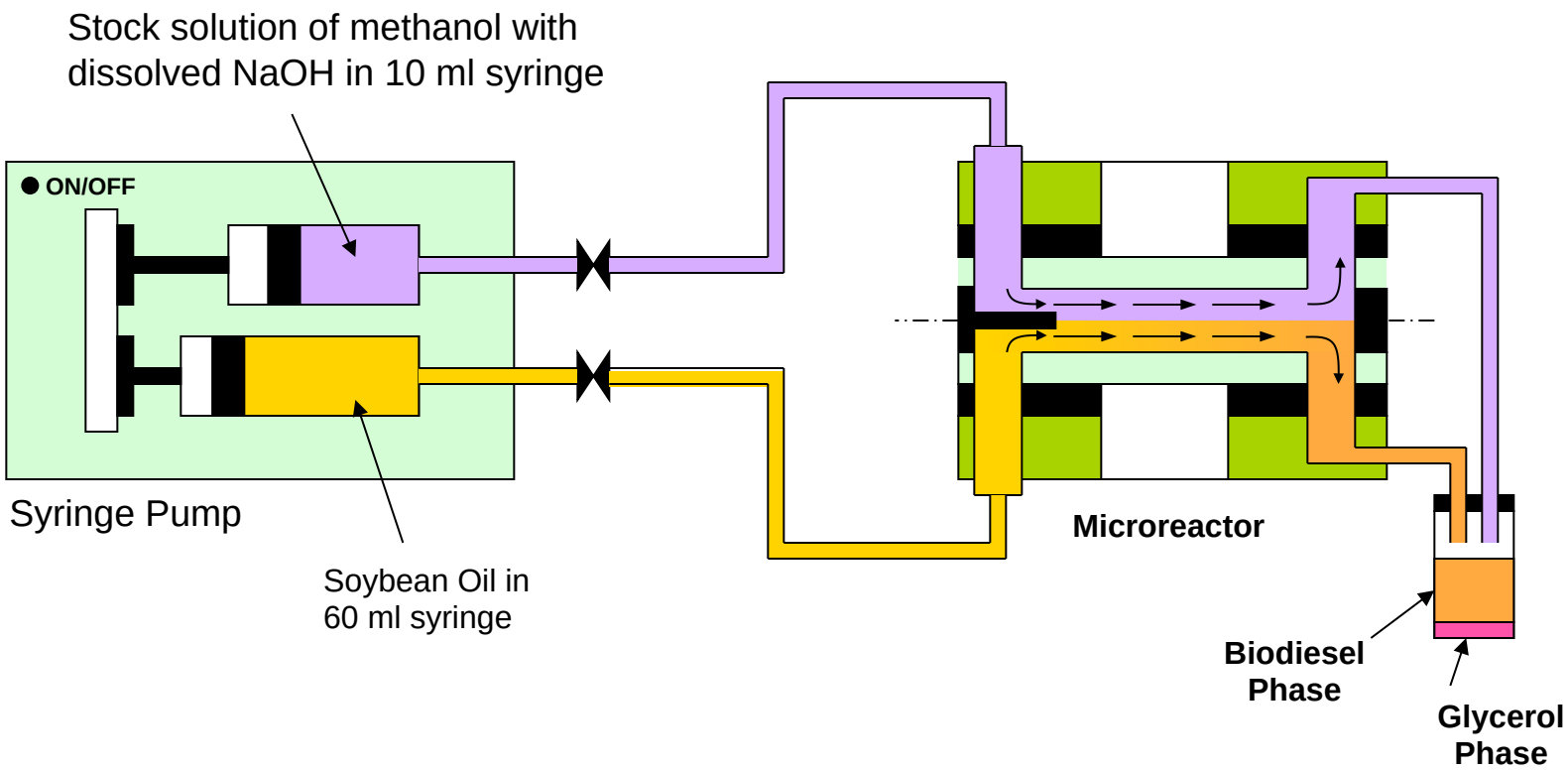


Syringe Pump

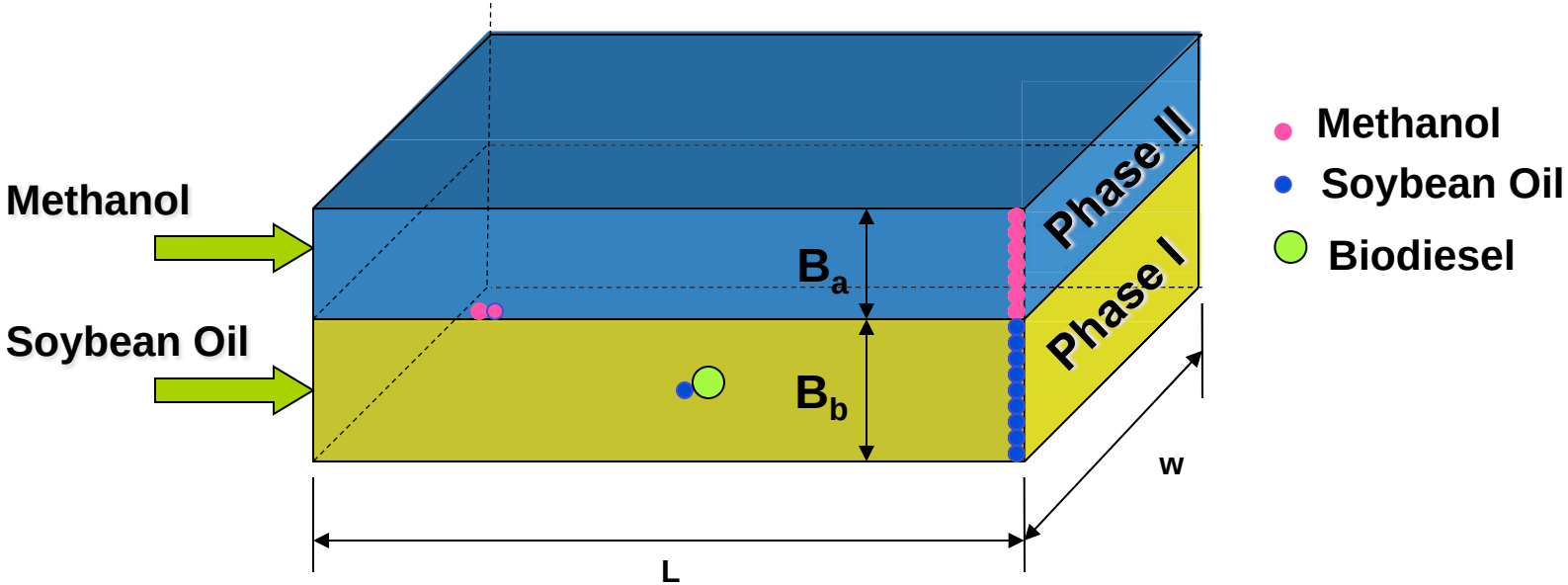
Experimental Setup



Experimental Setup - Animation



Experimental Setup - Animation

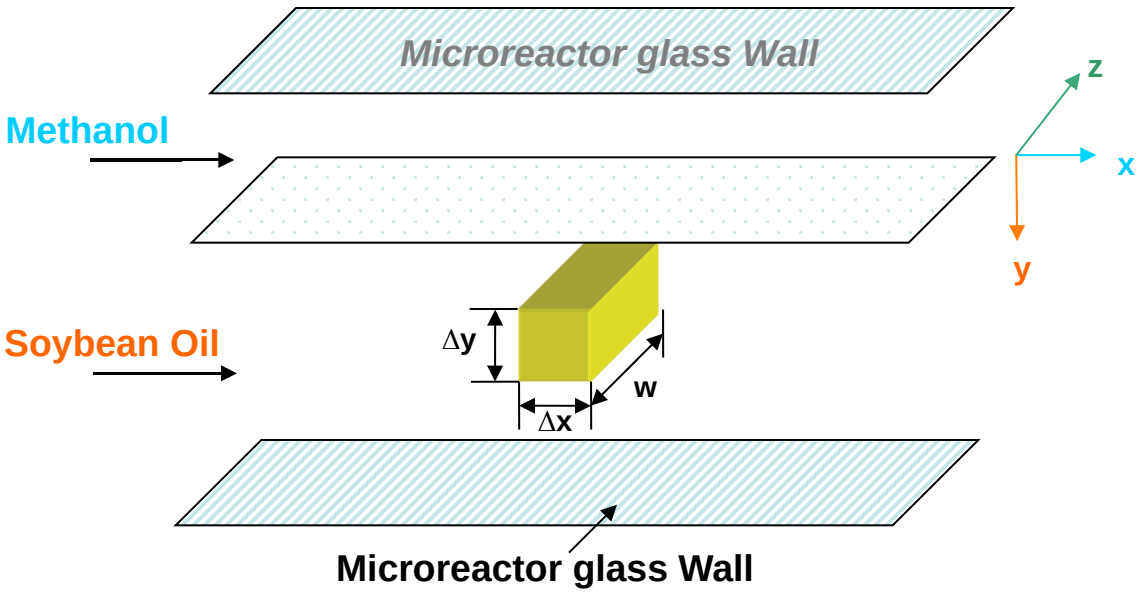


Schematic of the Microreactor.

