



**INVESTIGATING POINT-OF-USE UV-LED WATER PURIFICATION DEVICE
USING COMPUTATIONAL MULTIPHYSICS MODELING SOFTWARE**

THESIS

Shandon L. James, Captain, USAF

AFIT-ENV-MS-17-M-196
**DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY**

AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

DISTRIBUTION STATEMENT A.
APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

The views expressed in this thesis are those of the author and do not reflect the official policy or position of the United States Air Force, Department of Defense, or the United States Government. This material is declared a work of the U.S. Government and is not subject to copyright protection in the United States.

AFIT-ENV-MS-17-M-196

INVESTIGATING POINT-OF-USE UV-LED WATER PURIFICATION DEVICE
USING COMPUTATIONAL MULTIPHYSICS MODELING SOFTWARE

THESIS

Presented to the Faculty

Department of Engineering and Management

Graduate School of Engineering and Management

Air Force Institute of Technology

Air University

Air Education and Training Command

In Partial Fulfillment of the Requirements for the
Degree of Master of Science in Engineering Management

Shandon L. James, BS

Captain, USAF

March 2017

DISTRIBUTION STATEMENT A.
APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

INVESTIGATING POINT-OF-USE UV-LED WATER PURIFICATION DEVICE
USING COMPUTATIONAL MULTIPHYSICS MODELING SOFTWARE

Shandon L. James, BS
Captain, USAF

Committee Membership:

Dr. Michael E. Miller, PhD
Chair

Lt. Col. Kempisty, David, BSC, PhD, P.E.
Member

Dr. Prigge, Diedrich PhD, P.E.
Member

Abstract

The United States Air Force (USAF) often deploys personnel to remote locations or responds to disasters worldwide. Point-of-Use (PoU) ultraviolet (UV) water treatment could provide the DoD with the ability to provide water for small mobile entities that are incapable of providing the support network that larger water purification devices require. PoUs could be used as the water treatment system within the DoD for applications that include disaster response, austere locations, aircraft/helicopter survival kit or small unit for special operations teams. This research investigates the ability to use computer modeling software to predict and optimize the characteristics of a UV LED PoU water purification reactor for such applications. This research developed a working model using computational multiphysics software to predict reaction processes within a UV LED water purification reactor, and validated the model with laboratory data. The research also investigated the effect of altering the reactor geometry and the corresponding interactions with corresponding reactor rate effectiveness. The model demonstrated the ability to predict the reaction curves gathered from the lab data as well as illustrated trends in reactor geometry. When investigating the efficiency of various reactor geometries, minimizing the surface area:volume ratio was shown to result in the largest increases in efficiency. However the volume of the reactor, reflectance, and flow rates also played a role in reactor effectiveness.

Table of Contents

	Page
AFIT-ENV-MS-17-M-196.....	v
Abstract	v
Table of Contents.....	vi
List of Figures.....	x
List of Tables	xviii
 I. Introduction	 1
General Issue	1
Problem Statement.....	2
Research Objective	3
Research Focus	3
Investigative Questions.....	4
Methodology.....	4
Assumptions/Limitations	5
Implications	5
Preview	6
 II. Literature Review	 7
UV LED Development	7
History of Ultraviolet Water Treatment.....	8
Existing Means of Portable Water Treatment.....	9
Air Force Institute of Technology Research	15
COMSOL® Modeling Related Research	20

III. Methodology	22
Theory.....	23
COMSOL® Theory	24
Methods Utilized in COMSOL®	25
Lab Validation Data.....	28
COMSOL® Geometry Optimization.....	31
Summary.....	33
IV. Model Development and Construction	34
COMSOL® Multiphysics Model Development	34
Geometry	34
Parameterization	36
Meshing	39
Ray Optics Module	41
Laminar Flow Module	48
Transport of Diluted Species Module	49
3D Cut Line Data Collection	52
Significant Model Assumptions.....	53
Summary.....	54
V. Results and Analysis.....	56
Chapter Overview	56
Initial COMSOL® Model Results and Analysis	56
Adapted COMSOL® Model Results and Analysis.....	59
Original Geometry with 6 mL/min for BB-IIR and H ₂ O-IIR	61
Original Geometry with 8 mL/min for BB-IIR and H ₂ O-IIR	71
Original Geometry with 10 mL/min for BB-IIR and H ₂ O-IIR	76
Original Geometry with 10 mL/min at 100% Reflectance for H ₂ O-IIR	80

Adapted Model Analysis	84
Geometric Optimization Trends	86
Geometry Styles for Pure Water Imaginary Index of Refraction, H_2O -IIR.....	87
Geometry Styles for Brilliant Blue Absorption Imaginary Refractive Index, $k=8.80E-7$	89
Analysis	91
VI. Conclusions and Recommendations.....	101
Conclusions of Research.....	101
Investigate Questions.....	103
Significance of Research	105
Recommendations for Future Research	106
Summary.....	107
Appendix A- Brilliant Blue and Hydrogen Peroxide AOP UV LED Experimental Setup.....	108
Appendix B – Reactor Geometry, Mesh Layout, Ray Propagation, Velocity Field, Slice Concentration	112
<u>Original Geometry, 36.42 cm³, Pure Water $k=3.15E-$ at 6 mL/min</u>	116
<u>Original Geometry, 36.42 cm³, Brilliant Blue $k=8.80E-7$ at 8 mL/min</u>	121
<u>Original Geometry, 36.42 cm³, Pure Water $k=3.15E-$ at 8 mL/min</u>	125
<u>Original Geometry, 36.42 cm³, Brilliant Blue $k=8.80E-7$ at 10 mL/min</u>	130
<u>Original Geometry, 36.42 cm³, Pure Water $k=3.15E-$ at 10 mL/min</u>	134
<u>Original Geometry, 36.42 cm³, Pure Water $k=3.15E-$ at 10 mL/min, 100% Reflectance</u>	139
<u>Half Scale Original Geometry, 4.546 cm³, Brilliant Blue $k=8.80E-7$ at 10 mL/min</u>	143
<u>Half Scale Original Geometry, 4.546 cm³, Pure Water $k=3.15E-$ at 10 mL/min</u>	148
<u>Half Scale Original Geometry with Separator Plate, 4.546 cm³, Brilliant Blue $k=8.80E-7$ at 10 mL/min</u>	152
<u>Half Scale Original Geometry with Separator Plate, 4.546 cm³, Pure Water $k=3.15E-$ at 10 mL/min</u>	157
<u>Sphere Geometry, 4.546 cm³, Brilliant Blue $k=8.80E-7$ at 10 mL/min</u>	161

Sphere Geometry, 4.546 cm³, Pure Water k=3.15E- at 10 mL/min.....	166
<u>Sphere Geometry, 36.42 cm³, Brilliant Blue k=8.80E-7 at 10 mL/min.....</u>	170
<u>Sphere Geometry, 36.42 cm³, Pure Water k=3.15E- at 10 mL/min.....</u>	175
Appendix C – Supporting Data	180
Refractive Imaginary Index Power Conversion Table.....	180
Appendix D - COMSOL[®] Utilized Modules and Sub-nodes.....	181
Bibliography.....	184

List of Figures

Figure 1: Wavelength and Geometry Relationship, Image credit: COMSOL® (Walter 2015).....	27
Figure 2: Dual Inlet/Outlet Reactor	28
Figure 3: UV LED Reactor Geometry Modeled in COMSOL® (COMSOL® v. 5.2. 2017)	29
Figure 4: Experimental Test Setup	30
Figure 5: UV LED Original Reactor Geometry (COMSOL® v. 5.2. 2017).....	35
Figure 6: Geometry Node Parameters (COMSOL® v. 5.2. 2017)	36
Figure 7: Ray Optics Module Parameters (COMSOL® v. 5.2. 2017).....	37
Figure 8: Global Parameters (COMSOL® v. 5.2. 2017)	37
Figure 9: Initial Mesh Element Format for Original Geometry (COMSOL® v. 5.2. 2017).....	40
Figure 10: Final Mesh Element Format for Original Geometry (COMSOL® v. 5.2. 2017)	41
Figure 11: Imaginary Index of Refraction Model Geometry with Ray Particle (COMSOL® v. 5.2. 2017) .	45
Figure 12: Ray Release Locations Seen after 0.05ns (COMSOL® v. 5.2. 2017).....	47
Figure 13: Step Function Defined (COMSOL® v. 5.2. 2017)	52
Figure 14: Example 3D Cut Line Inputs with Red Plot Line (COMSOL® v. 5.2. 2017)	53
Figure 15: Degradation Curves Lab, Reactor Data and $RRC=1.2150E-6$ [mol/(W*s)] at 10 mL/min.....	57
Figure 16: Reaction Rate Constant Calibration Runs at 10 mL/min, ...	59
Figure 17: Ray Power for BB-IIR and Original Geometry Reactor, 95% Reflectance	60
Figure 18: Ray Power for H ₂ O-IIR and Original Geometry Reactor, 95% Reflectance.....	61
Figure 19: Original Geometry 6 mL/min, Isometric (COMSOL® v. 5.2. 2017).....	62
Figure 20: Original Geometry 6 mL/min, X-Axis (COMSOL® v. 5.2. 2017).....	62
Figure 21: Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)	63
Figure 22: Ray Propagation at 0.03 ns, 95% Reflectance (COMSOL® v. 5.2. 2017)	64
Figure 23: Ray Propagation at 0.35 ns, BB-IIR, 95% Reflectance (COMSOL® v. 5.2. 2017).....	64
Figure 24: Ray Propagation at 4.0 ns, H ₂ O-IIR, 95% Reflectance (COMSOL® v. 5.2. 2017)	65
Figure 25: 6 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017).....	66
Figure 26: 6 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)	66

Figure 27: Slice Concentration 6mL/min, BB-IIR, 60 seconds (COMSOL® v. 5.2. 2017).....	67
Figure 28: Slice Concentration 6mL/min, H ₂ O-IIR, 60 seconds (COMSOL® v. 5.2. 2017)	68
Figure 29: Slice Concentration 6mL/min, BB-IIR, 1500 seconds (COMSOL® v. 5.2. 2017).....	69
Figure 30: Slice Concentration 6mL/min, H ₂ O-IIR, 1500 seconds (COMSOL® v. 5.2. 2017)	69
Figure 31: Original Geometry Brilliant Blue Dye Degradation for Lab BB-IIR, Model BB-IIR, ...	70
Figure 32: 8 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017).....	71
Figure 33: 8 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017).....	72
Figure 34: Slice Concentration 8mL/min, BB-IIR, 60 seconds (COMSOL® v. 5.2. 2017).....	73
Figure 35: Slice Concentration 8mL/min, H ₂ O-IIR, 60 seconds (COMSOL® v. 5.2. 2017)	73
Figure 36: Slice Concentration 8mL/min, BB-IIR, 1128 seconds (COMSOL® v. 5.2. 2017).....	74
Figure 37: Slice Concentration 8mL/min, H ₂ O-IIR, 1128 seconds (COMSOL® v. 5.2. 2017).....	74
Figure 38: Original Geometry Brilliant Blue Dye Degradation for Lab BB-IIR, Model BB-IIR, Model H ₂ O at 8 mL/min Flow Rate	75
Figure 39: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017).....	76
Figure 40: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017).....	77
Figure 41: Slice Concentration 10mL/min, BB-IIR, 60 seconds (COMSOL® v. 5.2. 2017).....	78
Figure 42: Slice Concentration 10mL/min, H ₂ O-IIR, 60 seconds (COMSOL® v. 5.2. 2017)	78
Figure 43: Slice Concentration 10mL/min, BB-IIR, 900 seconds (COMSOL® v. 5.2. 2017).....	79
Figure 44: Slice Concentration 10mL/min, H ₂ O-IIR, 900 seconds (COMSOL® v. 5.2. 2017)	79
Figure 45: Original Geometry Brilliant Blue Dye Degradation for Lab BB-IIR, Model BB-IIR, ...	80
Figure 46: Power Loss from Water and 5% Wall Absorption, H ₂ O-IIR, 6mL/min (0-0.15 ns).....	81
Figure 47: Ray Power at 100% Reflection, H ₂ O-IIR, 10 mL/min	83
Figure 48: Original Geometry Brilliant Blue Dye Degradation, 100% Reflectance, 10 mL/min Flow Rate	84
Figure 49: Degradation of Original, Half Scale, Half Scale with Separator Plate, and Sphere 4.546cm ³ Geometry with H ₂ O-IIR, 10 mL/min Flow Rate	87
Figure 50: Degradation of Original, Sphere 4.546 cm ³ , and Sphere 36.42 cm ³ Geometry.....	88
Figure 51: Degradation of Original, Half Scale, Half Scale with Separator Plate, and Sphere 4.546cm ³	89

Figure 52: Degradation of Original Geometry 36.42cm^3 , Sphere 4.546cm^3 , and Sphere 36.42cm^3	90
Figure 53: 3D Cut Line (COMSOL® v. 5.2. 2017).....	92
Figure 54: Original Data Plot for Sphere Model, 36.42cm^3 , ...	93
Figure 55: Normalized Data Plot for Sphere Model, 36.42cm^3 ,.....	93
Figure 56: Reactor Assembly	109
Figure 57: Power Supply Settings	111
Figure 58: Original Geometry 6 mL/min, Isometric (COMSOL® v. 5.2. 2017).....	112
Figure 59: Original Geometry 6 mL/min, X-Axis (COMSOL® v. 5.2. 2017).....	112
Figure 60: Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)	113
Figure 61: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)	113
Figure 62: Ray Propagation at 0.35 ns, $k=8.80\text{E}-7$ (COMSOL® v. 5.2. 2017).....	114
Figure 63: 6 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017).....	114
Figure 64: 6 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017).....	115
Figure 65: Slice Concentration 6mL/min, $k=8.80\text{E}-7$, 60 seconds (COMSOL® v. 5.2. 2017).....	115
Figure 66: Slice Concentration 6mL/min, $k=8.80\text{E}-7$, 1500 seconds (COMSOL® v. 5.2. 2017).....	116
Figure 67: Original Geometry 6 mL/min, Isometric (COMSOL® v. 5.2. 2017).....	116
Figure 68: Original Geometry 6 mL/min, X-Axis (COMSOL® v. 5.2. 2017).....	117
Figure 69: Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)	117
Figure 70: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)	118
Figure 71: Ray Propagation at 4.0 ns, $k=3.15\text{E}-8$ (COMSOL® v. 5.2. 2017).....	118
Figure 72: 6 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017).....	119
Figure 73: 6 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017).....	119
Figure 74: Slice Concentration 6mL/min, $k=3.15\text{E}-8$, 60 seconds (COMSOL® v. 5.2. 2017).....	120
Figure 75: Slice Concentration 6mL/min, $k=3.15\text{E}-8$, 1500 seconds (COMSOL® v. 5.2. 2017).....	120
Figure 76: Original Geometry 8 mL/min, Isometric (COMSOL® v. 5.2. 2017).....	121
Figure 77: Original Geometry 8 mL/min, X-Axis (COMSOL® v. 5.2. 2017).....	121
Figure 78: Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)	122

Figure 79: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)	122
Figure 80: Ray Propagation at 0.35 ns, $k=8.80E-7$ (COMSOL® v. 5.2. 2017).....	123
Figure 81: 8 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017).....	123
Figure 82: 8 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017).....	124
Figure 83: Slice Concentration 8mL/min, $k=8.80E-7$, 60 seconds (COMSOL® v. 5.2. 2017).....	124
Figure 84: Slice Concentration 8mL/min, $k=8.80E-7$, 1128 seconds (COMSOL® v. 5.2. 2017).....	125
Figure 85: Original Geometry 8 mL/min, Isometric (COMSOL® v. 5.2. 2017).....	125
Figure 86: Original Geometry 8 mL/min, X-Axis (COMSOL® v. 5.2. 2017).....	126
Figure 87: Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)	126
Figure 88: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)	127
Figure 89: Ray Propagation at 4.0 ns, $k=3.15E-8$ (COMSOL® v. 5.2. 2017).....	127
Figure 90: 8 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017).....	128
Figure 91: 8 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017).....	128
Figure 92: Slice Concentration 8mL/min, $k=3.15E-8$, 60 seconds (COMSOL® v. 5.2. 2017).....	129
Figure 93: Slice Concentration 8mL/min, $k=3.15E-8$, 1128 seconds (COMSOL® v. 5.2. 2017).....	129
Figure 94: Original Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017).....	130
Figure 95: Original Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017).....	130
Figure 96: Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)	131
Figure 97: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)	131
Figure 98: Ray Propagation at 0.35 ns, $k=8.80E-7$ (COMSOL® v. 5.2. 2017).....	132
Figure 99: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017).....	132
Figure 100: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017).....	133
Figure 101: Slice Concentration 10mL/min, $k=8.80E-7$, 60 seconds (COMSOL® v. 5.2. 2017).....	133
Figure 102: Slice Concentration 10mL/min, $k=8.80E-7$, 900 seconds (COMSOL® v. 5.2. 2017).....	134
Figure 103: Original Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017).....	134
Figure 104: Original Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017).....	135
Figure 105: Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)	135

Figure 106: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017).....	136
Figure 107: Ray Propagation at 4.0 ns, $k=3.15E-8$ (COMSOL® v. 5.2. 2017).....	136
Figure 108: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017).....	137
Figure 109: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017).....	137
Figure 110: Slice Concentration 10mL/min, $k=3.15E-8$, 900 seconds (COMSOL® v. 5.2. 2017).....	138
Figure 111: Slice Concentration 10mL/min, $k=3.15E-8$, 60 seconds (COMSOL® v. 5.2. 2017).....	138
Figure 112: Original Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017).....	139
Figure 113: Original Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017).....	139
Figure 114: Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)	140
Figure 115: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017).....	140
Figure 116: Ray Propagation at 8.0 ns (COMSOL® v. 5.2. 2017)	141
Figure 117: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017).....	141
Figure 118: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017).....	142
Figure 119: Slice Concentration 10mL/min, $k=8.80E-7$, 60 seconds (COMSOL® v. 5.2. 2017).....	142
Figure 120: Slice Concentration 10mL/min, $k=8.80E-7$, 900 seconds (COMSOL® v. 5.2. 2017).....	143
Figure 121: Half Scale Original Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017)	143
Figure 122: Half Scale Original Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017)	144
Figure 123: Half Scale Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017).....	144
Figure 124: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017).....	145
Figure 125: Ray Propagation at 0.35 ns, $k=8.80E-7$ (COMSOL® v. 5.2. 2017).....	145
Figure 126: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017).....	146
Figure 127: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017).....	146
Figure 128: Slice Concentration 10mL/min, $k=8.80E-7$, 60 seconds (COMSOL® v. 5.2. 2017).....	147
Figure 129: Slice Concentration 10mL/min, $k=8.80E-7$, 900 seconds (COMSOL® v. 5.2. 2017).....	147
Figure 130: Half Scale Original Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017)	148
Figure 131: Half Scale Original Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017)	148
Figure 132: Half Scale Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017).....	149

Figure 133: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017).....	149
Figure 134: Ray Propagation at 4.0 ns, $k=3.15E-8$ (COMSOL® v. 5.2. 2017).....	150
Figure 135: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017).....	150
Figure 136: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017).....	151
Figure 137: Slice Concentration 10mL/min, $k=3.15E-8$, 60 seconds (COMSOL® v. 5.2. 2017).....	151
Figure 138: Slice Concentration 10mL/min, $k=3.15E-8$, 900 seconds (COMSOL® v. 5.2. 2017).....	152
Figure 139: Half Scale Original Geometry with Separator Plate 10 mL/min, Isometric (COMSOL® v. 5.2. 2017).....	152
Figure 140: Half Scale Original Geometry with Separator Plate 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017).....	153
Figure 141: Half Scale Original Geometry with Separator Plate Mesh Layout (COMSOL® v. 5.2. 2017)	153
Figure 142: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017).....	154
Figure 143: Ray Propagation at 0.35 ns, $k=8.80E-7$ (COMSOL® v. 5.2. 2017).....	154
Figure 144: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017).....	155
Figure 145: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017).....	155
Figure 146: Slice Concentration 10mL/min, $k=8.80E-7$, 60 seconds (COMSOL® v. 5.2. 2017).....	156
Figure 147: Slice Concentration 10mL/min, $k=8.80E-7$, 900 seconds (COMSOL® v. 5.2. 2017).....	156
Figure 148: Half Scale Original Geometry with Separator Plate 10 mL/min, Isometric (COMSOL® v. 5.2. 2017).....	157
Figure 149: Half Scale Original Geometry with Separator Plate 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017).....	157
Figure 150: Half Scale Original Geometry with Separator Plate Mesh Layout (COMSOL® v. 5.2. 2017)	158
Figure 151: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017).....	158
Figure 152: Ray Propagation at 4.0 ns, $k=3.15E-8$ (COMSOL® v. 5.2. 2017).....	159
Figure 153: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017).....	159
Figure 154: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017).....	160
Figure 155: Slice Concentration 10mL/min, $k=3.15E-8$, 60 seconds (COMSOL® v. 5.2. 2017).....	160

Figure 156: Slice Concentration 10mL/min, $k=3.15E-8$, 900 seconds (COMSOL® v. 5.2. 2017)	161
Figure 157: Sphere Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017)	161
Figure 158: Sphere Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017)	162
Figure 159: Sphere Geometry Mesh Layout (COMSOL® v. 5.2. 2017)	162
Figure 160: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)	163
Figure 161: Ray Propagation at 0.35 ns, $k=8.80E-7$ (COMSOL® v. 5.2. 2017)	163
Figure 162: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)	164
Figure 163: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)	164
Figure 164: Slice Concentration 10mL/min, $k=8.80E-7$, 60 seconds (COMSOL® v. 5.2. 2017)	165
Figure 165: Slice Concentration 10mL/min, $k=8.80E-7$, 900 seconds (COMSOL® v. 5.2. 2017)	165
Figure 166: Sphere Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017)	166
Figure 167: Sphere Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017)	166
Figure 168: Sphere Geometry Mesh Layout (COMSOL® v. 5.2. 2017)	167
Figure 169: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)	167
Figure 170: Ray Propagation at 4.0 ns, $k=3.15E-8$ (COMSOL® v. 5.2. 2017)	168
Figure 171: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)	168
Figure 172: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)	169
Figure 173: Slice Concentration 10mL/min, $k=3.15E-8$, 60 seconds (COMSOL® v. 5.2. 2017)	169
Figure 174: Slice Concentration 10mL/min, $k=3.15E-8$, 900 seconds (COMSOL® v. 5.2. 2017)	170
Figure 175: Sphere Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017)	170
Figure 176: Sphere Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017)	171
Figure 177: Sphere Geometry Mesh Layout (COMSOL® v. 5.2. 2017)	171
Figure 178: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)	172
Figure 179: Ray Propagation at 0.35 ns, $k=8.80E-7$ (COMSOL® v. 5.2. 2017)	172
Figure 180: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)	173
Figure 181: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)	173
Figure 182: Slice Concentration 10mL/min, $k=8.80E-7$, 60 seconds (COMSOL® v. 5.2. 2017)	174

Figure 183: Slice Concentration 10mL/min, $k=8.80E-7$, 900 seconds (COMSOL® v. 5.2. 2017).....	174
Figure 184: Sphere Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017).....	175
Figure 185: Sphere Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017).....	175
Figure 186: Sphere Geometry Mesh Layout (COMSOL® v. 5.2. 2017)	176
Figure 187: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017).....	176
Figure 188: Ray Propagation at 4.0 ns, $k=3.15E-8$ (COMSOL® v. 5.2. 2017).....	177
Figure 189: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017).....	177
Figure 190: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017).....	178
Figure 191: Slice Concentration 10mL/min, $k=3.15E-8$, 60 seconds (COMSOL® v. 5.2. 2017).....	178
Figure 192: Slice Concentration 10mL/min, $k=3.15E-8$, 900 seconds (COMSOL® v. 5.2. 2017).....	179
Figure 193: COMSOL® Operating System (COMSOL® v. 5.2. 2017).....	181
Figure 194: COMSOL® Modules and Sub-Nodes Utilized (COMSOL® v. 5.2. 2017).....	182
Figure 195: COMSOL® Ray Optics, Laminar Flow, Transport of Diluted Species Modules and Sub-Nodes (COMSOL® v. 5.2. 2017)	183

List of Tables

Table 1: AFIT UV LED Reactor Data Summary (Miller 2016).....	19
Table 2: Imaginary Index of Refraction Values	32
Table 3: Reactor Geometry Styles Analyzed for Geometric Optimization Process	33
Table 4: Reaction Rate Constant Sum of Squares Analysis from Laboratory Data	58
Table 5: Effluent Flow Variance	95
Table 6: Surface Area to Volume Ratio's.....	96
Table 7: 10 mL/min Reactor Flow Rates Percent Degraded Ranking.....	97
Table 8: Reactor Rankings, H ₂ O-IIR	98
Table 9: Reactor Rankings, BB-IIR.....	99

INVESTIGATING POINT-OF-USE UV-LED WATER PURIFICATION DEVICE USING COMPUTATIONAL MULTIPHYSICS MODELING SOFTWARE

I. Introduction

General Issue

The United States Air Force (USAF) often deploys personnel to remote locations or responds to disasters worldwide. These environments often don't have water that is safe for human consumption. In these locations USAF Civil Engineers (CE) have equipment that can be deployed to purify water through reverse osmosis (ROWPU) to produce safe drinking water. These units have the ability to provide large volumes of potable water. However they are large, consume copious amounts of power, and require a sizable supply chain to be operated. There are instances where USAF and other Department of Defense (DoD) entities would benefit from smaller, individual or squad sized water purification devices. Point-of-use ultraviolet (UV) water treatment could provide the DoD with the ability to provide water for small mobile entities that would not require the support network currently required by larger water purification devices.

UV radiation was used as early as the 1870s to disinfect water (Pirnie, Linden, and Malley 2006). UV radiation degrades nucleic acids in water borne organisms disabling DNA reproduction, thus preventing the microorganism from reproducing in its host (Pirnie, Linden, and Malley 2006). The first reliable municipal UV water treatment centers were in Switzerland and Austria in 1955, using mercury filled fluorescent lamps (Pirnie, Linden, and Malley 2006). Mercury bulbs require significant time to warm up to operating temperatures as well as suffer from relatively short life spans and contain toxic mercury metal vapors. For these reasons and because of the relative cost effectiveness of chlorine, chemical sanitizers have been adopted to treat and maintain relative safety within most municipal water

systems. These chemical sanitizers destroy microorganisms by degrading the cellular structures, preventing reproduction and residual chemicals remain in the water to prevent further microorganism growth.

Over the last few decades Light Emitting Diodes (LED) have been developed capable of producing UV radiation (Muramoto, Kimura, and Nouda 2014). Over the last decade UV LEDs have increased in power by 100 times for wavelengths 300 nm and greater while undergoing significant cost reductions (Muramoto, Kimura, and Nouda 2014). Recently, similar advances have begun to occur for UV LEDs with wavelengths between 220 and 300 nm. These advances are making UV LEDs viable for use in small scale water purification systems.

The USAF and DoD could have multiple uses for a small scale portable water purification system. In 2010 the USAF along with the Navy, Marines and Army responded to the Haiti earthquake to reopen the airport and provide immediate lifesaving actions, disaster relief, and humanitarian support, including food and clean water (Cecchine et al. 2013). Recently a hurricane in the same country left many residents without safe drinking water leading to a cholera outbreak. A small, point-of-use, water purification system that could be readily distributed among the populous could be greatly beneficial in an event of this magnitude, allowing rescuers to provide improved water from most water sources until public water systems are brought online. Other uses for a point-of-use water treatment system within the DoD include an aircraft/helicopter survival kit or small unit for special operations teams. This research investigates the ability for computer modeling software to predict and optimize the characteristics of a UV LED point source water purification reactor for such applications.

Problem Statement

The ability to provide safe drinking water in austere environments is essential for downed aviators,

special operators, and disaster search and response teams. USAF and DoD personnel need to be able to obtain safe drinking water while maintaining their mobility, precluding the use of ROWPUs or other large scale water purification methods. Although there are other small water purification devices on the market or in research, like Lifestraw (Vestergaard 2017b), Drinkable Book (Life is Water 2017), mercury fluorescent UV bulbs, among others; most of these purification methods have undesirable aspects for deployment in the target environments. A UV LED point-of-use water purification device can be light, use little power, and is durable; allowing operators to easily transport and apply such water treatment devices while focusing on their mission.

Air Force Institute of Technology (AFIT) has been studying the effects of UV LED reactors to purify water. Past devices have been large, fragile, and not practical for field use. These devices have undergone an iterative process of design, construction and laboratory evaluation. Unfortunately, this process is long and does not permit modification without completing the design, construction and evaluation steps. This thesis seeks to shorten this process through the application of computer modeling software to design and simulate test results to inform future design prior to construction.

Research Objective

This thesis seeks to develop a working model using computational multiphysics software to predict reaction processes within a UV LED water purification reactor, validate this model with laboratory data and investigate multiple geometry designs and their interaction with corresponding reaction rates.

Research Focus

The research will focus on validating the computer model using data from a current UV LED reactor and applying the model to improving the reactor design. The intent is to apply the model to aid the development of a small UV LED water purification device capable of producing clean water to supply a

single user or small unit comprised of multiple individuals. For example, such a method might strive to provide a more efficient reactor (e.g., one that requires minimal power to attain a system capable of meeting the NSF protocol P248 standard (International 2012)).

Investigative Questions

This thesis investigates the following questions:

- 1) What inputs are needed to develop a robust computer model that will successfully predict the reaction process of an UV LED reactor?
- 2) What methods can be used to validate the computer model?
- 3) How can COMSOL[®], Brilliant Blue and hydrogen peroxide be used to validate a model that utilizes UV radiation to degrade a known quantity of Brilliant Blue dye using laboratory data?
- 4) How does changing the reactor geometry and UV LED placement affect the efficiency of the reactor?

Methodology

The research methodology used in this thesis is computer modeling, validated through application of laboratory obtained, UV LED-based water reactor performance data. The first step was to gain proficiency with the modeling software package that would have the capability of modeling the complex interactions between fluid flow, propagation of UV LED energy in the reactor, as well as appropriate chemical reactions. The second step involved gathering an experimental data set involving Brilliant Blue dye and hydrogen peroxide to measure the degradation of the dye solution as it was circulated through the reactor. A model was then constructed in COMSOL[®] which permitted the estimation of the relative reduction in dye concentration as it flowed through the UV reactor. The laboratory degradation curves were compared to the reaction curves that COMSOL[®] produced. After the model was validated against the laboratory Brilliant Blue degradation curves, the model was tested by changing the reactor geometries,

volume, and imaginary refractive indices of the solution. These changes allowed the research to distinguish which variables had the greatest effect on the reactor efficiencies.

Assumptions/Limitations

Due to the USAF procurement process it was challenging to attain the COMSOL® Multiphysics software and delivery was significantly later than expected. Additionally, it was assumed that the simulation utilized water flow, ray tracing, and the chemical analysis correctly to produce the final model of the UV LED reactor.

Some limiting assumptions were utilized to reduce the scope of the research. The first being the device will be used as a point-of-use device, meaning that the device would be used by a single user and has to be small, light, and portable for ease of use. Another limiting assumption is the laboratory reactor data used to validate the model was correct, accurate, and precise. Therefore assuming that the if the model solution was comparable to the laboratory data that COMSOL® could effectively be used to model other reactors for future research and production. Additional detailed assumptions were made while calculating the necessary conversion values needed to input the correct reaction equation into COMSOL®. A few other limiting factors were the type and availability of the UV LEDs, reactor materials, reactor size, and power requirements used in the reactor.

Implications

If this research effort is successful it has the potential to exponentially increase the research speed for water purification devices at AFIT. The school will be able to investigate the attributes of multiple reactor designs in hours instead of months. The research also has the potential to lay the ground work for a multitude of divergent research efforts that utilize COMSOL® and water purification research.

Lastly, if the model successfully predicts the reaction process in the UV LED reactors, it could

move AFIT and the DoD one step closer to testing and implementing a point-of-use small scale water purification device for field applications. Once this step is achieved the possibilities for low energy point-of-use germicidal water purification devices are limitless. They could be used as personal water purification devices for hydration packs, or used in survival kits for crashed aviators. Additionally, they could be used on water faucets in a deployed remote location for bare base operations or used in conjunction with larger water purifiers similar to the current ROWPUs used within the DoD.

Preview

Chapter II will discuss the available literature on the history of UV water treatment, UV LED development, COMSOL® Multiphysics literature, and other related AFIT research. Chapter III will describe the methodology of this thesis modeling process, validation, and optimization using COMSOL® Multiphysics. Chapter IV will provide a summary of the model that was constructed. Chapter V will provide a summary and analysis of the results of the modeling, validation, and optimization process. Chapter VI will state the conclusions of this study and identify potential follow on research.

II. Literature Review

The purpose of this chapter is to examine the historical developments in UV LED technology, the application of ultraviolet illumination for water treatment, competitive means for portable water treatment, related Air Force Institute of Technology research, and COMSOL[®] Multiphysics modeling related research.

UV LED Development

The development of visible-spectrum light emitting diodes (LEDs) occurred over a 60 year period starting as early as the p-n junction design in 1940 (Dupuis and Krames 2008). The first visible spectrum LEDs used arsenic, gallium, and phosphorus compounds. These LEDs were of basic design composing a semiconductor chip and anionic junction design that was spearheaded by General Electric in 1962 (Holonyak and Bevacqua 1962). Later in the century, LED technology had progressed to be able to produce emission peaks in the regions of the visible spectrum associated with green, yellow, and orange light (Kovac, Peternai, and Lengyel 2003). Blue light LEDs were discovered in the 1990s and utilized Lanthanum Gallium Nitride compounds. This accomplishment was later acknowledged by a Nobel Prize in 2015 for Nakamura (Nakamura, Mukai, and Senoh 1994). LED technology has progressed to the point that commercial systems have attained white light sources with luminous efficacies of over 150 lm/W. These values are far above the efficacies attainable with traditional lighting technologies.

Despite visible spectrum LEDs existing since the 1960s, UV LEDs are relatively new. The UV LEDs were first created in 1992 around the same time as high energy blue LEDs (Goh et al. 2002). In 2000, only eight years after the first UV LED was created, a commercial grade, long wavelength UV LED was created and marketed (Muramoto, Kimura, and Nouda 2015).

Visible spectrum LEDs have improved dramatically since their inception in 1962. They have become more powerful, easier to mass produce, as well as inexpensive as their development has progressed. Their development has generally followed “Haitz’s Law,” which is similar in nature to “Moore’s Law” for computer processors. While Moore’s Law states that computer processing power doubles approximately every two years (Schaller 1997), Haitz’s Law states, “every 10 years the amount of light generated by an LED increases by a factor of 10, while the cost per lumen falls by a factor of 10 (Steele 2007).” This trend appears to be predictive of advances in the UV LED market as well (Ibrahim et al. 2014). The UV LED market has progressed from handmade devices to the early stages of mass-production. This drastic change of production has allowed the technology to progress to create more powerful and less costly UV LEDs every year.

History of Ultraviolet Water Treatment

Ultraviolet radiation has been used for water treatment for decades. The history of Ultraviolet water purification dates back to 1877 when Downs and Blunt (Downes and Blunt 1877) discovered that bacterial growth was inhibited by sunlight. Later in 1901 the mercury vapor bulb was created. This invention was used with a quartz tube to create the first artificial UV light source (Linden 1998). The year 1910 was important for water treatment practices. In Marseille, France the first implementation of an UV water treatment system was put into production (Dehghani, Jahed, and Zarei 2013). This achievement was followed by the discovery of the disinfection capabilities of chlorine gas. Chlorine was cheaper to implement and use than the UV radiation method, therefore efforts to implement UV radiation in water treatment plants were discontinued for the next few decades (Whitby 2004). Austria and Switzerland were the first countries to implement commercial scale UV water treatment processes in 1950 (Percival et al. 2013). The United States adopted UV water treatment later the same decade. The plant combined

filtration, UV radiation as well as chlorine in a process that is still used today across the world (Pontius 2003). This process was implemented due to the unique characteristics of the three methods. Filtration reduces the solids and other materials that reduce the effectiveness of the other two processes. Chlorine compounds eliminate most bacteria and viruses and, applied appropriately, provides a residual concentration that prevents regrowth. However, not all biological containments can be destroyed by chlorine. Therefore UV radiation treatment renders chlorine-resistant bacteria inert. This three prong approach provides a robust treatment process that has the ability to deactivate contaminants that the three processes could not attain individually, leading to the continued use of this treatment train (Pontius 2003).

Existing Means of Portable Water Treatment

This portion of the literature will focus on purification practices that are currently in use for small, portable water treatment systems. It has been speculated that the pursuit of clean drinking water began in prehistoric times. The earliest documentation of a form of water treatment has been found in Sanskrit writings and inscriptions in Egyptian tombs that date back as far as 2000 B.C. (Baker 1948). Some of the more notable methods mentioned are boiling water over fire, heating water in the sun, and filtration via gravel and sand (Baker 1948). Boiling water has been shown to eliminate nearly all waterborne organisms, but has very little effect on chemical compounds in the water (NY DOH 2017). To disinfect water the user must attain a water temperature of 100°C, and hold the water at a boil for over 30 minutes to provide proper disinfection (World Health Organization 2011). This process however is not ideal for DoD operations due to the time involved and the possibility of the heat source being detected. Therefore other methods of point-of-use water purification need to be investigated.

One of the widest used methods for water purification throughout the developed world is treating water with chlorine for disinfection. Often cities and rural entities disinfect both their drinking water and

waste water via the chlorine method. To attain mass quantity disinfection the plants need to be able to attain a 1ppm of chlorine at a pH of 7.5 and at a temperature of 25°C. This process needs to be able to treat the water for at least a minute to disinfect *E. coli*, and can take up to ten days to disinfect cryptosporidium (CDC 2017a). Some of the primary benefits of chlorine are its ability to stay dissolved in water for long durations to provide residual treatment of water after the initial disinfection. Additionally, chlorine is the DoDs preferred large scale water disinfectant (DoD 2010) after the water has been purified by reverse osmosis water purification devices.

However, there are disadvantages to using chlorine to disinfect water sources. It can create dangerous by-products such as hypobromous, and hypochlorous acids that can react with organic matter to create carcinogenic by-products (Grunwald et al. 2002). There are by-products from this process that the CDC states may cause long-term problems if an individual has extended exposure to them (CDC 2017c) such as endocrine system disruption, and cancer (Cray 2000). Furthermore, the DoD uses water purification devices where chlorine is passed over the reverse osmosis membrane it can damage the device. Therefore, DoD applications must ensure chlorine is only added post processing and cannot be re-disinfected which limits the devices that can be used (DoD 2010). Additionally, chlorine has been tied to environmental concerns such as ozone layer depletion. Finally, chlorine has been used successfully as an unconventional weapon in hostile locations. An intentional deployment of chlorine by terrorist, destruction of storage facilities, as well as industrial accidents of chlorine could produce thousands or casualties (Jones, Wills, and Kang 2010).

Iodine is also a well-developed method for treating water sources. It can be carried easily in tablet form lending its usefulness to point-of-use applications. The tablets are relatively cheap and easy to use, they also having a wide set of applications. Iodine is effective at disinfecting water by inactivating most bacteria and viruses however, as with chlorine, it has its shortcomings. The first issue with iodine is its

treatment process is determined by temperature. The user has to alter the treatment time depending on the water temperature to attain proper disinfection (Block 2001). Second, iodine does not treat *Legionella* bacteria. Therefore, in certain circumstances the method can lead the user to think the water has been disinfected when it has not (Cargill et al. 1992). Thirdly, iodine treatment must be performed in a dark vessel. Fourth, iodine has consumption restrictions that if surpassed can lead to goiter and other thyroid conditions (Teng et al. 2006). Fifth, though rare, individuals may be allergic to iodine. Additionally, iodine has an unpleasant taste which prevents it from being a widespread disinfection process, with the exception of emergency water disinfection practices (Curtis 1998).

Another method of purification is slow sand filtration, which has existed for the past century. Typically these devices are constructed using a diffuser plate, fine sand, coarse sand, and gravel (CAWST 2017). Sand filtration has the advantage of no energy use and has the ability to attain a variety of flow rates dependent on the dimensions of the device, allowing flexibility of use (CDC 2017d). Additional, benefits of sand filtration is the cheap readily available construction materials that have the ability to filter nearly all forms of protozoa and bacteria (W. A. M. Hijnen et al. 2004). As with all methods of disinfection it does come with disadvantages. Namely in its limited ability to filter viruses and heavy material weights (CDC 2017d). Therefore in DoD applications, sand filtration lends itself to home station and semi-permeant construction practices, not as a portable disinfection device.

Other commercially applied systems used today are granulated activated carbon (GAC) or the powdered activated carbon (PAC) processes. GAC is crushed carbon that has been treated to increase internal surface area and is used to remove organic hydrophobic contaminants from water by a process of adsorption (Tuncel et al. 2015). According to the EPA both GAC and PAC are capable of adsorbing soluble organic particles by adhering dissolved solids to their surfaces (EPA 2017). GAC and PAC processes filter organic compounds and some microorganisms, and are generally used to improve the taste

of the drinking water and remove organic contaminants. The negative aspects of these systems are the lack of ability to filter dissolved metals, they can develop microbial growth if not cleaned properly, and are not a good single source method for the disinfection of water (EPA 2017). They do work well with UV water treatment however to help reduce the dissolved solids leading to lower turbidity. This increases the effectiveness of UV radiation for disinfection as less of the UV radiation is absorption by dissolved solids.

