Use of hydrodynamic understanding of multiphase flows to improve performance of gas-liquid reactors

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Background

• Gas-liquid packed bed reactors are currently used for hydrotreating of petroleum, some waste treatment and other oxidation reactions

• Generic reactor system for gas-liquid w/solid catalyst that does not have real high heat removal requirements
  – heat removal is one problem in hydrotreating leading to “hot spots” and “coke balls”
Background (cont.)

• If selectivity can be improved and hydrodynamics better understood we envision these as a useful reactor to produce small quantities of hazardous chemicals “on location”, (closset scale production)
Objectives of our work

• Develop detailed knowledge about the hydrodynamics of gas-liquid flows and use it to understand and design multiphase reactors that take advantage of the specific dynamics of these flows

• Would like these reactors to be optimized as “smallest possible volume”, “highest reasonable selectivity”,

• Want: “No surprises”.

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Why do we think there is potential for something new and exciting here?

• The dynamics of these flows cause strong variations in pressure drop and heat and mass transfer

• These have not been understood or exploited to enhance reaction
Preview

- We will show the interesting dynamics of a gas-liquid packed bed flow
  - Time varying behavior, strong pressure fluctuations
- Pulses grow with distance like a convective instability
  - This allows us to do reaction studies both with and without pulses present
- Pulses significantly affect the reaction behavior
- Detailed studies of local heat transfer show
  - Most of the heat removal occurs during a pulse
  - The rate of heat removal in a pulse is about the same as only a liquid flow
  - Pressure drop and heat transfer do not scale exactly the same leading to some degree of possible optimization
Trickle flow
Intermittent pulsing

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Pulsing

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Pulse occurrence at increasing G

G = 0.33 kg/m²-s
L = 7.9 Kg/(m²-s)

G = 0.345 kg/m²-s

G = 0.40 kg/m²-s

G = 0.52 kg/m²-s

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Different flow regimes

- **Dispersed**
- **Stratified**
- **Slug (pulse)**
Surprising result: Pressure drop ratio

Using a simple model, air-water flow in a small channel
Effect of hydrodynamics

• We expect that the time-varying hydrodynamics plays a direct role on the reaction through the fluctuating heat and mass transfer rates.

• First check this with modeling
CSTR model with fluctuating mass transfer

Reaction Mechanism

Reaction Mechanism involving a gaseous reactant $A$, two catalyst sites, $S$ and $S^*$, and two products $B$ and $C$.

$$A(g) + S \rightleftharpoons_{k_1}^{k_1} AS$$
$$AS + A(g) \rightarrow_{k_2}^{k_2} 2B + S$$
$$A(g) + S^* \rightleftharpoons_{k^{-1}_2}^{k_2} AS^*$$
$$AS^* \rightarrow_{k^{-1}_1}^{k_1} C + S^*$$


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Mass transfer fluctuations

Define the fluctuating mass transfer coefficient

\[ \text{masst}[\omega, t, k_a, k_b] := \text{If}[\text{Sin}[\omega t] \geq 0, k_a + k_b \text{Sin}[\omega t], k_a] \]

\[ \text{Plot}[\text{masst}[\omega, t, k_a, k_b] / (k_a \rightarrow .01, k_b \rightarrow .06, \omega \rightarrow .01), \{t, 0, 4000\}]; \]
Calculated enhancement by pulsing

Significant enhancement, interesting frequency effect

Frequency is dimensionless with first order rate constant

http://www.nd.edu/~mjm/Reaction_Selectivity_Mult.nb

How can we do an experiment?

• Pulses behave as a “convective instability” which means they gain strength with distance in the flow direction.

• Thus you can find ranges of flowrates where pulses grow slow enough that the inception region is about 1/2 of the column

• At the top: no pulses

• At the bottom: pulses

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Wave measurements as function of distance showing the development of large disturbances.

Data of Bruno and McCready, 1988

\[ R_L = 300 \]
\[ R_G = 9975 \]
\[ \mu_L = 5 \text{ cP} \]
Location of the first appearance of pulsing
Catalyst configuration

"Lower Packing" Configuration

Trickling Regime

Transition

Pulsing Regime

"Upper Packing" Configuration

5 cm
25 cm
8 cm
25 cm
5 cm

5 cm
8 cm
25 cm

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Model reaction

Phenylacetylene (PA) + 2H₂ → Styrene (ST) + H₂ + H₂

Ethylbenzene (EB)
Reaction experiment results

- Pulses at bottom, no pulses at top
Reaction results

- Pulses at bottom, and top
More reaction results

![Graph showing reaction results for different conditions.](image-url)

- **C1**: Pulsing
- **C2**: Trickling

**Axes:**
- **X-Axis**: Time, Minutes
- **Y-Axis**: Dimensionless Concentration, $C_x / C_{PA,0}$

**Legend:**
- PA
- EB
- ST
Reaction model

• CSTR with reactor and catalyst

Reactor:

\[ V_r \cdot \frac{dC_{PA_r}}{dt} = K_{c,PA} \cdot A \cdot (C_{PA_p} - C_{PA_r}) \]
\[ V_r \cdot \frac{dC_{ST_r}}{dt} = K_{c,ST} \cdot A \cdot (C_{ST_p} - C_{ST_r}) \]
\[ V_r \cdot \frac{dC_{EB_r}}{dt} = K_{c,EB} \cdot A \cdot (C_{EB_p} - C_{EB_r}) \]