Assumptions:

- The system is operating at steady state conditions and at 25 ^{o}C temperature;
- Constant initial concentrations of methanol and soybean oil at the inlet;
- Concentration of methanol at the interface throughout the microreactor is constant and equals the equilibrium concentration;
- Methanol from phase II diffuses towards phase I and reacts with soybean oil to produce biodiesel

Differential Control Volume in Microreactor



Input –Output = Accumulation

Accumulation = 0 (at steady state)

Input = diffusion (x-direction) + convection (x-direction)+ diffusion (y –direction)

Output = diffusion (x-direction) + convection (x-direction)+ diffusion (y –direction)

Two-Dimensional Mathematical Model:

A steady state mass balance of soybean oil (A) in a control volume *dV=Wdydx*:

$$0 = v_x \left(W\Delta y\right) C_A\big|_x - v_x \left(W\Delta y\right) C_A\big|_{x+\Delta x} - D_A \left.\frac{dC_A}{dx}\right|_x \left(W\Delta y\right)$$

$$+ D_A \left.\frac{dC_A}{dx}\right|_{x+\Delta x} \left(W\Delta y\right) - D_A \left.\frac{dC_A}{dy}\right|_y \left(W\Delta x\right)$$

$$+ D_A \left.\frac{dC_A}{dy}\right|_{y+\Delta y} \left(W\Delta x\right) - [+k_1 C_A C_B - k_2 C_{DG} C_{ME}]\left(W\Delta y\Delta x\right)$$

By rearranging all terms into the form required for taking the limits and after division by control volume, we obtain:

$$-v_{Ax}\frac{\partial C_A}{\partial x}+D_A\frac{\partial^2 C_A}{\partial x^2}+D_A\frac{\partial^2 C_A}{\partial y^2}-k_1C_AC_B-k_2C_{DG}C_{ME}=0$$

The boundary conditions associated with the above equation are:

$$C_A(0,\mathrm{y})=C_{A0} \qquad 0\le y\le B_a; \qquad \frac{\partial C_A}{\partial y}(x,B_a)=0 \qquad 0\le x\le L$$

$$\frac{\partial C_A}{\partial x}(L,\mathrm{y})=0 \qquad 0\le y\le B_a; \qquad \frac{\partial C_A}{\partial y}(x,0)=0 \qquad 0\le x\le L$$

In the above equation v_{Ax} is velocity in x-direction in phase I and it is only a function of lateral position '*y*'; where $a=\mu_A/\mu_B$, $b=B_a/B_b$.

$$v_{Ax}=V_{\max}\left[1+\left(\frac{b^2-a^2}{aB_a(1+b)}\right)y-\left(\frac{a+b}{aB_aB_b(b+1)}\right)y^2\right]$$

Mathematical Model

Steady state mass balance of ***soybean oil*** in phase I for control volume (w$\Delta y \Delta x$)

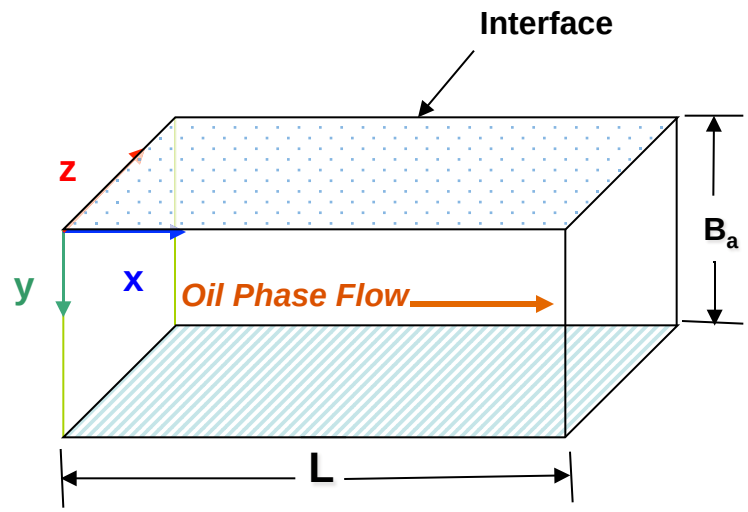
$$v_{A,x}\frac{\partial C_A}{\partial x} = D_{A,x}\frac{\partial^2 C_A}{\partial x^2} + D_{A,y}\frac{\partial^2 C_A}{\partial y^2} - k_1 C_A C_B + k_2 C_{DG} C_{ME}$$

$$C_A(0,y) = C_{A0}, \qquad 0 \le y \le B_a$$

$$\frac{\partial C_A}{\partial y}(x,B_a) = 0, \qquad 0 \le x \le L$$

$$\frac{\partial C_A}{\partial y}(x,0) = 0, \qquad 0 \le x \le L$$

$$\frac{\partial C_A}{\partial x}(L,y) = 0, \qquad 0 \le y \le B_a$$

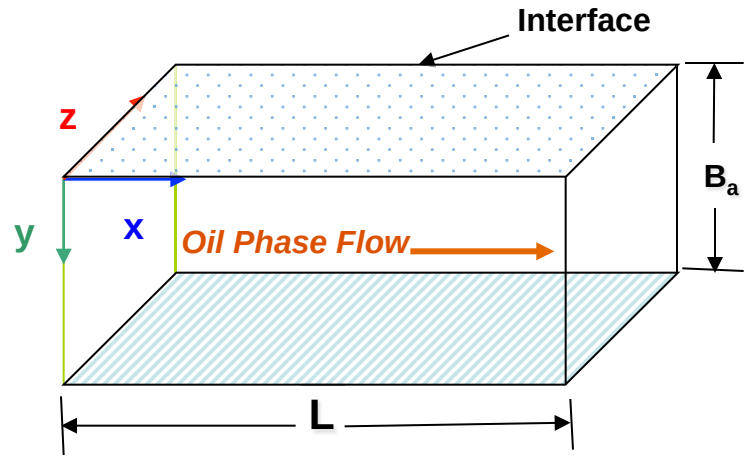


Mathematical Model

Steady state mass balance of ***methanol*** in phase I for control volume (w$\Delta y \Delta x$)

$$v_{A,x}\frac{\partial C_B}{\partial x} = D_{B,x}\frac{\partial^2 C_B}{\partial x^2} + D_{B,y}\frac{\partial^2 C_B}{\partial y^2} - k_1 C_A C_B + k_2 C_{DG} C_{ME}$$
$$-k_3 C_B C_{DG} + k_4 C_{MG} C_{ME} - k_5 C_B C_{MG} + k_6 C_{GL} C_{ME}$$

$$C_B(0,y) = 0, \qquad 0 \le y \le B_a$$
$$C_B(x,0) = C_B^*, \qquad 0 \le x \le L$$
$$\frac{\partial C_B}{\partial y}(x,B_a) = 0, \qquad 0 \le x \le L$$
$$\frac{\partial C_B}{\partial x}(L,y) = 0, \qquad 0 \le y \le B_a$$



Introduce dimensionless variables:

$$F_A = \frac{C_A}{C_{A0}};\ F_B = \frac{C_B^*}{C_{A0}};\ F_{DG} = \frac{C_{DG}}{C_{A0}};\ F_{MG} = \frac{C_{MG}}{C_{A0}};\ F_{ME} = \frac{C_{ME}}{C_{A0}};\ F_{GL} = \frac{C_{GL}}{C_{A0}};\ \Psi = \frac{y}{B_a};\ \xi = \frac{x}{L}$$

Mathematical Model

Soybean oil PDE in the dimensionless variables form:

$$v_{A,x} L B_a^2 \frac{\partial F_A}{\partial \xi} = D_{A,x} B_a^2 \frac{\partial^2 F_A}{\partial \xi^2} + D_{A,y} L^2 \frac{\partial^2 F_A}{\partial \Psi^2} + C_{A0} B_a^2 L^2 (-k_1 F_A F_B + k_2 F_{DG} F_{ME})$$

Soybean oil boundary conditions in the dimensionless variables form:

$$F_A(0,\Psi) = 1, \qquad 0 \le \Psi \le 1$$

$$\frac{\partial F_A}{\partial \Psi}(\xi,1) = 0, \qquad 0 \le \xi \le 1$$

$$\frac{\partial F_A}{\partial \xi}(1,\Psi) = 0, \qquad 0 \le \Psi \le 1$$

$$\frac{\partial F_A}{\partial \Psi}(\xi,0) = 0, \qquad 0 \le \xi \le 1$$

Mathematical Model

Methanol PDE in the dimensionless variables form:

$$v_{A,x} L\, B_a^2 \frac{\partial F_B}{\partial \xi} = D_{B,x} B_a^2 \frac{\partial^2 F_B}{\partial \xi^2} + D_{B,y} L^2 \frac{\partial^2 F_B}{\partial \Psi^2} + C_{A0} L^2 B_a^2 (-k_1 F_A F_B + k_2 F_{DG} F_{ME}$$
$$-k_3 F_B F_{DG} + k_4 F_{MG} F_{ME} - k_5 F_B F_{MG} + k_6 F_{GL} F_{ME})$$

Methanol boundary conditions in the dimensionless variables form:

$$F_B(0,\Psi) = 0, \qquad 0 \le \Psi \le 1$$
$$F_B(\xi,0) = F_{B0}, \qquad 0 \le \xi \le 1$$
$$\frac{\partial F_B}{\partial \xi}(1,\Psi) = 0, \qquad 0 \le \Psi \le 1$$
$$\frac{\partial F_B}{\partial \Psi}(\xi,1) = 0, \qquad 0 \le \xi \le 1$$

Mathematical Model

PDEs in the dimensionless form for ***diglycerides, monoglycerides, methyl esters,*** and ***glycerol*** respectively are shown below :

Diglycerides

$$v_{A,x} L B_a^2 \frac{\partial F_{DG}}{\partial \xi} = D_{DG,x} B_a^2 \frac{\partial^2 F_{DG}}{\partial \xi^2} + D_{DG,y} L^2 \frac{\partial^2 F_{DG}}{\partial \Psi^2} + C_{A0} L^2 B_a^2 (k_1 F_A F_B - k_2 F_{DG} F_{ME} - k_3 F_B F_{DG} + k_4 F_{MG} F_{ME})$$

Monoglycerides

$$v_{A,x} L B_a^2 \frac{\partial F_{MG}}{\partial \xi} = D_{DG,x} B_a^2 \frac{\partial^2 F_{MG}}{\partial \xi^2} + D_{DG,y} L^2 \frac{\partial^2 F_{MG}}{\partial \Psi^2} + C_{A0} L^2 B_a^2 (k_3 F_B F_{DG} - k_4 F_{MG} F_{ME} - k_5 F_{MG} F_B + k_6 F_{ME} F_{GL})$$

Methyl esters

$$v_{A,x} L\ B_a^2 \frac{\partial F_{ME}}{\partial \xi} = D_{M,x} B_a^2 \frac{\partial^2 F_{ME}}{\partial \xi^2} + D_{M,y} L^2 \frac{\partial^2 F_{ME}}{\partial \Psi^2} + C_{A0} L^2 B_a^2 (k_1 F_B F_A - k_2 F_{ME} F_{DG} + k_3 F_B F_{DG} - k_4 F_{MG} F_{ME} +$$