As mentioned previously another form of water treatment is reverse osmosis which has the ability to eliminate nearly all microorganisms. The reverse osmosis membrane has the ability to filter particles down to 0.0001 microns, effectively filtering pathogens, and smaller viruses (CDC 2017b). Some of the negatives of reverse osmosis is the process is so effective that it removes electrolytes from water sources. This process can be corrected through remineralization but is not required. The DoD's primary water purification devices utilize reverse osmosis for expeditionary locations but to date, these devices are large, heavy, and require a large supply chain for fuel and maintenance. Portable reverse osmosis systems are available, but similar to the DoD units, are bulky and not ideal for a light, portable, point-of-use system.

Another method of water disinfection that is the backbone of this thesis is ultraviolet radiation disinfection. UV radiation can deactivate vegetative and resistant bacteria that can be hard to treat via other methods (Morita et al. 2002). There are four main types of UV radiation; the first is UV-C with wavelengths of 100 to 280 nm. Until the advent of UV LEDs low-pressure mercury fluorescent bulbs utilized a germicidal wavelength of 254nm with limited ability to operate outside this wavelength (Pirnie, Linden, and Malley 2006). UV LEDs are not restricted to this single wavelength and currently have the ability to operate from 240-405nm. This is especially important as some organisms are more susceptible to differing UV wavelengths than others, allowing UV LED reactors to contain multiple wavelengths to target weaknesses in an organisms DNA for inactivation (W. Hijnen et al. 2006). Additionally, UV radiation has not been shown to produce harmful by-products as commonly seen when using chemical

treatments like chlorine. However, as with all methods discussed thus far, it does have some negative concerns. The primary concern with UV radiation is its limited ability to treat turbid water effectively due to the absorption of the radiation by total or dissolved solids in the water, limiting the effectiveness of the light source.

The processes already reviewed are highly effective at large scale water treatment but have significant downsides when applied to portable or point-of-use applications for water disinfection. The following water disinfection processes are geared more towards emergency and point-of-use applications and have limited effectiveness at full spectrum disinfection. The first this literature will look at is called the Lifestraw® and is marketed by the Vestergaard company. The device is highly portable and is 9 inch by 1 inch with the ability to filter water down to 0.2 microns (Vestergaard 2017a). At this level of filtration, the device has the ability to eliminate most microorganisms, to include cryptosporidium which chlorine has a hard time inactivating. Lifestraw® also has the ability to filter E. coli, giardia, and other protozoas. Unfortunately, Lifestraw® does not have the ability to filter out chemicals in the water and is relatively difficult to drink through. Lifestraw® has released their second generation products that have incorporated activated carbon capsule filtering to reduce chlorine and other organics but also addresses viral and chemical compounds (Vestergaard 2017b). This technology combined with UV disinfection would allow it to tackle the viral disinfection short falls of this technology.

Another point-of-use device on the market as of 2015 is the “drinkable book.” This device was developed for third world countries and uses paper that has been coated with silver nanoparticles that kill microorganisms when in contact with the paper (Life is Water 2017). The technology was tested and found that a page with a silver nanoparticle content of 6-mg/G of paper could cause a 7log reduction of E. coli (Dankovich and Gray 2011). One of the primary disadvantages of the drinkable book is limited validation of its ability to inactivate viruses. However, Shao performed a study that showed that 100 mg/L

of silver nanoparticles could deactivate viral bacteriophage (Shao 2014). Whereas a different study showed that a concentration of 440-910 mg/L of silver nanoparticles could prevent up to 50% of HIVs ability to infect (Lara et al. 2010). Unfortunately, the drinkable book pages don't contain these same levels of silver nanoparticles, therefore limiting its potential for viral inactivation. Other disadvantages of the silver nanoparticle approach is excessive silver can be toxic if ingested. The pages don't leech enough silver to be an issue, but prolonged exposure of higher doses could lead to potential issues. If this technology was combined with UV disinfection it has the potential to deactivate both bacteria and viruses to effectively work as an emergency water purification device.

The last process this literature will cover for current point-of-use water purification systems is created by CamelBak®. CamelBak® developed a point-of-use UV purification system that can be applied directly in the cap of their hydration packs. The UV bulb is a miniature florescent and CamelBak® claims this device takes approximately one minute to disinfect the water (CamelBak 2017). However, there are multiple variables to this system, first being how to determine if the pack is being mixed properly per design specifications. Secondly, it assumes the water lacks turbidity and does not determine if the water is too turbid to allow the device to function effectively. Lastly, the device is bulky and contains a mercury UV bulb which is a toxic material and is considered a hazardous waste material. However, a similar design utilizing UV LEDs for increased battery life, and instant on capability combined with a simple charcoal or carbon filter would cover contamination in a water source. This style of device, similar to the one outlined in this thesis, could provide effective emergency or point-of-use water disinfection for most situations where light weight, ease of use is necessary.

Each method of water disinfection has advantages and disadvantages. None of them have the ability to be portable, lightweight, and to disinfect against all forms of microorganisms. The concept of

combining a filter with UV radiation in a reactor may prove an appropriate solution to the complex problem of point-of-use water purification.

Air Force Institute of Technology Research

AFIT started its research in the UV LED reactor field with Spencer (Spencer 2014) creating the first generation of reactors at AFIT in 2013. Spencer's research focused on construction of the reactor as well as measuring the UV LED outputs in the reactor. The first reactor was constructed with 316 stainless steel walls and end caps. The reactor had a three inch diameter and was three inches tall with seven UV LEDs located on the top of the reactor, perpendicular to the water flow. Throughout Spencer's research a total of three reactor designs were constructed and tested multiple parameters of the reactor designs. Spencer's research highlighted that there were seven primary key characteristics that should be considered for future UV LED reactor design: LED placement, LED wavelength, UV radiation requirements, dispersion geometry, path length, reactor material, and LED power components (Spencer 2014). Due to Spencer's reactors being the first generation reactors at AFIT, multiple graduate students studied alternate aspects of the reactor for their own research on his reactor configurations.

Following in Spencer's research, Duckworth was the first at AFIT to utilize a witness dye in the reactor and measure the advanced oxidation process (AOP) and rates of UV LED reactor designs (Spencer 2014). Duckworth used a hydrogen peroxide and methylene blue solution, allowing UV LED radiation to decompose the peroxide, which oxidized her witness dye. As mentioned her research utilized Spencer's stainless steel reactor, however her research focused on analyzing the effects of cycling the UV LEDs and their corresponding energy efficiency to oxidize the witness dye. The research she performed concluded that a continuously driven UV LED reactor with a duty cycle of 100% caused a higher level of oxidization of the witness dye but was not as energy efficient as pulsing the UV LEDs (Duckworth 2014). This

process of using a witness dye and hydrogen peroxide solution to oxidize the dye has been used in further research at AFIT as a method to evaluate the different reactor performance and efficiencies of their varying designs.

Richwine's research concentrated on modeling the reactor and how the UV LEDs interaction with the geometry could be simulated (Richwine 2014). His model was designed to try to predict and provide insight into how differing reactor geometry's had an impact on reactor efficiencies of the AOP process as well as germicidal processes. A second aspect of his research focused on how UV LED placement and quantity affected reactor efficiency. Richwine discovered that certain UV LED configurations had the ability to reflect off the reactor walls and thus increased reactor efficiency by getting secondary benefits from reflection off reactor walls (Richwine 2014).

Spencer's reactor was also used by Tran for the purpose of germicidal disinfection research (Tran 2014). Tran's research utilized the concepts from Duckworth's research by using UV LEDs in a continuous and pulsed manor but instead of investigating the AOP process he investigated the inactivation of *Baccillus globigii* spores (Tran 2014). Tran found that when UV LEDs were pulsed versus continuous the reactor was 150% more effective at deactivating the *Baccillus* spores (Tran 2014). This discovery was contrary to Duckworth's AOP research that showed continuous radiation was more effective but less efficient when oxidizing dyes (Duckworth 2014). This information would later be used by Gallucci in his reactor design and research (Gallucci 2016).

Bates tackled a different aspect of the reactor in his research. His research focused on testing and analyzing the optical power of different UV LEDs with the use of a reactor (Bates 2014). To perform the tests a device called Labsphere shutter device was used to test the UV LEDs in both air and water mediums. In his research he found that for the wavelengths: 240nm, 260nm, 265nm, and 270nm there was

a linear relationship between optical power and current for the air medium. However, when using the water medium he was not able to obtain useful results due to optical losses in the water (Bates 2014).

Up to this point all AFIT research has used air, water, a witness dye of hydrogen peroxide and methane blue dye, and *Bacillus globigii* spores. Mudimbi was the first researcher to utilize a tartrazine dye as the witness dye (Mudimbi 2015), as well as investigate how the reactor mixed the solution as it passed through it. Similar to previous research, he studied the effects of pulsing the UV LEDs on the new AOP process using duty cycles ranging from 0% to 100% on the LEDs. Mudimbi's research showed similar to methylene blue dye that the higher the duty cycle rate the higher the witness dye degraded (Mudimbi 2015). When analyzing the mixing characteristics of the Spencer's reactor he utilized two different flow rates with and without mechanical stirring (Mudimbi 2015). The results showed that when the solution was being stirred, the data produced had smoother plot lines, and when the flow rates were higher the plots were smoother. These results have been seen in multiple other research efforts and have been considered in this research when setting up validation procedures.

Whereas Mudimbi researched the effects of tartrazine dye in the AOP process, Scott investigated a separate witness dye for his AOP process. Brilliant Blue FCF dye was combined again with one of Spencer's reactors to analyze the efficiency of Brilliant Blue in the AOP process for multiple duty cycles (Scott 2015). Scott determined that with low duty cycles from 5% to 10%, the efficiency of the reactor was almost twice that of one running a 100% duty cycle (Scott 2015). Scott also discovered that the Brilliant Blue witness dye was degraded up to 15 times greater than the tartrazine dye under similar conditions (Scott 2015).

Up to this point all of the AFIT research had been performed on the first generation reactor made of the 316 stainless steel with three inch diameter and three inches long that Spencer designed.

Researchers Almquist, Fyda, Godby, Harper, and Miller researched and designed alternate UV LED

reactor configurations (Fyda et al. 2015). The second reactor designed was a stainless steel body with dimensions of one inch in diameter and two and a half inches long. The reactor had silicon end caps with 245nm UV LEDs placed in the caps (Miller 2016). With this new reactor design they concluded that the methylene blue witness dye degraded linearly with corresponding duty cycle rates (Fyda et al. 2015). The research also discovered that the smaller reactor design yielded higher efficiencies compared to the larger reactor design (Fyda et al. 2015).

This research was followed by Gallucci in 2015 to examine the AOP process and germicidal effectiveness of new UV LED reactor designs by varying the construction materials and designs (Gallucci 2016). His research focused on changing the reactor construction materials while using a known testing process to attempt to increase reactor efficiencies and improve the ability for it to be used as a portable water treatment device. Gallucci investigated the effects of using Teflon instead of stainless steel for the end cap, and how varying the Teflon thickness in the reactor wall among thicknesses of 2, 6, and 12 mm would affected the AOP process (Gallucci 2016). He also investigated how the entry angle of the water entering the reactor would affect the mixing of the water and solution in the reactor and in terms of the efficiency of the reactor. Lastly, he investigated the effectiveness of the reactor to inactivate *Escherichia coli* strand 198 (ATCC® 11229TM) to the EPA drinking water standards (Gallucci 2016). During his research Gallucci utilized a multi-physics software package, COMSOL® that was utilized to investigate and analyze the fluid dynamics of the reactors and how differing flow rates and inlet/outlet configurations affected the flow in the reactors (Gallucci 2016). Gallucci concluded that utilizing Teflon as the reactor material and varying flow rates significantly affected reactor efficiencies (Gallucci 2016). Gallucci also discovered that the reactor in its current configuration had the capability to inactivate the E. coli with flow rates up to 15 mL/min (Gallucci 2016). During his research Gallucci was able to utilize COMSOL® multiphysics and laid the ground work for its future use at AFIT. This thesis effort is designed to

investigate if COMSOL® can be used entirely to predict reactor characteristics and exponentially increase the speed that research can precede in the future.

Following Gallucci's research Miller analyzed the relative efficiencies of all of AFIT UV LED reactors with their different configurations. Miller utilized the mean rate constant for the different reactors which showed a first order rate constant obtained from the loss of dye concentration that occurs from the witness dye being degraded from the hydroxyl radicals and UV radiation (Miller 2016). Miller additionally normalized the different reactors efficiencies by assuming the first reactor created by Spencer had a normalized efficiency of one or 100% with relation to the mean rate constants of the reactors and the number of LED used in the reactor design (Miller 2016). Miller concluded that Gallucci's reactor that utilized a 1/4" Teflon wall thickness and two LEDs obtained a normalized efficiency of 19.5 times greater than Spencer's three inch reactor (Miller 2016). The chart below describes the different reactor designs and normalized relative efficiencies that AFIT reactors have been able to obtain to date.

Table 1: AFIT UV LED Reactor Data Summary (Miller 2016)

Reactor	Chemical	LEDs	Mean Rate Constant/Min	Dimensions (length : diameter)	Wall Material	End Cap Material	Normalized Relative Efficiency
Reactor 1	Methylene Blue	7	0.011	3"	Stainless	Stainless	1
Reactor 2	Methylene Blue	2	0.008	1"	Stainless	Silicon	2.5
Reactor 1	Tartrazine	7	0.0013	3"	Stainless	Stainless	1
Reactor 3	Tartrazine	2	0.0058	1"	Stainless	Teflon	15.7
Reactor 4	Tartrazine	2	0.0059	1"	1/8" Teflon	Teflon	15.9
Reactor 5	Tartrazine	2	0.0072	1"	1/4" Teflon	Teflon	19.5
Reactor 6	Tartrazine	2	0.0070	1"	3/8" Teflon	Teflon	18.8

COMSOL® Modeling Related Research

Researchers Jenny, Jasper, Simmons, Shatalov, and Ducoste have investigated continuous flow point-of-use UV LED reactors using COMSOL® multiphysics software to change the modeling paradigm for reactor design (Jenny et al. 2014). The group modeled an existing UV LED continuous flow reactor and utilized COMSOL® and Mod-eFrontier™ optimization software package to model and optimize a UV LED reactor using 30, 254 nm UV LEDs and a flow rate of 109 mL/min. The modeling predictions they developed utilizing COMSOL® showed good agreement with their experimental results. Additionally, when utilizing the optimization software they were able to obtain a potentially near-optimal UV-LED reactor solution for their design (Jenny et al. 2014). The group determined that software modeling was an effective method to reduce the engineer's design decision process for how to create an optimal UV LED reactor while providing a near optimal solution given the engineers input (Jenny et al. 2014).

One of the methods that researchers use to quantify the number of photons inside a UV LED reactor is actinometry. This can be accomplished using potassium iodide and iodate solution as it passes over UV radiation. Rahn utilized a 0.6M iodide and 0.1M iodate solution to measure incident fluency from a low pressure mercury lamp (Rahn 1997). This method utilizes UV radiation to create Triiodide from the Iodide and Iodate solutions at a linear rate. Rahn was able to determine the quantum yield of this solution to show how much power was required per atom to create the triiodide solution. This process was originally considered for use in this thesis to help obtain the reaction equation that was needed for COMSOL® to correctly calculate the reaction for modeling purposes. However, after further research this process was determined to not be the best approach for UV LED reactor design with germicidal disinfection in mind. This is due to the high absorbance values of the potassium iodide and iodate solution unlike pure water that allows UV radiation to permeate over a long distance. A further detailed explanation can be found in the results section of the report.

Goldstein, Aschengrau, Diamant, and Rabani used methanol to measure the quantum yield of the hydroxyl radicals produced in the photolysis of hydrogen peroxide (Goldstein et al. 2007). The quantum yield of the hydroxyl radicals was re-determined due to inconsistencies in current literature to date that was available with the intent to provide more accurate values for the quantum yield of hydroxyl radicals (Goldstein et al. 2007). The research showed that the quantum yield of hydroxyl radicals was $\phi = 1.14$ within the excitation range of 205-280 nm UV radiation. This quantum yield value was used from this research effort to help create the reaction equation used in the COMSOL® model to predict results from lab data.

III. Methodology

The current research applied two complimentary research methods, namely modeling and laboratory experimentation, to answer the research questions previously outlined. The model was created in COMSOL[®] Multiphysics. This model was applied to generate dye degradation curves and the results were compared to data gathered from an UV LED reactor in a laboratory experiment. The model generation effort included learning to use COMSOL[®] Multiphysics software to create an effective model of the reactor. During this process many hours were spent researching the multiple facets of the software and understanding which modules would best suit the need of the research to create a model of a UV LED reactor. It was determined that three different modules would be needed in COMSOL[®]. The first module was the Laminar Flow Module to model and calculate the flow characteristics of the liquid solution within the reactor vessel. The second was the Ray Optics Module that allowed the UV radiation to be modeled as a ray or particle to reduce computational power. The last module utilized was the Transport of Diluted Species Module. This module allowed the model to interact with the data from the laminar flow and ray optics modules and perform the reaction process with the interaction of brilliant blue dye and UV radiation. The resulting model produced dye degradation curves for the AOP within the reactor. This model permitted parameters, including the flow rate of a solution containing dye and peroxide through the reactor, to be manipulated.

An existing UV LED reactor having the physical structure assumed in the model was used to conduct an AOP in the lab with three different flow rates. In the AOP, Brilliant Blue dye was degraded by hydroxyl radicals that were formed by exposing hydrogen peroxide to UV radiation from a pair of UV LEDs. The resulting degradation curves were compared to the degradation curves that the COMSOL[®] model produced.

This pair of activities was designed to answer questions one through three, thus laying the groundwork to answer the final questions posed in this research. The second component of the research was to analyze the geometry of the current reactor design using the COMSOL[®] model, to determine if there is a reactor geometry and LED placement that lends itself to higher reaction rates. This portion of the research assumed that the LED count and power that they produced were fixed. Various geometries were analyzed to determine if basic trends emerged to help determine if there was optimal geometry to pursue for UV LED germicidal reactors. The various geometries were analyzed by their reaction degradation efficiencies. The geometries were analyzed to discover if there would be a change of effectiveness of the UV LED reactor on degradation rate of the reactor. The second portion of the research was focused on analyzing and answering question four.

Theory

AFIT has been studying UV LED reactors and their ability to purify water. Past devices have evolved from large stainless steel units that were not practical for field use to small Teflon reactors that are light and somewhat robust. The design process of these devices has been an iterative process that creates a design, then builds the reactor and evaluates their performance in the laboratory. This process is long and has little ability for modification without a redesign and reconstruction. This iterative process has led to a slow development process. This thesis seeks to utilize COMSOL[®] computer modeling software to design, simulate test results, and determine a geometry that optimizes reaction rates before reactor construction, thus increasing research productivity. Other researchers have utilized COMSOL[®] to model similar UV LED reactors by comparing the laminar flow characteristics of COMSOL[®] compared to tracer tests, chemical actionometry, as well as microbial dose-response and inactivation using bio-dosimetry. The

results show COMSOL[®] was capable of running a model with good agreement to lab test data (Jenny et al. 2014).

This research utilized brilliant blue dye and hydrogen peroxide in an aqueous solution to evaluate UV LED reactor qualities through an advanced oxidation process (AOP). In the AOP, hydroxyl radicals were produced from the interaction between the UV radiation and hydrogen peroxide as indicated in Equation 1 (Scott 2015).



The hydroxyl radicals then degraded brilliant blue dye and the change in concentration of the brilliant blue dye was measured using an Agilent Technologies Cary 60 UV-Visible Spectrophotometer (Santa Clara, CA). This process was completed for multiple flow rates in a single reactor design. It was assumed that as the degradation rate increased for a fixed number of LEDs with a fixed power output, the efficiency of the reactor improved.

COMSOL[®] Theory

COMSOL[®] multiphysics was chosen as a general-purpose software package to model the reactor performance. The software utilizes numerical methods for modeling physics based problems (COMSOL[®] 2017c). The benefits to using COMSOL[®] are its ability to couple multiple forms of physics into one simulation. The software is a module based program with the base version being able to handle a multitude of standard physics based situations. For specialized applications COMSOL[®] Inc. offers over 30 add on modules to tailor the software to the user's needs. COMSOL[®] also allows the user to design and input their own equations to allow for increased user control and applicability (COMSOL[®] 2017c).

COMSOL® has a built in geometry package that allows users to create and design intricate geometries, or import their designs from a host of other products. COMSOL's® unique approach then meshes the geometry using Finite Element Analysis (FEA). When meshing the geometry the software defaults to a tetrahedral element. However a multitude of other meshing options, for example prismatic, hexahedral to name a few, are available as necessary to fit the geometry requirements (COMSOL® 2017c). The software has the ability to export all of the user's results into common files types like: .txt, .dat, .csv, .GIF, Adobe® Flash, .html, or .doc. Alternately the software has the ability to build custom report types. Combining the ability to analyze a couple different physics packages, the intuitive FEA meshing techniques, and its multitude of options to visualize the results COMSOL® was selected as the tool to develop the UV LED reactor model.

Methods Utilized in COMSOL®

To effectively model the UV LED reactor three different COMSOL® physics modules were utilized: Laminar Flow, Ray Optics, and Transport of Diluted Species modules. To verify if the Laminar Flow package would work for the expected flow rates the Reynolds number was calculated for the laboratory reactor expected parameters. Equation 2 shows the Reynolds number calculation.

$$R = \frac{\rho V D}{\mu} \quad (2)$$

Where:

ρ = Fluid Density

V = Fluid Velocity

D = Diameter

μ = Dynamic Fluid Viscosity

Using equation 2 and analyzing the flow rates in the influent/effluent pipes, a 1.6 mm diameter and a 0.2 m/s flow rate were assumed. The flow rate was faster than anticipated in the lab, providing a 250% margin of error over laboratory flow rates. The calculated Reynolds number was 358. This value is below the 2000 threshold for Laminar Flow (COMSOL[®] 2017a). Due to these considerations the fluid flow characteristics in the reactor were analyzed via COMSOL's[®] Laminar Flow package. It is important to note however that if in the modeling process the flow was to become transitional or turbulent COMSOL[®] would notify the user that the data might not be accurate due to turbulent flow characteristics present. If this were to happen COMSOL[®] still has the ability to analyze turbulent flow characteristics but a different module would have to be utilized. The Laminar Flow module employed a no-slip chamber wall condition which prescribes that fluid velocity is zero on the chamber walls. The module also utilized the incompressible flow Navier-Stokes equation to solve the Laminar Flow module as seen in Equation 3 (COMSOL[®] 2017a).

$$\rho(u \cdot \nabla) = \nabla \cdot [-pI + \mu(\nabla u + (\nabla u)^T)] + F \quad (3)$$

Where:

ρ = Density

u = Flow Velocity

p = pressure

∇ = del operator

I = Identity Matrix

T = Absolute Temperature

F = Volume Force Vector

The second module utilized was the Ray Optics module. The Ray Optics module can be used to model electromagnetic waves in models when the wavelength of the energy is much smaller than the smallest geometric detail being analyzed (COMSOL[®] 2017b). Figure 1 illustrates a chart for determining the COMSOL[®] module that should be utilized with the corresponding wavelengths being analyzed and geometry conditions.

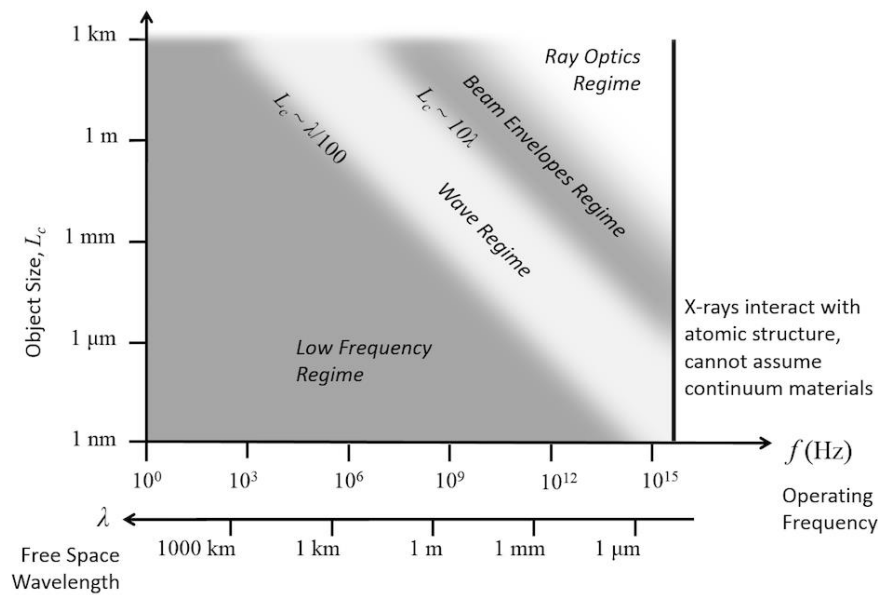


Figure 1: Wavelength and Geometry Relationship, Image credit: COMSOL[®] (Walter 2015)

<https://www.comsol.com/blogs/guide-to-frequency-domain-wave-electromagneticsmodeling/>

The wavelength fell off the chart on the right at 255nm and the scale of the UV LED reactor in the centimeter region. Therefore the Ray Optics package was the best choice to analyze the effects that the UV radiation would have on the water solution and how the rays would interact with the reactor vessel. The Ray Optics package treats the electromagnetic waves released from the UV LED as rays that propagate through the UV LED reactor solution. The primary benefit of utilizing the Ray Optics module instead of wave optics is that the rays can be calculated through the FEA mesh over long distances with

relatively low computational costs as compared to wave analysis (COMSOL® 2017b). The module that was used to bring the first two modules together was the Transport of Diluted Species module. This module contains the tools needed to simulate and create a model that can utilize the inputs from the laminar flow and ray optics model, as well as add a reaction equation that is used to simulate the reaction between the hydroxyl radicals, Brilliant Blue dye, and UV radiation.

Lab Validation Data

The reactor utilized was constructed at the AFIT machine shop of McMaster-Carr brand polytetrafluoroethylene (PTFE). The physical reactor shape and configuration is shown in Figure 2 and the interior volume geometry that was modeled in COMSOL® is shown in Figure 3. The reactor design shows dual inlets and dual outlet pipes. However during lab flow testing the flow rates for inlet and outlet tubes were not equal, therefore a single in and out configuration was chosen.



Figure 2: Dual Inlet/Outlet Reactor

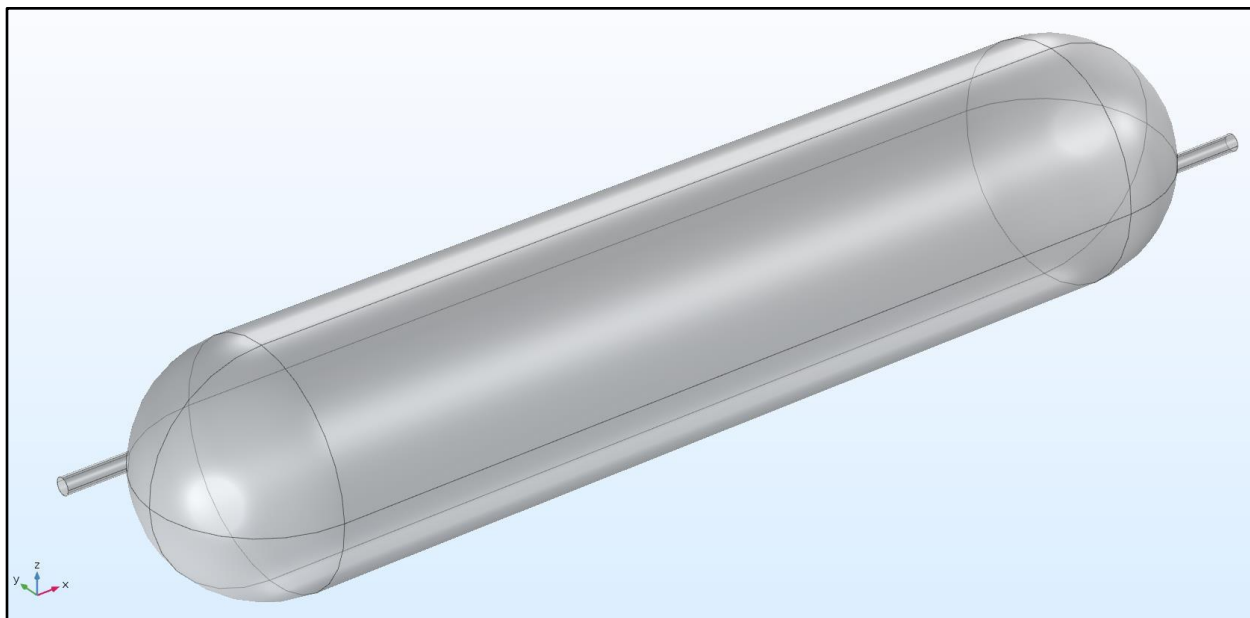


Figure 3: UV LED Reactor Geometry Modeled in COMSOL® (COMSOL® v. 5.2. 2017)

This decision would minimize a source of error between lab data and model data that was produced in COMSOL®. The reactor caps had the solution enter the reactor at 90° from the body as seen in Figure 2 but when entering the reactor chamber, the flow entered parallel to the long axis and thus was modeled in COMSOL® in this manner as seen in Figure 3. The two UV LEDs were manufactured at Sensor Electronic Technology, Inc. (SETi) and were located in the center of the endcaps, emitting along the long axis of the reactor into the reactor chamber. The LEDs power was measured using a Labsphere® (North Sutton, NH) integrating sphere. The SETi LEDs part number S-T39B-F1-255-01-1-020 had a measured output of 0.00032W each while being driven at 200 mA (Russell 2017). To create the solution, 250 mL of deionized water was mixed with 0.01mmol of Brilliant Blue and 5 mmol of hydrogen peroxide or a 500:1 H₂O₂ to Brilliant Blue concentration (Stubbs 2017). The solution was mixed on a magnetic stir plate using a stir bar for 15 minutes before the test to ensure complete mixing. During the test runs the solution was continuously mixed to ensure no separation or settling could occur. The solution was

pumped through Masterflex 14 tubing using a Masterflex pump (model 77200-50, Cole-Parmer, Gelsenkirchen, Germany) and calibration was performed at flow rates of 6 mL/min, 8 mL/min, and 10 mL/min. The aqueous solution was pumped through the reactor from the bottom to the top at the three flow rates and then passed through an Agilent Technologies Cary 60 UV-Visible Spectrophotometer (Santa Clara, CA) in a configuration as seen in Figure 4.

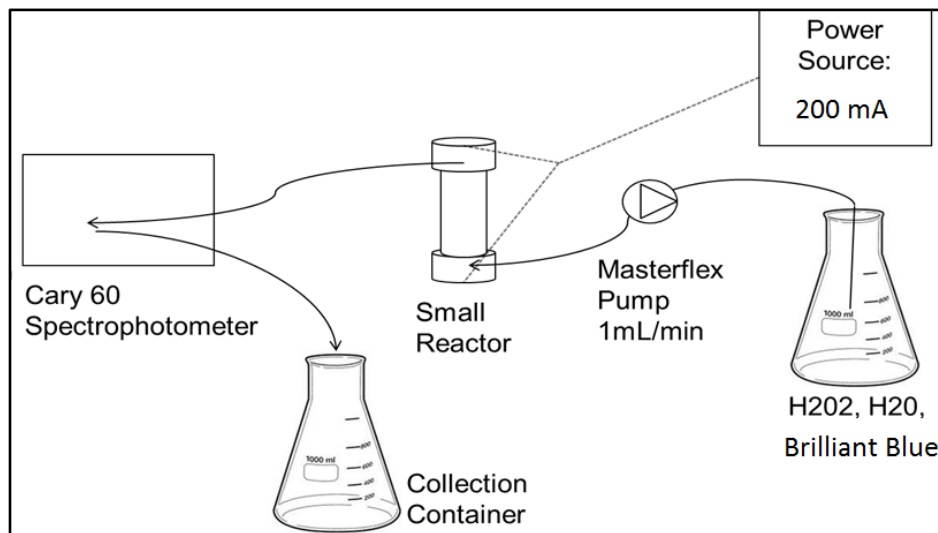


Figure 4: Experimental Test Setup

The Cary 60 was used to measure the visible wavelength peak absorption of the Brilliant Blue dye at 630 nm, with a reduction in peak absorption used as an indication of dye degradation. The Cary 60 took measurements every six seconds for the three flow rate tests. The tests were run to allow the reactor chamber volume to be replaced three times with the 6 mL/min run at 25 minutes (1500 sec.), 8 mL/min at 19 minutes (1140 sec.), and 10 mL/min at 15 minutes (900 sec.). At the end of each test run the reactor was drained, rinsed out with deionized water and fresh Brilliant Blue, hydrogen peroxide solution was run through it to prime it for the next test run. The absorption data was saved and converted to a mol/m^3 . With

the concentration of the Brilliant Blue dye it was easily comparable with the COMSOL[®] model concentration degradation curves. See Equation 4 for conversion equation. Adsorption

$$Absorption * \frac{0.1^{mol}/250\ mL}{Original\ Absorption} * 4\ mL/L \quad (4)$$

Where:

Absorption = Data Point Absorption

Original Adsorption = Starting Absorption Value

COMSOL[®] Geometry Optimization

The second component of the research focused on utilizing the COMSOL[®] model to change the differing aspects of the geometry and investigate the corresponding degradation curves the new reactors produced. Due to time constraints, creation of a fully optimized reactor that maximized reactor efficiency using UV LED placement, geometry, flow rates, and number of UV LEDs was not possible. However, by changing the UV LED placement and reactor geometry while keeping the flow rates, power, and UV LED count the same, a comparative analysis could be performed to show trends in reactor design. To perform this analysis, the reactor geometry was altered using different shapes, and influent/effluent locations. Each reactor geometry style was analyzed utilizing the Brilliant Blue Imaginary Index of Refraction for the Brilliant Blue dye solution as well as the Pure Water Imaginary Index of Refraction to compare the relative reactor efficiencies. It's important to note that the Brilliant Blue Imaginary Index of Refraction is not referring to the Brilliant Blue dye concentration, but referring to the Imaginary Index of Refraction value for this solution. Imaginary Index of Refraction refers to the extension coefficient of a solution and how long it takes for power to dissipate in the solution. A detailed explanation of the Refractive Indices can be

found in chapter four under the Ray Optics section. The reason the research wanted to investigate the difference in the Brilliant Blue Imaginary Index of Refraction and the Pure Water Imaginary Index of Refraction and their interactions in the reactors has to do with the end goal of developing germicidal water purification devices. The absorption of the Brilliant Blue dye is significantly higher than pure water and thus the output characteristics of the reactors with the same geometries might be different with differing Imaginary Index of Refraction values. Therefore, throughout this document all models will analyze the Imaginary Index of Refraction for the Brilliant Blue dye solution and for pure water. From this point on the Imaginary Index of Refraction (IIR) term will be IIR. The Imaginary Index of Refraction for the Brilliant Blue dye solution will be (BB-IIR), and for pure water (H₂O-IIR). The IIR values are unit-less and the specific values for each can be seen in Table 2 below. The process showing how these values were determined can be found in chapter four.

Table 2: Imaginary Index of Refraction Values

Imaginary Index of Refraction Values		
	Brilliant Blue Lab Solution	Pure Water
Designator	<i>BB-IIR</i>	<i>H₂O-IIR</i>
Value	k=8.80E-07	k=3.15E-08

Table 3 outlines key aspects of each geometry, volume, and UV LED placement. The results are discussed in detail in chapter 5.

Table 3: Reactor Geometry Styles Analyzed for Geometric Optimization Process

Geometry Type	Flow Rate (mL/min)	Imaginary Index of Refraction	Volume (cm ³)
Original Geometry	6	BB-IIR, H2O-IIR	36.42
Original Geometry	8	BB-IIR, H2O-IIR	36.42
Original Geometry	10	BB-IIR, H2O-IIR	36.42
Half Scale Original Geometry	10	BB-IIR, H2O-IIR	4.546
Half Scale Original Geometry with Separator Plate	10	BB-IIR, H2O-IIR	4.546
Sphere	10	BB-IIR, H2O-IIR	4.546
Sphere	10	BB-IIR, H2O-IIR	36.42

Summary

The research of the UV LED reactor consisted of two major efforts, the COMSOL[®] model development, including validation with lab data and model manipulation to understand the effect of reactor properties on reactor efficiency. The software used three modules; the Laminar Flow, Ray Optics, and the Transport in Diluted Species module. Lab validation data was the flow rates of 6, 8, and 10 mL/min to produce three Brilliant Blue degradation curves to compare to COMSOL[®] Multiphysics model. The following chapter will focus on a detailed outline of the model construction and development process.

IV. Model Development and Construction

COMSOL® Multiphysics Model Development

COMSOL® is a module-based software that progressively builds on itself in an unified workflow that starts with the geometry of the project, and then moves onto meshing the geometry. After this, the individual modules are implemented, analyzed and then the user can add a multitude of post processing graphs, graphics, charts, or animations. The following sections will describe and outline the methods for how the validation model was set up in COMSOL®.

Geometry

The geometry portion in COMSOL® can be used to create solid or boundary modeling in 1D, 2D, or 3D space. For the UV LED reactor validation, 3D solid modeling was utilized and created using the same dimensions as the existing UV LED reactor. It is important to note that the reactor water volume was modeled, not the actual reactor vessel itself. This process allowed the exterior walls of the model to be considered the boundary of the model or the interior walls of the reactor chamber. This method cut down on the time involved to create the physical geometry as well as greatly reduced the number of mesh elements in the model. This greatly reduced the computational demand on the model. The software also has the ability to utilize multiple materials in the design, depending on how the geometry domains built up. In the UV LED reactor geometry the interior domain was set to water and the surface boundary was set to Teflon. This feature allowed the model to have differing properties as needed to solve the model. The solid modeling technique is built using a combination of solid objects and *Boolean operations* like union, intersection, or difference (COMSOL® 2017a). Figure 5 shows the final geometry that was created by the software, creating multiple cylinders and spheres and when compiling the final geometry the feature that

removed all interior boundaries was selected. This process allows the user to create one uniform geometrical shape that was meshed.

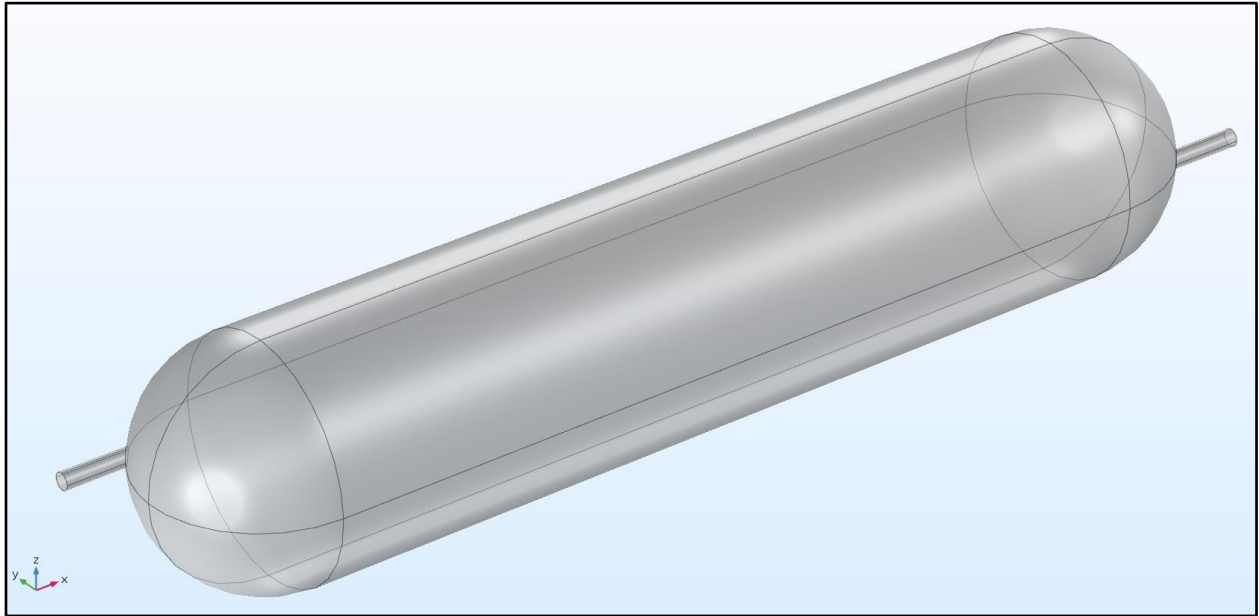
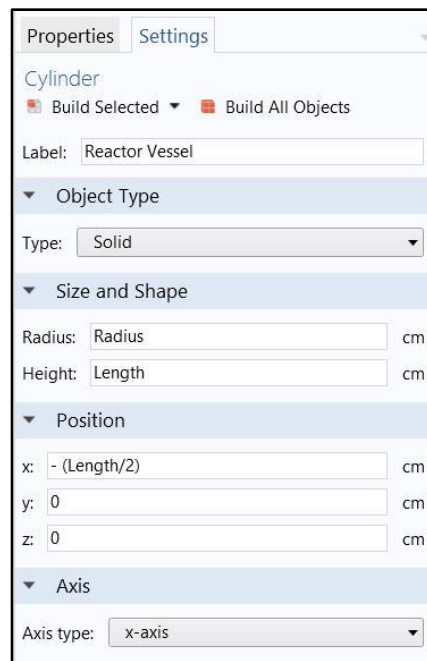


Figure 5: UV LED Original Reactor Geometry (COMSOL® v. 5.2. 2017)

Parameterization

COMSOL[®] is designed to be able to input all the variables and parameters directly in the different modules or a feature that is termed Global Parameters. This feature allows all modules to pull values from a global location without having to input them in multiple locations. This process prevents the user from forgetting to update a value in a module when changes are made. This feature is especially important when wanting to make quick changes to the geometry or if the COMSOL[®] optimization module is being used. As seen in Figures 6, 7 and 8, the geometry and ray optics module pulled the dimensional data from a single source in the Global Parameters section.



