Application of Submerged Hydrodynamic Cavitating Jets (DynaJets®) to Oxidation Of Organic Compounds in Water

Greg Loraine

November 17, 2010

AOT 16

Dynaflow, Inc.
10621-J Iron Bridge Road
Jessup, MD
www.dynaflow-inc.com

www.dynaflow-inc.com
Outline

- Cavitation and Formation of Free Radicals
- Acoustic (Ultrasonic) Cavitation vs. Hydrodynamic Cavitation
- Hydrodynamic Cavitating Jets
- Oxidation / Reduction in Water
- Applications
- Conclusions

Underwater explosion from 6000 V spark. Collapse is analogous to cavitation.
Cavitation

- Bubble nuclei in water expand & collapse when the local pressure changes very quickly.
- Collapsing bubbles produce tremendous pressures & temperatures in localized area (~5,200 K, ~200 Atm).
- Water vapor dissociates into OH• and H•
  \[ \text{H}_2\text{O} \rightarrow \text{OH}^\cdot + \text{H}^\cdot \]
- Volatile compounds can also dissociate into radicals
  \[ \text{CCl}_4 \rightarrow \text{Cl}^\cdot + \text{Cl}_3\text{C}^\cdot \]
- Inside collapsing bubble or at interface
- Volatile compounds enter the expanding bubble and decompose during collapse
- $\text{OH}^\cdot$ and $\text{H}^\cdot$ concentrations highest in center, decrease toward bubble wall
- Hydrophobic compounds partition to air-water interface
- Local depletion of starting compound and build up of products
Hydrodynamic & Ultrasonic Cavitation

- Ultrasonic (US) cavitation produced by mechanical vibration in a liquid localized at the face of the probe.
- US- high intensity, localized cavitation, energy intensive, scaling up difficult
- Hydrodynamic Cavitation (HD) is produced by motion of fluid.
- Large pressure fluctuations in shear layer of the liquid cause cavitation.
- HD – wider area of cavitation, 1/10 – 1/100 energy required, easy to scale
DYNAJETS® Cavitating Jets

- Specially designed nozzles intensify cavitation and generate cavitation at lower pump pressures
- This is achieved through:
  - Passive acoustic excitation
  - Swirling the flow
- Both enhance vorticity and reduce pressure in the vortices

STRATJOET®

DYNASWIRL®
Hydrodynamic Cavitation for Oxidation

- Hydrodynamic cavitation can be 10 – 100 times more energy efficient than acoustic cavitation
- No addition of oxidizer
- Optical opacity or particulates are no problem
- Other than nozzle no special equipment required
- DYNAJETS®
  - Cavitation at lower pressures
  - Lower pressures lower electrical requirements
    - Hydraulic Energy = Flow Rate x Pressure change x time
  - Cavitation in wider area
  - Easier to scale up than US
Energy: Acoustic & Hydrodynamic

25 ppm \( p \)-Nitrophenol

Hydrodynamic cavitation can be 10 – 100 times more energy efficient than acoustic cavitation*

Applications of DYNAJETS®

- **Oxidation**
  - Chlorinated solvents
  - Toluene, Acetone
  - Pesticides: Malathion, Carbaryl, 2,4-D
  - Pharmaceuticals and Personal Care Products
- **Disinfection**
  - Water
  - Wastewater
  - Storm water
- **Recovery of Cellular Matter – Algae**
- **Pretreatment of lignocellulose biomass**
- **Biodiesel production**
Selectivity of HD Cavitation Oxidation

- Volatile (high vapor pressure) can be oxidized easily
- pH can be used to adjust degree of ionization of weak acids and bases
- Hydrophobic compounds (high octanol-water partition coefficient log \( K_{OW} \)) oxidize faster than hydrophilic compounds
- Reaction intermediates are formed in regions of high radical concentrations, lower by-product concentrations
- Operating parameters (pump pressure, jet velocity, etc.), and nozzle design can be varied to improve oxidation performance
Volatile Compounds: Mineralization of Chloroform

2-Jet DYNASWIRL® 65 psi, Chloroform = 344 mg/L
Vapor Pressure = 160 mm Hg @ 20 C
Oxidation of Toluene

DYNASWIRL® 30 psi

Toluene:
Vapor Pressure= 28.4 mmHg @25 C
Log $K_{OW}$=2.69
Hydrophobicity: pH effects & Methyl Orange

Decoloration of acid dye, Methyl Orange – pKa = 3.44

DYNASWIRL® dual jet 30 psi 

www.dynaflow-inc.com  AOT 16 11-17-10
Solubility Effects: DMMP and Malathion

DMMP – dimethyl methylphosphonate,
  sol = >100g/L, log $K_{OW}$=-1.88 Vp = <0.1 mmHg

Malathion – organophosphate pesticide
  Sol = 145 mg/L, log $K_{OW}$=2.89, Vp = $3 \times 10^{-6}$ mmHg
Malathion Oxidation Products
GC/MS data from Malathion oxidation: Dual Jet DYNASWIRL® at 30 psi

Malathion Oxidation Products

GC/MS data from Malathion oxidation: Dual Jet DYNASWIRL® at 30 psi

Int. Std – Tributyl phosphate

Int. Std – Tributyl phosphate

1: Scan El+
TIC
5.16e9

www.dynaflow-inc.com  AOT 16 11-17-10
Mass Balance Of Malathion Oxidation

Mass Balance

[C]/[Mal]0

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1

Oxidation Time (mins)