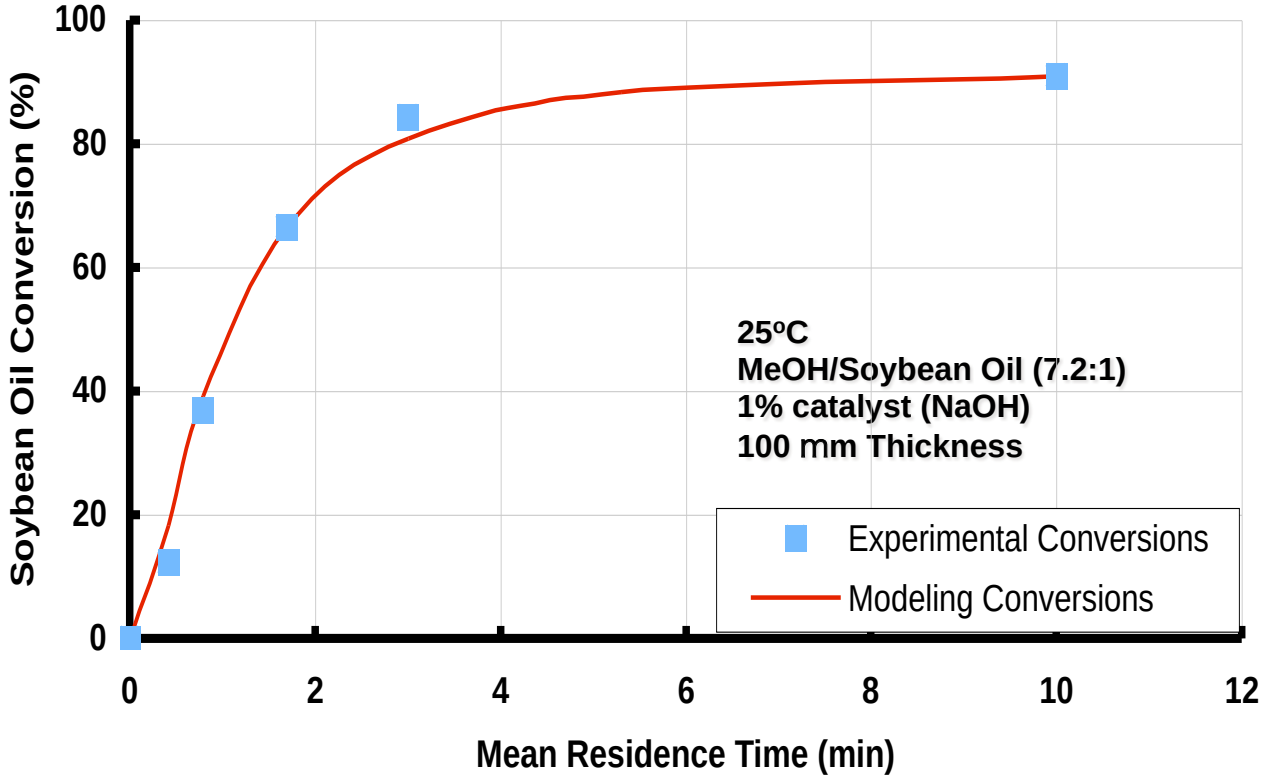
$$+ k_5 F_{MG} F_B - k_6 F_{ME} F_{GL})$$

Glycerol

$$v_{A,x} L\ B_a^2 \frac{\partial F_{GL}}{\partial \xi} = D_{GL,x} B_a^2 \frac{\partial^2 F_{GL}}{\partial \xi^2} + D_{GL,y} L^2 \frac{\partial^2 F_{GL}}{\partial \Psi^2} + C_{A0} L^2 B_a^2 (k_5 F_{MG} F_B - k_6 F_{ME} F_{GL})$$

Experimental Results

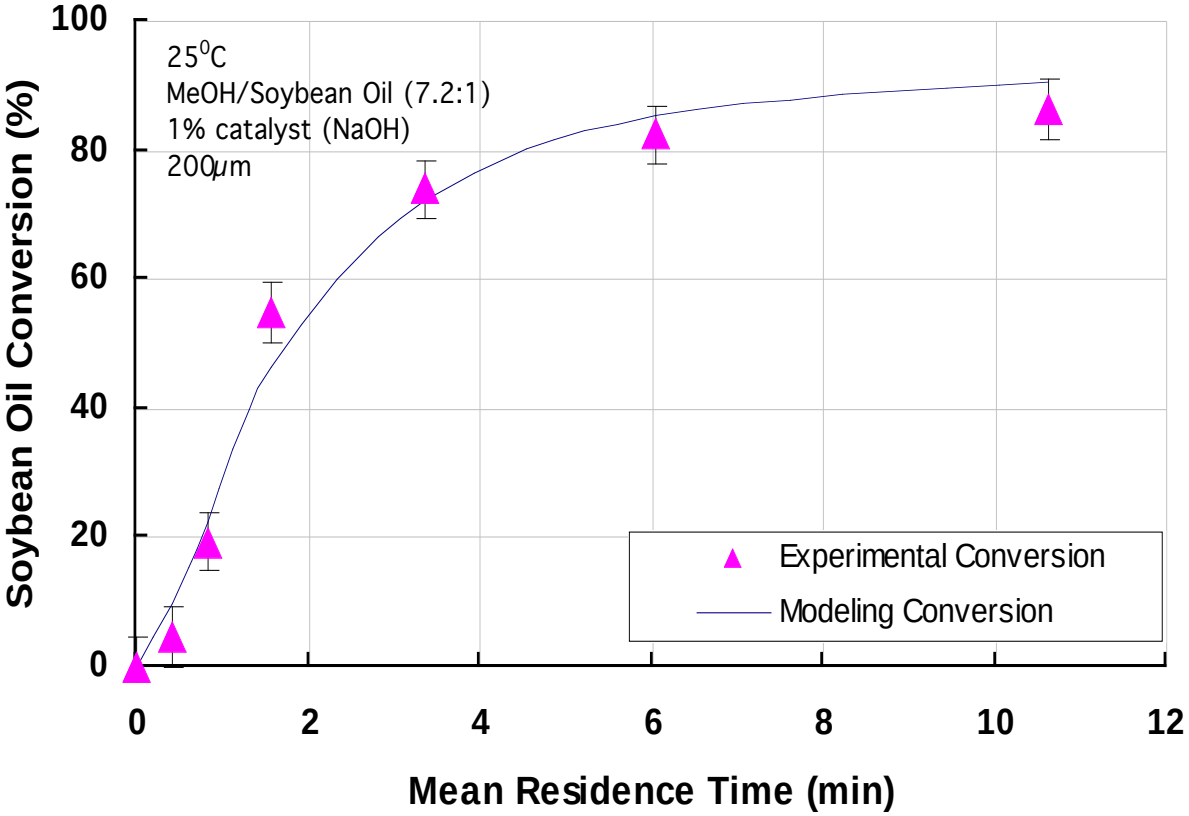
The reaction rate constants (k_i) are estimated by fitting the experimentally obtained conversion data for 100 μm microreactor using the above mathematical model.



k_i	Values (m3/ mol sec)
k_1	$4.37*10^{-6}$
k_2	$9.62*10^{-6}$
k_3	$1.88*10^{-5}$
k_4	$1.07*10^{-4}$
k_5	$2.12*10^{-5}$
k_6	$9.01*10^{-7}$

Experimental Results

The model conversions with estimated reaction rate constants (k_i) show good fit for experimentally obtained conversion data at 200 µm.