The image shows a screenshot of the 'Properties' and 'Settings' tabs for a 'Cylinder' object in COMSOL. The 'Settings' tab is active, showing various parameters for the cylinder. The 'Label' is set to 'Reactor Vessel'. Under 'Object Type', the 'Type' is set to 'Solid'. Under 'Size and Shape', the 'Radius' is set to 'Radius' and the 'Height' is set to 'Length', both with units of 'cm'. Under 'Position', the 'x' coordinate is set to $-(Length/2)$, 'y' is set to '0', and 'z' is set to '0', all with units of 'cm'. Under 'Axis', the 'Axis type' is set to 'x-axis'.

Property	Value	Unit
Label	Reactor Vessel	
Object Type	Solid	
Radius	Radius	cm
Height	Length	cm
x	$-(Length/2)$	cm
y	0	cm
z	0	cm
Axis type	x-axis	

Figure 6: Geometry Node Parameters (COMSOL[®] v. 5.2. 2017)

Figure 7: Ray Optics Module Parameters (COMSOL® v. 5.2. 2017)

Parameters			
Parameters			
Name	Expression	Value	Description
con	0.04	0.04	Concentration Brilliant Blue
Diff_Coeff	1e-9[m^2/s]	1E-9 m²/s	Diffusion Coefficient
End_Radius	0.435 [in]	0.011049 m	Reactor End Cap Radius
Groove_Length	Length	0.080518 m	NA
Groove_Radius	Radius + (0.1 [in])	0.013589 m	NA
Groove_Width	.05 [in]	0.00127 m	NA
Inlet_Length	20 [cm]	0.2 m	Reactor Inflow Pipe Length
Inlet_Radius	0.8 [mm]	8E-4 m	Reactor Inflow Radius
Inlet_Yaxis	(0.54/2) [in]	0.006858 m	Reactor Inflow Y Axis Factor
Length	3.17 [in]	0.080518 m	Reactor Body Length
Radius	0.435 [in]	0.011049 m	Reactor Body Radius
Ray_Angle	60 [deg]	1.0472 rad	Ray Release Angle from Center Axis in Degrees
Ray_Int	1	1	Ray Intensity
Ray_Number	300	300	Number of Rays Emmited
Ray_Power	3.2e-3 [W]	0.0032 W	LED Power
Ref_Img	8.8e-7	8.8E-7	Refractive Imaginary Index (Absorbtion)
Ref_Real	1.35	1.35	Refractive Real Index
Temp	293.15[K]	293.15 K	Water Temp
Velocity	0.0663	0.0663	Water Velocity
Wave_Length	255 [nm]	2.55E-7 m	LED Wave Length

Figure 8: Global Parameters (COMSOL® v. 5.2. 2017)

Some of the parameters shown in Figure 8 never changed throughout the model building process.

However, some changed frequently and were important to the research effort. One of the most important

parameters was the IIR for both the Brilliant Blue solution and pure water. The BB-IIR value was one of the most difficult values to obtain and will be covered in detail later in the Ray Optics module section. Other parameters that changed frequently were the flow rates, ray count (to minimize computational time), and ray power.

Meshing

Creating mesh elements in COMSOL[®] is possibly the most important step in the process as this step creates the building blocks of the entire model. COMSOL[®] has a multitude of different options for creating mesh elements for the model. It boasts automatic and semi-automatic meshing tools that are exclusive to the software package (COMSOL[®] 2017c). The standard algorithm defaults to a tetrahedral mesh and adds a boundary-layer mesh when a fluid property is being analyzed. COMSOL's[®] unique approach to meshing separates the geometric model into finite elements that can be adjusted by the user to fit the specific requirements. This process provides maximum flexibility for most geometric shapes and supports first, second, third and in some cases higher order model geometries (COMSOL[®] 2017c). This proprietary algorithm is one of the software's strongest features and allows the program to automatically select the meshing sequence that best fits the model to allow for the highest mesh element quality for analysis. In addition, the program also allows for a multitude of modifications of the mesh to allow for user flexibility as well as refinement. The UV LED reactor model utilized the automatic meshing algorithm to start as a base line to create a uniform and a strong mesh layout. This mesh had around 200,000 mesh elements that were more refined in the influent and effluent tubes that entered the main reactor volume as seen in Figure 9.

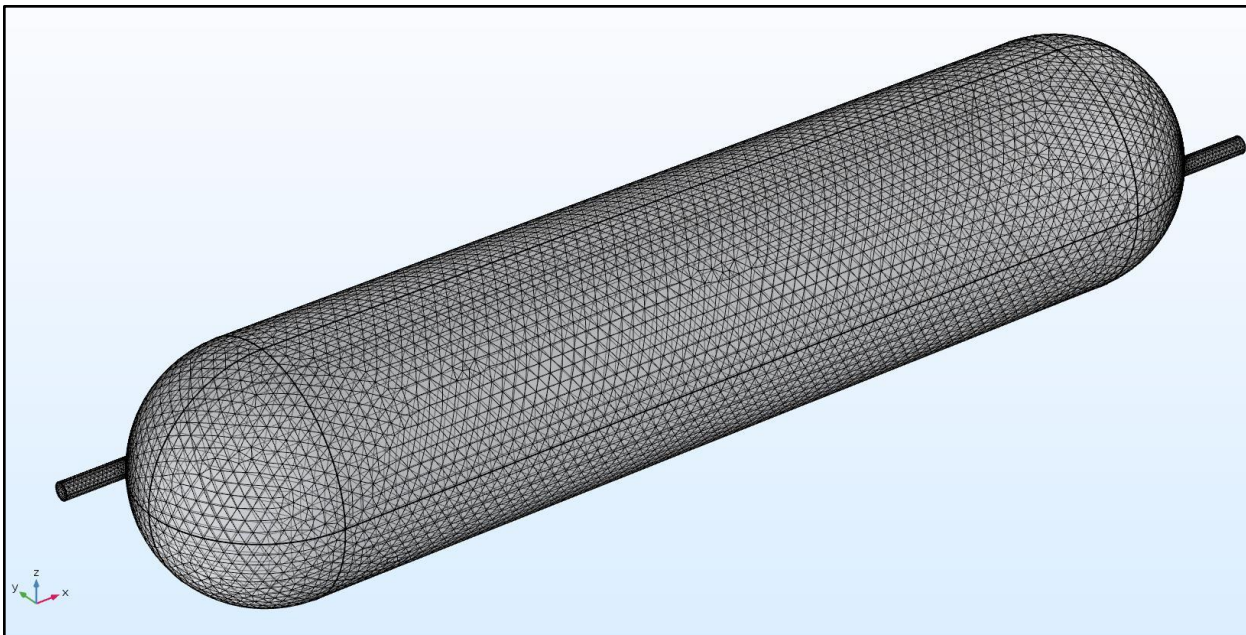


Figure 9: Initial Mesh Element Format for Original Geometry (COMSOL® v. 5.2. 2017)

The mesh was then refined to decrease computational requirements by lowering the mesh count where less resolution was needed. The model also has mesh refinement points on the ends of the reactor volume where the UV LEDs rays release into the reactor chamber. This step was added to allow for greater refinement where the UV LED rays would release into the volume of the reactor. The greater mesh refinement at the release points allows the software to have increased resolution when the ray power is changing the most and has the highest energy. This process also provided the ability for the transport of diluted species module to analyze the reaction between the UV radiation and Brilliant Blue dye more accurately with smaller mesh elements. This process produced a mesh that dropped from around 200,000 to 156,435 domain elements while still increasing the refinement around the UV LED release points. COMSOL® analyzes each element at the point of the tetrahedral elements. Therefore, with this mesh element reduction, the amount of calculations per time interval the software had to analyze was reduced from around 800,000 elements to 625,740 elements, a decrease of 21.79%. This

reduction in computational requirements for every time step allowed faster analysis of the model per cycle. The final mesh element format can be seen below in Figure 10.

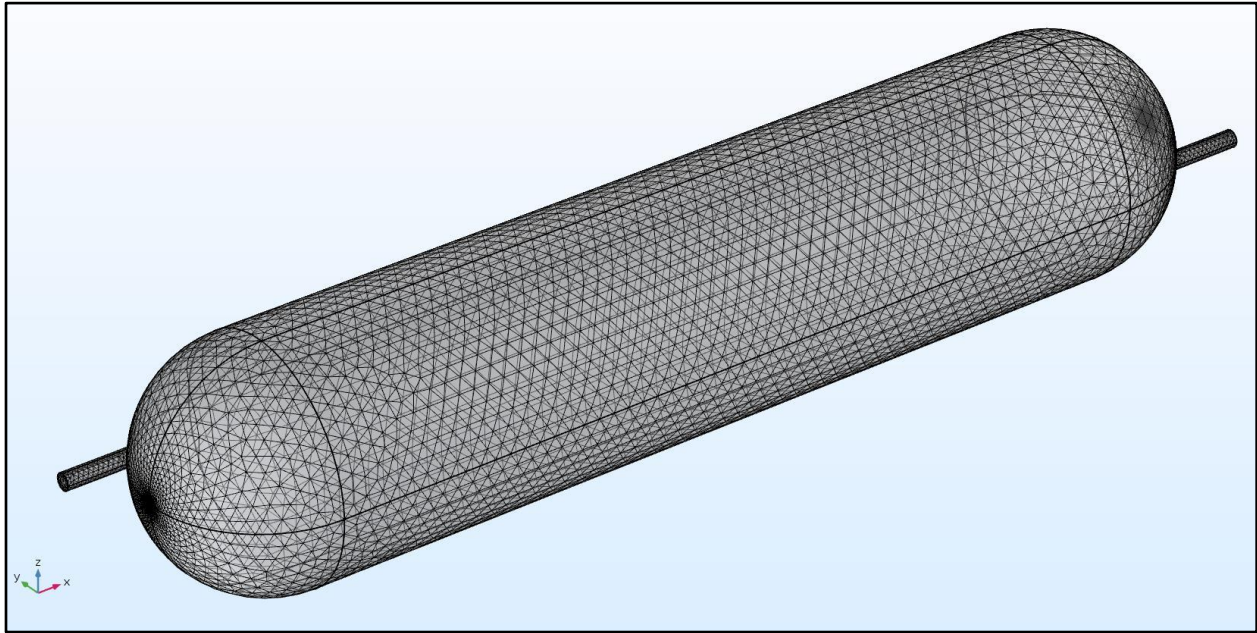


Figure 10: Final Mesh Element Format for Original Geometry (COMSOL® v. 5.2. 2017)

Ray Optics Module

The Ray Optics module computes the path of electromagnetic rays. Additionally, it can compute ray intensity, ray power, polarization, phase, optical path length among many other features (COMSOL® 2017a). The module allows for multiple release options, as well as the ability to track a multitude of methods that the rays interact with the environment and deposit their relative power. The UV LED reactor model utilized the following sub-nodes within the Ray Optics module: Medium Properties, Material Discontinuity, Ray properties, Wall, Deposited Ray Power (Domain), and Release from Grid. The medium properties sub-node was utilized to specify the IIR for the solution. This sub-node was the most

important node in the module due to the refractive indices. COMSOL[®] is a physics based software package, however the model would have to be validated via lab data to ensure an effective model could be implemented. The Refractive Index is a complex number with both an imaginary component and a real part. The real part represents how light bends as it enters and exits a domain. The imaginary component indicates the strength of absorption or loss through a domain and is known as the extinction coefficient. The real component is ‘n’ and the imaginary component is ‘k’. However this concept is based in the physics realm and is typically applied to characterize a pure material based upon theoretical computation. This concept does not readily cross over to the chemistry and engineering field where mixtures of materials, such as the solution of water, dye and peroxide applied in this research, must be modeled. The chemistry and engineering fields’ measure absorption, usually assuming that absorption occurs as explained by *Beers – Law*. The process applied to derive the IIR value of ‘k’ based upon laboratory measurements is illustrated in the following pages. The first part of Beers Law relates transmittance to measured power, as shown in equation 5.

$$T = \frac{P}{P_0} \text{ or } \%T = 100 * T \quad (5)$$

Where:

T = Transmittance

%T = Percent Transmittance

P = Radiant Power leaving sample

P₀ = Radiant Power

The transmittance can then be converted to absorbance as seen in equation 6.

$$A = 2 - \log_{10} \%T = \log_{10} * \frac{P}{P_0} \quad (6)$$

Where:

A = Absorbance

Log₁₀ = Log base 10

The next step in Beers Law is to be tied to Lambert Law to form the Beer – Lambert Law found in equation 7.

$$A = \varepsilon * b * c \quad (7)$$

Where:

A = Absorbance

ε = Molar Absorptivity

b = Path Length

c = Concentration

The law now can be converted to equation 8.

$$\%T = 100 * \frac{P}{P_0} = e^{-\varepsilon bc} \quad (8)$$

As stated above the research had to bridge the gap between the physics realm and the chemistry engineering realm. There was no effective literature found to describe how to determine the IIR ‘k’, required as in input to COMSOL[®], from transmittance or absorbance.

To determine the IIR, the Brilliant Blue and hydrogen peroxide solution was analyzed using an Agilent Technologies Cary 60 UV- Vis Spectrophotometer (Santa Clara, CA) to determine the absorbance of the solution at 255 nm using a one cm³ sample vessel. The solution was analyzed nine times and found to have an average absorbance of 0.1906 and can be seen in Appendix C. Utilizing Equation 5, the measured percent transmittance was determined to be 64.48%.

The next step of the conversion from lab absorbance values to COMSOL's[®] IIR value and to do this a new model was created. The model was of a one cm³ cube and passed a ray from one side to the other. The side that the ray hit had a Deposited Ray Power (Boundary) sub-node added to it. This node within the Ray Optics module allowed COMSOL[®] to compute the total incident energy flux on the boundary surface based on the power of the ray that strikes it (COMSOL[®] 2017a). Since the percent transmittance of the Brilliant Blue solution was found to be 64.48% the amount of UV energy that was absorbed by the solution was the compliment at 35.52%. Therefore to convert the lab data from absorbance to IIR when the model passed the ray through the one cm³ cube it would need to have a 35.52% power loss. This meant the one cm³ cube should absorb 35.52% of the ray release power. Therefore, the IIR for the Brilliant Blue dye was adjusted through an iterative process with a 1 (W) ray passing through the cube till the output power on Deposited Ray Power boundary was 0.6448 (W). This value corresponded to the target 35.52% power loss, thus allowing the research to effectively bridge the gap between the physics realm and the engineering/chemistry laboratory realm despite the lack of literature on the subject. The calibration model can be seen below Figure 11 and the IIR conversion table can be seen in Appendix C.

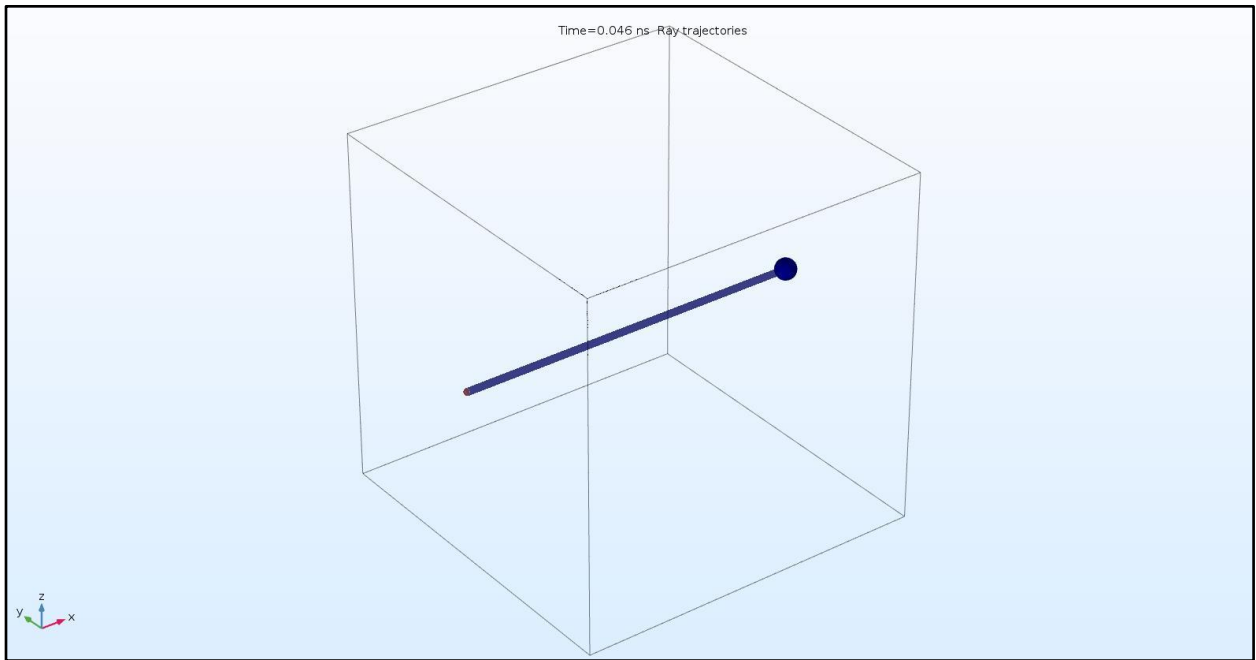


Figure 11: Imaginary Index of Refraction Model Geometry with Ray Particle (COMSOL® v. 5.2. 2017)

To verify that the IIR value obtained by the calibration model had the prospect of being correct, the IIR value obtained was compared to other known values. Pure water was analyzed first with an IIR of $k = 3.15\text{E-}8$ at the target 255nm (Polyanskiy 2017c). The IIR that was computed via the model for the Brilliant Blue and hydrogen peroxide solution was $k = 8.80\text{E-}7$. Since Brilliant Blue dye is an organic compound classified in the triarylmethane dye family (Contributors 2017), the IIR value was compared against the IIR of a similar alcohol based organic compound. It was found that pure Ethanol had a IIR of $k = 4.20\text{E-}6$ (Polyanskiy 2017a) and pure Propanol had a IIR of $k = 6.2872\text{E-}6$ (Polyanskiy 2017b) at the respective 255nm wavelength. Since the calibrated IIR was less than the pure alcohol based IIR values but higher than the IIR for pure water, it was used to calibrate the COMSOL® physics model to effectively replicate the conditions of the solution in the lab.

After the IIR was calibrated for the model, the next step was to build the ray optics module and determine the other important parameters. Under the wall sub-node the wall condition of diffuse scattering was selected to model Teflon's unique reflective properties. The diffuse scattering option had the rays reflect utilizing Lambert's cosine law for diffuse reflection unlike following the typical specular reflection profile (COMSOL® 2017a). Under the same sub-node the probability of the ray's reflection is selected, in this case a 95% reflection was selected instead of the literature's stated nearly 92-100% reflection to allow for a conservative model. Therefore every time a ray would strike the Teflon reactor wall it had a 5% chance of being absorbed by the reactor chamber and not continuing to radiate back into the solution. A second wall sub-node was additionally selected for the influent and effluent tubes surfaces so that rays that passed through them would disappear instead of traveling through open model space for long distances, thus improving the model's computational efficiency. Another sub-node that was utilized was the release from grid node. This node allowed the UV LEDs to be placed anywhere in Cartesian model space and emit in any direction that was needed. Figure 12 illustrates how the UV LEDs were set up to release from the reactor chamber end caps.

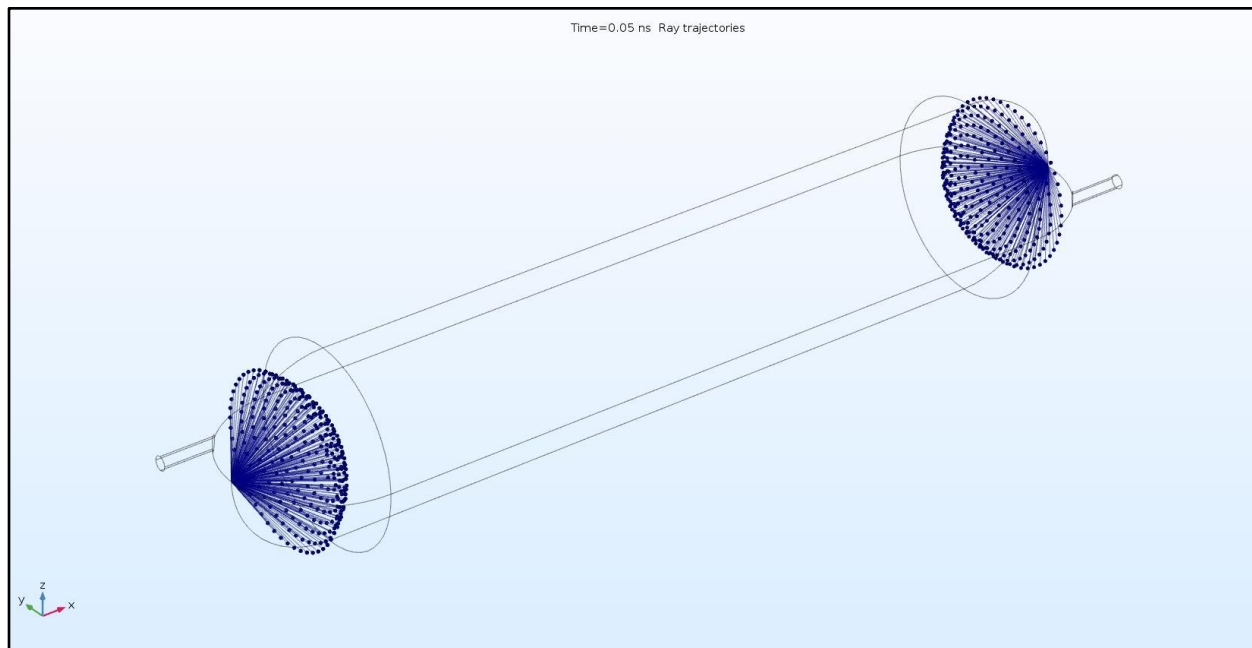


Figure 12: Ray Release Locations Seen after 0.05ns (COMSOL® v. 5.2. 2017)

The last notable sub-node used in the Ray Optics module was the deposited ray power on the domain of the reactor chambers volume. As mentioned in the calibration model, this node allows COMSOL® to track all the rays as they pass the individual mesh elements in the model and tally the power they deposit on that finite mesh area. This node is essential for the mode as it allows the Transport of Diluted Species module to calculate the reaction/interaction between the Brilliant Blue solution and the ray power on each mesh element as the solution flows through the reactor chamber. The data produced in the module was sent to the Laminar Flow module to be used later with the Transport of Diluted Species module. To see a screen shot of all sub-nodes used and their corresponding input values for the original geometry design, refer to APENDEX D.

Laminar Flow Module

The laminar Flow interface is used to calculate the velocity and pressure fields for the flow of a fluid that falls under the laminar flow realm. The modules utilized in the Laminar Flow model were the Laminar Flow Interface, Fluid Properties, Initial Values, Wall, Inlet, and Outlet. As stated previously the flow remains laminar as long as the Reynolds number stays below 2000 (COMSOL® 2017a). The laminar flow module has the ability to support incompressible flow, weakly compressible flow, compressible flow at Mach number below 0.3, as well as support for non-Newtonian fluids. The module solves laminar flows utilizing the Navier-Stokes equations for the conservation of momentum and the continuity equation for conservation of mass (COMSOL® 2017a). The UV LED model utilized the incompressible flow option which utilizes the before mentioned Navier-Stokes equations as well as fluid density and temperature are used as reference values. The model was analyzed at a temperature of 293.15 K (68° F) with flow rate of 0.04973 m/s, 0.06631 m/s, and 0.08289 m/s. The above velocities were determined off of flow rates of 6 mL/min, 8 mL/min, and 10 mL/min utilizing equation 9.

$$V = \frac{Q}{A} = \frac{4*Q}{\pi*D^2} \quad (9)$$

Where:

V = Velocity

Q = Flow Rate

A = Area

D = Diameter of Pipe

The two dependent variables needed for the Laminar Flow module were velocity and pressure. The velocity could be added as a velocity field or broken down into the components x, y, and z velocity

vectors. The influent sub-node in the Fluid Flow module was set to have one of the above mentioned velocities and the effluent sub-node was set to have a pressure of zero. This is an important aspect to point out due to the difference between computer modeling versus real world flow characteristics. In physics, the velocity in must equal the velocity out for a non-changing volume. However in computational modeling this is not always the correct approach. If the laminar flow module was set up this way, it would fail to converge on the correct values. Therefore the outlet tube must be set to have a designated pressure, in the model the pressure was set to zero. This allowed the software to solve the flow rate correctly. The underlying reason for this is due to the numerical approach to solving the flow rates. COMSOL[®] would have to solve the flow rates with no margin of error for every mesh element to the point where the flow rate out is exactly equal to the flow rate in. This is not possible and causes the model to not converge and fail to solve. Stating the output pressure is zero allows the software to have a small margin for error and converge if the flow rates are not exactly equal at the inlet and the outlet. The laminar flow was then analyzed using a steady state analysis, not a time based analysis where the flow starts from zero and ramps up to the steady state flow rate. The data produced from this process was then pushed to the Transport of Diluted Species module for processing and analysis.

Transport of Diluted Species Module

The Transport of Diluted Species Module provides COMSOL[®] the ability to model diluted species reactions. The software defines diluted species when their concentration is less than 90% of the molar concentration of the solvent; in this case water. Due to this principle, the solution properties such as density and viscosity can be assumed to correspond to those of water (COMSOL[®] 2017a). The sub nodes used in this module were: Transport Properties, No Flux, Initial Values, Inflow, Outflow, and Reactions. The Transport of Diluted Species module was used to calculate the concentration field of the Brilliant Blue

and hydrogen peroxide aqueous solution and its interaction with the Ray Optics module. The first step in this module was similar to the previous modules of setting up the domains and boundary conditions in the reactor chamber. Then the initial values sub-node was addressed by setting the reactor chamber solution to have a concentration of 0.04 mol/m^3 using Equation 10.

$$\frac{0.01 \text{ mmol}}{250 \text{ mL}} * \frac{1000 \text{ mL}}{1 \text{ L}} = 0.04 \frac{\text{mmol}}{\text{L}} = 0.04 \frac{\text{mol}}{\text{m}^3} \quad (10)$$

Although the lab data utilized a Brilliant Blue and hydrogen peroxide solution, the solution that was analyzed in COMSOL[®] was the Brilliant Blue dye and water. The reason for this approach is outlined in chapter three with the hydrogen peroxide being used as a source for the hydroxyl radicals that degrade the Brilliant Blue dye. This approach simplified the model by eliminating the chemical equations for the UV radiation interaction with the hydrogen peroxide that creates hydroxyl radicals as well as simplifying the process of building equations to simulate the hydroxyl radicals degrading the brilliant blue dye. To account for this simplification, the reaction equation used in the reaction sub-node was developed to account for these interactions. With the initial reactor chamber condition set to 0.04 mol/m^3 , the next step was to set the inflow sub-node to have the same concentration as the initial condition. The outlet boundary was set to be the pipe outflow and the transport properties sub-node was set to diffusion utilizing the diffusion properties of water with isotropic diffusion.

The final reactions sub-node addressed the primary feature of the model, which was the reaction between the ray's power and how that power reacted on each mesh element. This was then multiplied by a constant that was calculated to account for Avogadro's number, photon power at 255nm, as well as the quantum yield of hydrogen peroxide. One limiting factor with this approach was that for each hydrogen peroxide, two hydroxyl radicals were created and the assumption was made that every

hydroxyl radical would degrade a Brilliant Blue dye molecule. This assumption also assumed the hydroxyl radicals would not degrade other stray organic matter in the solution or recombine to reform hydrogen peroxide. This assumption while likely incorrect, provided an initial condition for the model. This assumption was necessary as a review of the literature failed to provide an estimate of the quantum efficiency of the hydroxyl radical-dye reaction. The equation that was utilized for the reaction rate constant is shown below in Equation 11.

$$\frac{\phi}{2*N_A*\epsilon} = \frac{1.14}{2*\frac{6.022140857\ E23}{mol}*7.78998E-19\ (W*s)} = 1.215032\ E-06\ \frac{mol}{(W*s)} \quad (11)$$

Where:

Φ = Quantum Yield, Per Hydrogen Peroxide (Goldstein et al. 2007)

2 = Multiplier to Convert H_2O_2 to 2*(-OH) Molecules

N_A = Avogadro's Number

ϵ = Energy of Photon at 255nm (Shipway and Shipway 2008)

With the reaction equation constant calculated, the last step for Transport of Diluted Species module was to input Equation 12 into the reaction sub-node in COMSOL[®]. This equation combined the Ray Optics power density variable and combined reaction rate constant with the quantum yield, Avogadro's number, and energy of a 255nm wave length photon. The step function defines the reaction rate constant as a function of concentration 'c', such that when 'c' approaches zero, so does the reaction rate constant. The step function is designed to smoothly turn off the reaction rate constant when the local mesh concentration goes to zero. This step function prevents the model from creating a negative

concentration near the UV LED release points due to the extreme local power density at the source. The step function was defined under the definitions node as seen below in Figure 13.

$$gop.dsc1.Qsrc \left[\frac{W}{m^3} \right] * 1.215032 E - 06 \left\{ \left[\frac{mol}{W*s} \right] * step1 \left(\frac{c}{1 \left(\frac{mol}{m^3} \right)} \right) \right\} \quad (12)$$

Where:

$gop.dsc1.Qsrc$ = Power Density, Ray Power over Mesh Elements

$1.215032 E-06$ = Reaction Rate Constant

$step1(c/1(mol/m^3))$ = Step Function for Reaction Rate Constant Smooth Shut Off

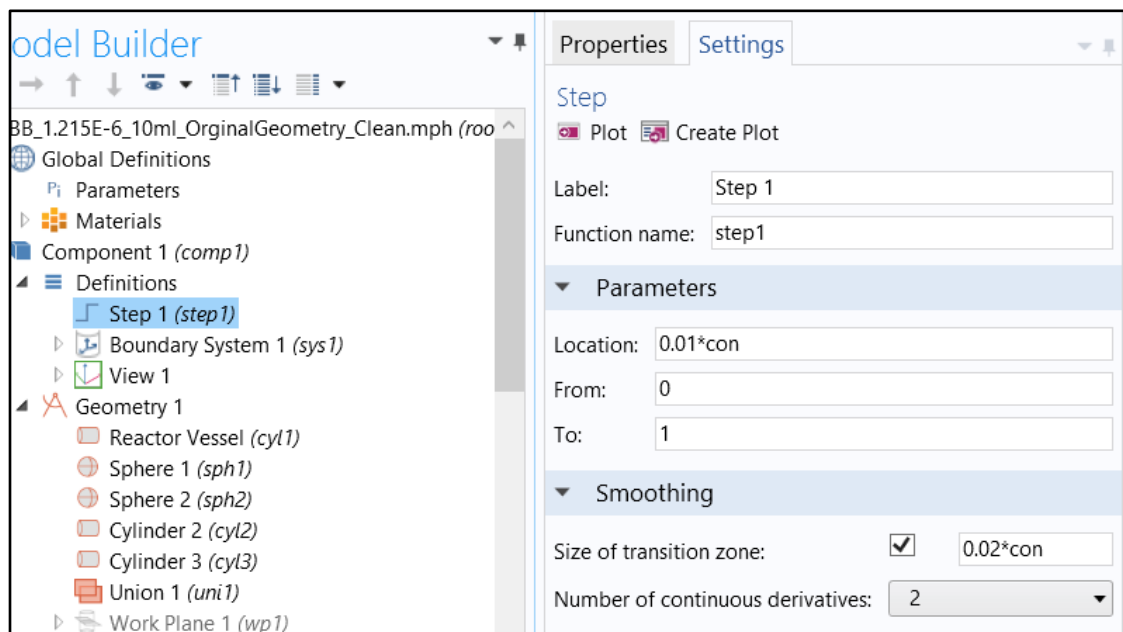


Figure 13: Step Function Defined (COMSOL® v. 5.2. 2017)

3D Cut Line Data Collection

The final step for model development was selecting additional data collection cut lines. This process allowed COMSOL® to be able to show 1D graphs along physical geometry of the outlet pipe to

provide a better analysis of the output effluent concentration. COMSOL® has a built in variable for average concentration that can be selected to show the average concentration at the outflow surface boundary. However to provide a higher level of resolution, cut lines were added in the outlet pipe surface as well as along the long axis of the chamber, connecting the release points for the UV LEDs. This process is performed by selecting the 3D cut line sub node under the Data section in COMSOL®. Then the two point line entry method is selected from the line data section to input the Cartesian coordinates needed to create the cut line. COMSOL® required the two points to be input via Cartesian coordinates and can be seen in Figure 14.

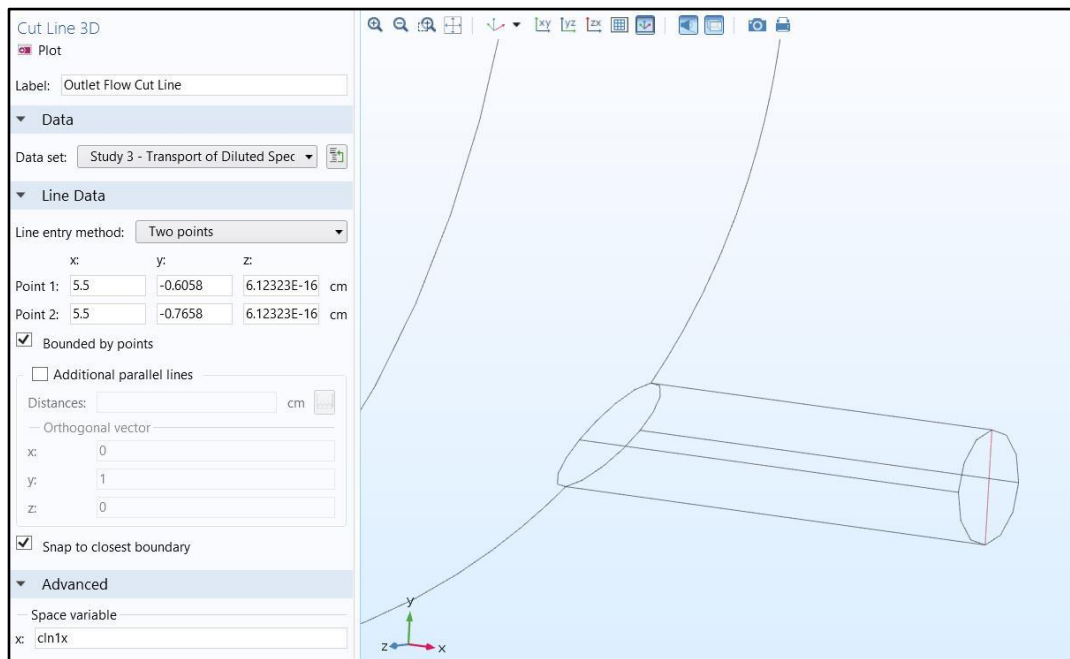


Figure 14: Example 3D Cut Line Inputs with Red Plot Line (COMSOL® v. 5.2. 2017)

Significant Model Assumptions

There are three significant model assumptions utilized when developing the COMSOL® model. The first is previously outlined under the Transport of Diluted Species section which states every

hydroxyl radical degrades a Brilliant Blue dye molecule. This assumption is likely incorrect but was needed to create the reaction equation as a starting point for model development. The second significant assumption is that the IIR value of 'k' would stay constant throughout the reaction process. This assumption is likely not correct. However further lab research would need to be performed and analyzed to provide a working equation to correctly vary the IIR in relation to the reaction process in the COMSOL[®] model. This process would provide a more robust COMSOL[®] model that considered varying IIR values. This assumption will affect the BB-IIR more than the H₂O-IIR due to the Brilliant Blue dye degrading over time in the reaction process. This will decrease the absorbance of the rays on the solution allowing the ray energy to travel longer in the reactor chamber. The third significant assumption is that the quantum efficiency of the reaction process is independent of the IIR value. This assumption is likely not correct but is needed to help develop a more robust model that accounts for the quantum yield of the hydroxyl radicals while varying the absorbance of the solution analyzed. This assumption however falls outside the scope of this research effort and won't be addressed. Therefore, this value was held constant.

Summary

This chapter outlined the three modules that were used in the research, how they were developed, and some of the key input parameters. The Ray Optics module utilized a method to convert the IIR from the chemistry/engineering domain to the physics domain. The Laminar Flow module was used to analyze the reactor in a steady state flow condition as there was no interest in ramp up characteristics of the reactor for this research. The Transport of Diluted Species module utilized the data from the Ray Optics and Laminar Flow module to allow COMSOL[®] to create a reaction between the UV Ray Power

Density on the mesh elements that was used to degrade the brilliant blue dye using the reaction rate equation. The following chapter will focus on the results and analysis of the model and laboratory data.

V. Results and Analysis

Chapter Overview

This chapter will report and discuss the results from the laboratory model validation process for the advanced oxidation process (AOP) of the Brilliant Blue dye. It will also outline the initial COMSOL[®] results, the adapted COMSOL[®] model results and analysis as well as results from the geometric optimization trends analysis.

Initial COMSOL[®] Model Results and Analysis

The initial process used to build the COMSOL[®] model utilized the Ray Optics, Laminar Flow, and Transport of Diluted Species modules. After all the correct parameters had been input into COMSOL[®] for the corresponding modules, the first data run was performed using the reaction rate constant (RRC) of $1.2150\text{E-}6$ [mol/(W*s)], shown in chapter four.

The first analysis was performed using a 10 ml/min flow rate with the BB-IIR value. The initial data seen in Figure 15 produced by the COMSOL[®] model used the reaction rate equation seen in chapter 4, Equation 11. The data followed the laboratory data degradation curve along the time axis visually; however the percent concentration remaining axis was off by final value of 59.98% and had a sum of squares difference of 0.065213 as seen in Table 4. The COMSOL[®] model was able to predict the laboratory data degradation curve satisfactorily but was not able to provide the correct concentration in mol/m³.