Pellet:

\[ \varepsilon_p \cdot \frac{\partial C_{PA_p}}{\partial t} = D_{e,PA} \cdot \frac{\partial^2 C_{PA_p}}{\partial r^2} - (k_1 \cdot C_{PA_p} + k_3 \cdot C_{PA_p}) \]
\[ \varepsilon_p \cdot \frac{\partial C_{ST_p}}{\partial t} = D_{e,ST} \cdot \frac{\partial^2 C_{ST_p}}{\partial r^2} + (k_1 \cdot C_{PA_p} - k_2 \cdot C_{ST_p}) \]
\[ \varepsilon_p \cdot \frac{\partial C_{EB_p}}{\partial t} = D_{e,EB} \cdot \frac{\partial^2 C_{EB_p}}{\partial r^2} + (k_2 \cdot C_{ST_p} + k_3 \cdot C_{PA_p}) \]
Detailed modeling results
Effect of pulses on reaction

• We can observe an effect of pulses on selectivity -- 40% max effect for our system
• Reaction modeling suggests that time-varying mass transfer is the reason
• To further test and fully exploit we need to be able to control strength and frequency of pulses
• We to understand the mechanism of formation!
How do we think about the flow in the column?

• Are the gas and liquid homogenously dispersed?
• Is the other limit where there are liquid-rich and gas rich regions?
Heterogeneous base state?

Gas

Liquid

Liquid

liquid rich regions

liquid rich regions
Pulsing in a horizontal column

Pressure tracings as a function of gas velocity ranging from mild waves to pulses:

- **L = 15.5 Kg/m² s**
- **G = 0.41 Kg/m² s**

- **Disturbed**

- **L = 15.5 Kg/m² s**
- **G = 0.49 Kg/m² s**

- **Pulsing**

- **L = 15.5 Kg/m² s**
- **G = 0.58 Kg/m² s**

- **Heavy Pulsing**

- **L = 15.5 Kg/m² s**
- **G = 0.66 Kg/m² s**
Detailed measurements of pulsing in vertical column, local heat transfer
Local instantaneous heat transfer compared to pressure drop

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Heat transfer enhancement by pulsing

- Ratio of pulse/base heat transfer rate
Effect of gas and liquid on heat transfer
Can heat transfer be optimized?

Heat transfer

Pressure drop
Ratio of thermal energy removed to mechanical energy expended
Ratio of thermal energy removed to mechanical energy expended
Continuing work

• Hydrodynamics
  – “2D” packed bed

• Reaction
  – Catalysts that have pore sizes that enable convective transport within the pellets caused by pressure fluctuations from the pulses.
Configuration of two-dimensional beds
Pressure tracing in 2D bed

$L = 30000 \text{ kg/(hr-m}^2\text{)} \quad G = 130571 \text{ kg/(hr-m}^2\text{)}$

$L = 59000 \text{ kg/(hr-m}^2\text{)} \quad G = 2.57e6 \text{ kg/(hr-m}^2\text{)}$
Pressure tracing in 2D bed

L = 30000 kg/(hr-m²)  G = 130571 kg/(hr-m²)

L = 59000 kg/(hr-m²)  G = 2.57e6 kg/(hr-m²)
Catalyst structure

Macro channels span catalyst pellet.

Nanoporous structure with macro channels.

blow up of region
Conclusions

• Complex time-varying hydrodynamics occur in gas-liquid packed bed systems
  – These occur in pipe flow as well.
  – Flow regime significantly affects the pressure drop and transport rates

• Because pulses behave as a convective instability, it is possible to do experiments where the flow rates are the same for pulsing and non-pulsing flows
Conclusions (cont.)

• These experiments show that pulses definitely affect the selectivity of a sequential reaction.
  – Modeling suggests this is because of the fluctuating mass transfer coefficient having a *time scale* that allows interaction between mass transfer and reaction

• Detailed measurements of the local instantaneous heat transfer suggest
  – Most of the heat removal occurs during a pulse
  – The rate of heat removal in a pulse is about the same as only a liquid flow
  – Pressure drop and heat transfer do not scale exactly the same leading to some degree of possible optimization
Dimensionless groups are ratios of important effects in a problem.

\[ \text{Re} \equiv \frac{\text{Inertia Forces}}{\text{Viscous Forces}} \]
Dimensionless groups do not need to be on technical subjects

\[ Cr \equiv \frac{\text{How Smart You Are}}{\text{How Smart You Think You Are}} \]
Dimensionless

Confucius Proverb

• He who knows not and knows he knows not is a child, teach him, $C_r \sim 1$
• He who knows not and knows not he knows not is a fool, shun him, $C_r \ll 1$
• He who knows and knows not he knows is asleep, awaken him, $C_r \gg 1$
• He who knows and knows he knows is wise, follow him $C_r \sim 1$