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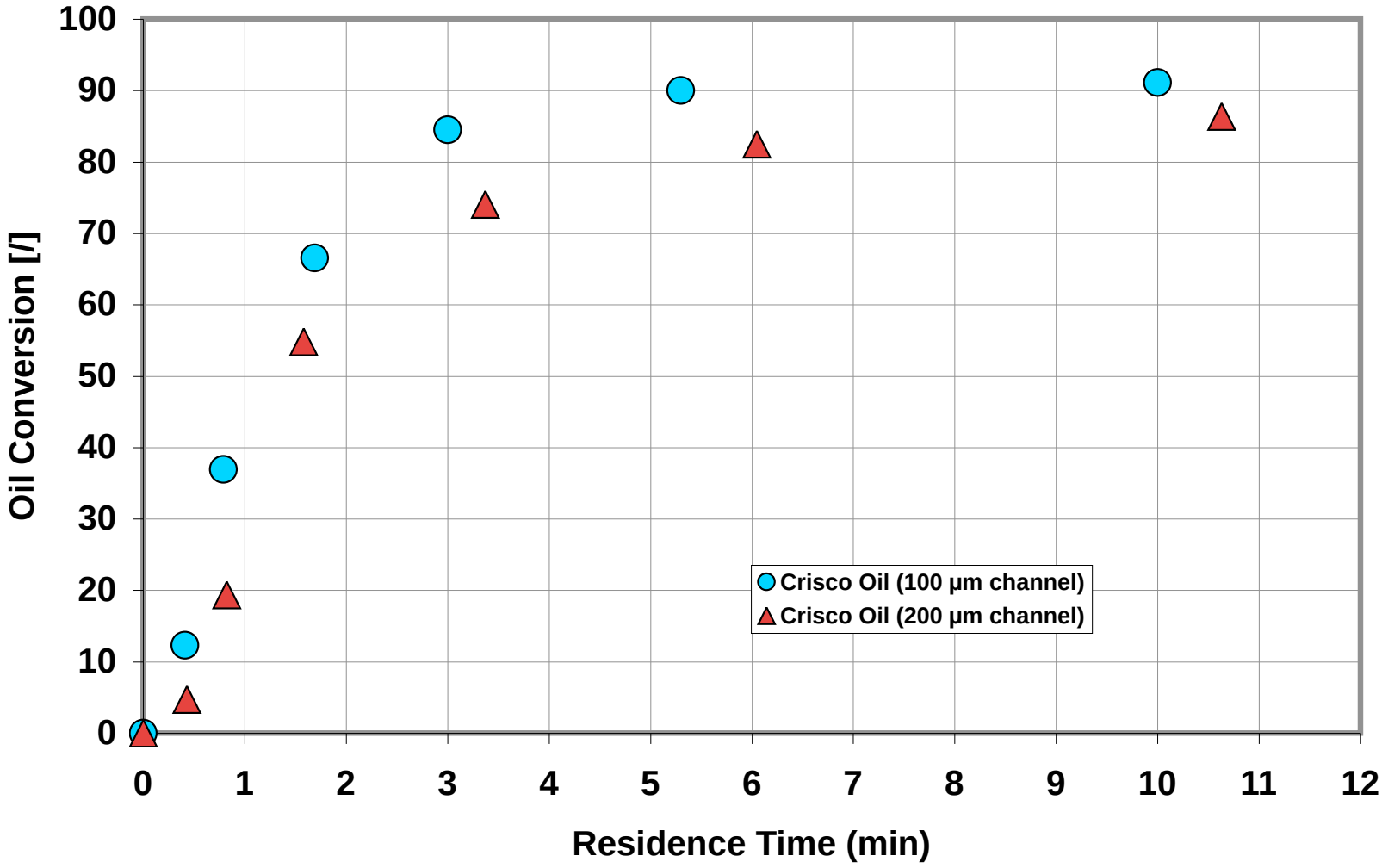
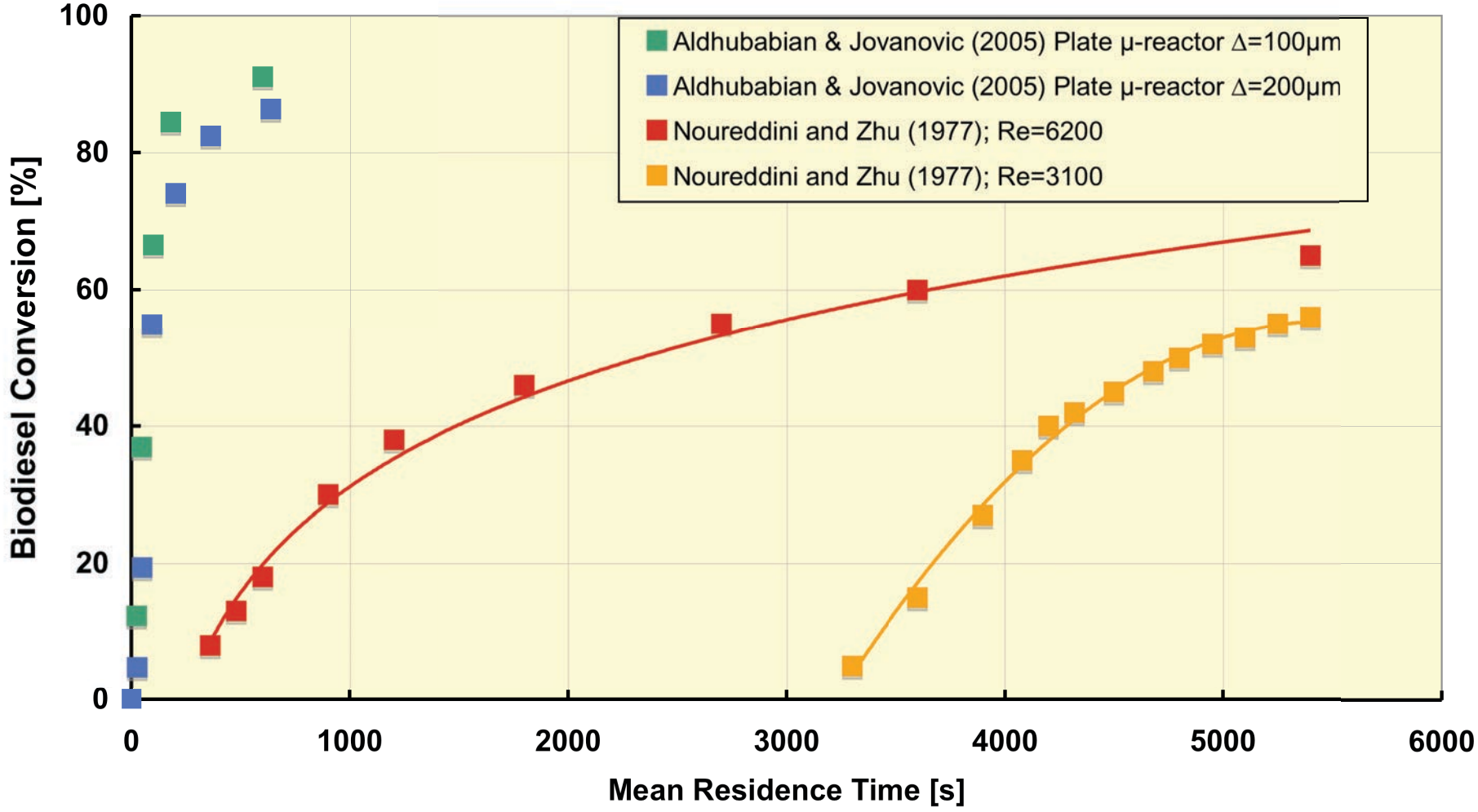
k_4	$1.07*10^{-4}$
k_5	$2.12*10^{-5}$
k_6	$9.01*10^{-7}$

Experimental Results

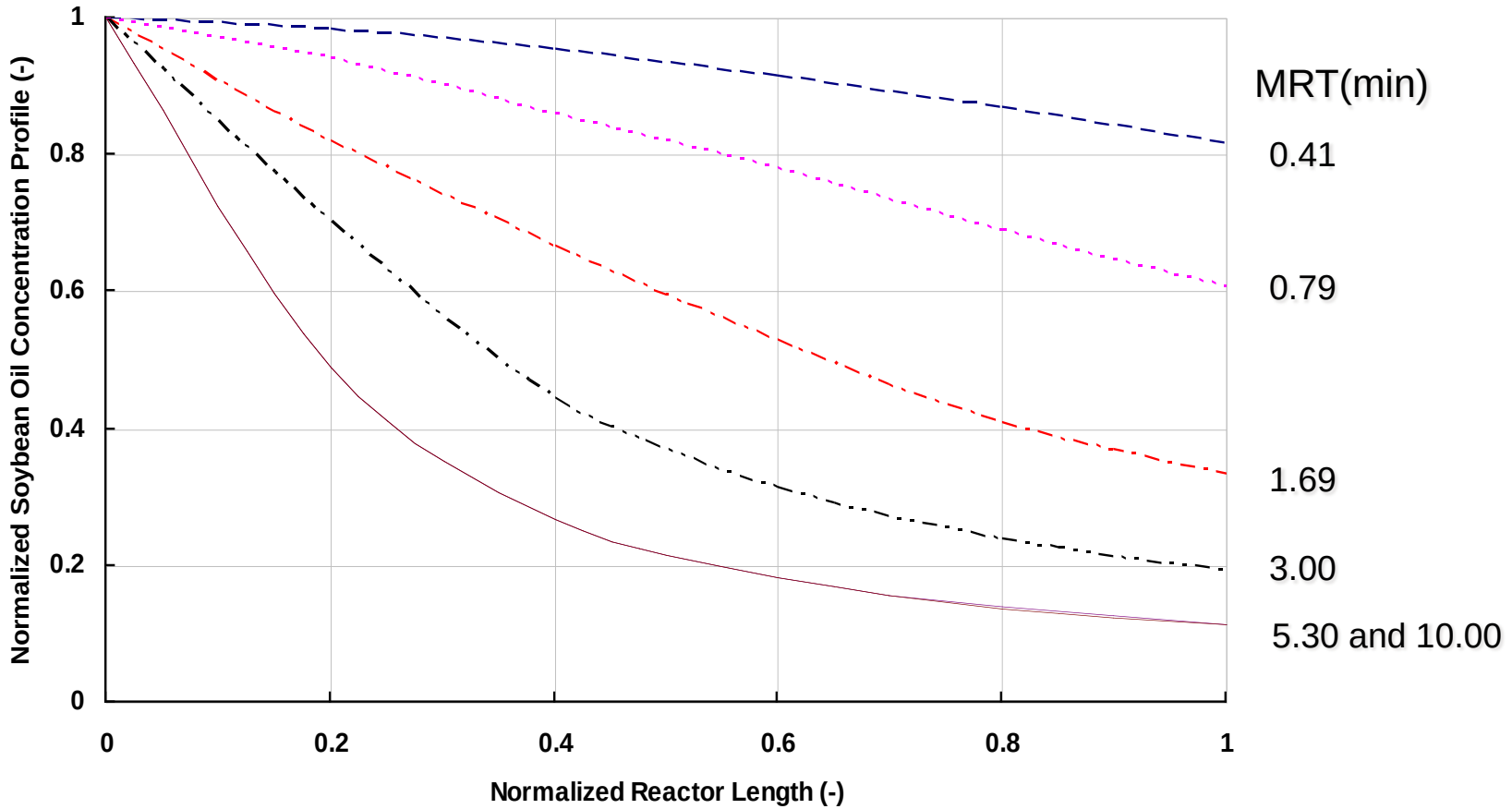


Experimental Results comparison



Comsol Simulation Results

Model output for soybean oil concentration profiles in the microreactor-100 µm at different mean residence times (MRT).