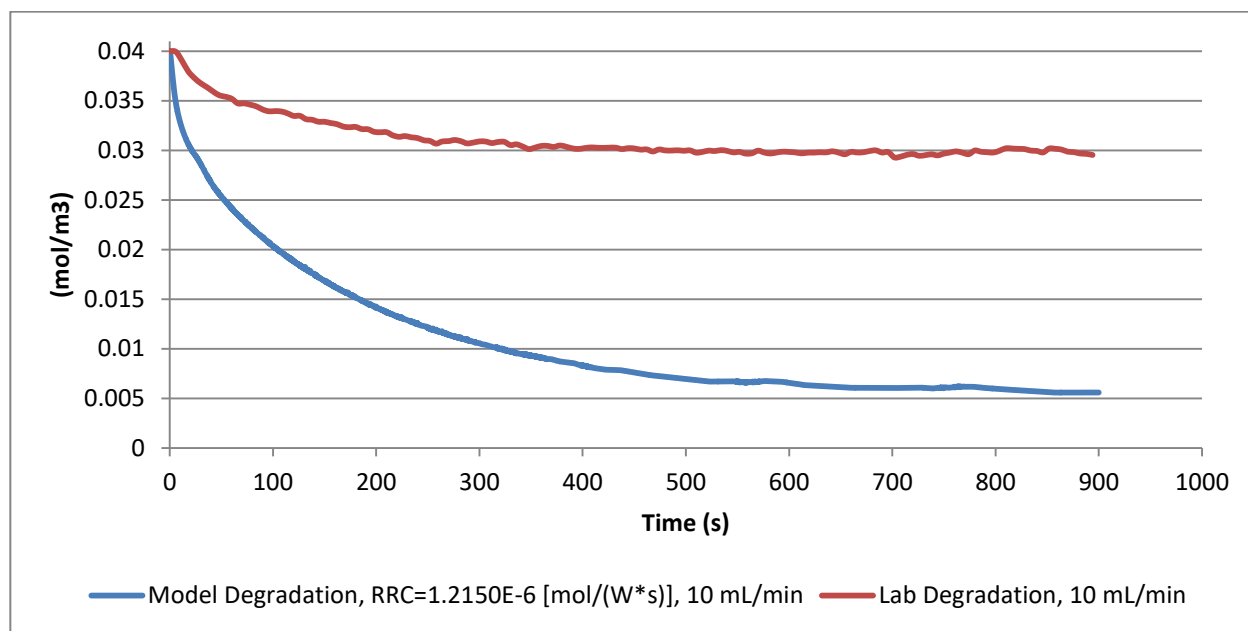


Figure 15: Degradation Curves Lab, Reactor Data and RRC=1.2150E-6 [mol/(W*s)] at 10 mL/min

It was hypothesized that the difference between the laboratory data and the COMSOL[®] model output data was due to the assumption that for every hydroxyl radical created with the reaction equation constant, a Brilliant Blue dye molecule would be degraded. As previously mentioned, this assumption was likely inaccurate but due to a lack of available literature to support any alternative assumption, this undesirable assumption was required. To correct for this factor, the RRC was modified in the reaction rate equation through an iterative process. The first iteration of this process changed the value from a RRC=1.2150E-6 [mol/(W*s)] to RRC=1.2150E-7 [mol/(W*s)]. This changed the assumed efficiency of the hydroxyl radicals from a rate of 100% to 10% when degrading the Brilliant Blue dye molecules. To analyze how close the new output data matched the laboratory data, the laboratory data was compared to each RRC run with a sum of squares method. This approach was used due to the similarity of the laboratory data and COMSOL[®] model output data curves. This rigorous method would provide insight to the relationship of the data between the RRC values and the laboratory data. The Spectrophotometer

collected data every six seconds and the COMSOL[®] model data was pulled for every six seconds instead of the natural time interval of 0.1 seconds, thus allowing a simple sum of square methods to be performed on the degradation curves. The final RRC used was 2.90E-7 [mol/(W*s)] which resulted in a sum of squares value of 0.000059 difference between the RRC model and laboratory data. Each model ran averaged 12 hours to compute. Therefore the RRC=2.9E-7 [mol(W*s)] value was deemed acceptably close to the optimal zero value and was selected. See Table 4 and Figure 16 for the series of values investigated. The true RRC minimum is likely between 2.90E-07 [mol/(W*s)] and 2.80E-07 [mol/(W*s)] as calculated from the mean of their individual degradation curves.

Table 4: Reaction Rate Constant Sum of Squares Analysis from Laboratory Data

Sum of Squares Analysis	
Run	Sum Squares Vs Laboratory Data
RRC=1.2150E-6	0.065213
RRC=1.2150E-7	0.004063
RRC=3.1500E-7	0.000490
RRC=2.9000E-7	0.000059
RRC=2.8000E-7	0.000076

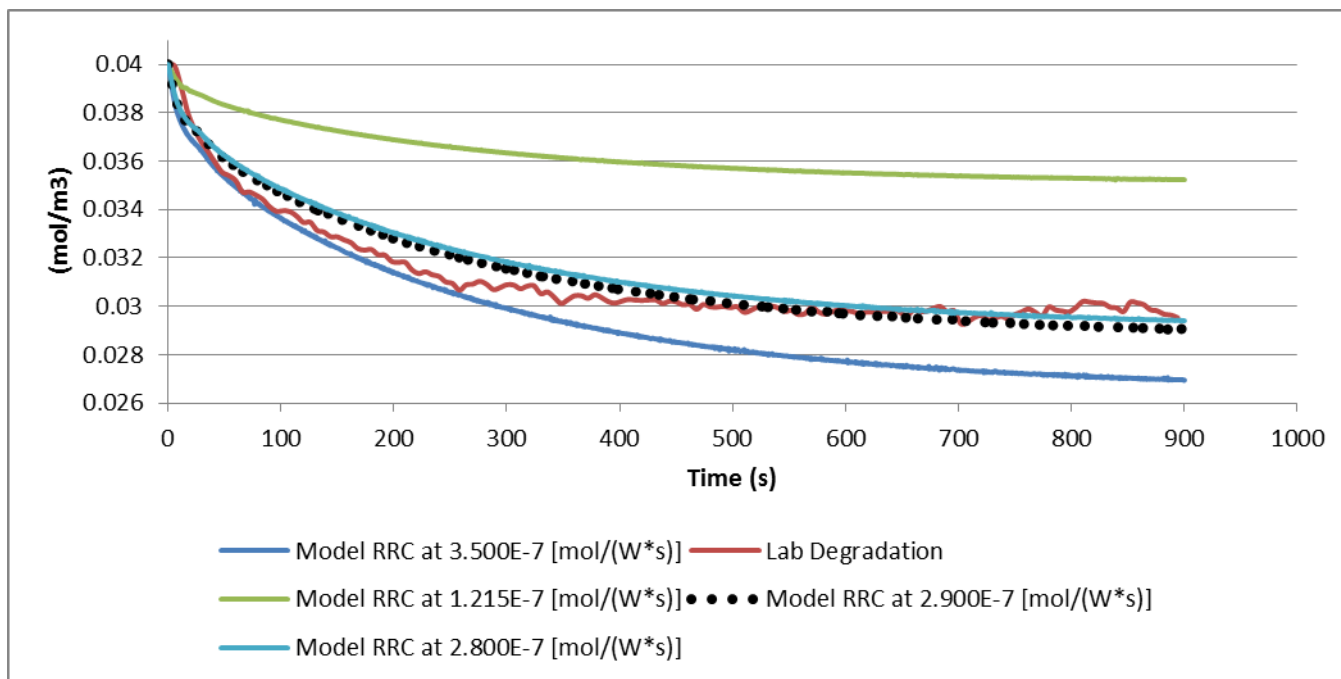


Figure 16: Reaction Rate Constant Calibration Runs at 10 mL/min,
Final RRC = 2.900×10^{-7} [mol/(W*s)] selected for best fit.

With the adapted reaction rate equation the COMSOL[®] model was used to compare the ability of the model to predict the laboratory data at flow rates of 6, 8, and 10 mL/min. Additionally, the IIR of the solution was varied to represent BB-IIR and H₂O-IIR data sets. These results and analysis are covered in the following section.

Adapted COMSOL[®] Model Results and Analysis

Using the adapted reaction rate equation the reactor model in COMSOL[®] was ran using the respective flow rates of 6, 8, and 10 mL/min with the original geometry reactor design. These conditions were explored in combination with the IIR values for pure water at 255 nm ($k = 3.15 \times 10^{-8}$), as well for the Brilliant Blue dye solution ($k = 8.80 \times 10^{-7}$). The intent of using two IIR values was to show how the reactor geometry would affect the efficiency of the reactor when the rays were allowed to

travel further in the water compared to the semitransparent solution of the Brilliant Blue dye solution. For the Brilliant Blue dye solution it was deemed that the Ray Optics module would simulate the rays for 0.35 ns. The initial power was found to be 0.0064W at time zero and 0.000183W after 0.35 ns. Figure 17 illustrates the power fall off for the BB-IIR using the original geometry reactor.

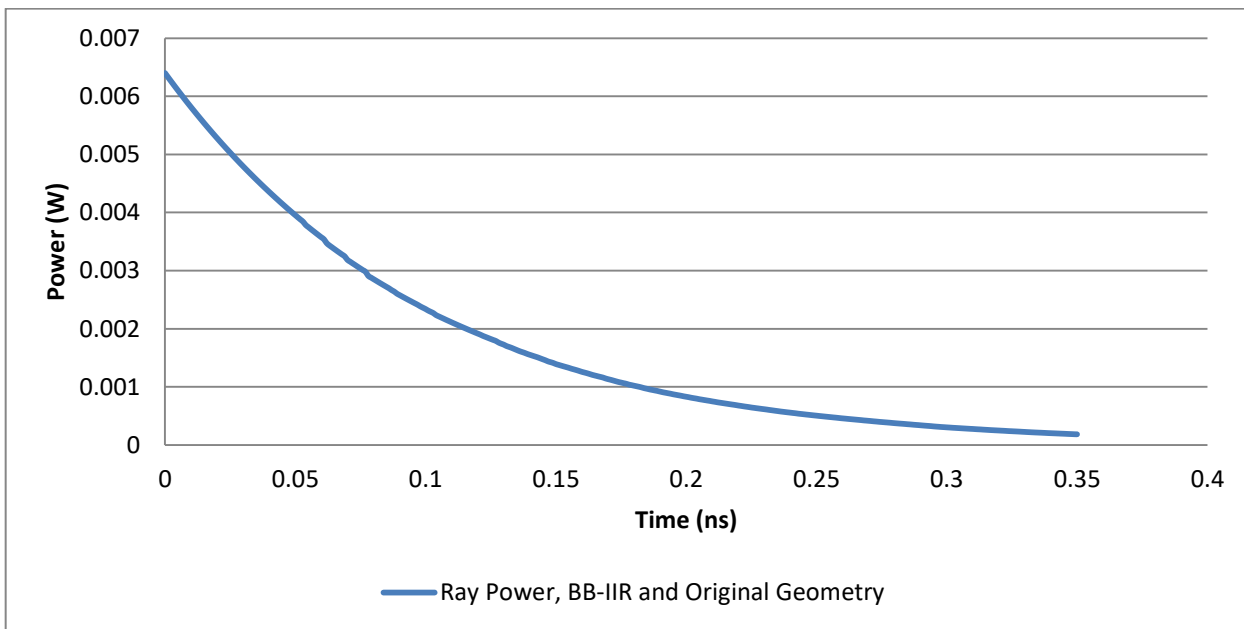


Figure 17: Ray Power for BB-IIR and Original Geometry Reactor, 95% Reflectance

For the H₂O-IIR the Ray Optics package was used to simulate ray paths for 4 ns. The initial power decreased from 0.0064W at time zero to 0.000206W after 4 ns. The two different ending power values were not identical, but for modeling purposes deemed to be within acceptable limits. The pure water power curve can be seen below in Figure 18.

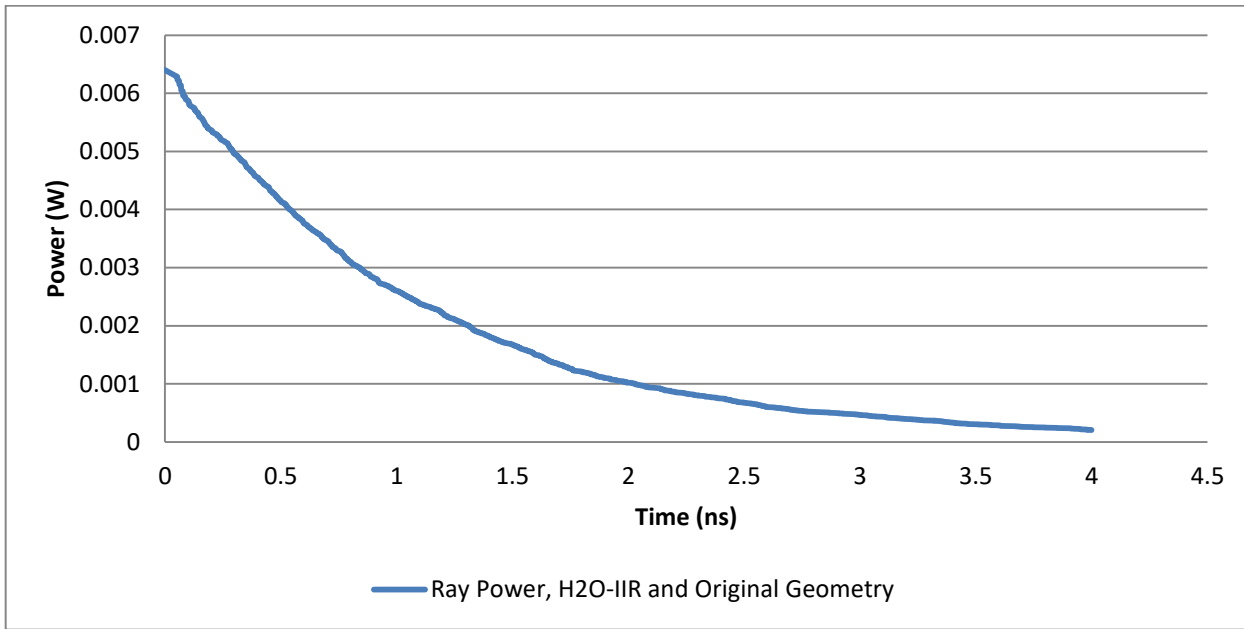


Figure 18: Ray Power for H₂O-IIR and Original Geometry Reactor, 95% Reflectance

After the ray duration had been determined for both BB-IIR and H₂O-IIR values, the model was ran using the two IIR indices for 6, 8, and 10 mL/min flow rates for a total of six runs. These data runs are outlined in the following sub sections.

Original Geometry with 6 mL/min for BB-IIR and H₂O-IIR

The first run was 6 mL/min and BB-IIR and H₂O-IIR values. The geometry, mesh layout, ray propagation, velocity field, and slice concentration fields for this model will be outlined below since it is the first time they are described. However, since all six of the following models share the similar traits: geometry, mesh layout, and ray propagation the follow on sections will only have the velocity field, and slice concentration fields data. Refer to Appendix B for a visual representation of all models outputs and images. The geometry for the 6 mL/min reactor can be seen below in Figures 19 and 20.

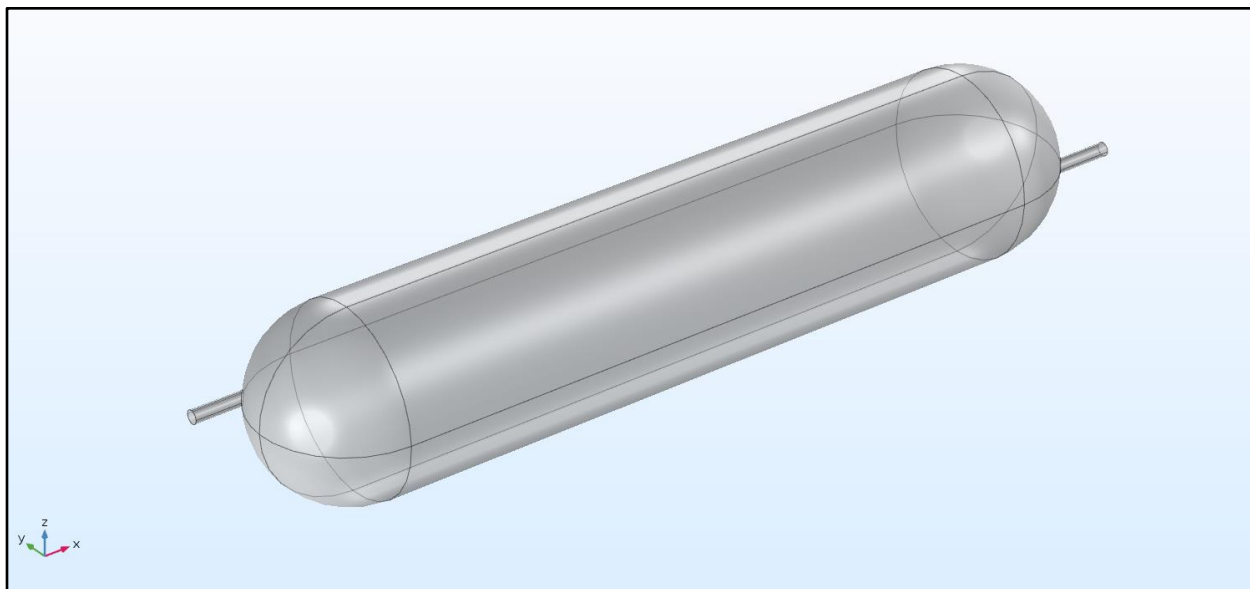


Figure 19: Original Geometry 6 mL/min, Isometric (COMSOL® v. 5.2. 2017)

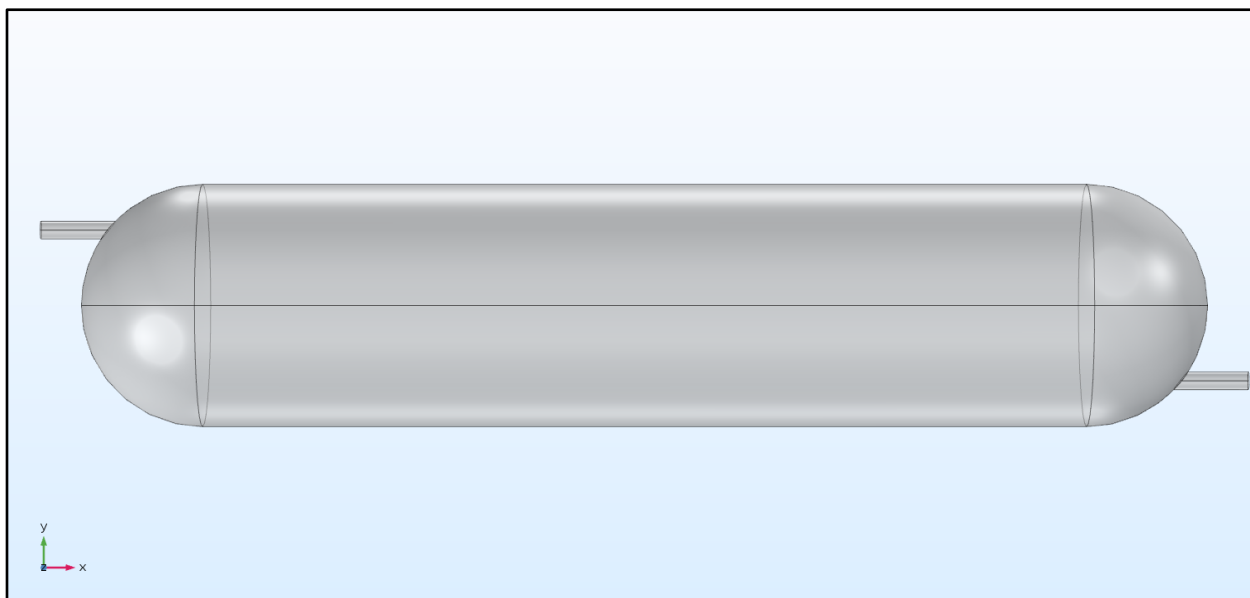


Figure 20: Original Geometry 6 mL/min, X-Axis (COMSOL® v. 5.2. 2017)

The Brilliant Blue solution enters the reactor from the influent pipe on the left side in Figure 20 and exits the effluent pipe to the right side or along the positive x-axis. The mesh layout below illustrates how the mesh was refined at the UV LED release points on the center line of the reactor along

the X-Axis to provide greater resolution for COMSOL® to resolve the fine detail around the UV LED release points.

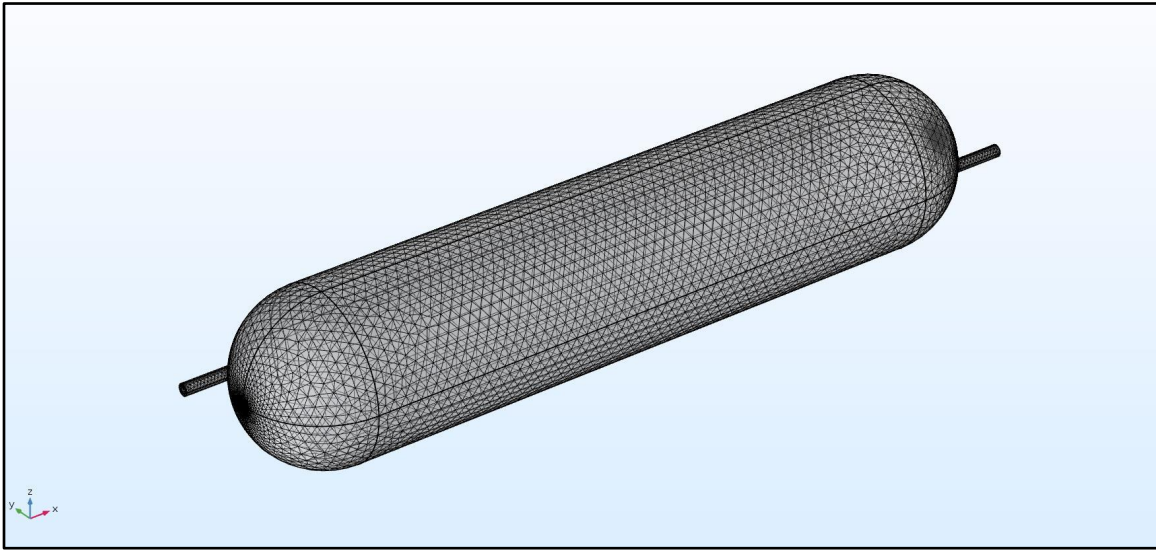


Figure 21: Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)

The Ray Optics package was the next step in the model and was used to calculate the ray power throughout the reactor chamber for the 0.35 ns ray simulation. Figures 22-24 illustrate how the rays propagated in the reaction chamber showing three different time intervals; the first at 0.03 ns showing the release point and the ray wave front. Figure 23 illustrates the rays after the full 0.35 ns for the BB-IIR. Figure 24 illustrates the rays after the full 4.0 ns for H₂O-IIR. Figures 23 and 24 also show a unique issue of COMSOL® allowing rays to escape the reactor chamber on rare occasions. This issue was not a concern due to the low power of the individual rays. The initial UV LED power was 0.0032 W per LED and was divided by 300 rays. The rays additionally experienced power losses as they moved through the reactor chamber; therefore the occasional accidental ray release was not considered an issue.



Figure 22: Ray Propagation at 0.03 ns, 95% Reflectance (COMSOL® v. 5.2. 2017)

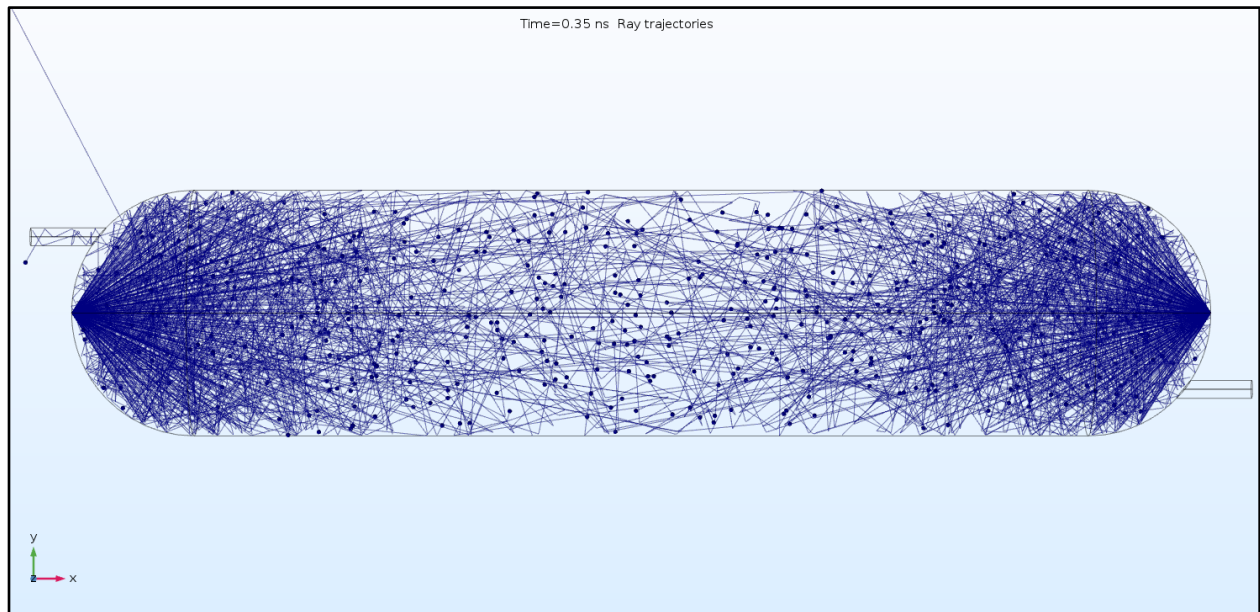


Figure 23: Ray Propagation at 0.35 ns, BB-IIR, 95% Reflectance (COMSOL® v. 5.2. 2017)

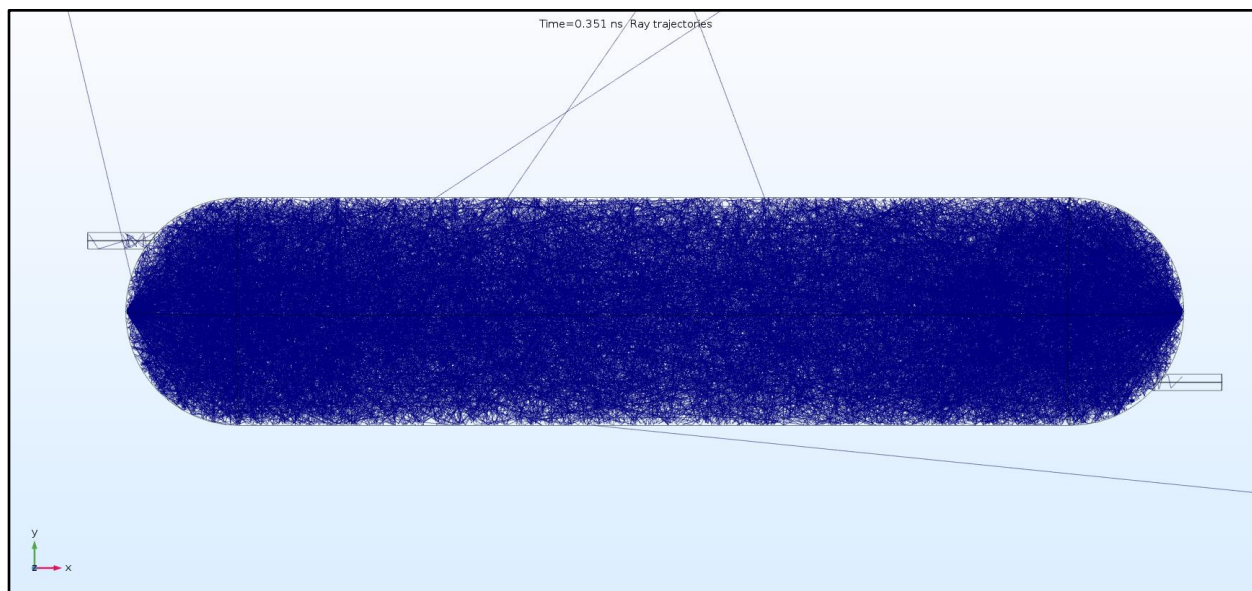


Figure 24: Ray Propagation at 4.0 ns, H₂O-IIR, 95% Reflectance (COMSOL® v. 5.2. 2017)

After the Ray Optics package solved for the ray propagation in the chamber, the Laminar flow package calculated the velocity fields within the reactors. Figure 25 illustrates the x and y -axis components of the velocity field. Figure 26 illustrates the y and z-axis velocity field with the effluent pipe going into the page. Due to the 6 mL/min flow rate, very little mixing was seen in the reactor flow profile and two distinct dead zones are evident in the upper and lower portion of the reactor along the x-axis.

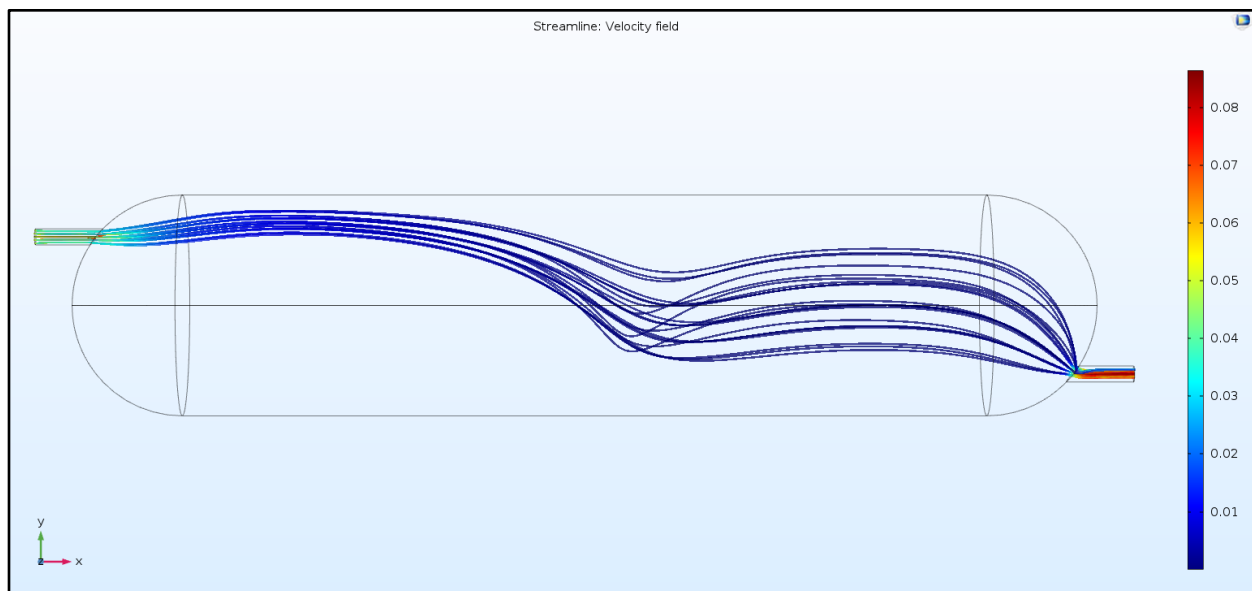


Figure 25: 6 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

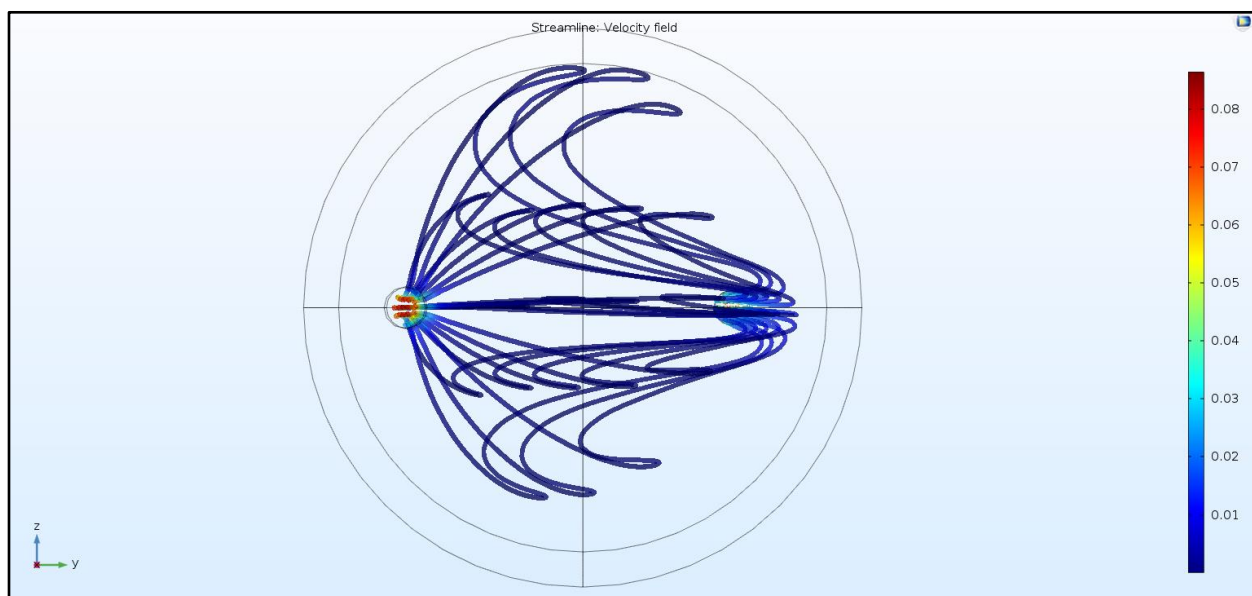


Figure 26: 6 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

After the velocity fields were calculated, the Transport of Diluted Species module was used to simulate the reaction between the rays and the power they deposited on the mesh elements and Brilliant Blue dye

solution as it passed through the reactor. The simulation was run for 1500 seconds to allow over three reactor chamber volumes to pass through the reactor at 6 mL/min. The module analyzed the reactions in the reactor every 0.1 seconds and recomputed the degradation of the concentration of Brilliant Blue dye over the entire reactor chamber domain for every time interval. Figure 27 and 28 outlines a slice concentration of the reactor chamber using the BB-IIR and H₂O-IIR after the first 60 seconds of the simulation. It's important to reiterate that the BB-IIR and H₂O-IIR should not be confused with the concentration of the Brilliant Blue dye in the reactor. These values are different and have no direct correlation between each other.

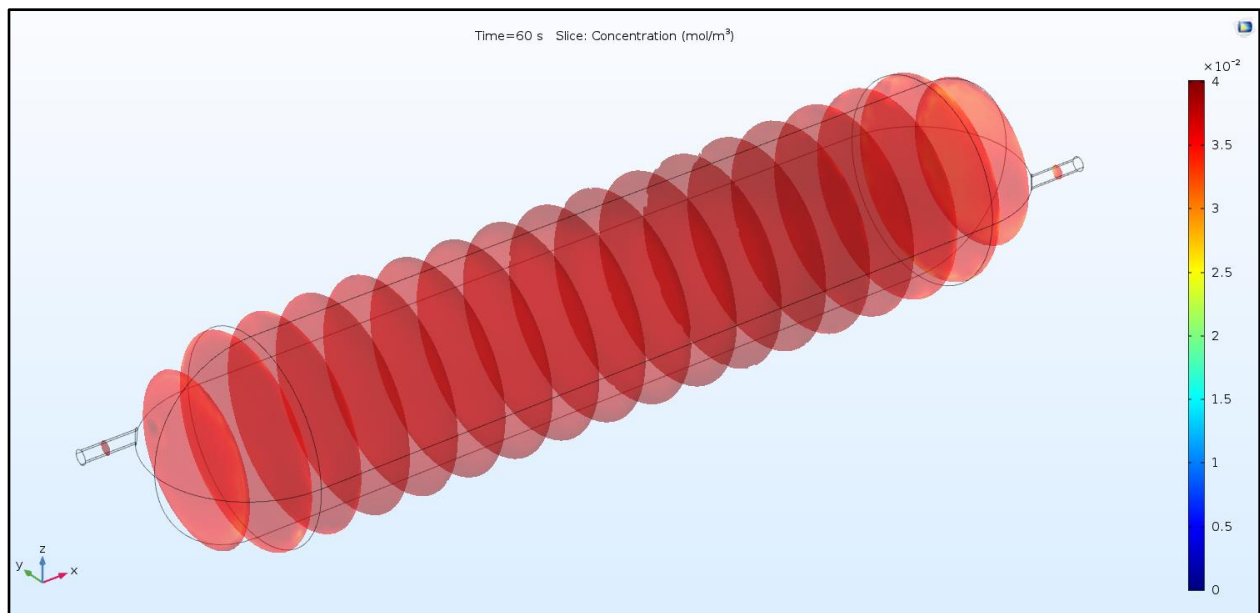


Figure 27: Slice Concentration 6mL/min, BB-IIR, 60 seconds (COMSOL® v. 5.2. 2017)

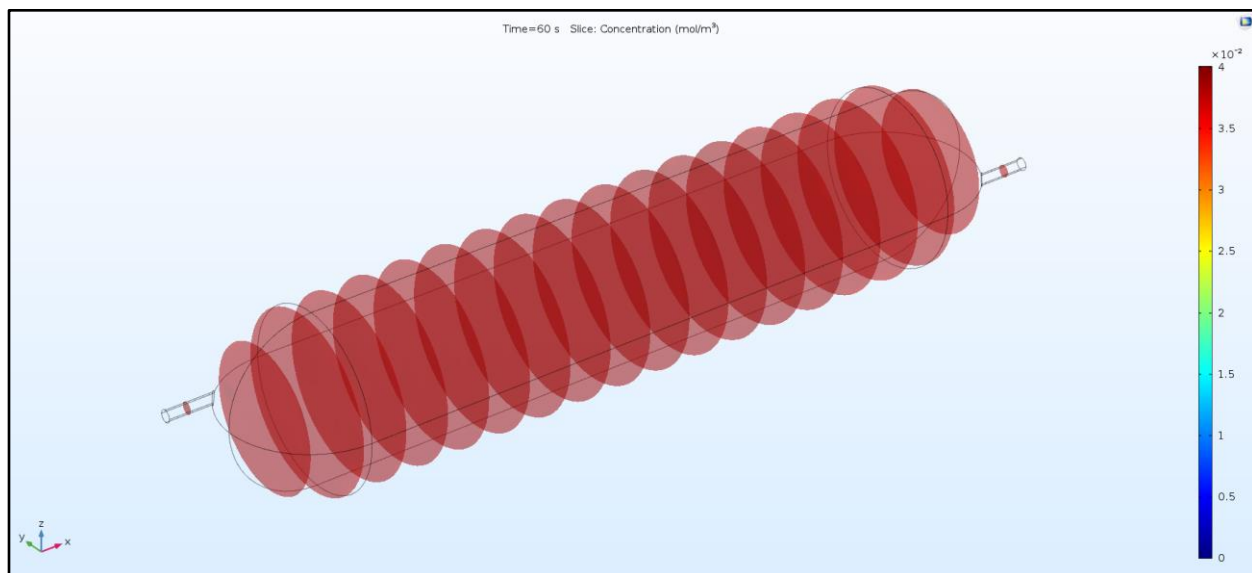


Figure 28: Slice Concentration 6mL/min, H₂O-IIR, 60 seconds (COMSOL® v. 5.2. 2017)

When analyzing the slice concentration of the reactor with BB-IIR the image shows higher reaction rates around the UV LED release locations after 60 seconds. The concentration around the end caps appeared to be significantly lower than in the middle of the reactor with the least degradation occurring about 2/3rds down the reactor length. This occurs due to the higher absorption of the BB-IIR. As the rays pass through the liquid they discharge their power faster than in pure water, resulting in higher reaction rates near the release points. This condition can be seen with the ray power graphs in Figures 17 and 18 as well. This condition reappears with the H₂O-IIR with the reaction being uniformly degraded over the reactor and slightly below the initial 0.04 mol/m^3 value set as the initial condition. This trend can be seen as well at the final time interval of 1500 seconds; providing validation for the proposed explanation. The BB-IIR slice concentration image had an overall lower concentration than the pure water index as well. Figures 29 and 30 show the dye concentration at slices along the reactor after 1500 seconds. Figure 29 shows the concentration for the BB-IIR while Figure 30 shows the concentration for the H₂O-IIR.