0 20 40 60 80 100 120 140

DYNASWIRL® duo jet, 30 psi

Malathion

Diethyl Fumarate

Hydroxydimethyl Phosphorodithioic Acid

Dimethyl Phosphorodithioic Acid
Selective Oxidation of Mixtures: log $K_{OW}$

- 7 pharmaceuticals and personal care products were mixed in wastewater treatment plant effluent
- Mixture oxidized using DYNASWIRL® nozzle at 60 psi for 30 minutes
- Mixture had a range of log $K_{OW}$ values 1.4 – 5.9
- More hydrophobic compounds reacted faster
Oxidation of Mixture of PPCP in Wastewater

DYNASWIRL® nozzle at 60 psi

Log $K_{OW}$

Chloroxylenol
Tris (2-chloroethyl)Phosphate
Galaxolide
Musk Ketone
Oxybenzone
Triclosan
Ibuprofen

www.dynaflow-inc.com  AOT 16 11-17-10
In a mixture more hydrophobic compounds react faster.

The relationship between log $K_{ow}$ and reaction extent is described by the linear equation:

$$y = 0.0523x - 0.0536$$

with a correlation coefficient $R^2 = 0.7922$. The graph shows a positive linear relationship with data points plotted against log $K_{ow}$ on the x-axis and $(1-C/C_0)$ on the y-axis.
Increasing Reaction Rates

- Nozzle design
- Pressure drop through the nozzle affects the quality of cavitation and oxidation efficiency
- Tweeking the system can increase reaction efficiency

DYNASWIRL® nozzle

20 psi
100 psi
Chloramphenicol antibiotic used in aquaculture and veterinary applications
Removal of Chloramphenicol using centerbody CaviJet at 45 and 65 psi

Initial concentrations = 27 mg/l, and total volume 11 liters
Effect of Pressure Drop on Removal Rate

Initial conc = 30 mg/L, Volume = 10 L. Oxidation with DYNASWIRL®

Chloramphenicol mg/L vs Oxidation Time (minutes)

- 30 psi
- 90 psi
- 60 psi
Chloramphenicol Removal per kilowatt-hour

Graph showing the removal of Chloramphenicol as a function of kilojoules (kJ). The graph compares different methods:
- CaviJet 65 psi
- CaviJet 45 psi
- DynaSwirl 30 psi
- DynaSwirl 60 psi
- DynaSwirl 90 psi

The x-axis represents the kilojoules (kJ), and the y-axis represents the ratio of Chloramphenicol concentration ([C] / [C]₀). The plot shows the effectiveness of each method in reducing the concentration of Chloramphenicol.
Conclusions

- Cavitation initiated reactions are similar regardless of how the cavitation is initiated.
- Hydrodynamic cavitation can be more energy efficient and easier to scale up than ultrasonic devices.
- Selective removal of volatile and hydrophobic compounds can be accomplished.
- Selective removal by pH adjustment.
- Oxidation rates have non-linear dependence on pump pressure.
- Nozzle geometry can affect oxidation rates.
Collaboration

- [www.dynaflow-inc.com](http://www.dynaflow-inc.com), technology descriptions and papers
- Testing, design, and production services
- Collaborative research
  - Feasibility studies
  - Small business STTR
  - Grant proposal writing
Acknowledgements & Contact Information

- US Environmental Protection Agency
- NASA
- Office Naval Research
- NOAA
- NIEHS

- DYNAFLOW, INC.
  www.dynaflow-inc.com
  10621-J Iron Bridge Road, Jessup, MD 20794. USA

- Dr. Greg Loraine
  Sr. Research Scientist
  (301) 604-3688
  gregl@dynaflow-inc.com

- Dr. Georges L. Chahine
  President
  (301) 604-3688
  glchahine@dynaflow-inc.com

- Business POC: Dr. Jin-Keun Choi
  Principal Research Scientist
  (301) 604-3688
  jkchoi@dynaflow-inc.com
Oxidation of As (III) to As(V)

![Graph showing oxidation of As (III) to As(V)](image)

<table>
<thead>
<tr>
<th>AOP</th>
<th>Lamp Power kW</th>
<th>Pump Power kW</th>
<th>kW/1000 gal</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV/H₂O₂</td>
<td>0.004</td>
<td>0.004</td>
<td>31</td>
</tr>
<tr>
<td>UV/TiO₂</td>
<td>0.004</td>
<td>0.004</td>
<td>17.4</td>
</tr>
<tr>
<td>DYNAJETS®</td>
<td>0.173</td>
<td>0.173</td>
<td>4.6</td>
</tr>
</tbody>
</table>

UV/H₂O₂ & UV/TiO₂ data Yoon and Lee 2005

www.dynaflow-inc.com  AOT 16 11-17-10
Disinfection Efficiency: E coli & B subtilis

Effects of nozzle geometry, and nozzle pressure were investigated using E. coli and B. subtilis.

E. coli

B. subtilis

Same conditions - DYNASWIRL® nozzle at 2.1 bar

www.dynaflow-inc.com  AOT 16 11-17-10