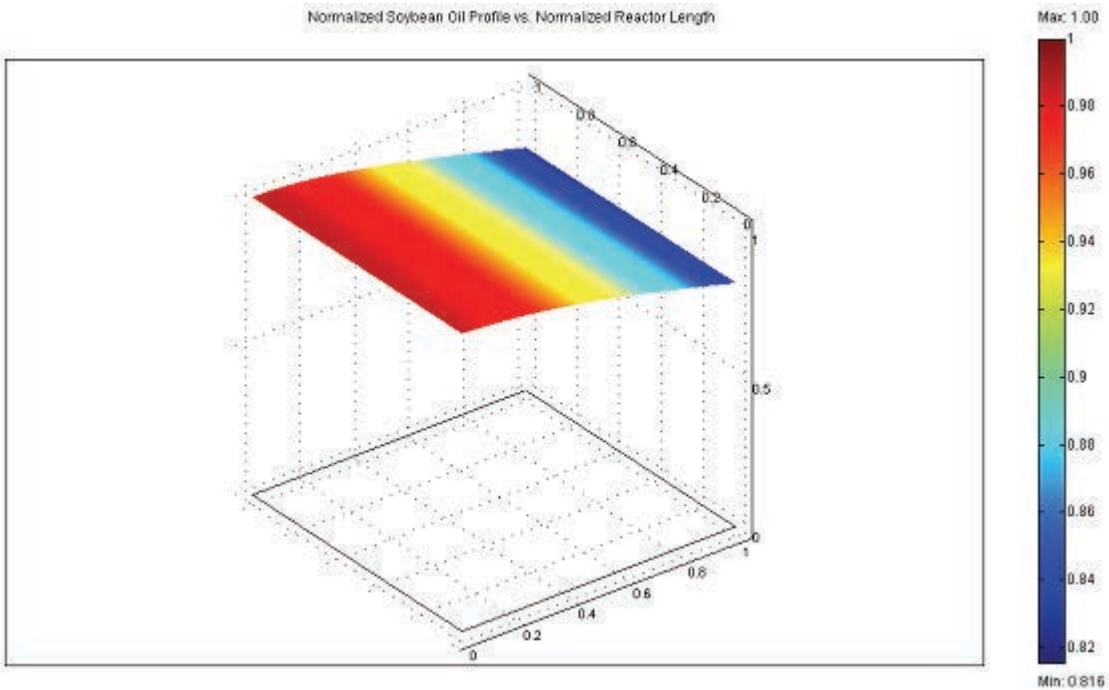
Comsol Simulation Results

Effect of Mean Residence Time

Molar Ratio (Methanol : Soybean Oil) = **7.2 : 1.0**

T = 25 ^{o}C

Thickness = 100 μm



MRT = **0.41 min**

Conv. = **18.40 %**

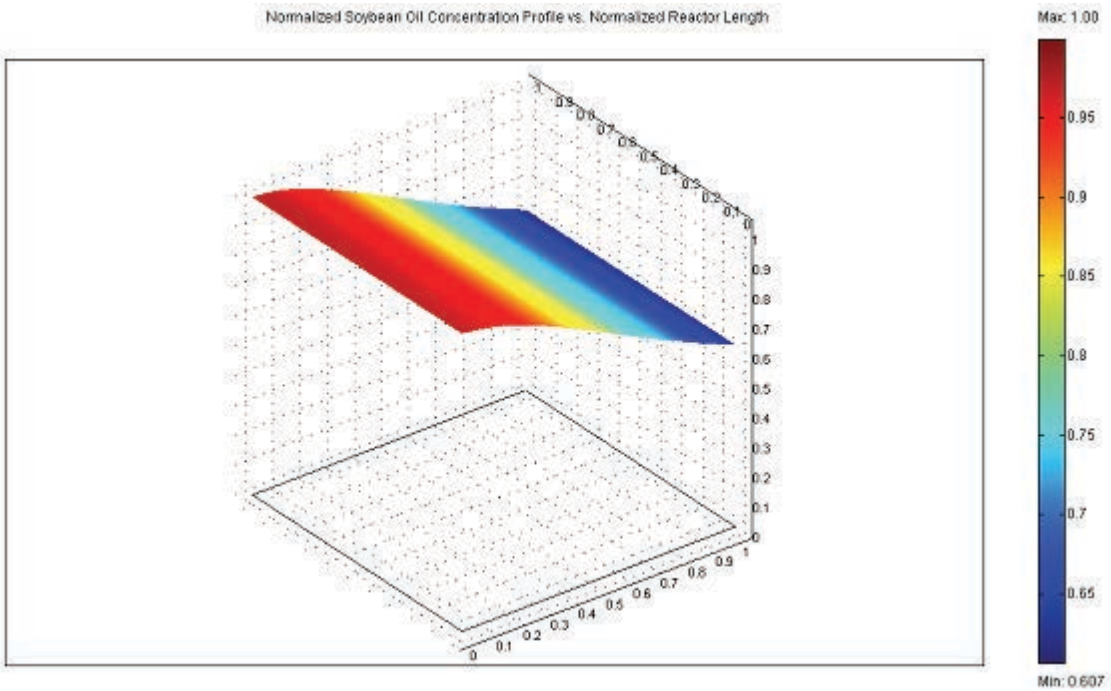
Comsol Simulation Results

Effect of Mean Residence Time

Molar Ratio (Methanol : Soybean Oil) = **7.2 : 1.0**

T = 25 ^{o}C

Thickness = 100 mm



MRT = **0.79 min**

Conv. = **39.30 %**

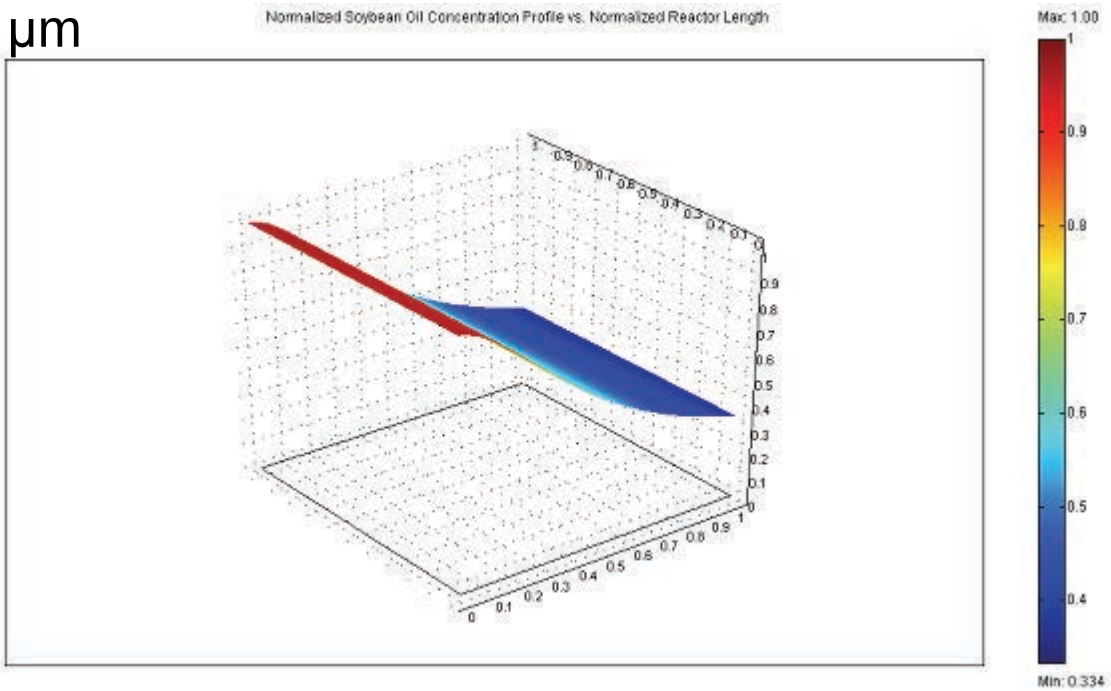
Comsol Simulation Results

Effect of Mean Residence Time

Molar Ratio (Methanol : Soybean Oil) = **7.2 : 1.0**

T = 25 ^{o}C

Thickness = 100 μm



MRT = **1.69 min**

Conv. = **66.60 %**