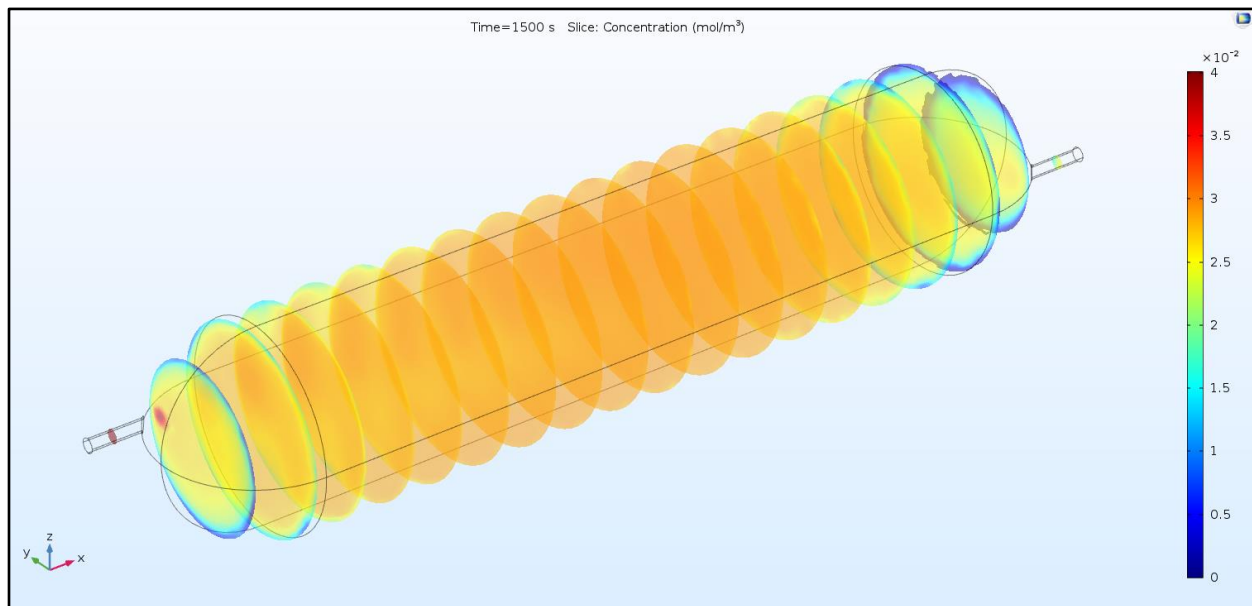


Figure 29: Slice Concentration 6mL/min, BB-IIR, 1500 seconds (COMSOL® v. 5.2. 2017)

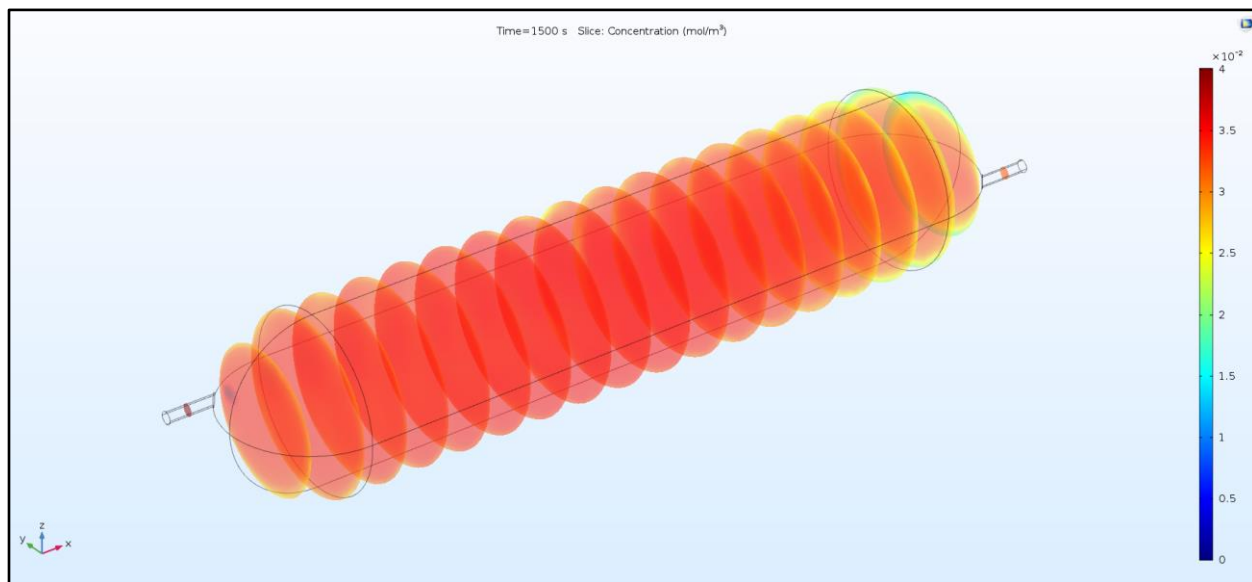


Figure 30: Slice Concentration 6mL/min, H2O-IIR, 1500 seconds (COMSOL® v. 5.2. 2017)

The next step was to plot the data for the average concentration as it exited the effluent pipe for both BB-IIR and H₂O-IIR and compare these results with the laboratory data. Figure 31 shows the concentration for the 6 mL/min flow rate.

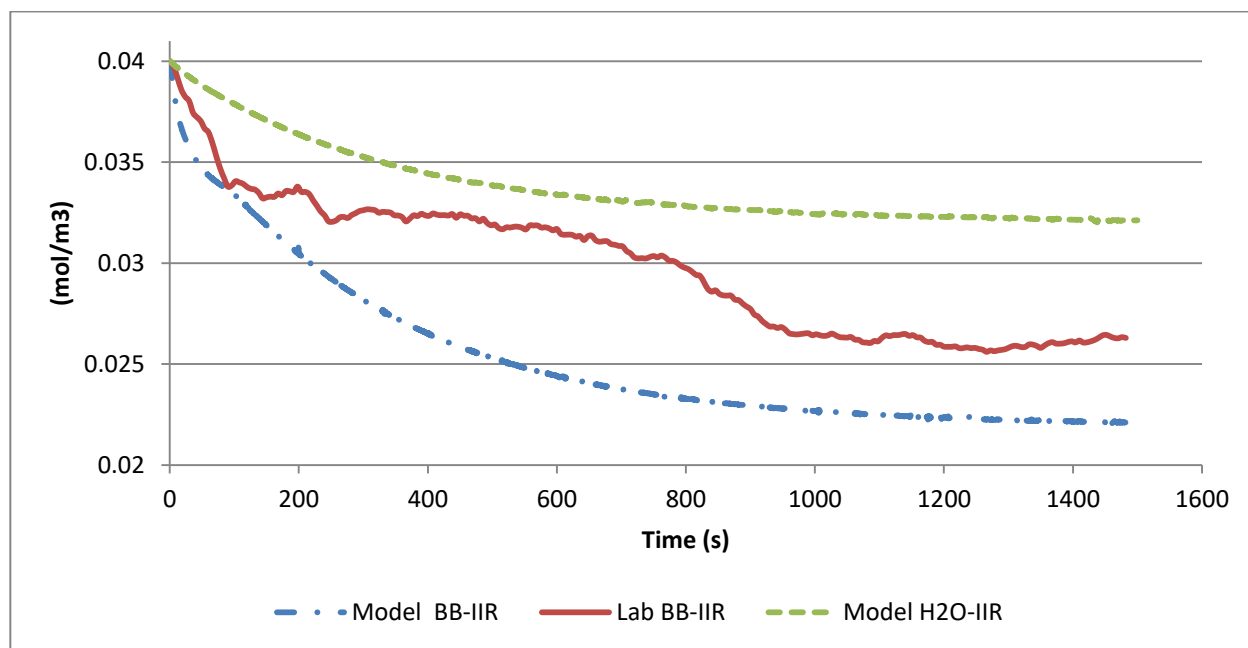


Figure 31: Original Geometry Brilliant Blue Dye Degradation for Lab BB-IIR, Model BB-IIR, Model H₂O-IIR at 6 mL/min Flow Rate

Figure 31 illustrates that the BB-IIR plot provided a reasonable fit to the curve of laboratory data for 6 mL/min flow rate, however, the final concentration is substantially below the laboratory data points for the entire plot. The H₂O-IIR provided concentrations above the laboratory data curve line, or proved to be less efficient. This result was unexpected due to the assumption that the rays would travel longer in the reactor and, in turn, contribute to a greater overall reaction rate in the reactor. This subject will be readdressed later.

Original Geometry with 8 mL/min for BB-IIR and H₂O-IIR

This section will discuss the results for the original geometry reactor at the 8 mL/min flow rate for both the BB-IIR and H₂O-IIR. Since the 8 mL/min original geometry reactor utilized the same ray optics data, geometry, mesh design as was used in the 6 mL/min models seen in Figures 19-24 they will not be covered in this section. However, the velocity fields for the 8 mL/min flow rate did produce different results than the 6 mL/min models and can be seen below in Figures 32 and 33.

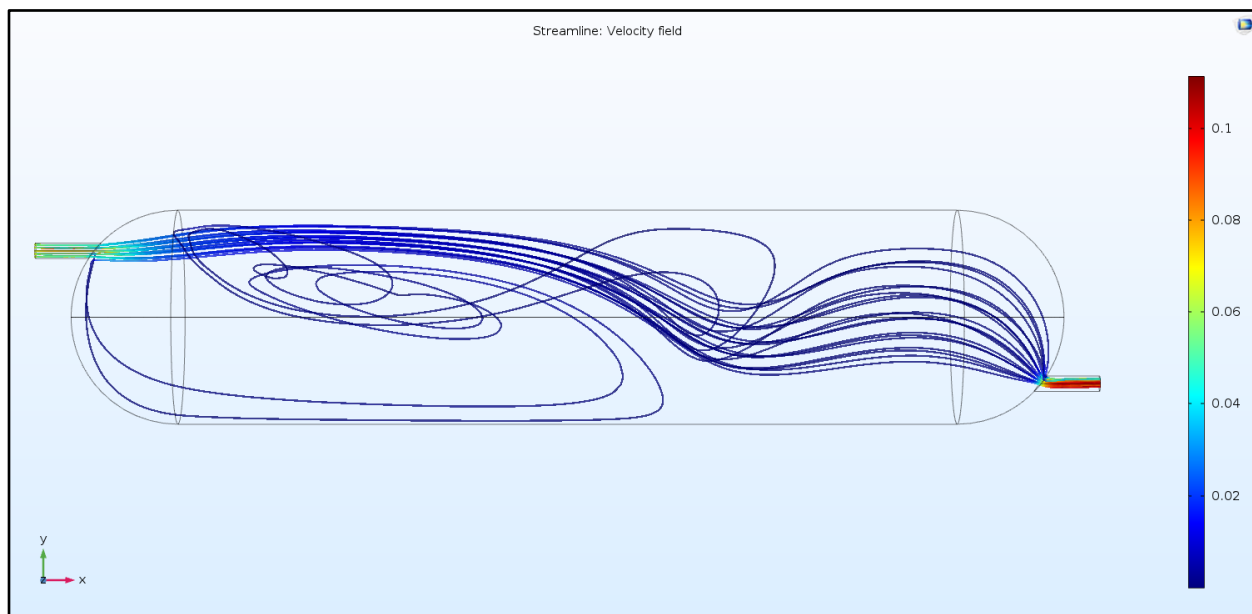


Figure 32: 8 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

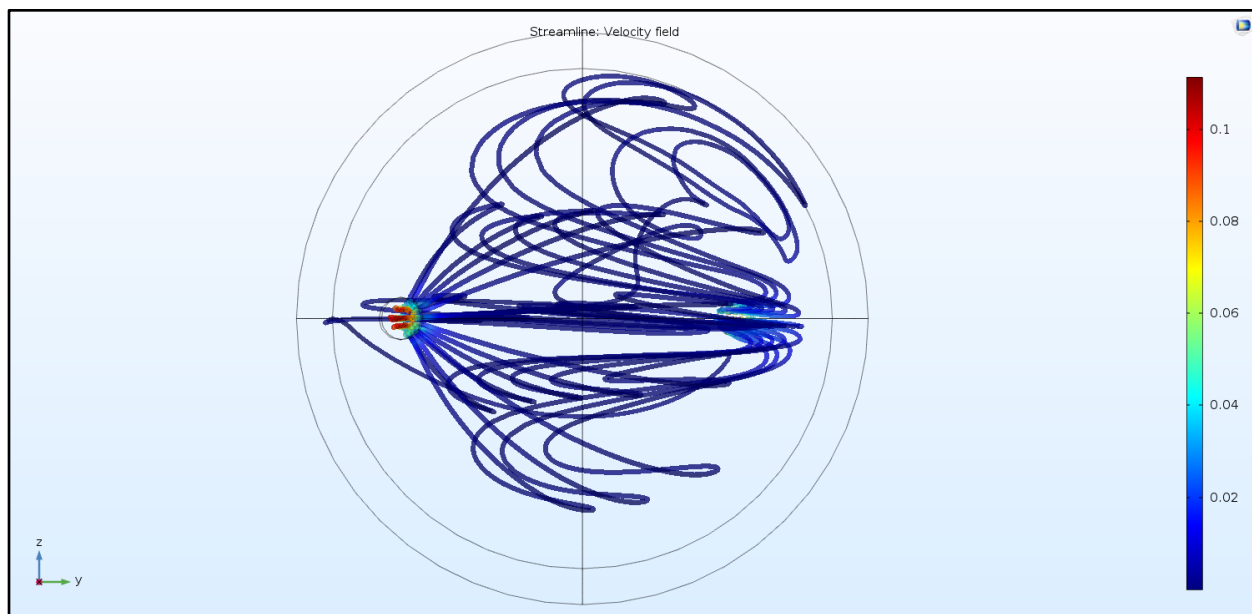


Figure 33: 8 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

The 6 mL/min velocity field seen in Figures 25 and 26 showed a primary channel passing through the reactor with very little dissipation or mixing outside the primary flow path. When analyzing the 8 mL/min velocity field, the flow has particle paths that diverge from the primary flow profile and primarily swirl along the x-axis dead zones. Therefore the velocity field for the 8 mL/min reactor has more internal mixing than the 6 mL/min reactor.

As with the previous flow rate, the simulation was ran to allow for over three reactor volumes to be replaced; in this case at 1128 seconds. The same trends can be seen when comparing BB-IIR and H₂O-IIR between the 6 and 8 mL/min flow rates. The BB-IIR shows greater degradation at the end caps where the UV LEDs release and less degradation of the Brilliant Blue dye near 2/3 of the way down the reactor along the X-Axis as seen in Figure 34. Again the higher transparency of the water allowed the rays to travel longer distances in the reactor before they lost power, thus a more uniformly distributed concentration was seen in Figure 35.

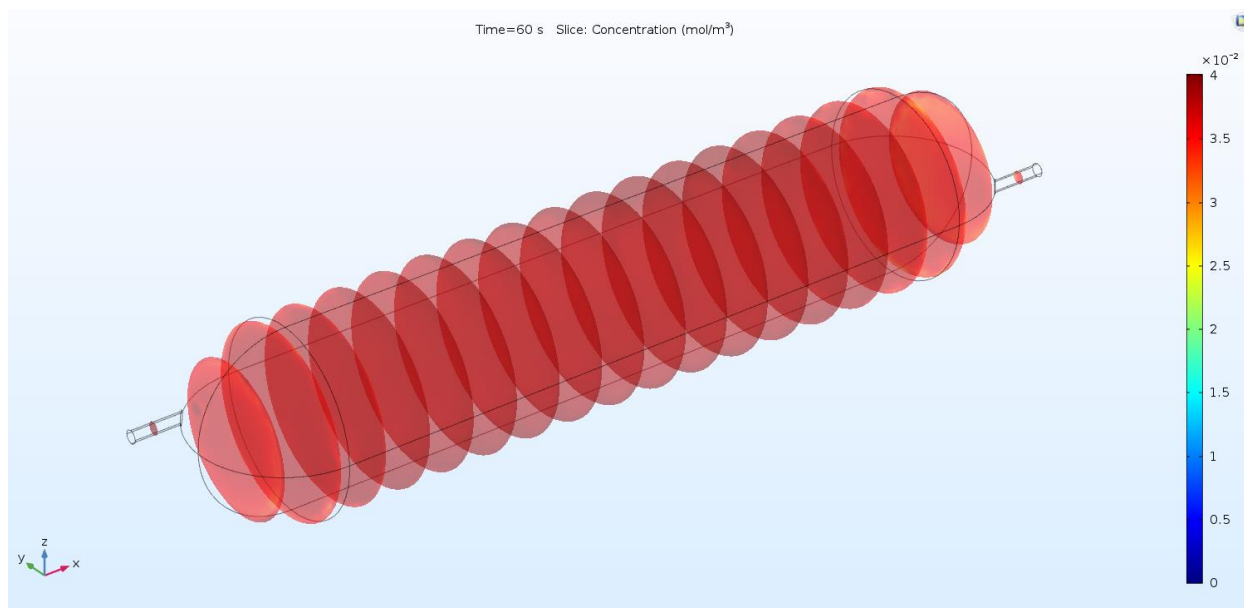


Figure 34: Slice Concentration 8mL/min, BB-IIR, 60 seconds (COMSOL® v. 5.2. 2017)

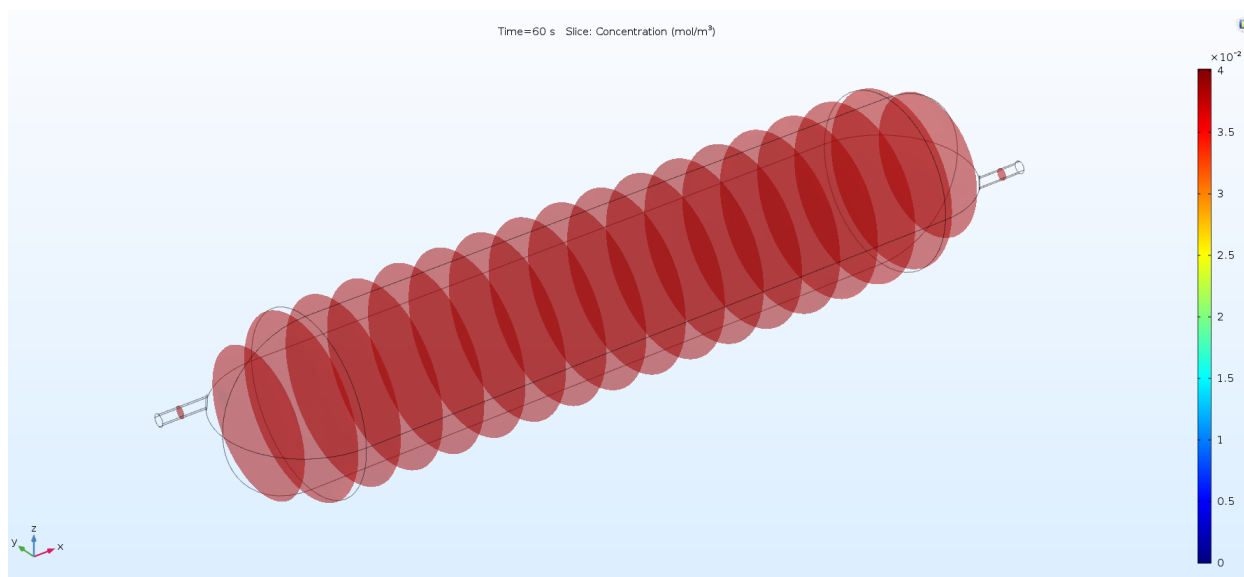


Figure 35: Slice Concentration 8mL/min, H₂O-IIR, 60 seconds (COMSOL® v. 5.2. 2017)

At the final last time interval of 1128 seconds the BB-IIR and H₂O-IIR reactors showed similar results as the 6 mL/min flow rate models, with the BB-IIR degrading the Brilliant Blue dye more thus being more efficient. However, as seen in Figure 36 and 37 the average concentrations in mol/m³ was not

as low as the respective 6 mL/min flow rates in Figures 29 and 30. This result was expected due to the solution having a lower dwell time as it passed through the reactor chamber due to higher flow rates.

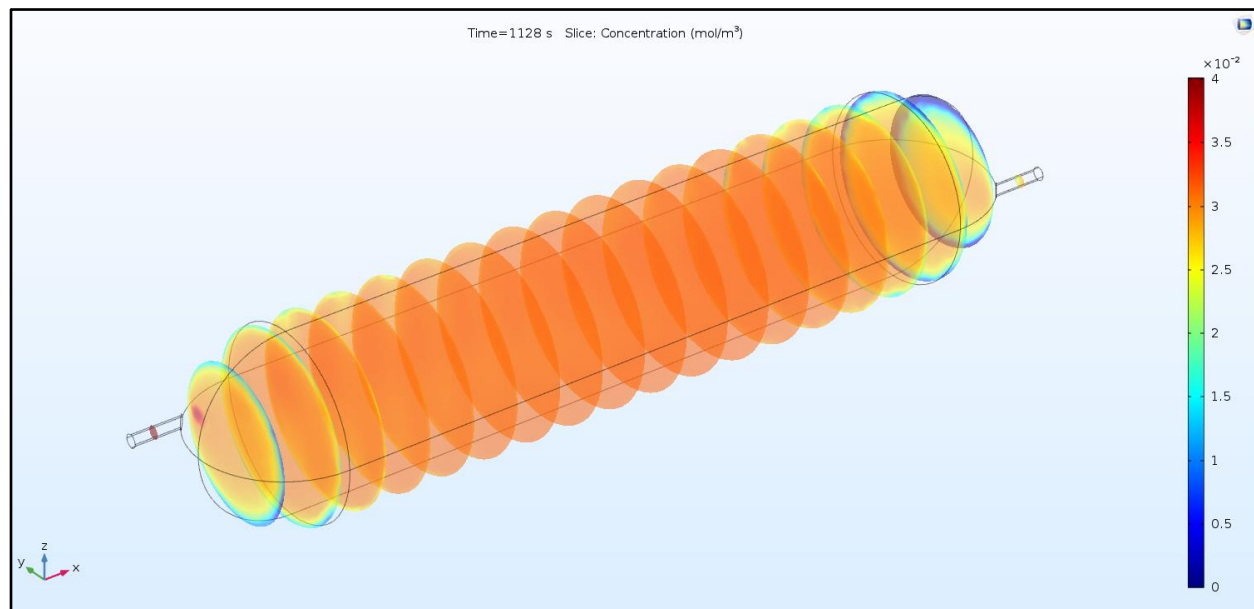


Figure 36: Slice Concentration 8mL/min, BB-IIR, 1128 seconds (COMSOL® v. 5.2. 2017)

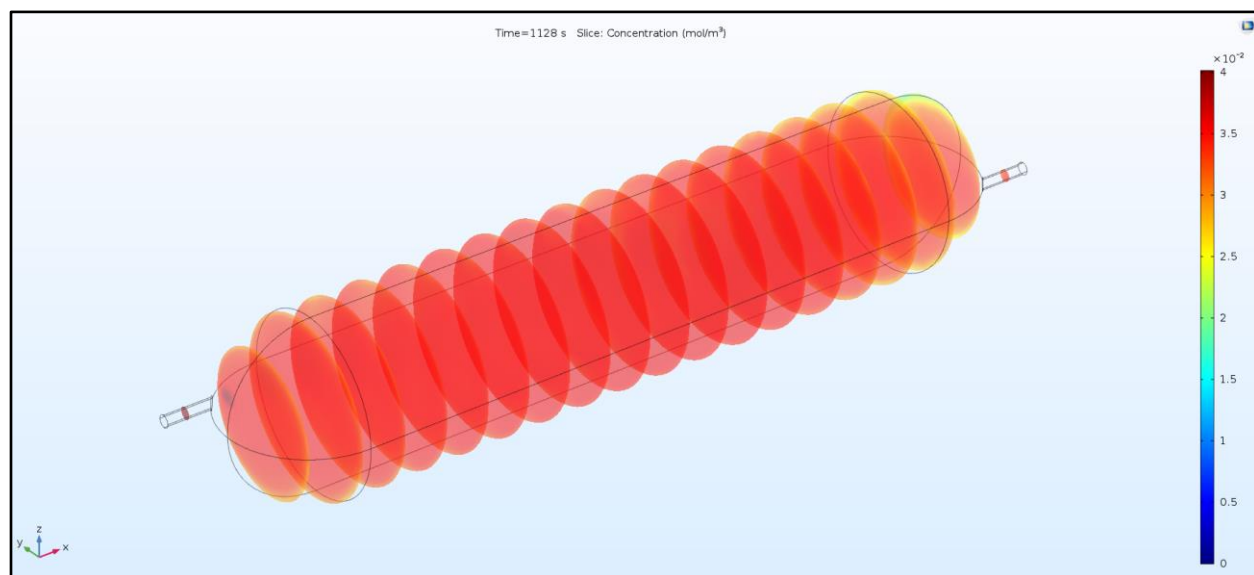


Figure 37: Slice Concentration 8mL/min, H₂O-IIR, 1128 seconds (COMSOL® v. 5.2. 2017)

When graphing the output values for both reactors and comparing it to the laboratory data, the same trends were seen as with the 6mL/min flow rate models. The BB-IIR followed the laboratory curve well and was slightly lower than the laboratory data. The H₂O-IIR again was less efficient than the BB-IIR model.

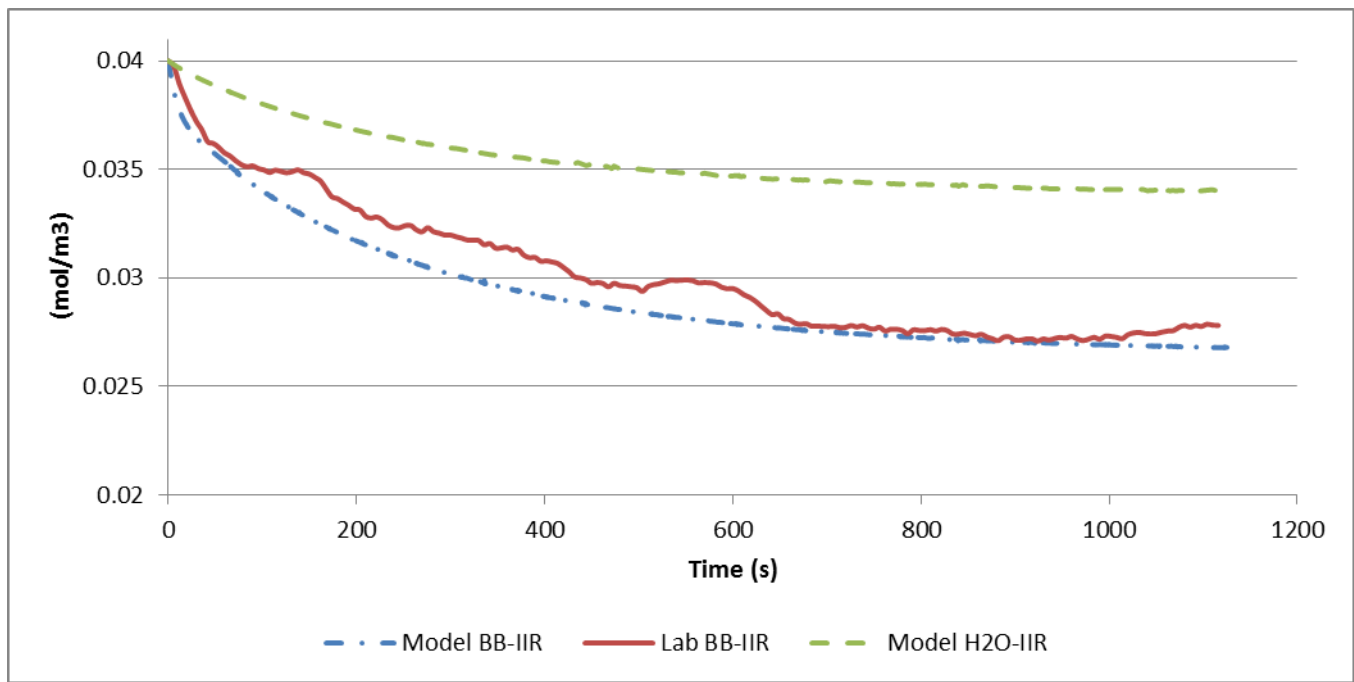


Figure 38: Original Geometry Brilliant Blue Dye Degradation for Lab BB-IIR, Model BB-IIR, Model H₂O at 8 mL/min Flow Rate

As shown in Figure 38, the difference between the laboratory data and the COMSOL[®] curve was smaller than for the 6 mL/min condition, meaning that the COMSOL[®] model was able to better predict the laboratory results with more accuracy with a flow rate of 8 mL/min than at 6 mL/min.

Original Geometry with 10 mL/min for BB-IIR and H₂O-IIR

The 10 mL/min original geometry reactor utilized the same Ray Optics data as the 6 and 8 mL/min models as well as the same geometry and mesh layout as seen in Figures 19-24. Therefore they will not be readdressed in this section. The velocity fields for the 10 mL/min differed from the 6 and 8 mL/min conditions and can be seen in Figure 39 and 40.

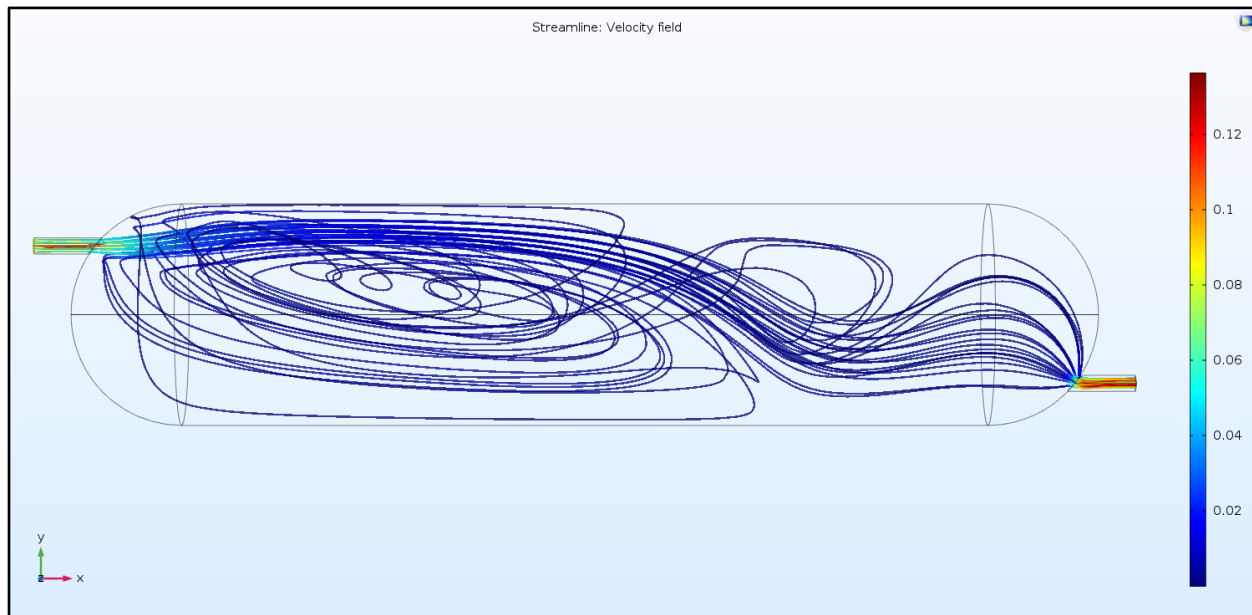


Figure 39: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

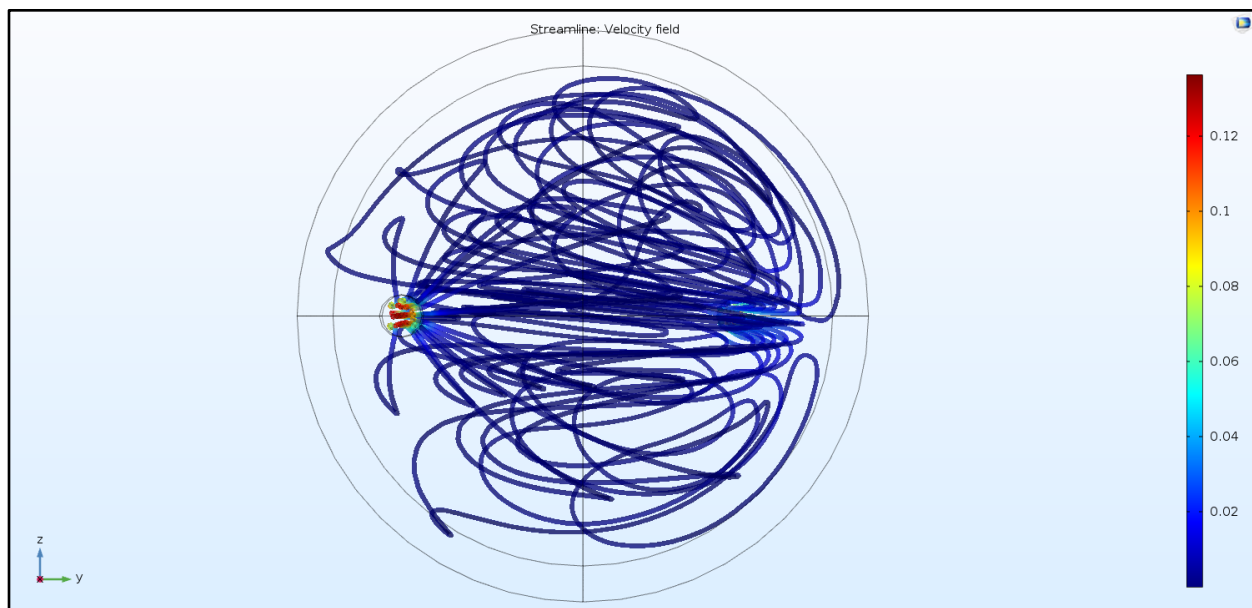


Figure 40: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

The 10 mL/min velocity field followed a similar trend as the 8 mL/min field. However, the velocity field for the 10 mL/min reactor showed more internal mixing than both the 6 and 8 mL/min reactor.

As with the previous flow rates, the simulation was run to allow over three reactor volumes to be replaced, in this case 900 seconds. The same trends were seen when analyzing BB-IIR and H₂O-IIR indices for the 60 and 900 time intervals. The BB-IIR showed greater degradation at the end caps where the UV LEDs released and a higher Brilliant Blue dye concentration near 2/3 of the way down the reactor along the x-axis as seen in Figure 41. The H₂O-IIR was lower and therefore allowed the rays to travel longer distances in the reactor before they lost power. The same trends appeared with this condition showing uniform degradation throughout the reactor at the 60 second time interval as seen in Figure 42.

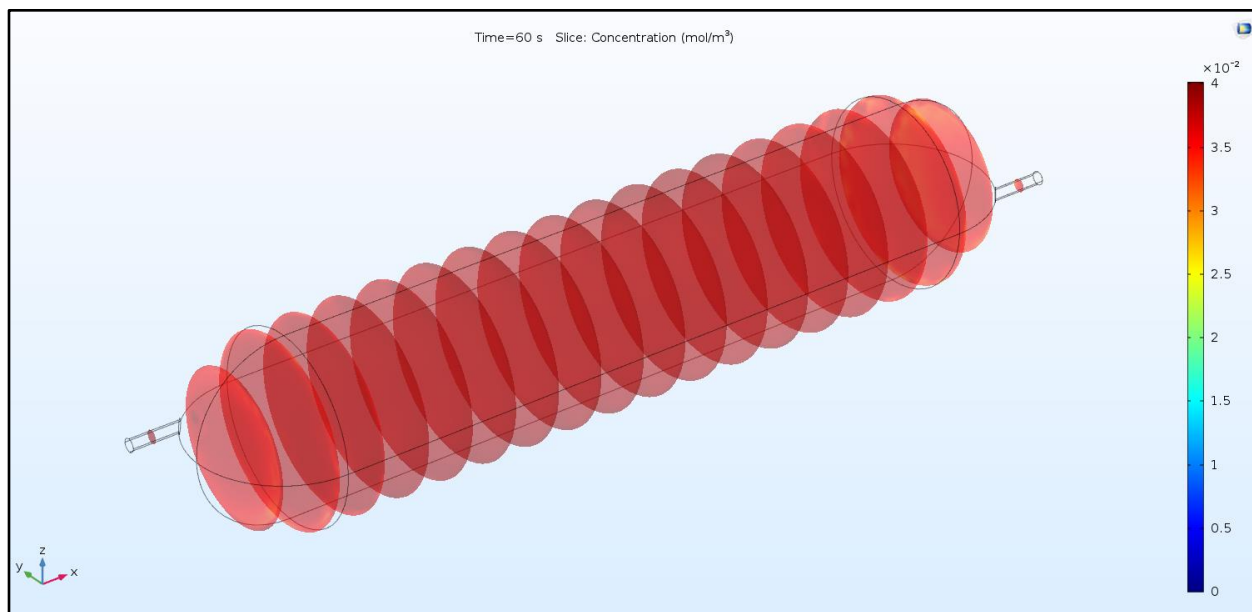


Figure 41: Slice Concentration 10mL/min, BB-IIR, 60 seconds (COMSOL® v. 5.2. 2017)

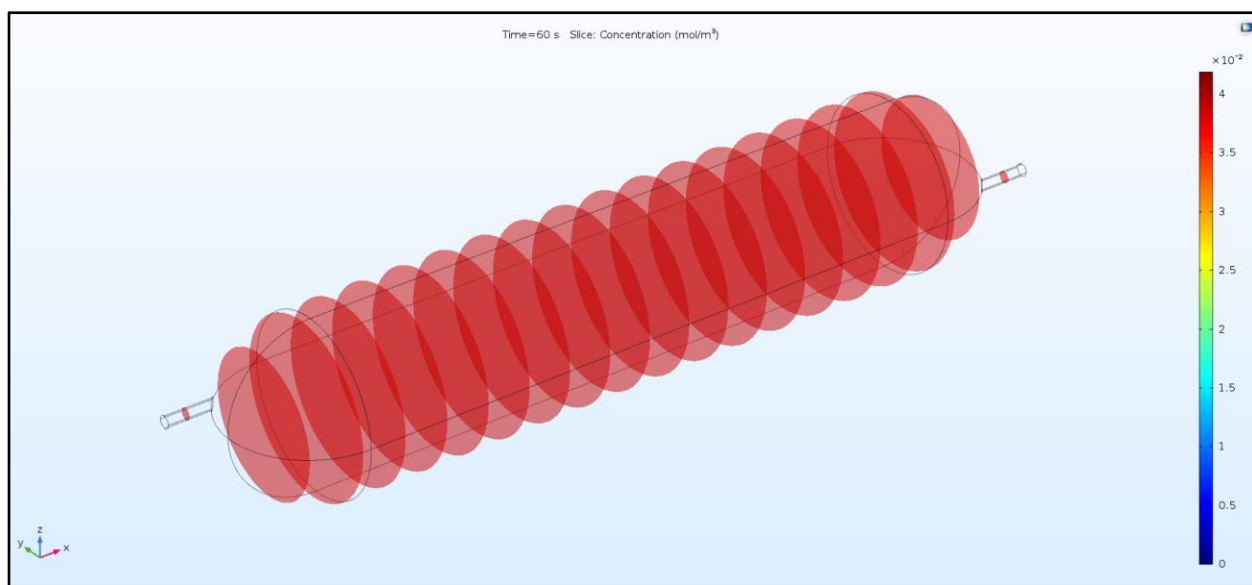


Figure 42: Slice Concentration 10mL/min, H₂O-IIR, 60 seconds (COMSOL® v. 5.2. 2017)

The final time interval of 900 seconds for the reactor showed similar results as the 6 and 8 mL/min flow rates with the BB-IIR degrading more than the H₂O-IIR. As seen in Figures 43 and 44 the average concentration in mol/m³ was not as low as the respective 6 and 8 mL/min flow rates as can be seen in

Figures 29-30 and 36-37. This result was expected due to the solution having a shorter dwell time as it passed through the reactor chamber due to higher flow rates.

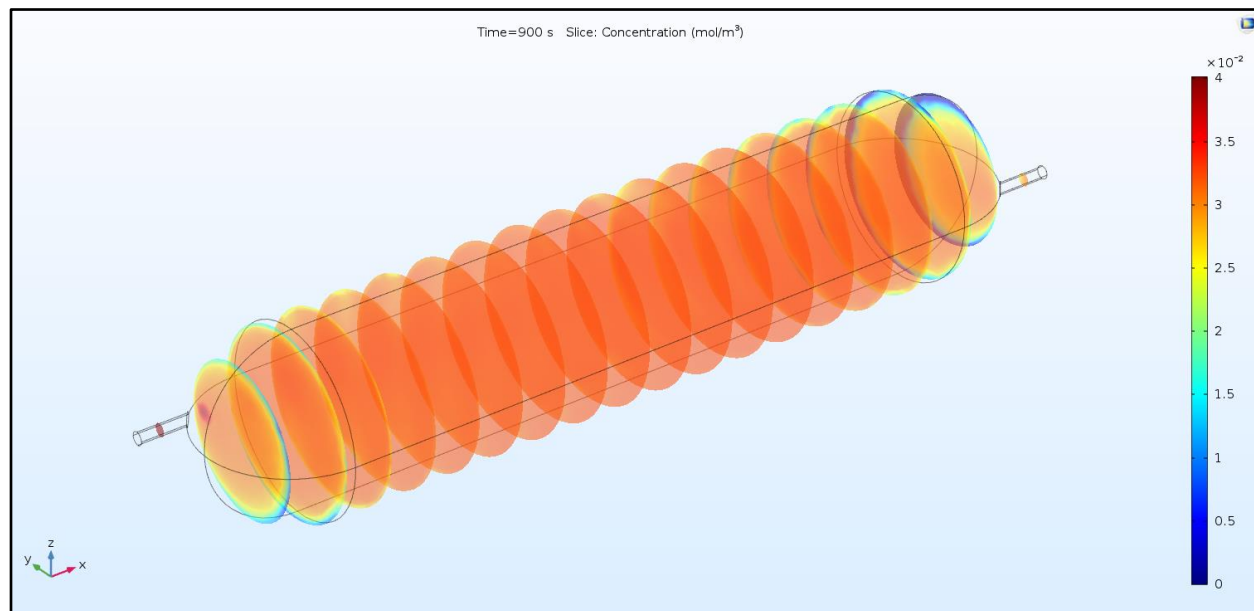


Figure 43: Slice Concentration 10mL/min, BB-IIR, 900 seconds(COMSOL® v. 5.2. 2017)

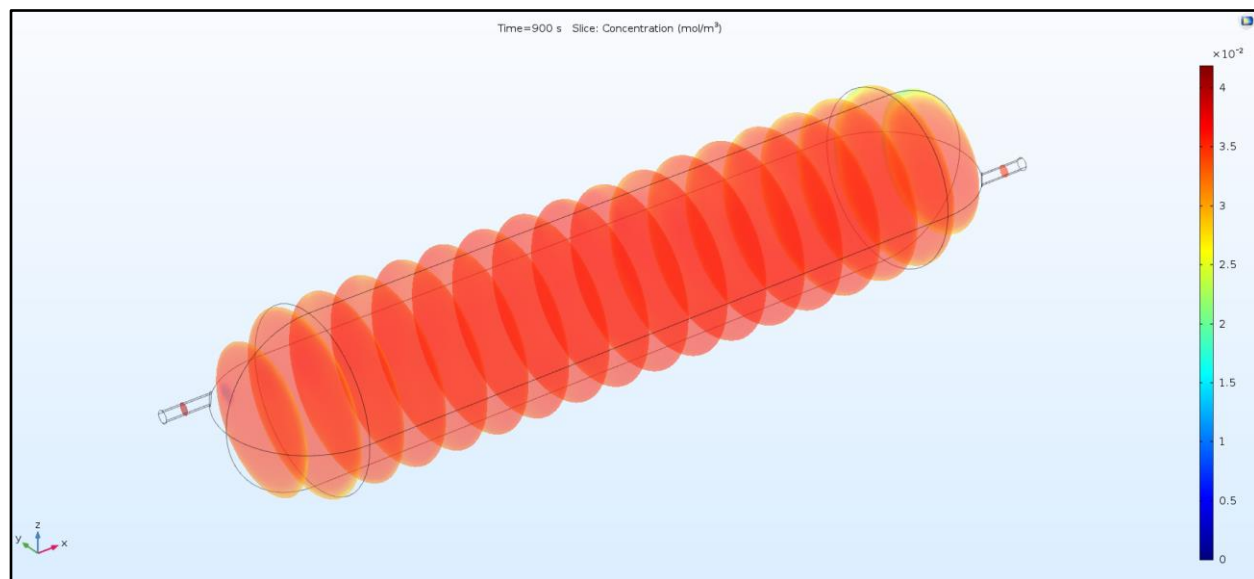


Figure 44: Slice Concentration 10mL/min, H2O-IIR, 900 seconds (COMSOL® v. 5.2. 2017)

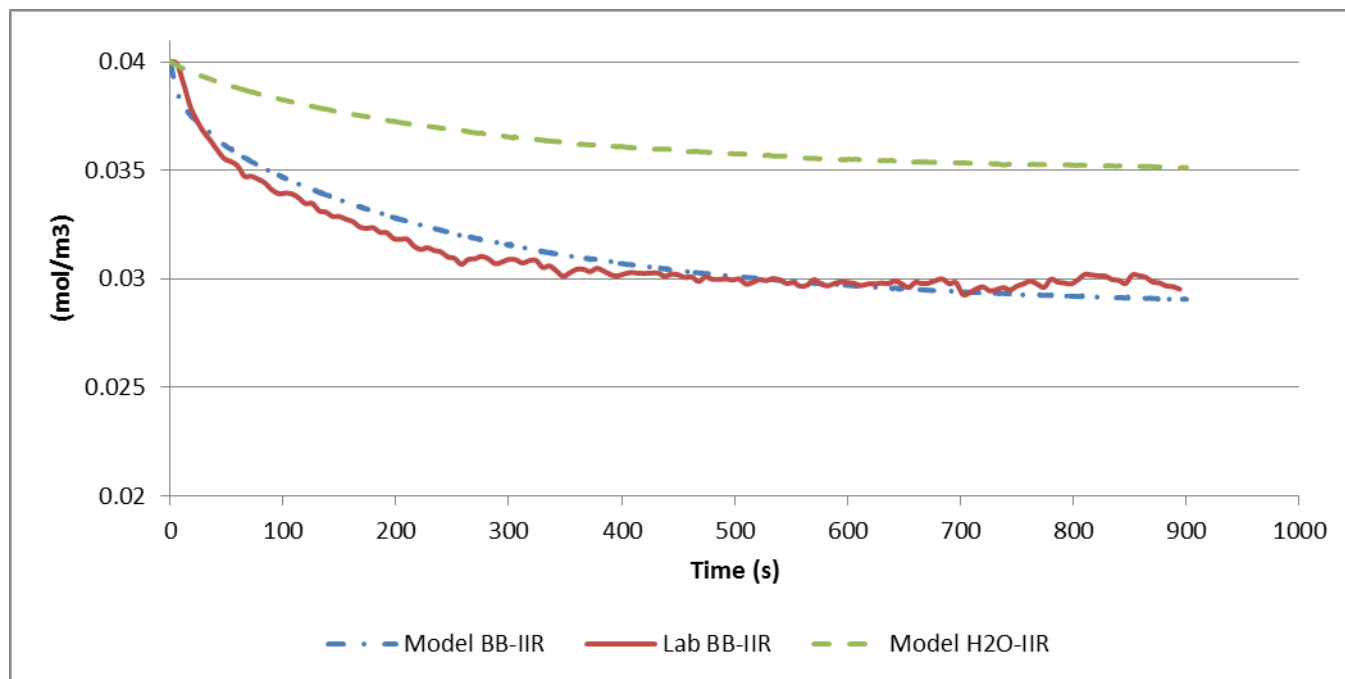


Figure 45: Original Geometry Brilliant Blue Dye Degradation for Lab BB-IIR, Model BB-IIR, Model H₂O at 10 mL/min Flow Rate

When graphing the values for both reactors and the laboratory data, the same trends appeared as was seen in the 6 and 8 mL/min flow rates. The BB-IIR followed the laboratory curve and obtained an average difference of 0.21% lower than the laboratory data curve. The adapted model had been calibrated for the 10 mL/min flow rate; therefore the 10 mL/min curves matched the best of the 6, 8, 10 mL/min flow rates. The H₂O-IIR was less efficient than the BB-IIR value following the same trends as the 6 and 8 mL/min flow models.

Original Geometry with 10 mL/min at 100% Reflectance for H₂O-IIR

During the model validation process, the H₂O-IIR resulted in a less efficient reaction (i.e., higher steady state dye concentration) than the higher absorbent BB-IIR. This was an unexpected result and was not easily explained. However, it was hypothesized that the reduction in efficiency could be due to the 5%

wall absorption value. After analyzing the power curves for the two absorption values, the research team noticed that the rays were losing energy in the water as well as being absorbed by the reactor walls. This was calculated to occur at the rate of a 5% chance every time a ray struck a reactor wall (i.e., the complement of the 95% reflectance value). This concept can be seen in greater detail in Figure 46, which shows the ray power when the 4 ns ray power curve was zoomed in on to show the initial few nanoseconds of the simulation. The first few nanoseconds from 0 – 0.06 ns indicates power loss or absorption by the solution. The power then drops rapidly as the rays strike the walls of the reactor for the first time. A large portion of the rays strike the walls at roughly the same time and incur a large loss due to the 5% reactor wall absorption parameter. After the initial encounter with the wall, the rays steadily decrease in power via absorption in the solution as well as wall absorption until the simulation is stopped at 4 ns as seen in Figure 46.

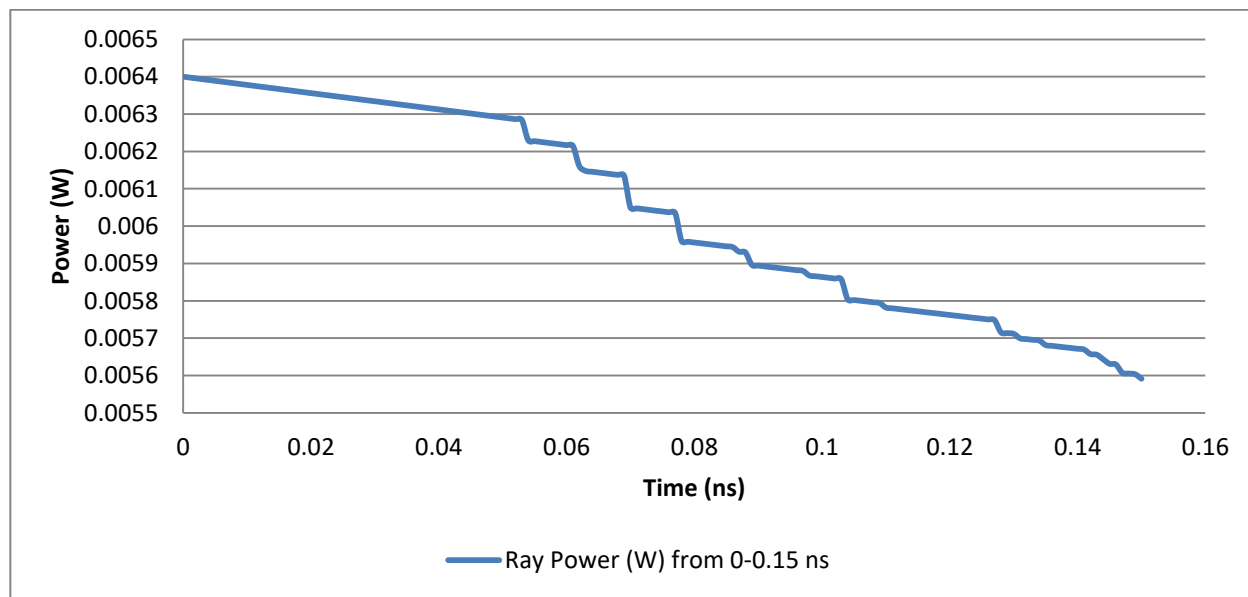


Figure 46: Power Loss from Water and 5% Wall Absorption, H₂O-IIR, 6mL/min (0-0.15 ns)

After investigating this issue the research team hypothesized that since the rays traveled almost 1.2 meters after 4 ns, as seen in Equation 13, with a reactor that was roughly 10.26 cm long and 1.11 cm wide, each ray could have easily experienced over 100 wall strikes if not absorbed. At a 5% chance of wall absorption for each wall strike, this interaction results in a significant average power reduction over the ray's duration.

$$299,792,458 \text{ m/s} * \frac{1.0E-9 \text{ s}}{1 \text{ ns}} * 4 \text{ ns} = 1.1992 \text{ m} \quad (13)$$

To verify this theory, a model was ran using 100% reflection for the original geometry and H₂O-IIR at a flow rate of 10 mL/min. It was assumed that if the reduction in efficiency for H₂O-IIR was due to wall absorption, this condition should produce results for pure water that is comparable to the BB-IIR. Figure 47 illustrates this concept with the rays no longer losing power to reactor wall absorption. To compensate for the lack of ray absorption from 95% reflectance, the ray optics simulation duration had to be extended to 8 ns to experience a similar power loss.

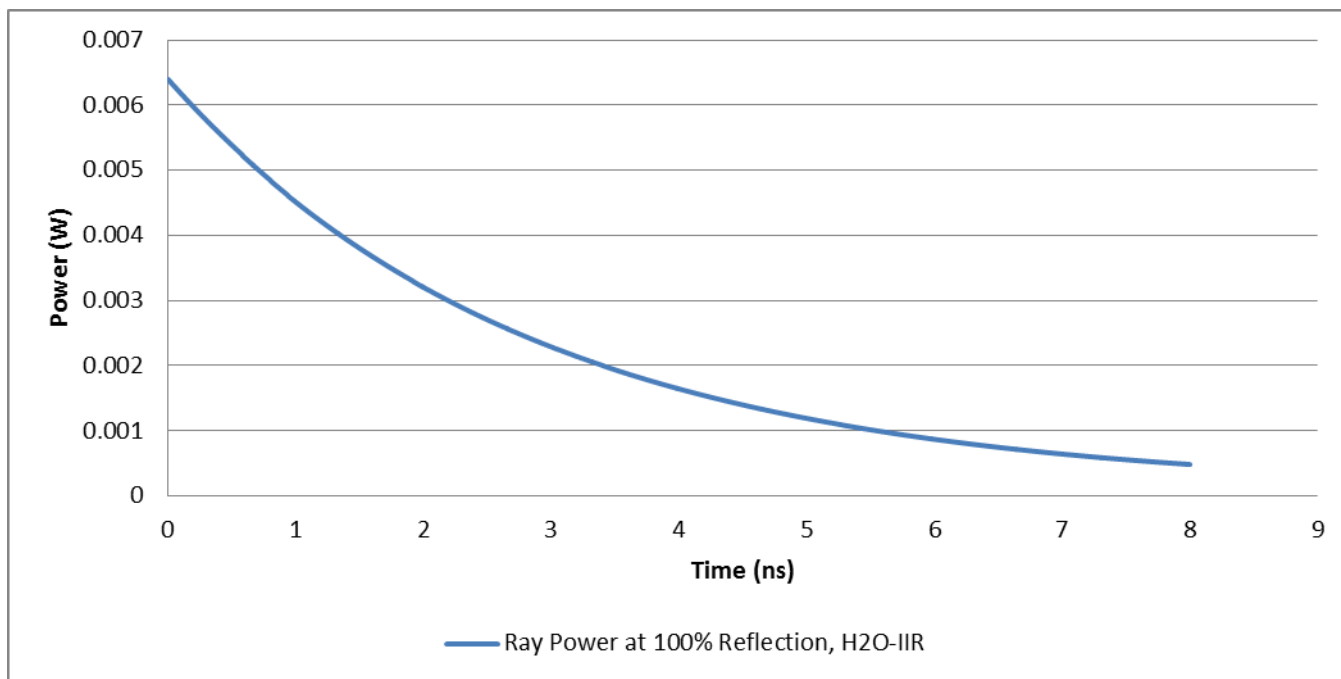


Figure 47: Ray Power at 100% Reflection, H2O-IIR, 10 mL/min

The final ray power value for the 8 ns simulation was 0.00048264W compared to the 4 ns simulations final power value of 0.00020561W. To obtain the same power value as the 4 ns run the simulation would have had to run longer and thus greatly increased an already large 27 Gigabyte output file size and greatly increased computational time. Therefore since this was a proof of concept model to test a hypothesis and not a data analysis simulation, the 8 ns time was determined to be satisfactory. The result of this test is outlined in Figure 48. As shown, the efficiency improved significantly for this condition as compared to the original result with the H₂O-IIR and had a final concentration below concentration obtained for the BB-IIR condition.

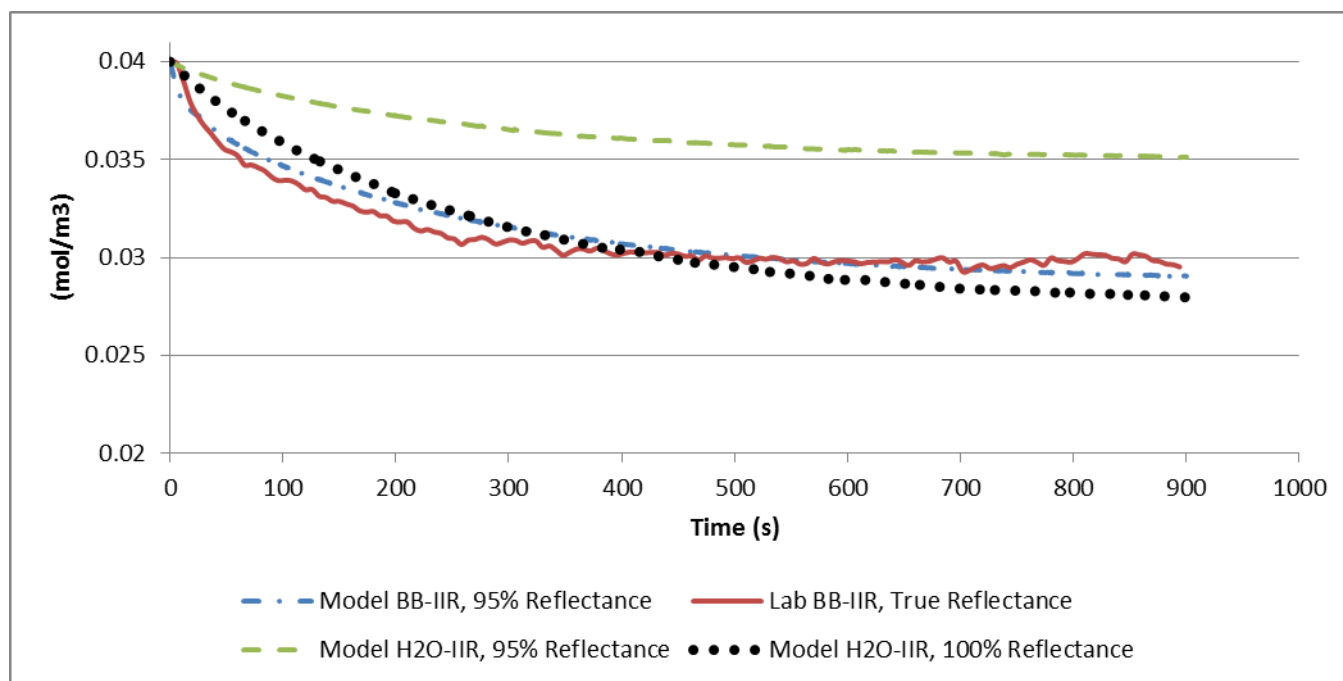


Figure 48: Original Geometry Brilliant Blue Dye Degradation, 100% Reflectance, 10 mL/min Flow Rate

Adapted Model Analysis

When analysing the data from the adapted model, it was determined that the model was sufficient at correctly predicting the reaction processes experienced in the laboratory with the Brilliant Blue dye degradation. However, a few major matters presented themselves while performing the model validation process. The first item was the assumption that every hydroxyl radical produced would degrade a Brilliant Blue dye molecule appeared to be incorrect, as was anticipated. This can be seen when looking at Figure 15 in the Initial COMSOL[®] Model Results and Analysis section. The original reaction rate equation that accounted for the quantum yield, the creation of two hydroxyl radicals for every hydrogen peroxide molecule, Avagadro's number, and the energy per photon produced a final concentration far lower than observed in the laboratory data, with an error of over 59.98% and a sum of squares difference of 0.065213. Therefore the reaction equation constant was changed from $1.2150\text{E-}6$ [mol/(W*s)] to $2.9000\text{E-}7$

[mol/(W*s)], a 76.13% reduction. This means that on average about one in every four (23.87%) of the hydroxal radicals was effective in degrading a Brilliant Blue dye molecule. This however was adapted for the higher flow rate of 10 mL/min which provided a model that provided a good fit to the laboratory data. However when analyzing the 6 and 8 mL/min flow rate plots, the modeled dye concentration was below the laboratory data curves as seen in Figures 31 and 38. This result indicates that other factors were contributing to the efficiencies at different flow rates.

To explain this result, it is important to focus on the velocity fields for the three flow rates. The 10 mL/min flow rate had a significant amount of velocity induced mixing in the reactor, as can be seen in Figures 39 and 40. The 8 mL/min condition had less mixing than the 10 mL/min. The 6 mL/min velocity field was the smoothest and appeared to have minimal natural mixing. Therefore, mixing within the reactor might be a potential cause for the decreased efficiency from the laboratory data. The model was adapted using the 10 mL/min flow rate and it was assumed that the normalized reaction equation would be constant. Therefore it is possible that as the flow rates decreased from 10 to 6 mL/min the natural mixing effect lessened. In turn it is possible that the reaction between the hydroxyl radicals and dye molecules was reduced, potentially due to a reduction in the ratio of dye to hydroxyl concentration within unmixed regions of the reactor. This might have affected the efficiency of dye degradation. Unfortunately, no literature was found explaining the efficiency of the hydroxyl radical to Brilliant Blue degradation rates, nor how flow rates affected the mixing process in the reactor. Since this research was outside the scope of this thesis, the answer was not investigated beyond the proposed explanation. Unfortunately, the assumption that IIR was constant throughout the reaction process as well as that the quantum efficiency of the reaction process was independent of the IIR values could be affecting the results. However, improving this portion of the model was also outside the scope of this thesis and could not be addressed. Since the COMSOL[®] models were built using IIR values instead of a

concentration dependent equation for IIR, there is no way to improve upon this assumption until further research is performed to develop the correct equation for the IIR as the concentrations changes within the reactor. Likewise the assumption that the reaction rate equation constant does not change as the Brilliant Blue dye degrades could not be assessed. Future research will have to investigate these assumptions to help create a more robust COMSOL[®] model.

In summary the COMSOL[®] model was able to predict the laboratory degradation curves satisfactorily for a single flow rate when the reaction rate constant was adapted to fit the model. Additionally, it was found that the reflectance of the reactor walls had a large impact on efficiency of the pure water absorption models due to the rays traveling long distances and being absorbed in the reactor walls. Therefore, reactor geometry might not play a less important role on reactor efficiency as previously if the reflectance value is high. However, even the reduction from 100 to 95% reflectance had a very significant effect on the efficiency of the reactor when assuming the H₂O-IIR.

Geometric Optimization Trends

With the reaction rate constant adapted for 10 mL/min flow rates, a variety of geometries were analyzed by combining five different geometry styles and different reactor volumes. The purpose of this analysis was to investigate and analyze how changing the geometry and volume of the reactor would affect the efficiency of the reactors in the presence of the BB-IIR and H₂O-IIR indices. The underlying purpose for this part of the study was to determine if there was a geometry style or trend that outperformed other design styles for water, H₂O-IIR. The reason H₂O-IIR is important is its similarity to characteristics of a germicidal purification device for point-of-use applications. For geometries and mesh layouts refer to Appendix B for screen shots of the varying reactor designs.

Geometry Styles for Pure Water Imaginary Index of Refraction, H₂O-IIR

The models in this section used the H₂O-IIR index. The results of the original geometry design with a volume of 36.42 cm³, and three other reactor designs that all had the same volume of 4.546 cm³ can be seen in Figure 49. The three smaller reactors have the half scale reactor geometry, half scale with separator plate, and sphere. The average outflow concentration values were plotted and can be seen in Figure 49.

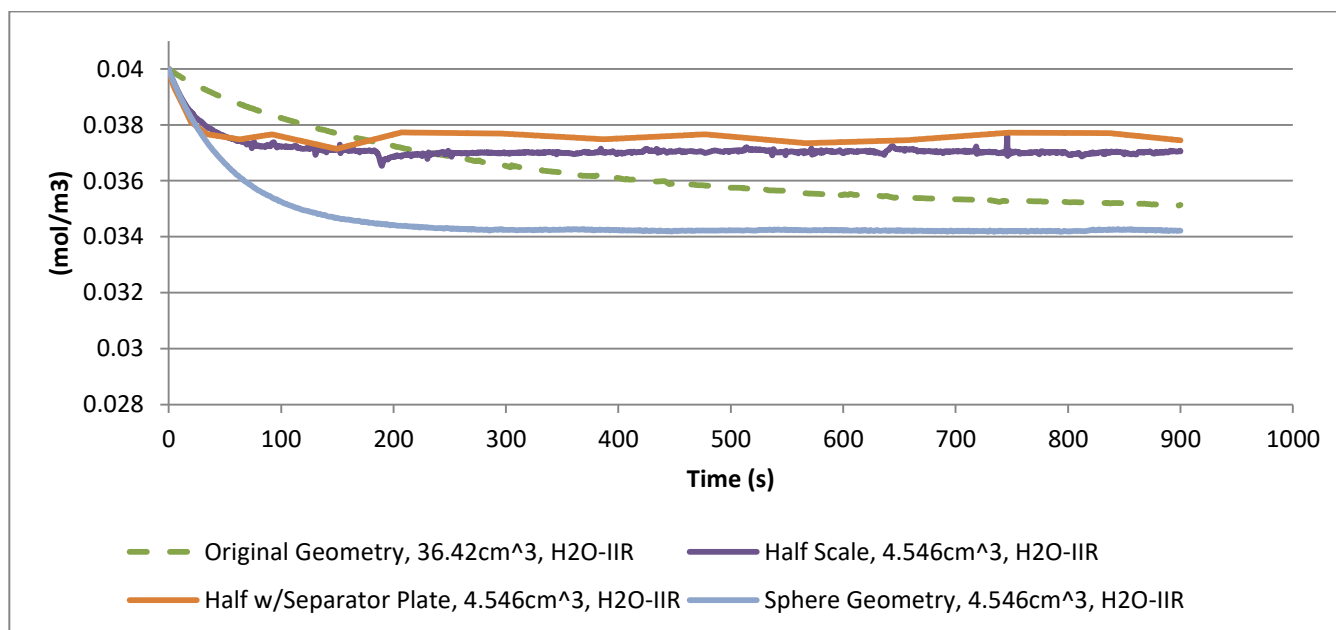


Figure 49: Degradation of Original, Half Scale, Half Scale with Separator Plate, and Sphere 4.546cm³ Geometry with H₂O-IIR, 10 mL/min Flow Rate

The dotted green line provides dye concentration for the original reactor geometry as seen previously in this chapter and was used as a baseline. The half scale and half scale with separator plate

reactors were not as efficient as the full size original reactor. However, they were able to attain steady state faster as they reached a steady state condition at around 60 seconds. The original geometry reactor did not obtain a steady state condition despite the longer duration of 900 seconds. Therefore the smaller volume reactors appeared to be more efficient at the beginning by degrading the concentration very quickly but were not able to reach as low of a final concentration as the larger original reactor volume of 36.42 cm^3 . The sphere reactor design with a volume of 4.546 cm^3 was substantially more efficient at reducing the Brilliant Blue dye concentration and was able to obtain a final value 0.0342 mol/m^3 from the original 0.04 mol/m^3 . This was a 14.47% reduction and the lowest value obtained during the research effort for the H_2O -IIR, with the exception of the 100% reflectance model. This discovery prompted the research team to test one more reactor design using a sphere with the higher volume of 36.42 cm^3 and investigate the results. Figure 50 outlines the findings of this model.

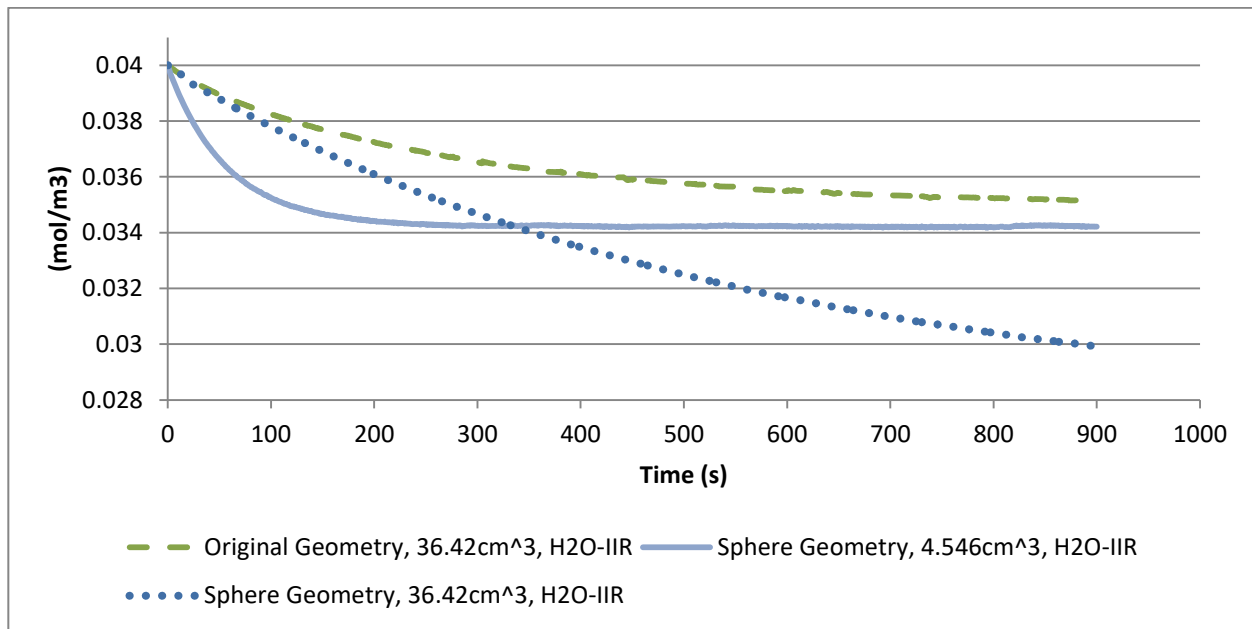


Figure 50: Degradation of Original, Sphere 4.546 cm^3 , and Sphere 36.42 cm^3 Geometry with H_2O -IIR, 10 mL/min Flow Rate

The result of this model was a surprise and was significantly lower than any H₂O-IIR values analyzed; again with the exception of the 100% reflectance model. The final concentration value for the larger sphere was 0.0299 mol/m³ from the initial 0.04 mol/m³ for a 25.19% reduction. Additionally, the curve was still degrading and had not yet approached a steady state condition when the simulation reached the 900 s end point.

Geometry Styles for Brilliant Blue Absorption Imaginary Refractive Index, $k=8.80E-7$

The models in this section used the BB-IIR. The results of the original geometry design with a volume of 36.42cm³, and three other reactor designs that all had the same volume of 4.546 cm³ can be seen in Figure 51. The three smaller reactors have the half scale reactor geometry, half scale with separator plate, and sphere. The average outflow concentration values were plotted and can be seen in Figure 51.

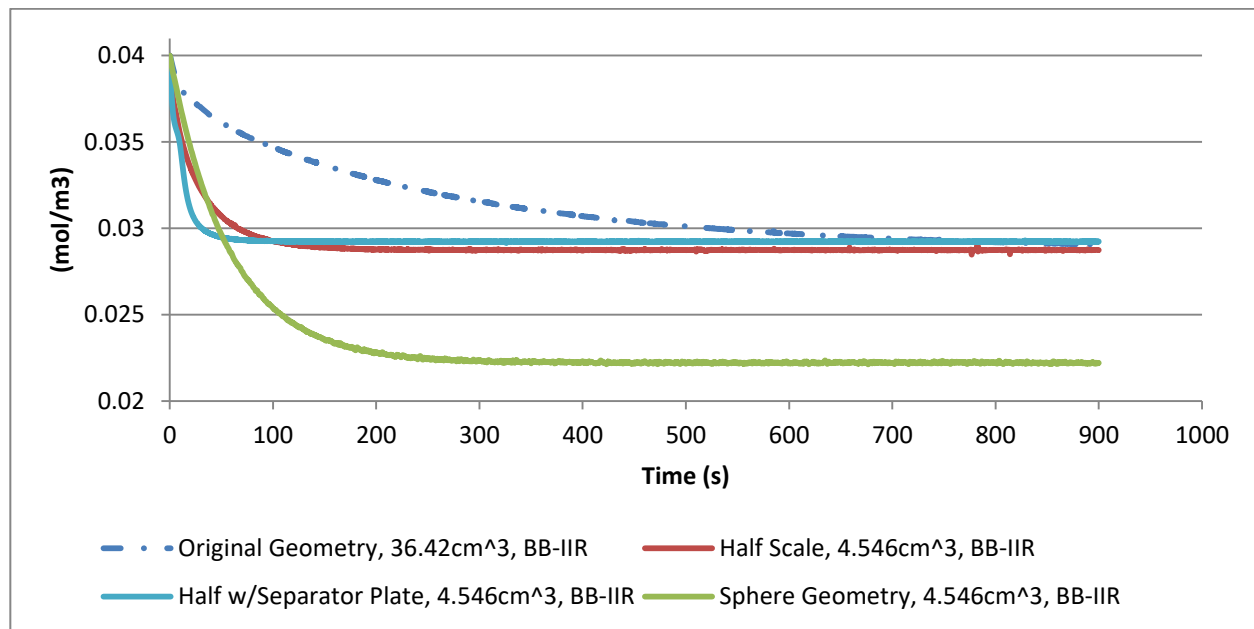


Figure 51: Degradation of Original, Half Scale, Half Scale with Separator Plate, and Sphere 4.546cm³

The original geometry, half scale, and half scale with separator plate geometries all had similar values around 0.028 mol/m^3 . The half scale being the most degraded of the three at 0.0273 mol/m^3 remaining. The two small volume reactors had similar degradation curves and obtained steady state by 120 seconds. However the larger volume of the original reactor was much slower to obtain a steady state value as its smaller brethren. The outlier was the sphere geometry again, similar to the H_2O -IIR models. The sphere geometry obtained a final value of 0.0222 mol/m^3 from an initial value of 0.04 mol/m^3 for a 44.50% reduction in concentration. Additionally, this reactor had one of the fastest degradation curves evaluated. This was a rapid reduction rate and was higher than anything observed for any of the models. As with the H_2O -IIR models, a larger 36.42 cm^3 volume sphere was tested. The results of this test can be seen in Figure 52.

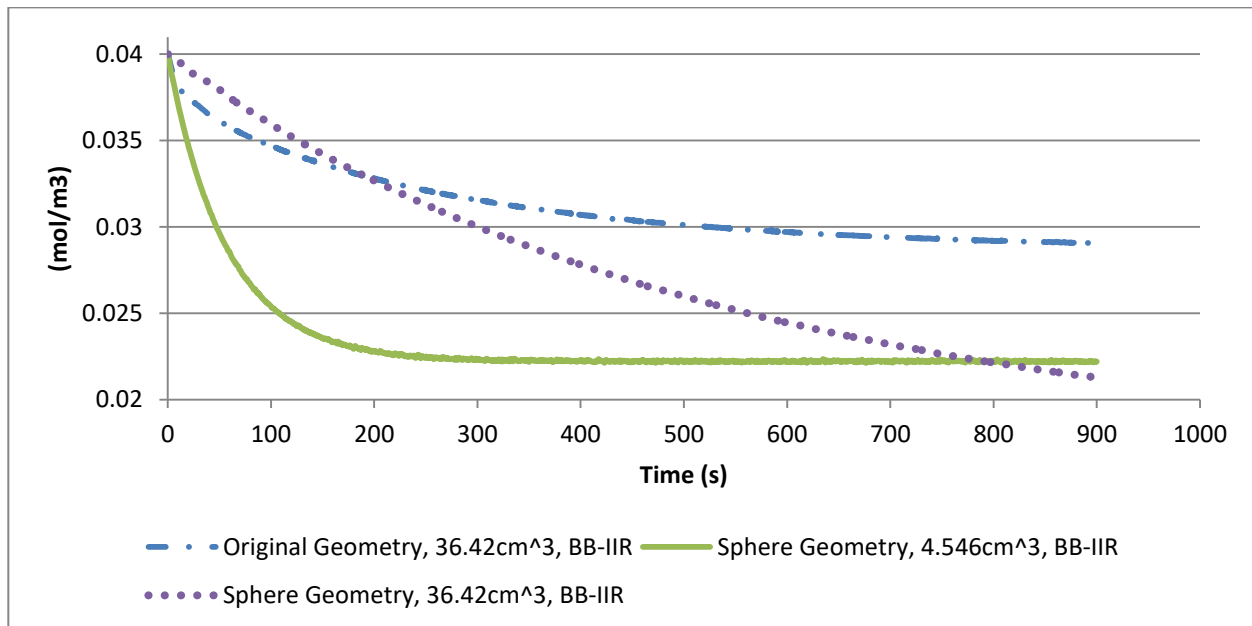


Figure 52: Degradation of Original Geometry 36.42 cm^3 , Sphere 4.546 cm^3 , and Sphere 36.42 cm^3

with BB-IIR, 10 mL/min Flow Rate

Similar to the H₂O-IIR large sphere geometry, the BB-IIR large sphere model obtained a reduction value that was higher than any others before it, for a final concentration value of 0.0213 mol/m³ with a reduction of 46.84%.

Analysis

One of the data gathering techniques was analyzing and logging the average concentration of the effluent pipe as it left the reactor. However, the average concentration values did not always outline the whole story. Some reactors had less variance and were mixed better than others, therefore providing a more uniform reduction rate as the solution exited the effluent pipe. When analyzing a chemical degradation process like the Brilliant Blue dye this is not a large concern, but when researching germicidal purification reactor designs, it is a very important factor. The variance of the effluent pipe could mean that some of the liquid and biological contaminants have been inactivated while others slip through the purification process. Therefore an important post processing technique was to analyze which reactor designs had the lowest variance from the effluent pipe. Figure 53 illustrates with the red line on the effluent pipe where the typical variance data was obtained for the reactors.

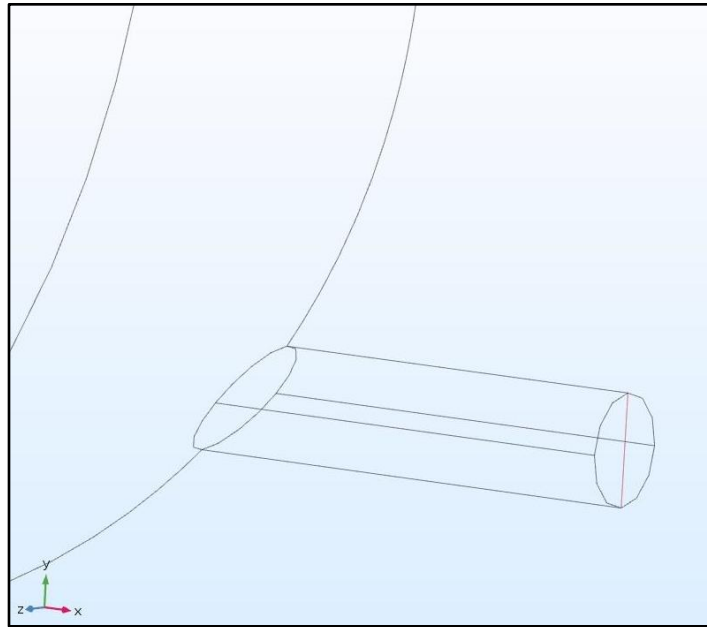


Figure 53: 3D Cut Line (COMSOL® v. 5.2. 2017)

The effluent pipe was measured using the 3D cut line feature and had data collected every 60 seconds starting at time zero for each reactor model. The data obtained was normalized by the average amount of the Brilliant Blue dye degraded at each point in time, permitting only the variance across the effluent pipe to be captured. This process allowed the variance to only show how much difference was present from the top of the cut line to the bottom with regards to change in concentration. Figure 54 illustrates the original data plot for the Sphere Model with a volume of 36.42 cm^3 which had lowest effluent flow variance and Figure 55 illustrates how the data appeared after normalization.

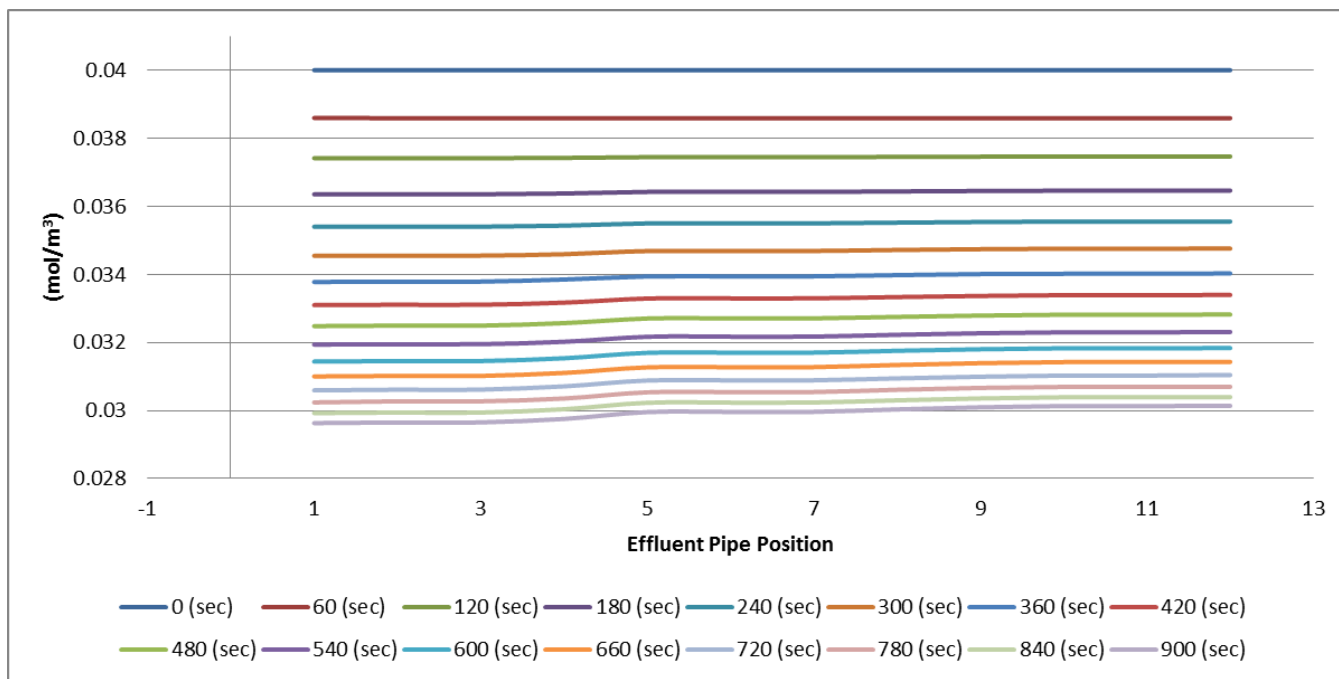


Figure 54: Original Data Plot for Sphere Model, 36.42cm³,
Effluent Pipe Concentration, 60 seconds Intervals

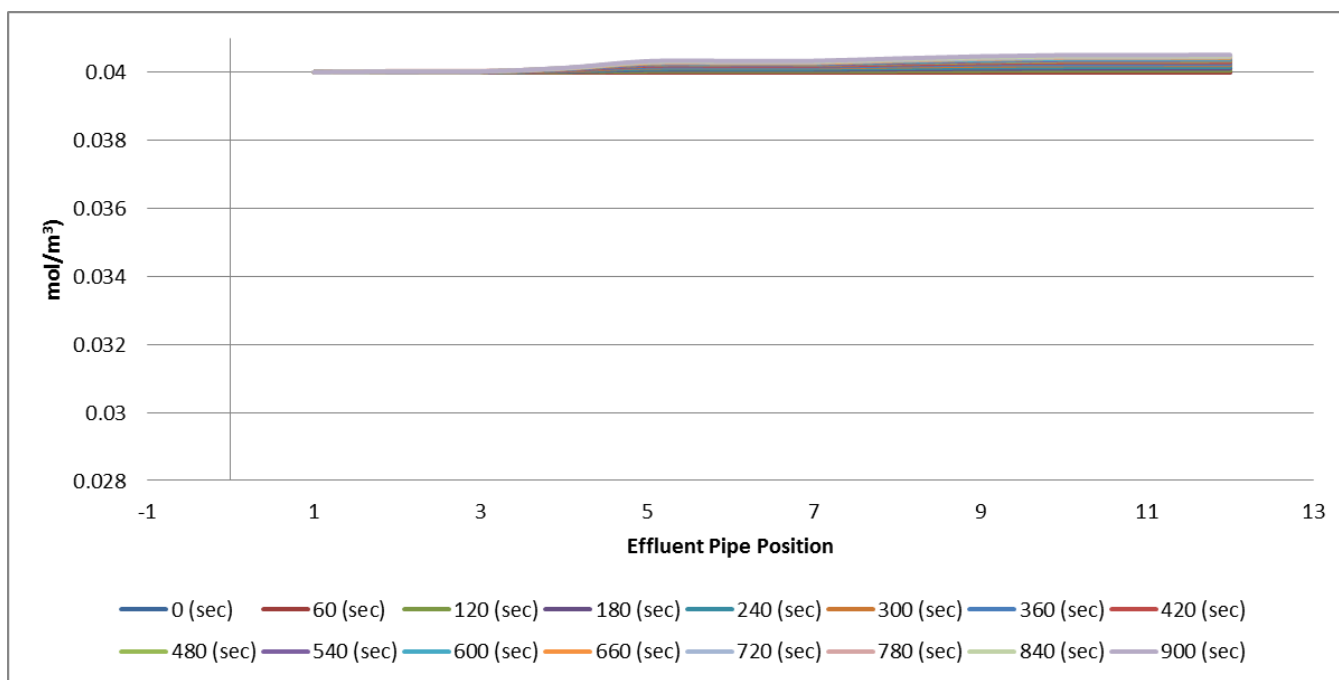


Figure 55: Normalized Data Plot for Sphere Model, 36.42cm³,
Effluent Pipe Concentration, 60 seconds Intervals

Figure 54 had virtually no change in concentration from the top position in the effluent pipe to the bottom, as illustrated with the small variation in vertical variance of the lines for each time interval. However the model had large concentration changes between the 60 second time intervals due to the degradation of the dye. When the data was normalized as seen in Figure 55 the only variance being analyzed is the difference in concentration along the vertical axis of the effluent pipe. This process illustrates how well the reactors have mixed the effluent concentration while removing any analysis of how effective the reactors are at overall concentration reduction. The variance was calculated for each reactor, compiled and sorted from lowest variance to highest in Table 5. This is an accurate representation of how the variance analysis can provide insight into the flow and reaction characteristics of a reactor design for germicidal disinfection purposes.