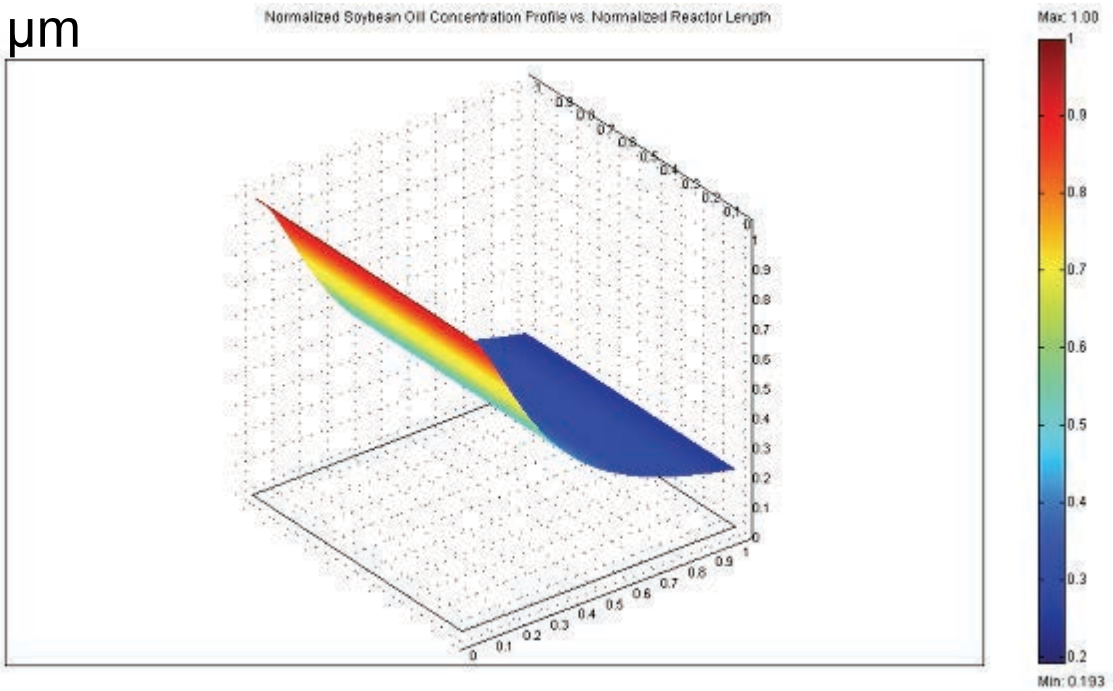
Comsol Simulation Results

Effect of Mean Residence Time

Molar Ratio (Methanol : Soybean Oil) = **7.2 : 1.0**

T = 25 ^{o}C

Thickness = 100 μm



MRT = **3.00 min**

Conv. = **81.00 %**

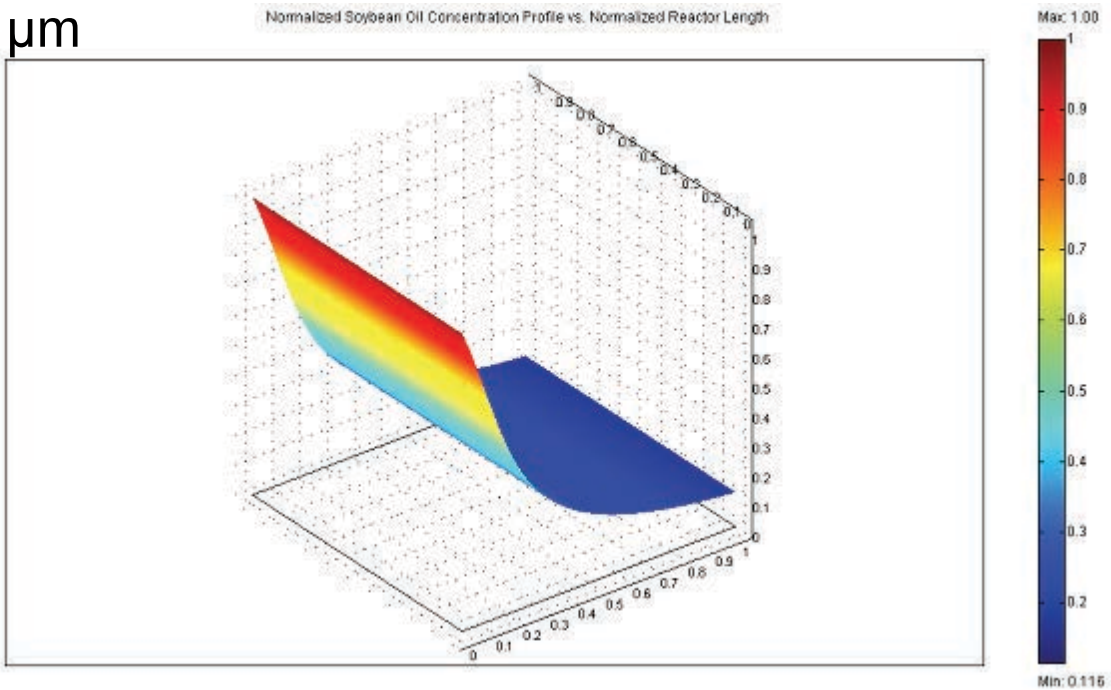
Comsol Simulation Results

Effect of Mean Residence Time

Molar Ratio (Methanol : Soybean Oil) = **7.2 : 1.0**

T = 25 ^{o}C

Thickness = 100 μm



MRT = **5.30 min**

Conv. = **88.40 %**

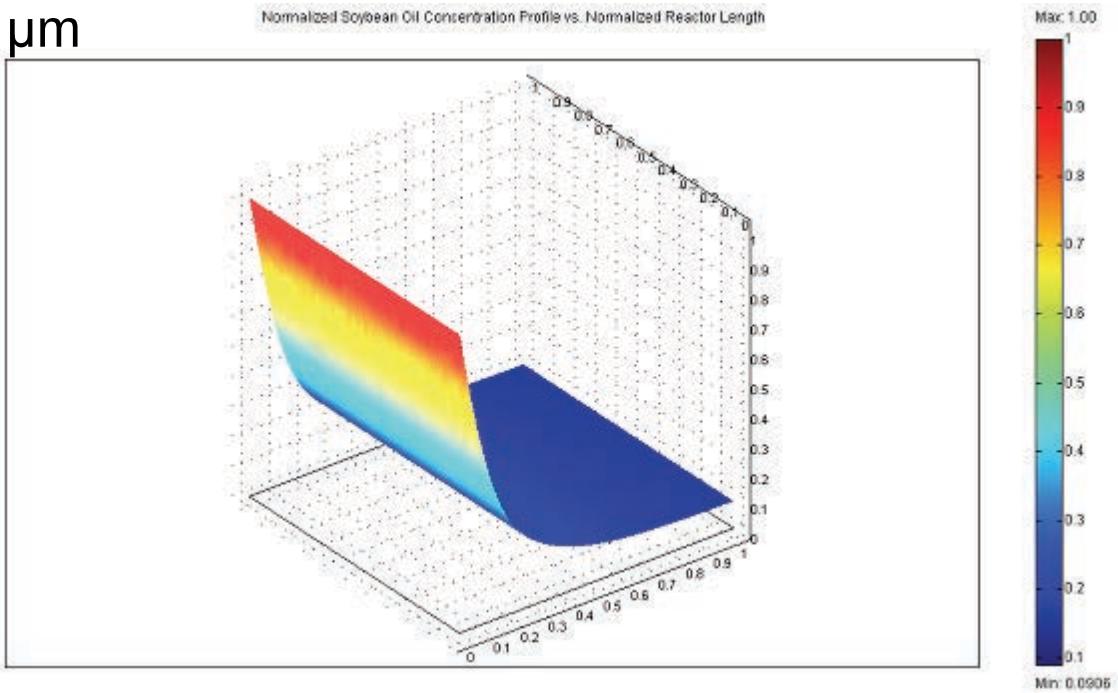
Comsol Simulation Results

Effect of Mean Residence Time

Molar Ratio (Methanol : Soybean Oil) = **7.2 : 1.0**

T = 25 ^{o}C

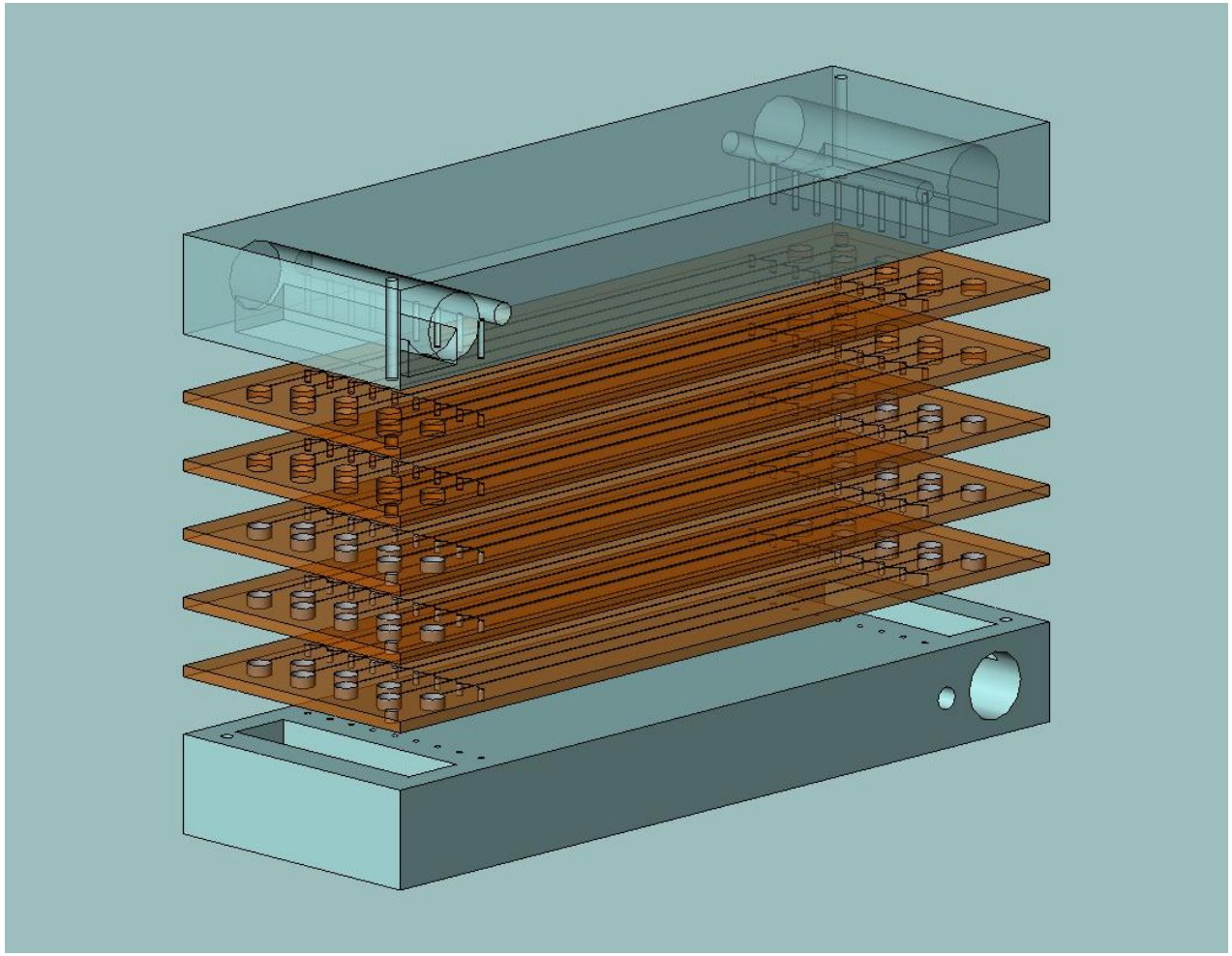
Thickness = 100 μm



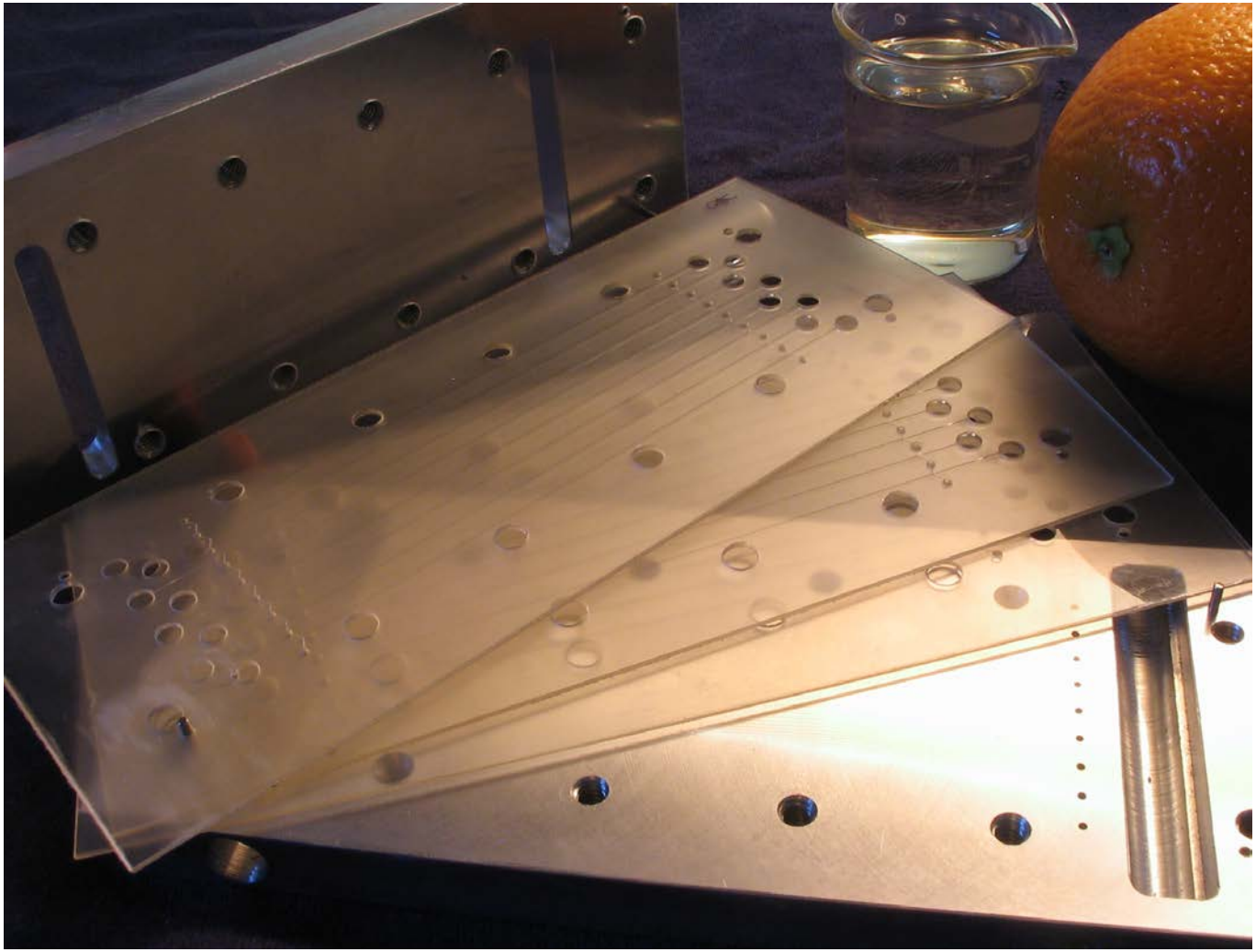