Table 5: Effluent Flow Variance

Geometry Type	Flow Rate (mL/min)	Refractive Imaginary Index (k)	Volume (cm ³)	Effluent Flow Variance
Sphere	10	H ₂ O-IIR	36.42	2.501E-08
Sphere	10	BB-IIR	36.42	4.917E-08
Original Geometry	10	H ₂ O-IIR	36.42	7.241E-08
Half Scale Original Geometry	10	H ₂ O-IIR	4.546	7.842E-08
Original Geometry	8	H ₂ O-IIR	36.42	9.628E-08
Half Scale Original Geometry with Separator Plate	10	H ₂ O-IIR	4.546	1.131E-07
Sphere	10	H ₂ O-IIR	4.546	1.444E-07
Original Geometry	6	H ₂ O-IIR	36.42	2.050E-07
Half Scale Original Geometry with Separator Plate	10	BB-IIR	4.546	7.830E-07
Sphere	10	BB-IIR	4.546	1.186E-06
Original Geometry	10	BB-IIR	36.42	4.734E-06
Half Scale Original Geometry	10	BB-IIR	4.546	6.003E-06
Original Geometry	8	BB-IIR	36.42	6.138E-06
Original Geometry	6	BB-IIR	36.42	9.293E-06

When analyzing the different reactor designs it was evident that the sphere design was the most efficient respectfully for both volumes and IIR indices. This result was a surprise to the research team, especially since Ducoste (Jenny et al. 2014) utilized a plate separator reactor design similar in design parameters to the half scale original geometry with separator plate design. It was thought that the longer flow profile of the water while in the reactor volume would be more efficient then reactors of the same volume. This hypothesis was disproved however when the sphere designs where substantially more efficient. The research team investigated the parameters of each reactor and discovered a pattern emerging when relating the volume of the geometries and the surface areas. Table 6 illustrates the five reactor designs and their corresponding volumes and internal surface areas. A simple surface area to volume ratio was calculated to compare designs to each other.

Table 6: Surface Area to Volume Ratio's

Reactor	Surface Area (cm ²)	Volume (cm ³)	Ratio (Surface/Volume)
Sphere	53.62	36.42	1.47
Original Geometry	71.75	36.42	1.97
Sphere	13.50	4.55	2.97
Half Scale Geometry	18.30	4.55	4.03
Half Scale Geometry with Separator Plate	28.51	4.55	6.27

The next step was to rank all the reactors that were analyzed and to attempt to illustrate numerically which reactor was the most efficient at reducing the Brilliant Blue dye concentration as seen in Table 7 for all 10 mL/min flow rate reactors.

Table 7: 10 mL/min Reactor Flow Rates Percent Degraded Ranking

<u>Only 10 mL/min Flow Rates</u>					
Geometry Type	Flow Rate (mL/min)	Imaginary Index of Refraction (k)	Volume (cm ³)	Final Outlet Flow Value (mol/m ³)	% Degraded, Final Data Point
Sphere	10	BB-IIR	36.42	0.0213	46.84%
Sphere	10	BB-IIR	4.546	0.0222	44.50%
Original Geometry, 100% Reflectance	10	H ₂ O-IIR	36.42	0.0280	30.05%
Half Scale Original Geometry	10	BB-IIR	4.546	0.0287	28.16%
Original Geometry	10	BB-IIR	36.42	0.0291	27.35%
Half Scale Original Geometry with Separator Plate	10	BB-IIR	4.546	0.0293	26.65%
Sphere	10	H ₂ O-IIR	36.42	0.0299	25.19%
Sphere	10	H ₂ O-IIR	4.546	0.0342	14.47%
Original Geometry	10	H ₂ O-IIR	36.42	0.0351	12.16%
Half Scale Original Geometry	10	H ₂ O-IIR	4.546	0.0370	7.38%
Half Scale Original Geometry with Separator Plate	10	H ₂ O-IIR	4.546	0.0374	6.39%

After this step was performed a clear pattern emerged. The spheres were both the most efficient for their respective IIR values with the larger volume being slightly more efficient than the smaller device. However, the smaller devices were able to obtain their steady state conditions within the first 120 seconds and the larger volume spheres had still not obtained their steady state conditions at 900 seconds. When comparing the surface area to volume ratio it to the percent degraded value for the H₂O-IIR the reactor rankings almost matched up perfectly as seen in Table 8.

Table 8: Reactor Rankings, H₂O-IIR

Reactor	Ratio Rank (Surface/Volume)	% Degraded Rank for $k=3.15E-8$	Rank Difference
Sphere, 36.42cm ³	1	1	0
Original Geometry, 36.42cm ³	2	3	-1
Sphere, 4.546cm ³	3	2	1
Half Scale Geometry, 4.546cm ³	4	4	0
Half Scale Geometry with Separator Plate, 4.546cm ³	5	5	0

The surface area to volume ratio is lowest for the spheres. The proposed explanation to this relationship has to do with surface area to volume ratio and the connection to the Teflon absorption value of 5%. The lower the surface area:volume ratio, the longer the average ray can travel before encountering a reactor wall. With a 5% chance of absorption for these models, the more opportunities a ray has to strike a wall and be absorbed, the higher the chance that the reactor will lose power due to ray wall interaction verses power loss in the liquid. Therefore, reactors with lower surface:volume ratios appear to be more efficient by design for their respective volumes. There also seems to be a relationship between the reactor volumes to the reactor efficiency value as well. According to the surface area:volume ratio theory the original geometry reactor should be the second most efficient tested, however it is the third. Therefore there is a relation between the volume of the reactor and the surface area:volume ratio. This relationship is something that could be investigated further using COMSOLs[®] optimization modules for future research. To validate this theory the research team investigated if the surface area:volume ratio and reactor volume theory held up when analyzing the different BB-IIR index. At first glance it appeared not apply as well as for the H₂O-IIR, as shown in Table 9.

Table 9: Reactor Rankings, BB-IIR

Reactor	Ratio (Surface/Volume)	% Degraded, Final Data Point	Difference
Sphere, 36.42cm ³	1	1	0
Original Geometry, 36.42cm ³	2	4	-2
Sphere, 4.546cm ³	3	2	1
Half Scale Geometry, 4.546cm ³	4	3	1
Half Scale Geometry with Separator Plate, 4.546cm ³	5	5	0

Investigation of the effects of the Brilliant Blue absorption index and how it discharges the ray's power around the ray release point created a concentrated reaction zone near the UV LED release points. This effect would cause the reactor to be effected more by the surface area:volume ratio than a reactor with a larger overall volume. There still appears to be a relationship between surface area:volume ratios and the overall reactor volume. However, the original geometry reactor moved from third to fourth when being evaluated for percent concentration reduction and the other geometry styles didn't change positions. This highlights that the volume has less of an impact on reactor efficiency than the surface area:volume ratio for high absorbent solutions.

This effect is further supported when analyzing the power curve for 100% reflectance H₂O-IIR model. Without the rays being absorbed by the reactor walls to dissipate the ray power, the simulation required over twice as long, increasing from 4 ns to 8 ns. For a low absorbent solution, like pure water, as might be used for a germicidal point-of-use disinfection device, keeping the surface area:volume ratio as

low as possible will produce a reactor that has the highest efficiency compared to other reactor designs of the same volume. Additionally, the results showed that increasing the reactor volume on a spherical reactor design would potentially provide a higher steady state reactor efficiency value but at the cost of increasing the time required to reach steady state. This tradeoff between reactor efficiency and reaction rate should be investigated further using the COMSOL[®] optimization module and verified experimentally.

VI. Conclusions and Recommendations

Conclusions of Research

A primary goal of this thesis was to construct a COMSOL[®] model which could be used to predict the degradation of Brilliant Blue dye in an AOP conducted in a flow-through reactor. Although the concentration produced by the model was normalized compared to the laboratory data, the model successfully predicted the general shape of the degradation curve. The model was then calibrated through an iterative process that adapted the model to fit the 10 mL/min flow rate curve for the laboratory data. This change was an attempt to account for an incorrect assumption that every hydroxyl radical created via the reaction rate equation would degrade a Brilliant Blue dye molecule. Although it was predicted that this assumption was likely incorrect, literature was not identified to justify any alternate assumption. Based upon this calibration, it would appear that approximately 1 in 4 (i.e., 23.87%) Brilliant Blue dye molecules were degraded for every hydroxyl radical generated under this condition.

After the model was adapted for the 10 mL/min flow rate, a series of runs using 6, 8, and 10 mL/min flow rates and the BB-IIR and H₂O-IIR values were conducted. The IIR indices were selected to represent the absorbance of the Brilliant Blue dye solution, based on laboratory results, and for pure water, as published within the literature. Reduction in the flow rate, resulted in model-generated degradation curves which were progressively lower than the laboratory-obtained degradation curves. This issue was believed to be caused by higher hydroxyl radical-dye molecule reaction rates with the increased mixing that was present at higher flow rates, a factor not accounted for in the COMSOL[®] model. Future models should therefore consider inclusion of this factor. When the IIR was adjusted to represent pure water absorption rates, it was found that the reactors performed significantly less efficiently (resulted in less dye degradation) than when the IIR represented the Brilliant Blue solution

absorption. It was discovered that this issue was related to the reactor wall absorption rate, as each light ray had a 5% chance of being absorbed every time a wall was struck. When the reactor wall reflection was changed to 100%, the reactor was more efficient using the H₂O-IIR than the BB-IIR value. Although the models were not able to perfectly predict their corresponding laboratory data sets, they did predict the shape of the curves reasonably considering the course assumptions regarding chemical reactions within the reactor.

After the model was validated for 10 mL/min flow rates, five different reactor geometries were analyzed using the same BB-IIR and H₂O-IIR indices. The analysis revealed a distinct relationship between the efficiency of the reactor and the ratio of the internal surface area to volume of the reactor geometry. Larger ratios of reactor internal surface area to volume resulted in less efficient reactors. The research also showed that increases in reactor volume generally resulted in improvements in reactor efficiency, at least for reactors with the same general reactor designs (i.e. sphere to sphere), but higher volumes also resulted in lower final concentration values and a more gradual reduction in dye concentration for the same flow rate and time interval (i.e. 10 mL/min, 900 seconds). Whereas the smaller volume reactors degraded the dye less and obtained steady state conditions much faster than their larger counterparts. This analysis is extremely important to future reactor research. Reactors with higher volumes have the ability to obtain much higher degradation values with equal flow rates but it takes much longer for them to obtain a steady state condition. Therefore reactors which are likely to require frequent on-off cycling similar to a hydration pack point-of-use device should have as low as possible internal surface:volume ratio, as well as, a low overall volume. This will allow the device to obtain a steady state condition very quickly while maximizing the efficiency of the device for the given volume. Due to this design parameter, a very small reactor volume with the same flow rate will not be able to obtain as high of a final degradation value and is therefore disadvantaged when maximum efficiency is required. The

tradeoff between surface area/volume ratio, flow rates, and volumes will dictate the reactor designs for future reactors, depending on requirements of high efficiency or high flow rates. The research data shows that as reactor reflectance approaches 100%, the geometry of reactor has less of an effect on the performance of the device. Efficiency of these reactors will depend more on the volume of the device, as well as the absorbance of the liquid being treated.

Investigate Questions

This thesis sought to answer multiple research questions. Research question one asked “What inputs were needed to develop a strong computer model that will successfully predict the reaction process of an UV LED reactor?” Throughout the research effort, significant parameters and input values were needed to successfully create a model that had the ability to predict the reaction conditions seen in the laboratory data. Many expected parameters regarding the geometry of the reactor, reflectance of the reactor material, light output of the LEDs, placement of the LEDs, and solution flow rate were included in the model. Two difficult to obtain parameters were also required for the research models. The first was the Imaginary Index of Refraction (IIR) value for the Brilliant Blue dye solution. As stated in chapter three, COMSOL[®] is a physics based modeling program and is not always designed to accept the direct data gathered in laboratories. Through an exhaustive literature search, conversations with experts in the field and COMSOL[®] technical support there was not a convenient method to convert the absorption values found in the laboratory to the COMSOL[®] parameter of IIR, which was necessary to determine the extinction coefficient of light rays within the reactor. Through modeling known parameters, a method was developed to convert from the chemistry/engineering domain absorption values obtained in the laboratory to the IIR applied in the physics realm. The second difficult to obtain parameter arose during development of the reaction rate equation used in the Transport of Diluted Species module. This

equation was the lynch pin to the research effort and was the method that COMSOL[®] used to calculate the degradation curves. This equation was derived, but the efficiency of hydroxyl radical-dye combination rate was simply assumed, and then later calibrated.

The second and third questions asked what methods could be used to validate the computer model. This research answered these questions by using an existing reactor that had been developed for other purposes and analyzed it using multiple flow rates in a laboratory AOP experiment. The UV LED reactor utilized a Brilliant Blue dye and hydrogen peroxide solution to perform an advanced oxidation process (AOP) to gather the degradation curves as the solution was passed through the reactor. These curves were then compared to output curves that COMSOL[®] produced. It was found that the initial reaction equation constant was incorrect and had to be adjusted to account for the unknown hydroxyl radical to Brilliant Blue molecule degradation efficiency value. An initial degradation curve was similar in shape to the laboratory data but the scale of the degradation axis was incorrect. After the correction was made, the degradation curves for three flow rates were compared to their respective laboratory curves. The research pointed to an unknown parameter that involved natural mixing of the reactor and flow rates. This parameter is necessary to alter the degradation rate of the dye by hydroxyl radicals as flow rates change. This relationship could be accounted for in future research to provide a more accurate and robust model. Overall the COMSOL[®] model provided a reasonable prediction of the laboratory degradation curves for a first generation model.

The final question asked, “What effect does changing the reactor geometry and UV LED placements have on the efficiency of a reactor?” This question led to analyzing five different reactor designs and volumes for both the BB-IIR and H₂O-IIR values. The data indicated that the lower the surface area to volume ratio of the reactor, the more efficient the reactor is when reactor volume is held constant. The research also illustrated that different volumes of reactors would produce different

concentration reduction curves. The data illustrated that as the volume of a reactor decreased, the rate of degradation increased and obtained a steady state value much quicker than larger volume reactors. However, a larger reactor volume was able to obtain a higher degradation value than the smaller reactors. This trade off was due to the dwell time of the solution as it stayed in a larger reactor longer, therefore enabling it to absorb more energy and degrade more of the solution.

Significance of Research

The ability for COMSOL[®] to successfully predict the degradation curves from laboratory tests shows that the software has the ability to predict the complex reaction processes that occur in a UV LED reactor with an AOP process. This research also showed that there was a direct relationship between the surface area to volume ratio, reactor volume, and flow rates to reactor performance. Reactors with lower internal surface area;volume ratio had higher reaction efficiencies than alternate reactors of the same volume. Additionally, changing the volume to flow rate ratio would have an effect on the reactor characteristics. This was seen when analyzing the effluent outflow cut line data and the variance. A reactor that was mixed well usually produced a lower variance value thus indicating a more uniform reaction process within the reactor. Furthermore, a reactor with the same flow rate, but lower volume would degrade the solution much faster and obtain a steady state condition significantly faster than a reactor of larger volume.

This discovery is critical to furthering the germicidal water purification reactor research effort. For example, if the reactor is to be a point-of-use reactor, this research shows that the lower the surface area to volume ratio obtained, the more efficient the reactor will be for liquids with low optical absorbance. This results from the interaction between the ray path length and the absorbance of the reactor walls. Maximizing the volume of a reactor while minimizing the area of walls encountered will

reduce the chance the UV rays lose power due to wall interactions versus losing power in the liquid. Secondly, having a lower volume will ensure the reactor chamber will inactivate the biological contaminants faster than a larger volume. Conversely if the reactor will be a larger reactor, like seen in a semi-permanent water purification devices like a ROWPU's used by the DoD in remote environments, a slower flow rate, large volume reactor that has time to obtain a steady state condition will provide a more efficient solution.

Recommendations for Future Research

Throughout the research, other parameters were discovered that needed to be researched to produce a more robust model. The two most important unknown parameters would be developing an Imaginary Index of Refraction equation that varied the 'k' value of the model as the dye solution was degraded. This research is not as important for germicidal research efforts but would be a must for further research of the Advanced Oxidation Process. The second key parameter to investigate would be the effect that natural reactor mixing has on the reaction equation, specifically the reaction rate constant. This constant needs to be converted to a reaction rate constant equation that incorporates flow rates and mixing characteristics within the reactor for optimal results or the model needs to be expanded to further describe the chemical reactions.

Other research efforts should investigate the relationships between the surface area to volume ratio and a more detailed analysis of its relationship between flow rates, reactor volumes, and the effect that reactor vessel reflectance has on concentration reduction. Specifically, these relationships should be validated through laboratory evaluation. Other research efforts could include analyzing the effects of varying the UV LED release locations in the reactor and the impact it has on reactor efficiency. Another important research effort should investigate COMSOL's[®] ability to analyze individual particles as they

flow through the reactor to ensure all particles have received the target 40 mJ/cm^2 set forth in the NSF P248 for germicidal water purification devices (International 2012). Lastly, this thesis was limited to the number of geometries and reactor configurations that could be evaluated within a reasonable time as each run required between 3 and 22 hours to complete. Future efforts should investigate installing COMSOL[®] on a network with super computing capabilities to expedite the computational requirements.

Summary

This research effort was able to successfully validate that COMSOL[®] multiphysics models have the ability to successfully predict the advanced oxidization process (AOP) with Brilliant Blue dye from laboratory tests. The process of validation discovered a few items where more research is needed to be able to implement future models before a fully robust model can be developed. However for a first generation model, COMSOL[®] was able to successfully predict the AOP process performed in the laboratory reactor. Additionally, the research discovered that the surface area to volume ratio, flow rate, reactor volume, and reactor material reflectance values played a large role in the efficiency of a reactor design. The research showed that for a given volume and flow rate the most efficient reactor was one that minimized the surface area to volume ratio.

Appendix A- Brilliant Blue and Hydrogen Peroxide AOP UV LED Experimental Setup

Mix hydrogen peroxide (5 mmol) and Brilliant Blue dye (0.01 mmol) solution:

- 1) Fill 1L volumetric flask with 700mL of reverse osmosis deionized water then add stir bar
- 2) Add 0.03 mmol Brilliant Blue dye to 700mL of reverse osmosis deionized water
- 3) Add 15.0 mmol Hydrogen Peroxide to 700mL of reverse osmosis deionized water and Brilliant Blue dye solution
- 4) Fill flask with reverse osmosis deionized water to 750 mL and use stir plate to stir solution for 15 minutes

UV LED and Heat Sink Assembly:

The reactor was already assembled from previous research efforts. However, the copper slug was located over the UV LED. The positive wire led and negative wires were soldered to the UV LED leads with heat shrink material in place.

Reactor Assembly:

The reactor assembly consisted of the center body and two end caps with heatsinks mounted to the end caps via two hex-head screws. The end caps had o-rings installed in the respective o-ring grooves to ensure the reactor would not leak between the body and end caps. Refer to Figure 56 for UV LED Reactor assembly.

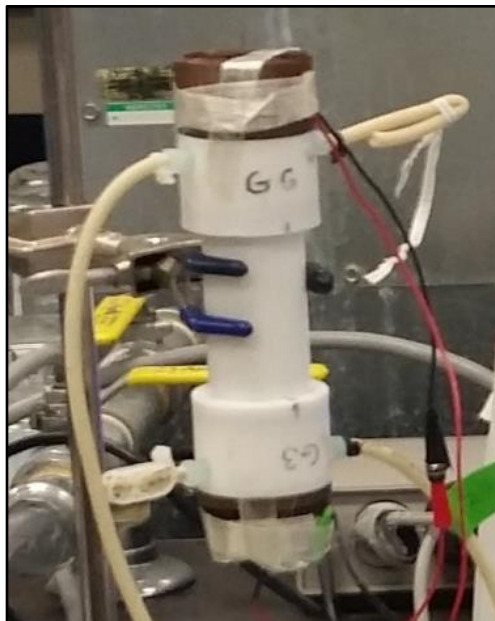


Figure 56: Reactor Assembly

Set up Cary-60 UV-Vis Spectrophotometer:

- 1) Log on to desktop- Username:Cary60; no password
- 2) Open “Cary 60” program
- 3) Open “Scan” File
- 4) Click “setup”
- 5) X-mode= Start at 625nm Stop at 635nm
- 6) Cycle Mode= Count=151, Time=10 Minute
- 7) Scan controls=Fastest
- 8) Insert DI water into Cuvette, and insert Cuvette into Spectrophotometer
- 9) Click “Zero”

Run Experiment

- 1) Setup tubing through peristaltic pump

- 2) Insert one end of tubing into Brilliant Blue dye and hydrogen peroxide solution and the other end to bottom cap of reactor (DO NOT ATTACH TUBING TO TOP CAP YET- It may cause an air bubble in the next step, which may pop apart the reactor)
- 3) Rotate reactor's clamp so that it is holding the reactor horizontally- This is done to release air out of the top hose barb while filling with solution
- 4) Start pump and increase flow rate to desired speed- Be careful not to load too fast, as this may cause excess pressure in reactor, and pop it apart
- 5) Once solution starts to flow out of top hose barb, stop pump, rotate and tighten down clamp so that reactor is vertical again, start pump, and adjust pump to experimental speed
- 6) Attach tubing to top cap and run to UV-Vis Cuvette
- 7) Watch the cuvette fill and make sure there are no air bubbles
- 8) Attach final tubing from cuvette to collection container
- 9) Close UV-Vis lid as close to tubing as possible, and then place a piece of paper over the remaining opening of lid
- 10) Start UV-Vis program and turn on the UV LEDs set at 200 mA

These experimental process steps were modified from Capt. Drew Gallucci research(Gallucci 2016).

Figure 58 illustrates the BK Precision power supply settings.



Figure 57: Power Supply Settings

**Appendix B – Reactor Geometry, Mesh Layout, Ray Propagation, Velocity Field, Slice
Concentration**

Original Geometry, 36.42 cm³, Brilliant Blue k=8.80E-7 at 6 mL/min

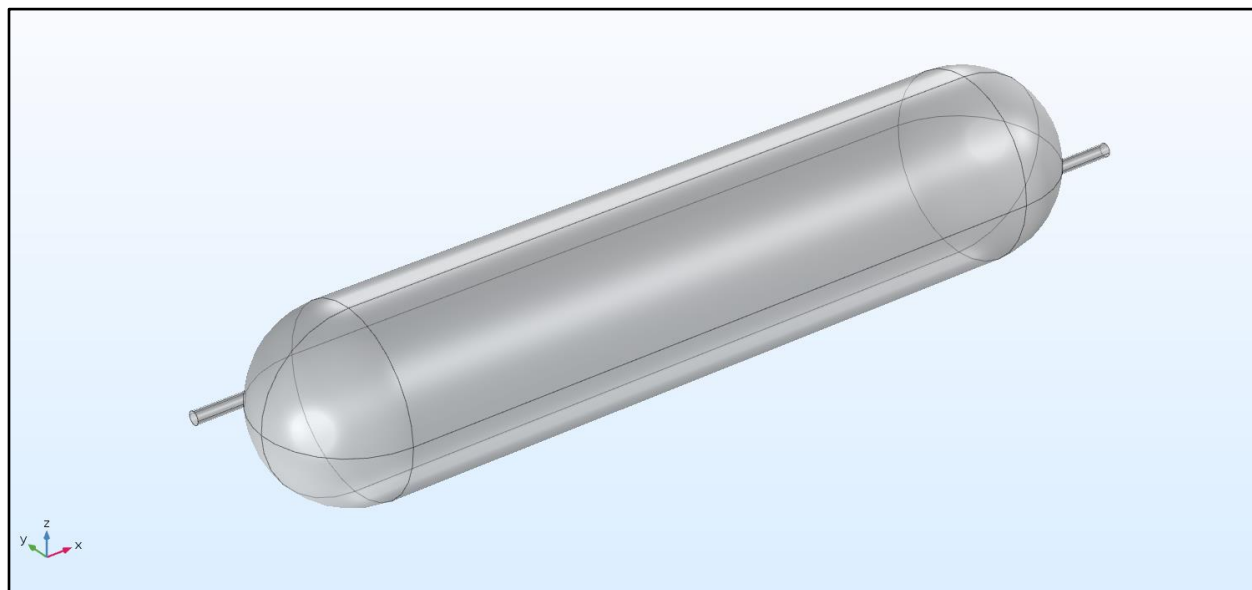


Figure 58: Original Geometry 6 mL/min, Isometric (COMSOL® v. 5.2. 2017)

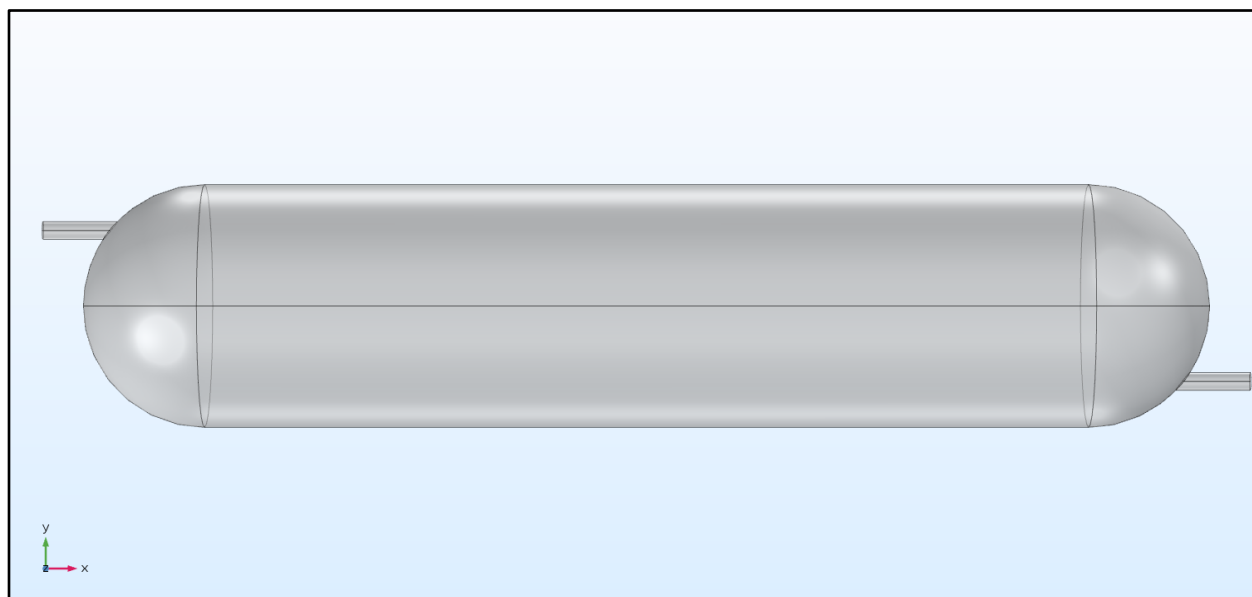


Figure 59: Original Geometry 6 mL/min, X-Axis (COMSOL® v. 5.2. 2017)

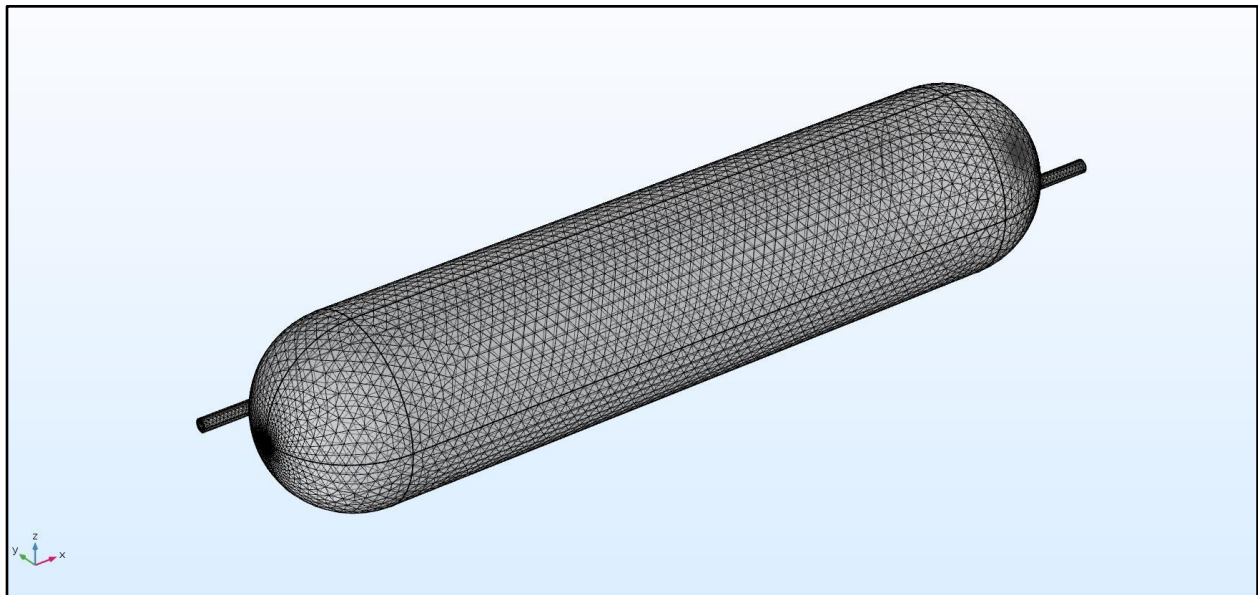


Figure 60: Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)



Figure 61: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)

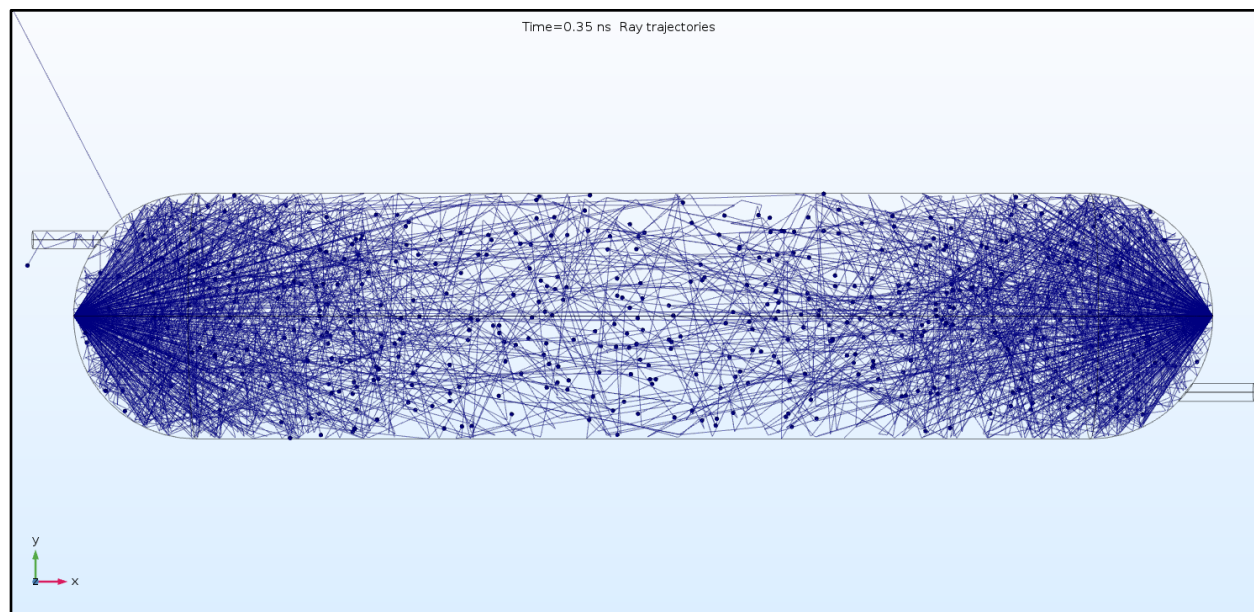


Figure 62: Ray Propagation at 0.35 ns, $k=8.80E-7$ (COMSOL® v. 5.2. 2017)

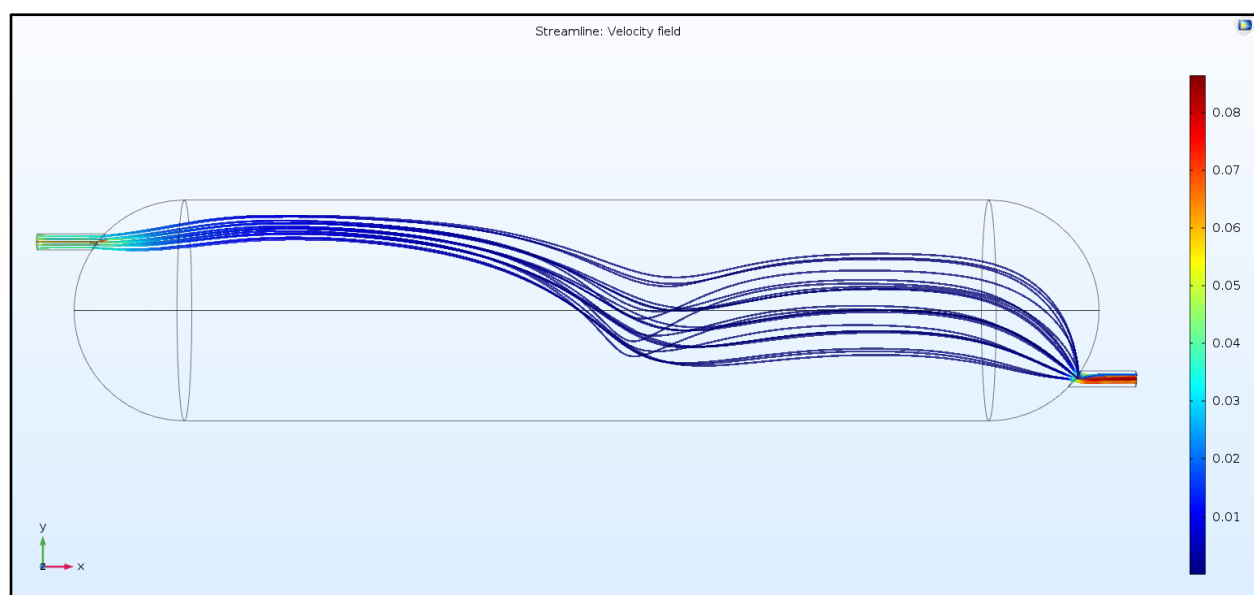


Figure 63: 6 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

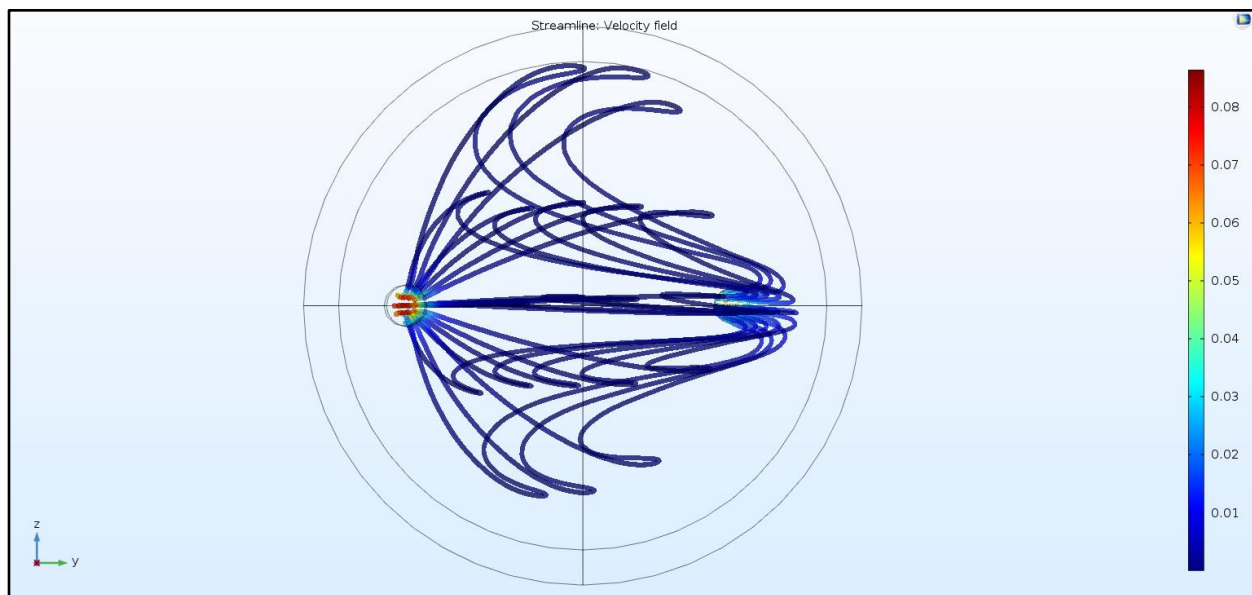


Figure 64: 6 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

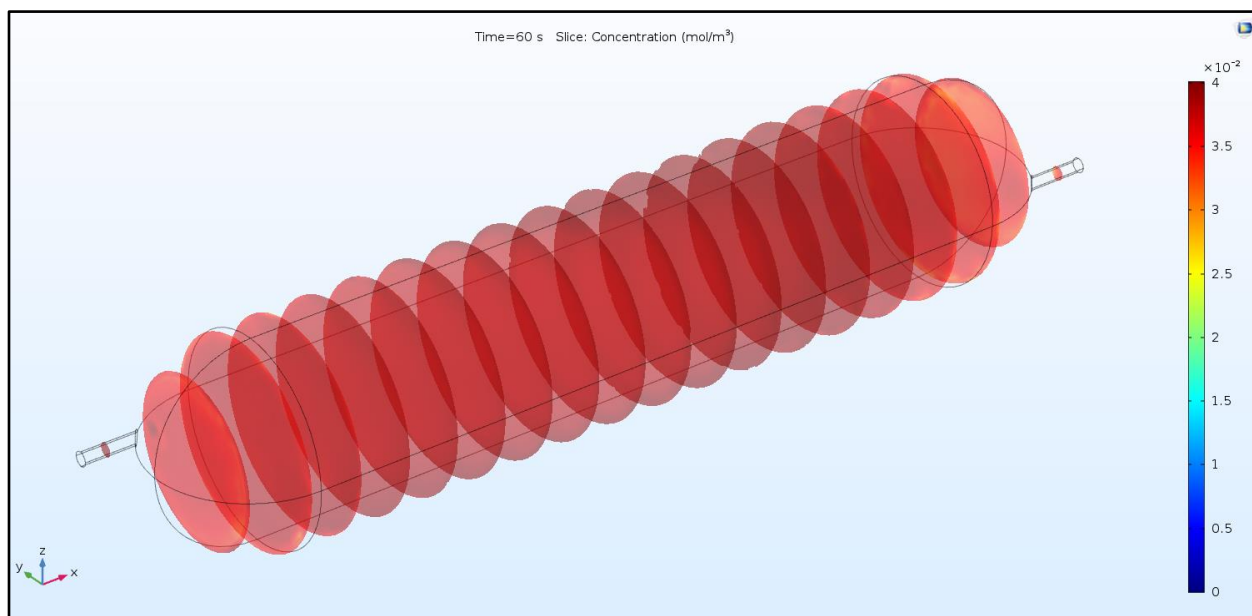


Figure 65: Slice Concentration 6mL/min, $k=8.80E-7$, 60 seconds (COMSOL® v. 5.2. 2017)