MRT = **10.00 min**

Conv. = **91.00 %**

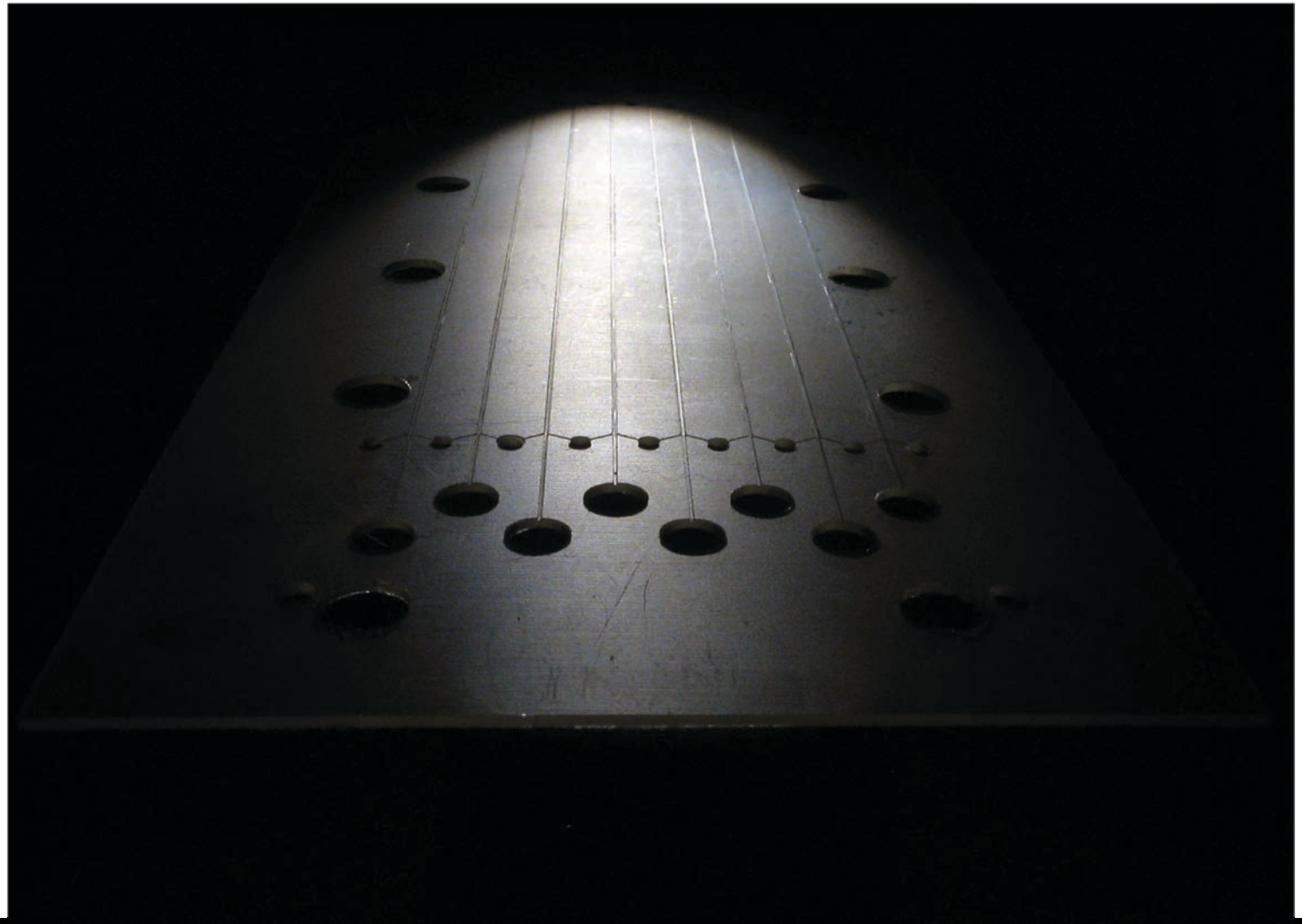
Numbering-up of Microscale Reactors



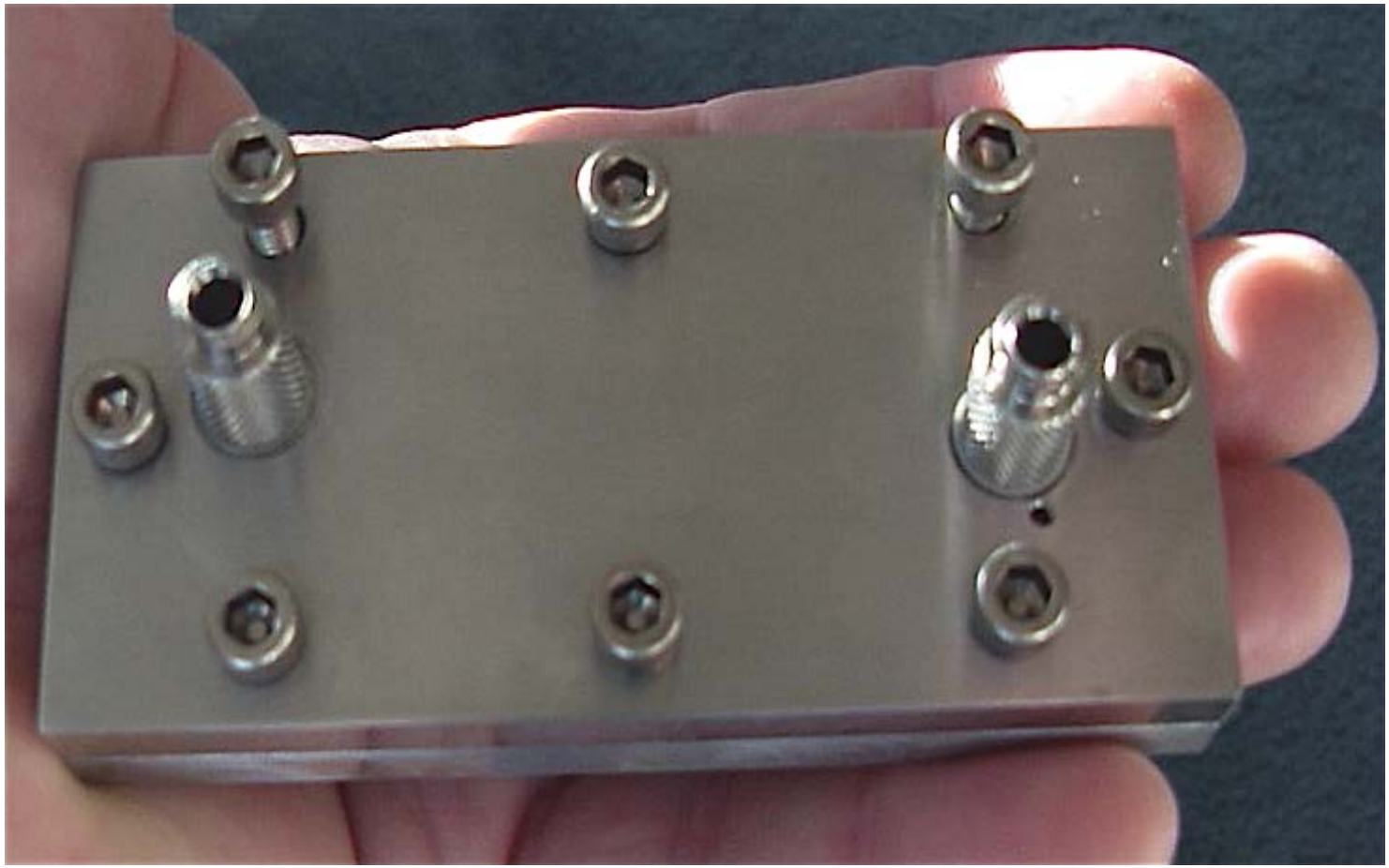
Numbering-up of Microscale Reactors



Numbering-up of Microscale Reactors



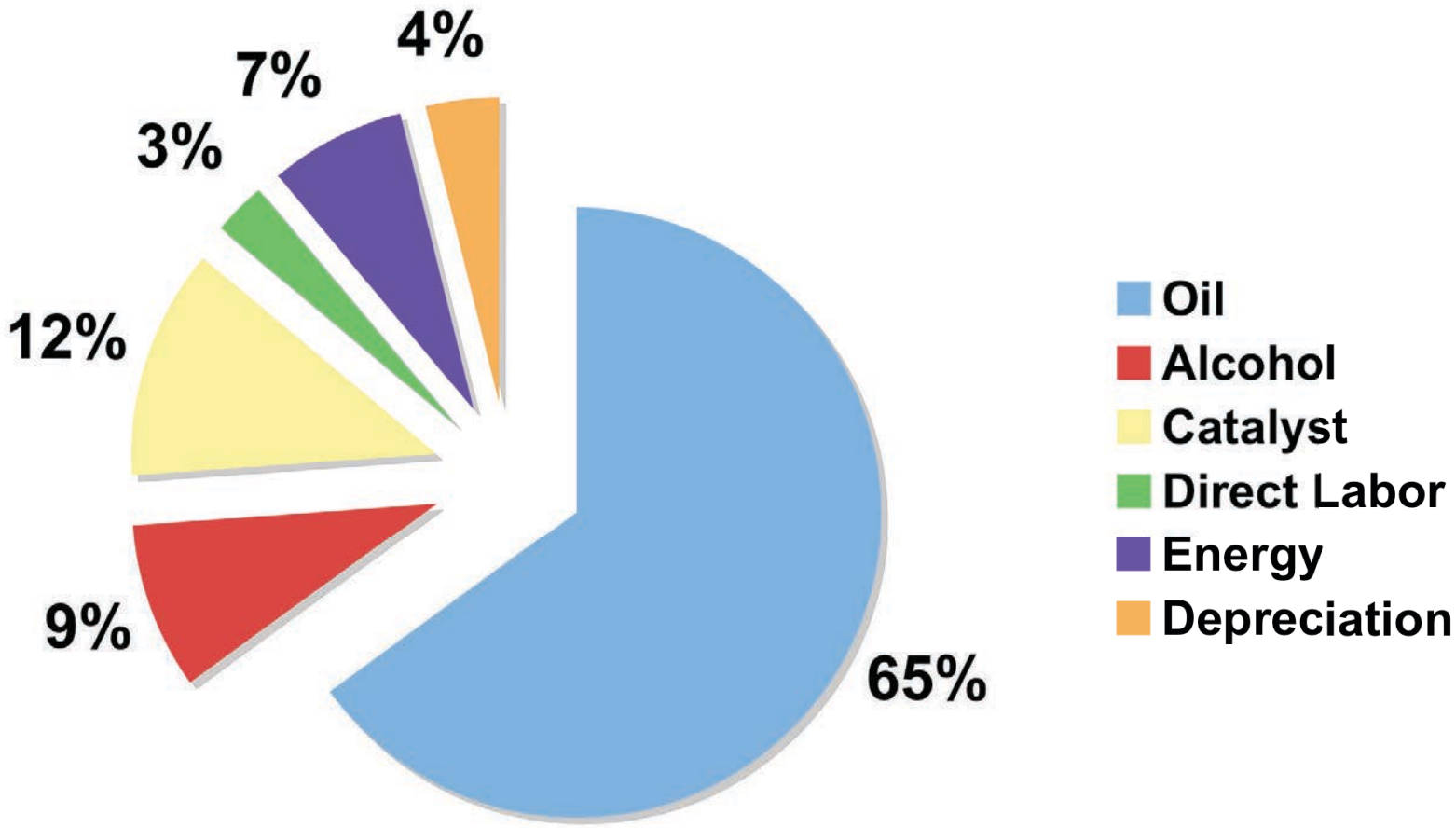
OSU first microscale biodiesel reactor



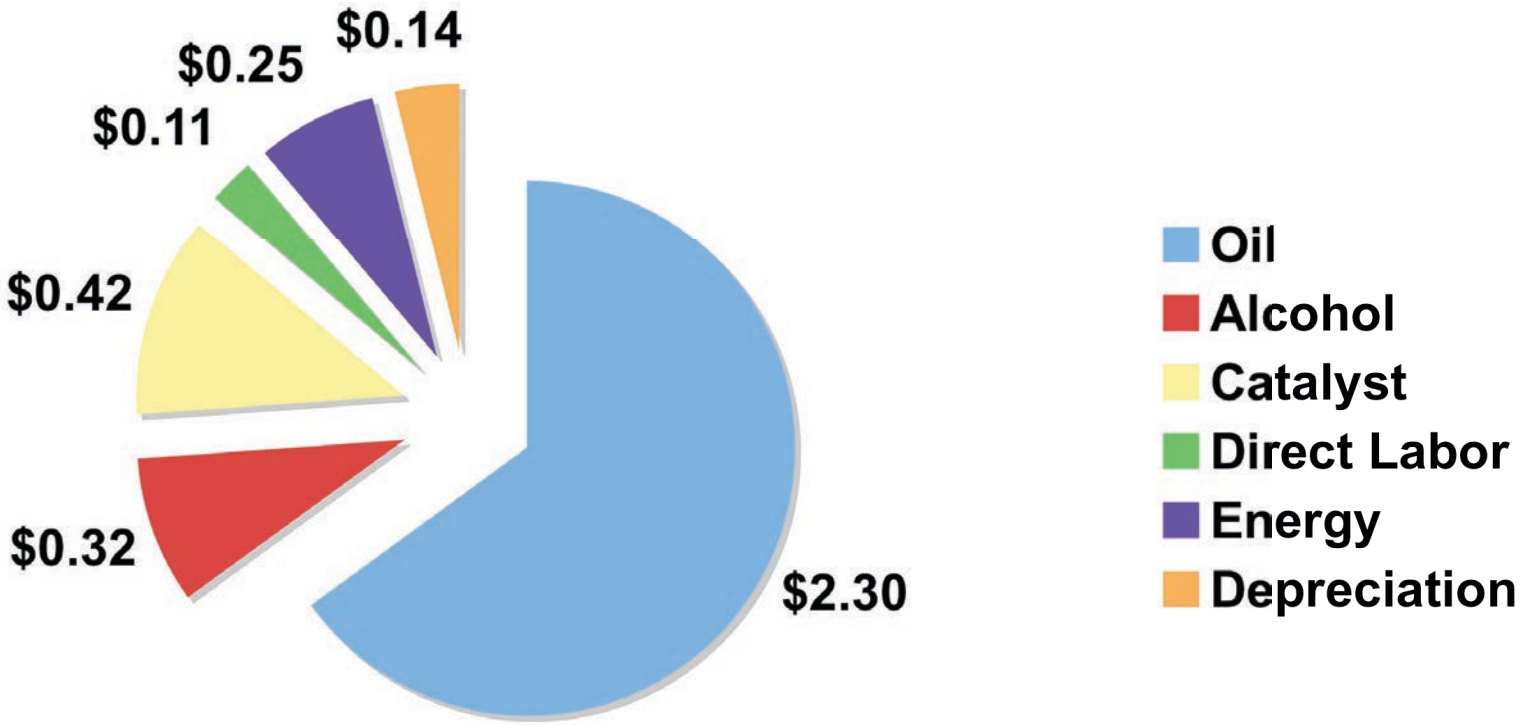
References

Ahmad Al-Dhubabian, M.Sc. Thesis, Oregon State University, Corvallis (2006)

Production Cost of Biodiesel
(Conventional Large Biorifinery - Soybean Oil)

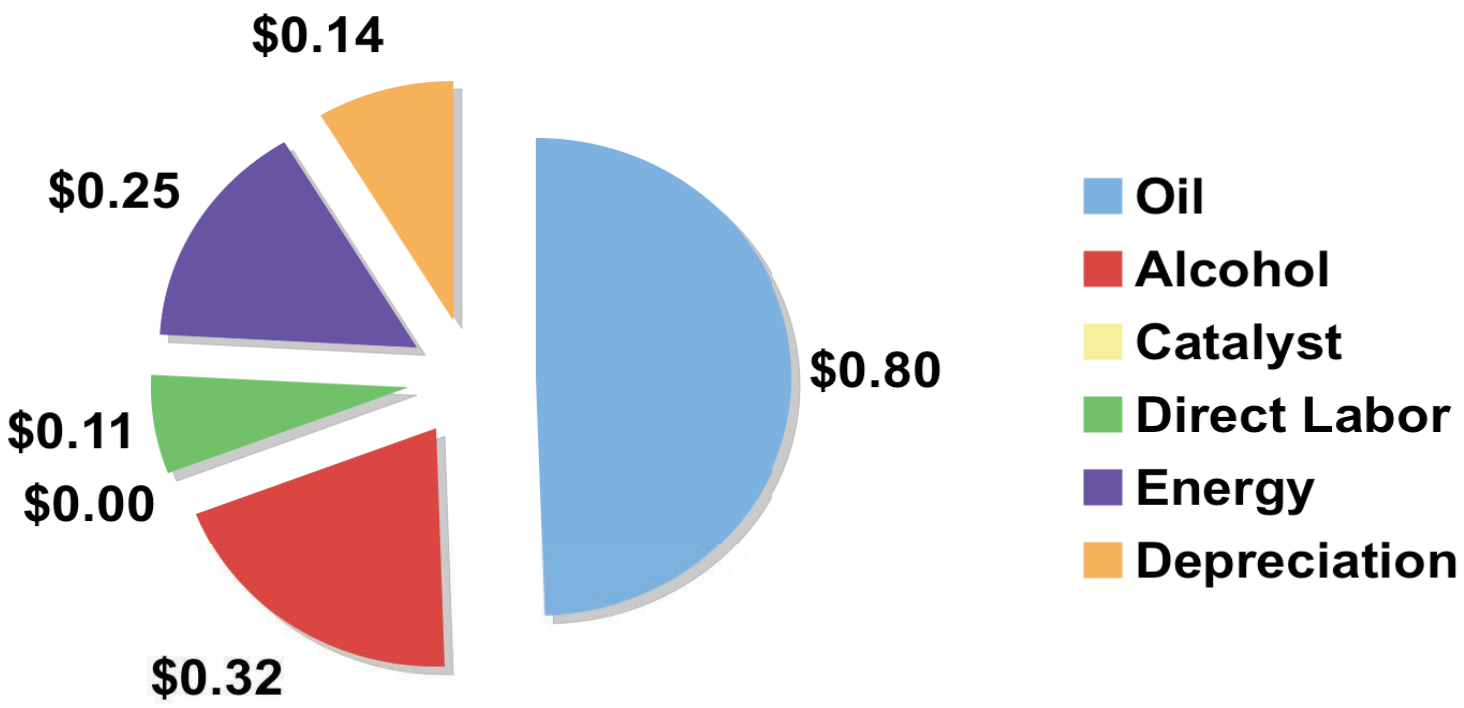


Production Cost of Biodiesel in US $
(Conventional Large Biorifinery - Soybean Oil)



Total Cost per Gallon US $ 3.54

Production Cost of Biodiesel in US $
(1-5 M gal/year Secondary Triglycerides - Animal Fat)



Total Cost per Gallon US $ 1.62

Opportunities in the Development of Biodiesel Synthesis in Micro-technology

- *Classical* Biodiesel Synthesis With Homogenous Catalyst.
- Biodiesel Process With Solid Catalyst.
- Biodiesel Process at Sub-critical Conditions With Homogenous Catalyst.
- Biodiesel Process at Sub-critical Conditions With Solid Catalyst.
- Biodiesel Process at Super-critical Conditions With or Without Solid Catalyst.

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People. Ideas. Innovation.

Thank you for your attention!

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