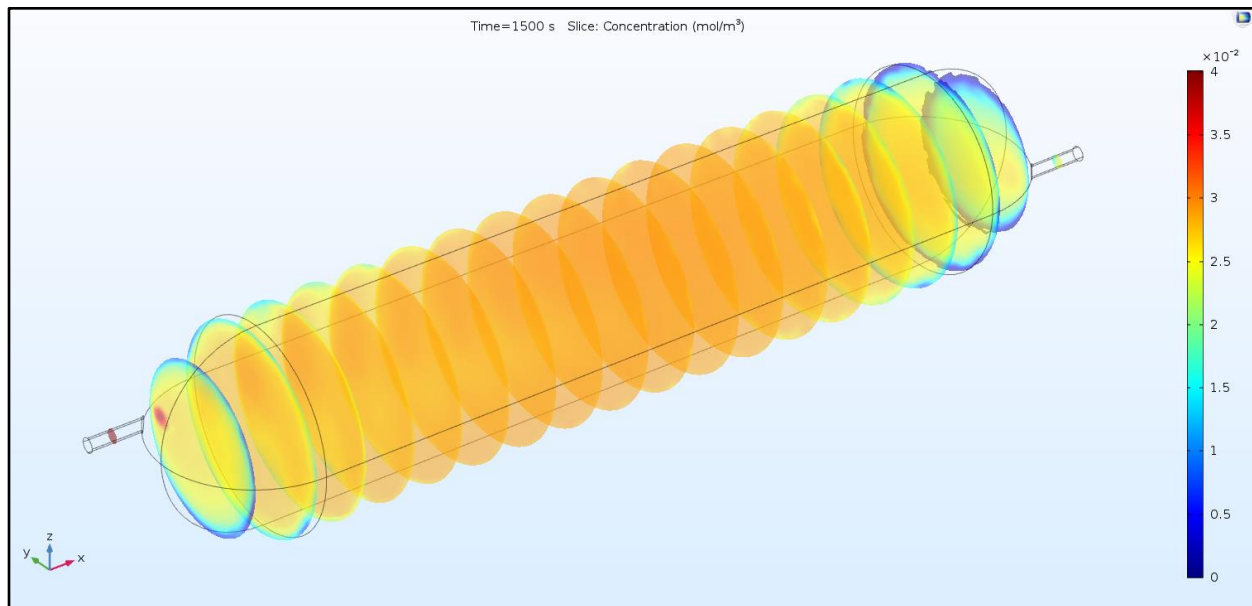


Figure 66: Slice Concentration 6mL/min, $k=8.80\text{E-}7$, 1500 seconds (COMSOL® v. 5.2. 2017)

Original Geometry, 36.42 cm³, Pure Water $k=3.15\text{E-}$ at 6 mL/min

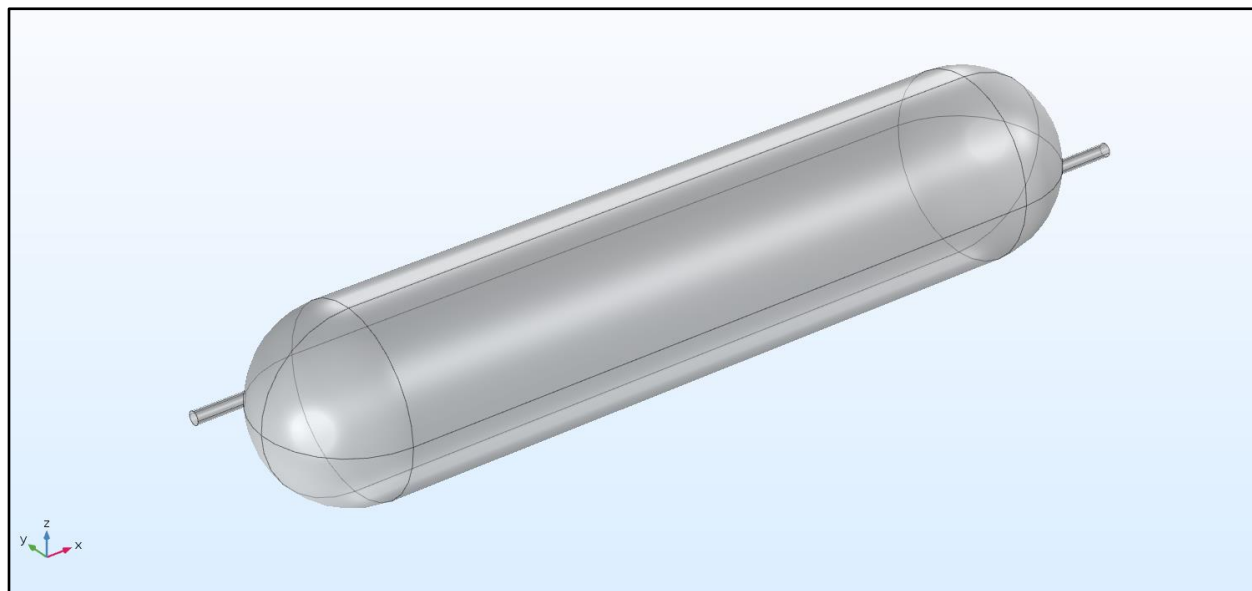


Figure 67: Original Geometry 6 mL/min, Isometric (COMSOL® v. 5.2. 2017)

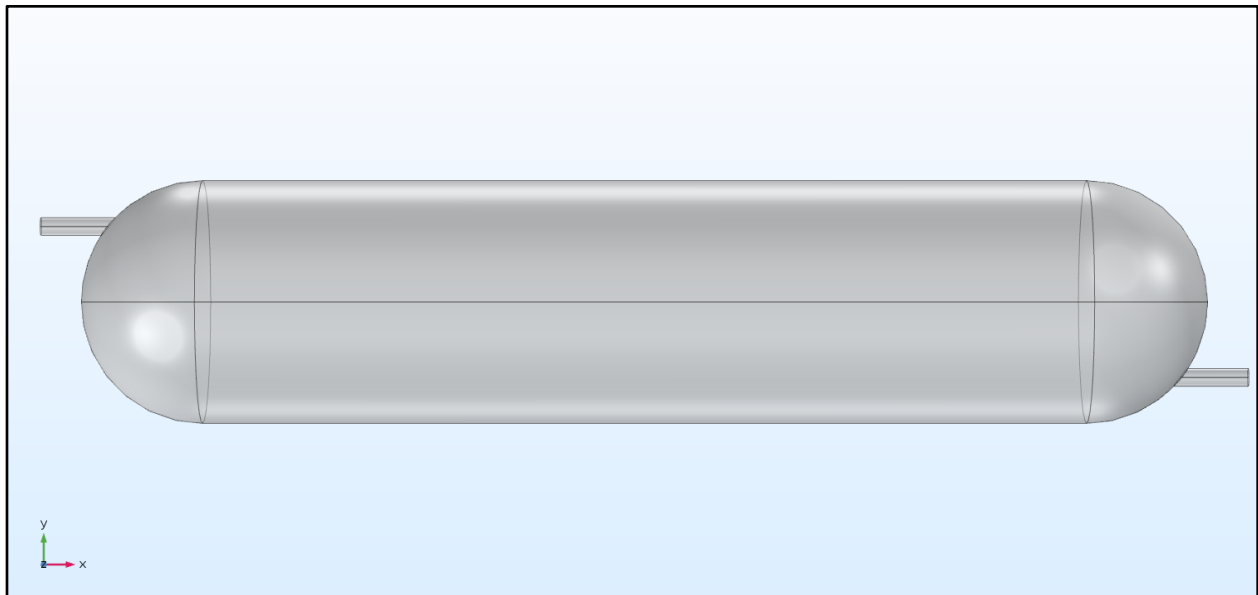


Figure 68: Original Geometry 6 mL/min, X-Axis (COMSOL® v. 5.2. 2017)

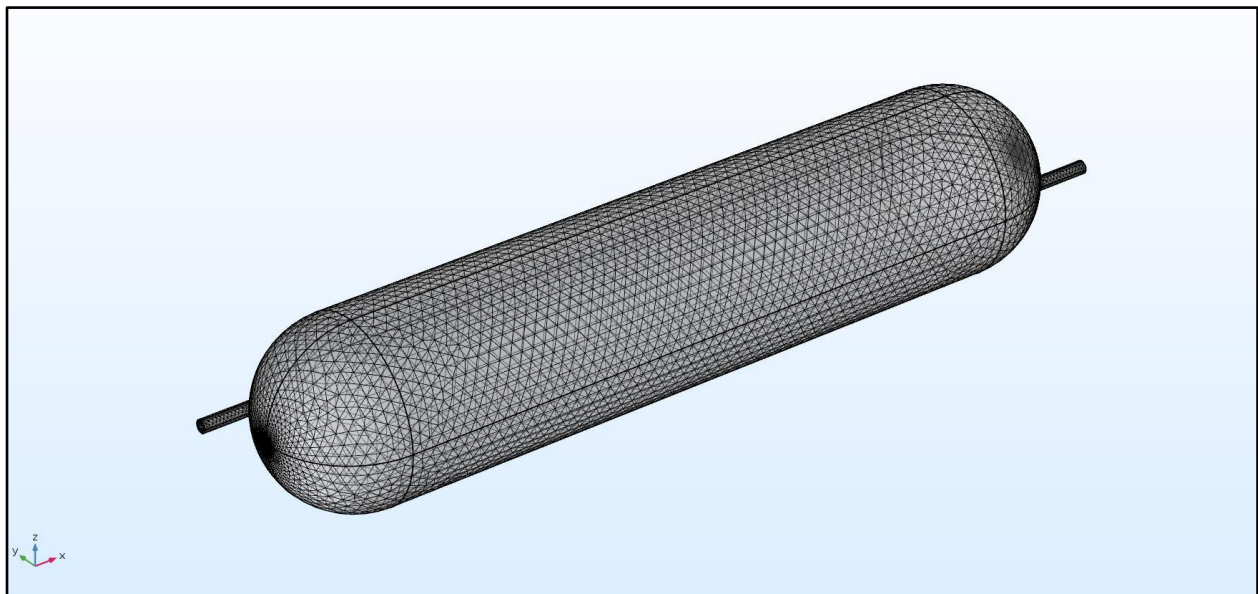


Figure 69: Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)



Figure 70: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)

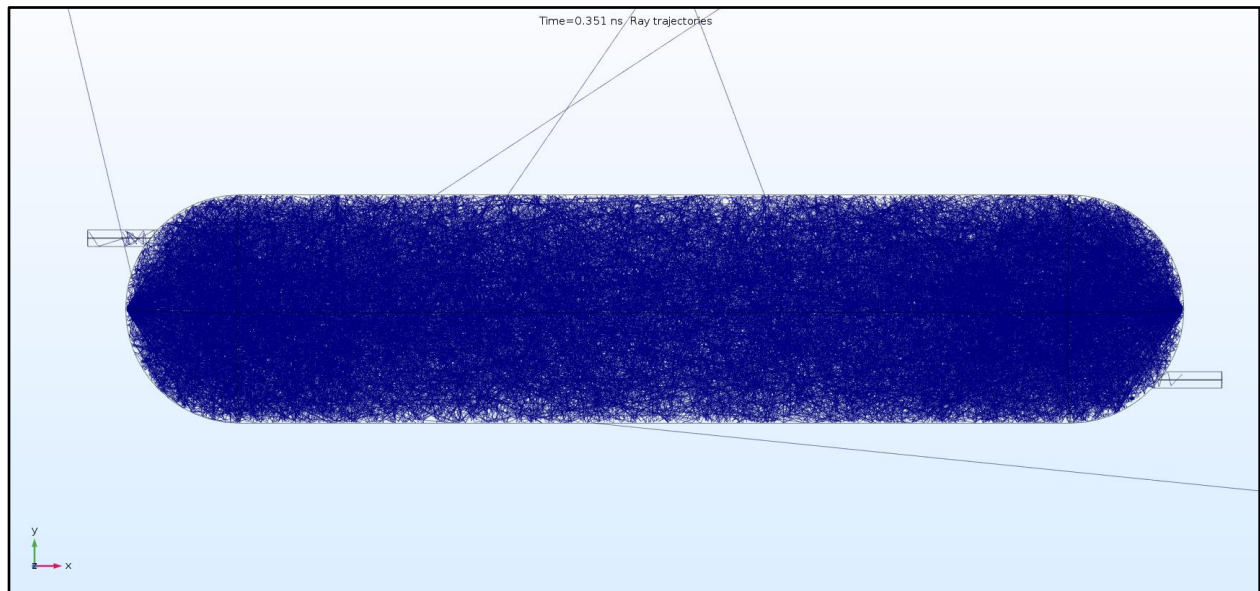


Figure 71: Ray Propagation at 4.0 ns, $k=3.15E-8$ (COMSOL® v. 5.2. 2017)

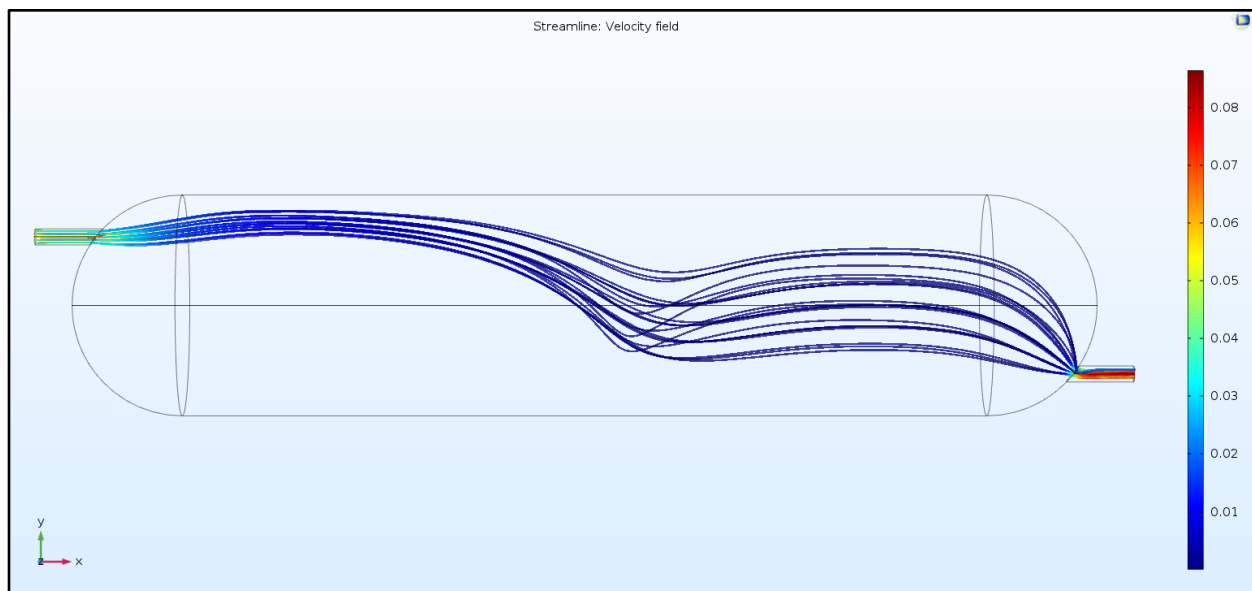


Figure 72: 6 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

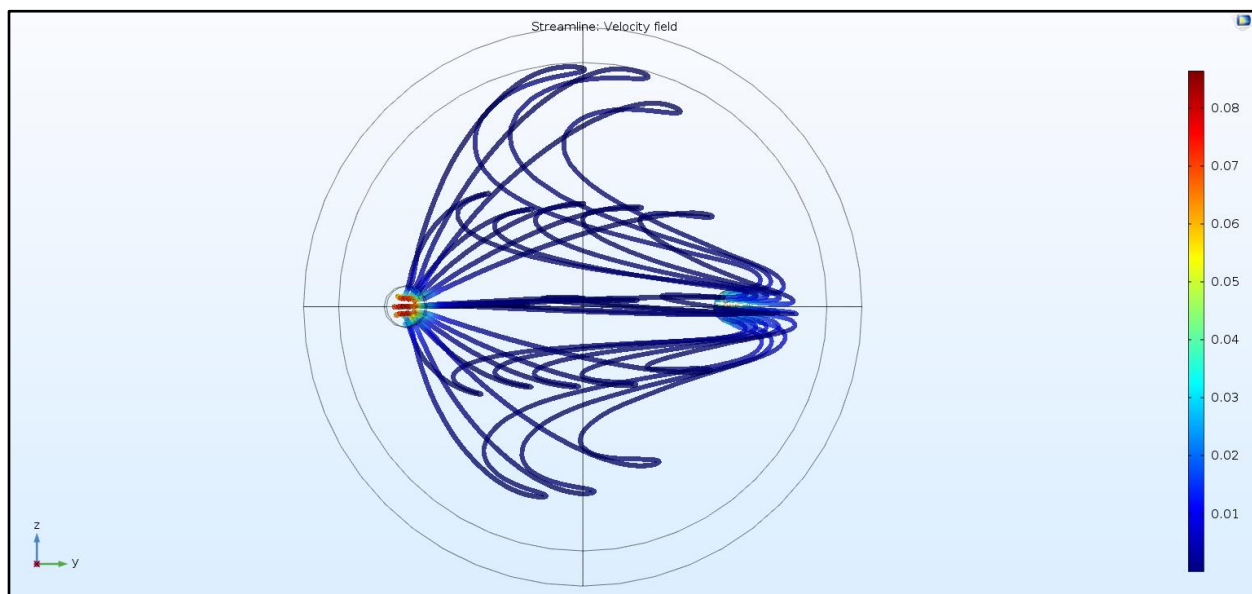


Figure 73: 6 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

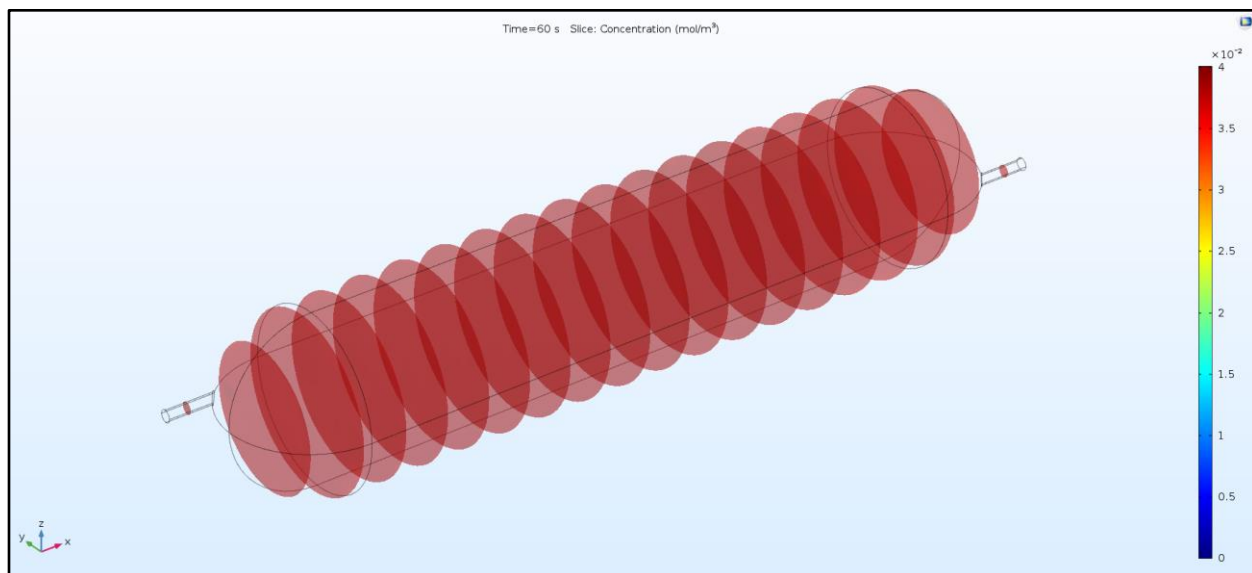


Figure 74: Slice Concentration 6mL/min, $k=3.15E-8$, 60 seconds (COMSOL® v. 5.2. 2017)

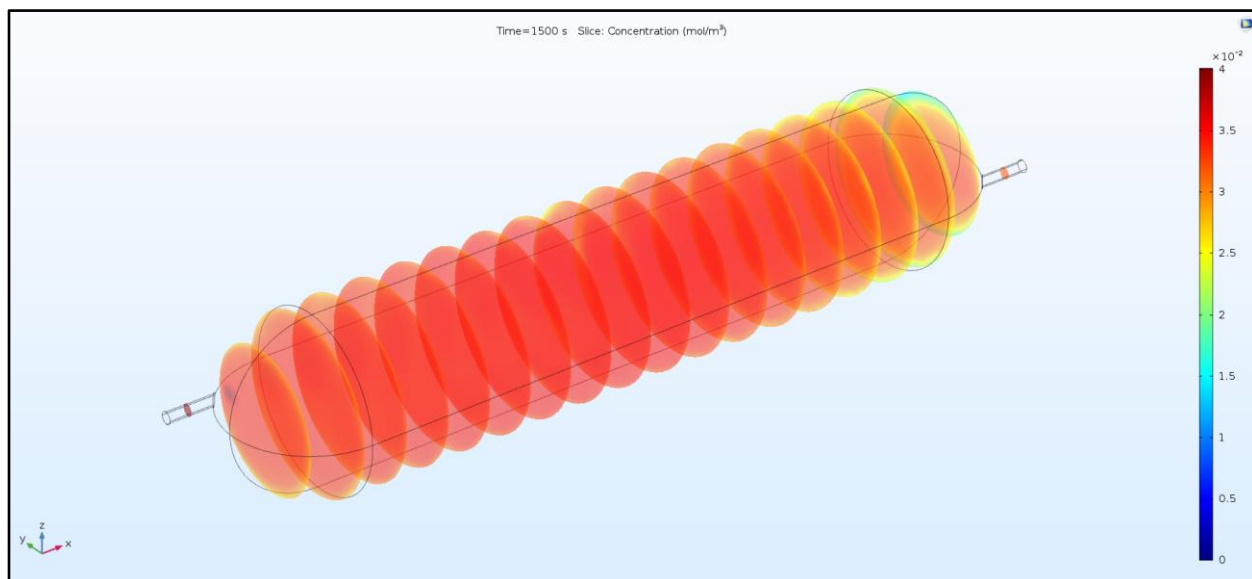


Figure 75: Slice Concentration 6mL/min, $k=3.15E-8$, 1500 seconds (COMSOL® v. 5.2. 2017)

Original Geometry, 36.42 cm³, Brilliant Blue k=8.80E-7 at 8 mL/min

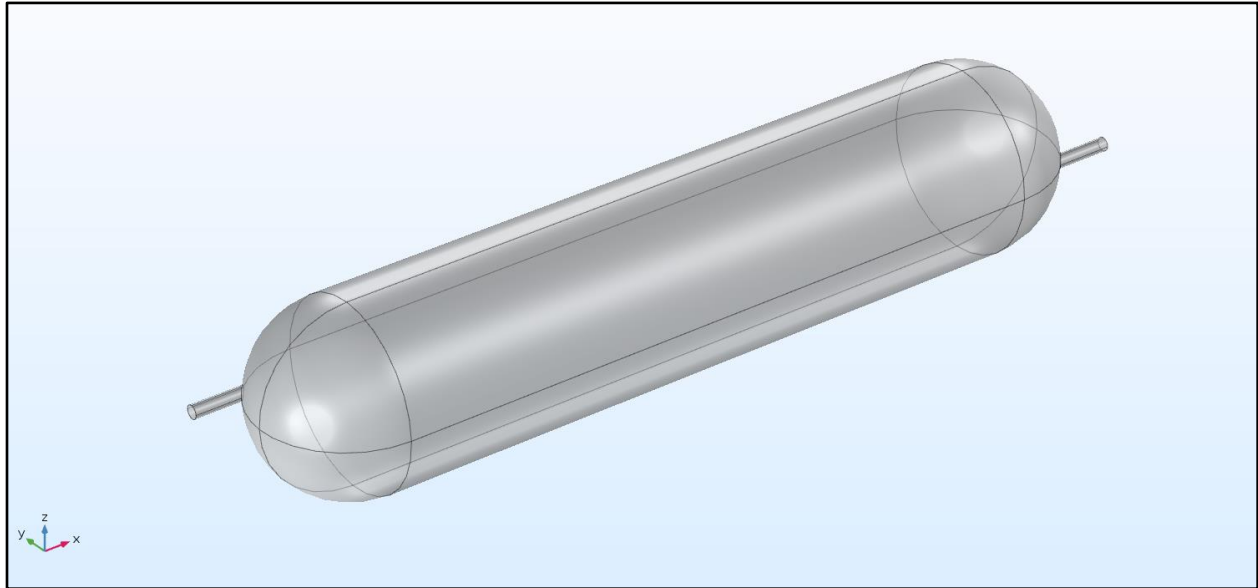


Figure 76: Original Geometry 8 mL/min, Isometric (COMSOL® v. 5.2. 2017)

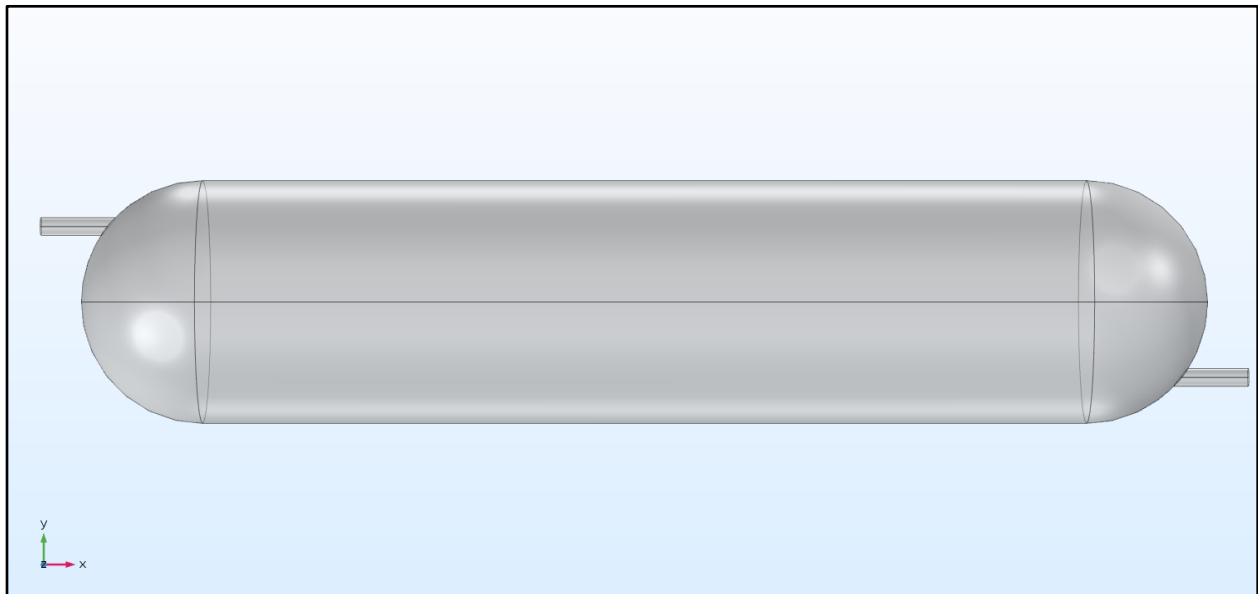


Figure 77: Original Geometry 8 mL/min, X-Axis (COMSOL® v. 5.2. 2017)

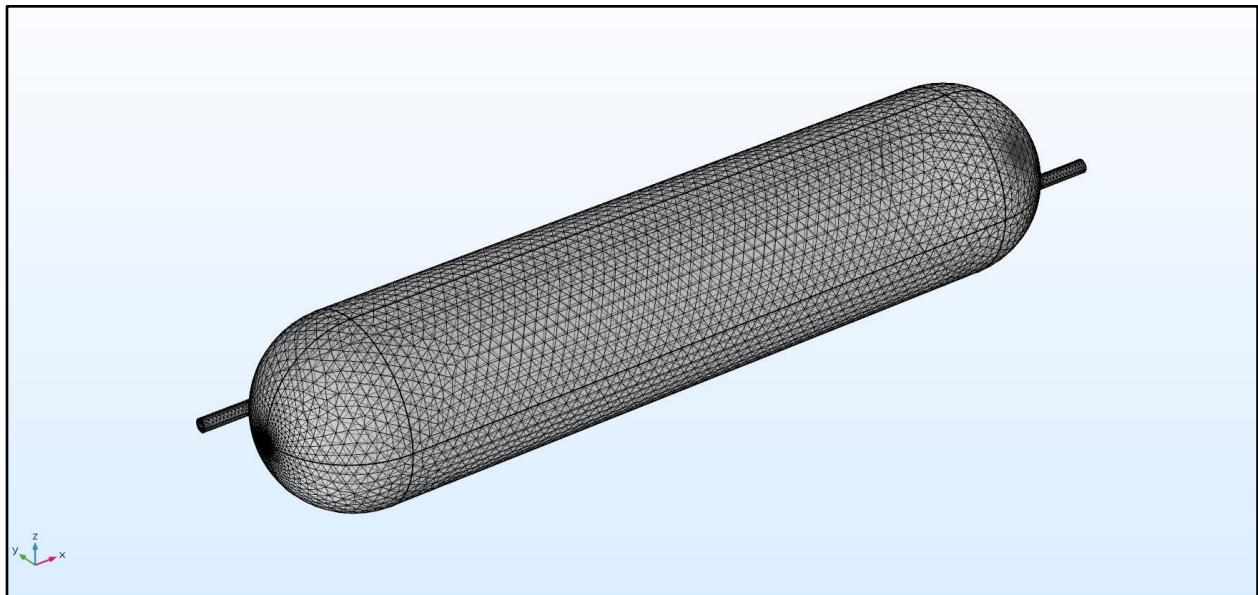


Figure 78: Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)



Figure 79: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)

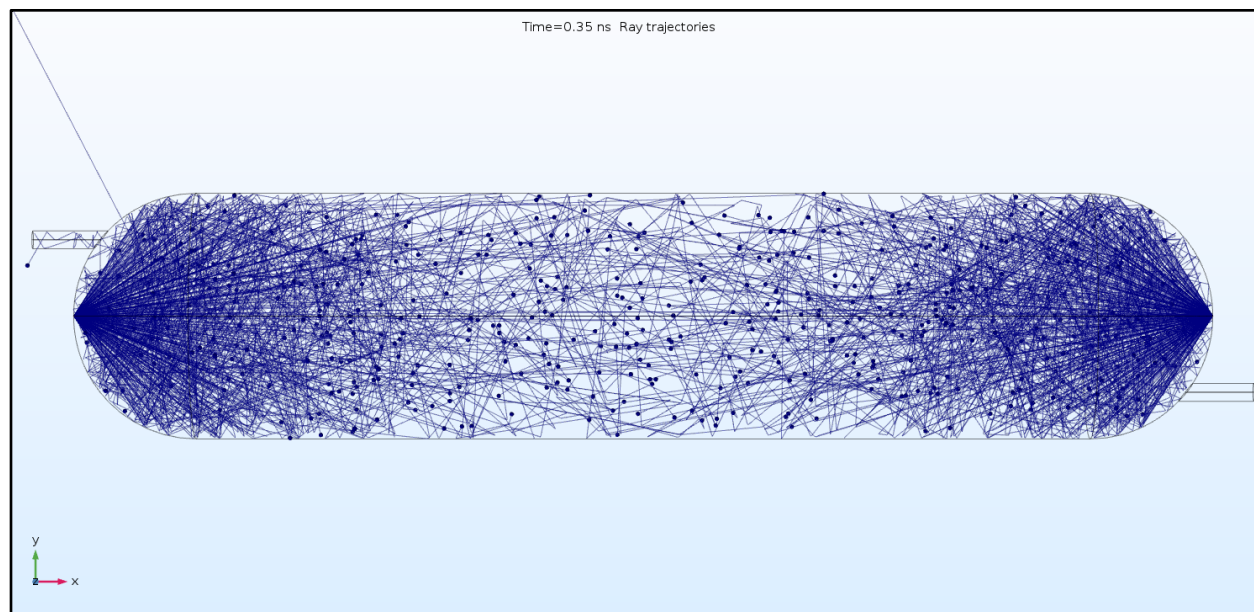


Figure 80: Ray Propagation at 0.35 ns, $k=8.80E-7$ (COMSOL® v. 5.2. 2017)

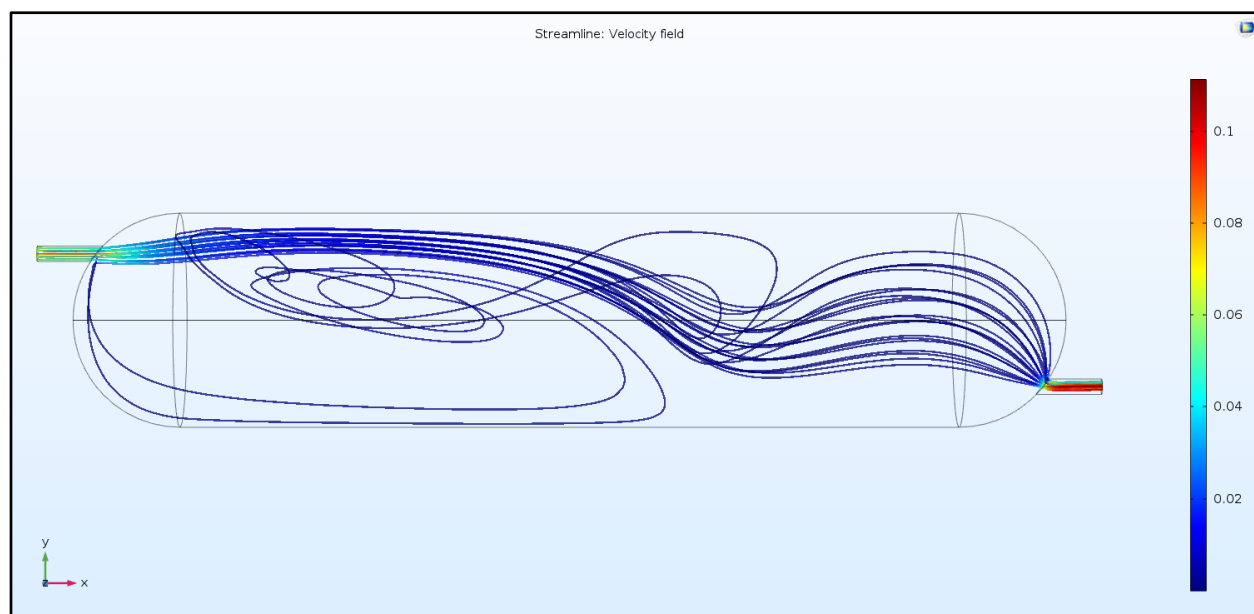


Figure 81: 8 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

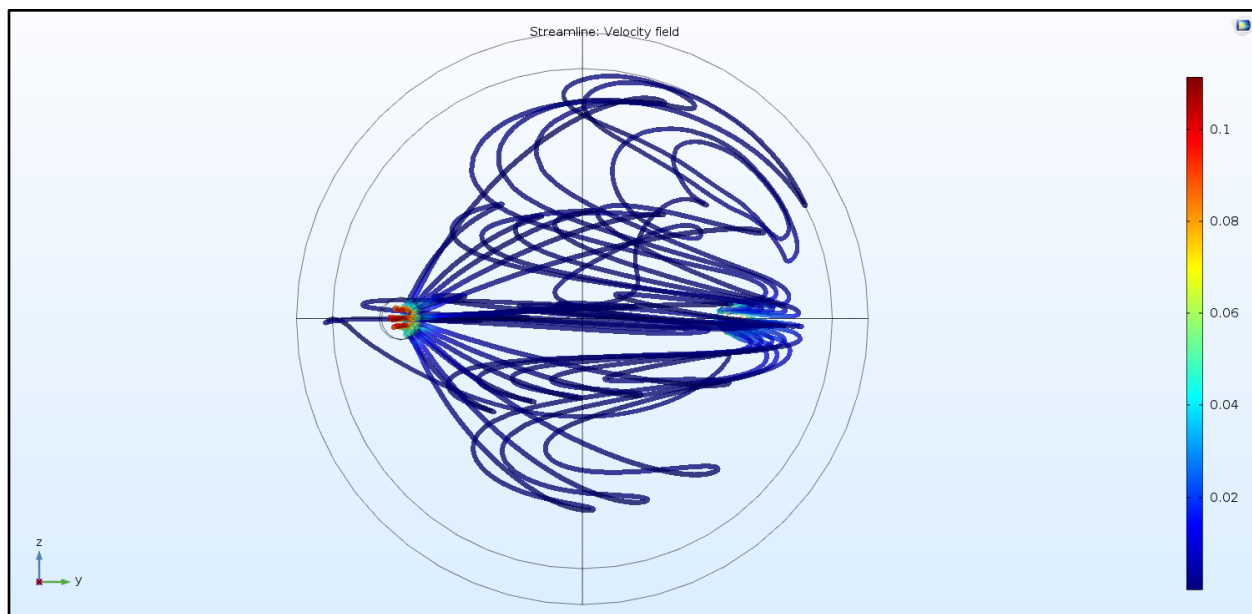


Figure 82: 8 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

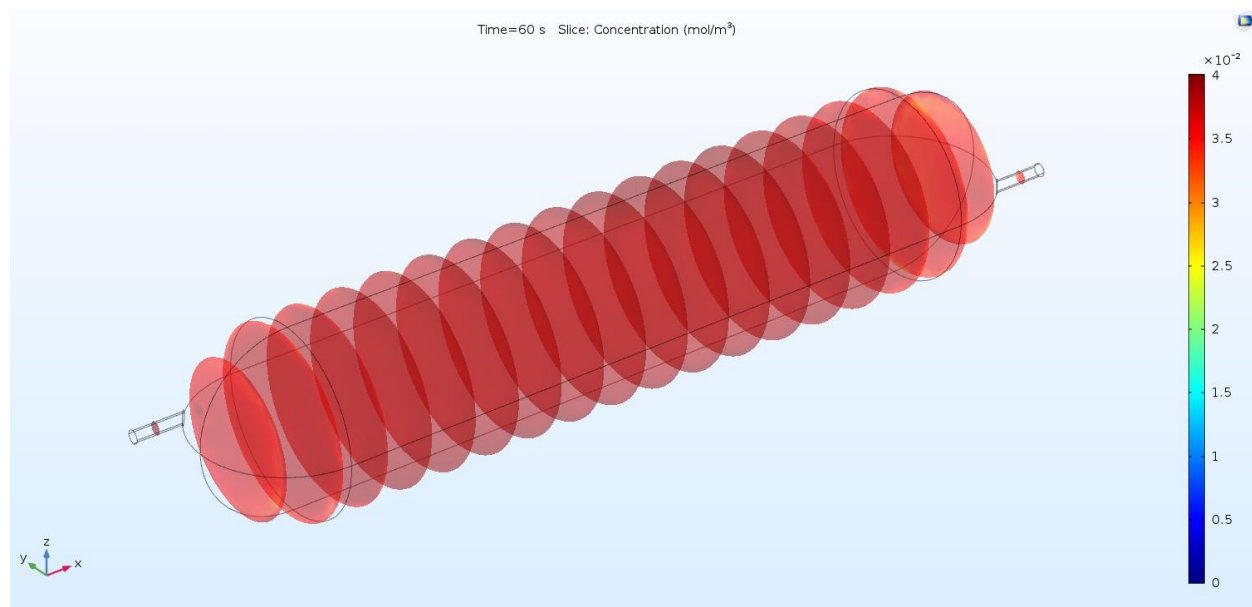


Figure 83: Slice Concentration 8mL/min, $k=8.80E-7$, 60 seconds (COMSOL® v. 5.2. 2017)

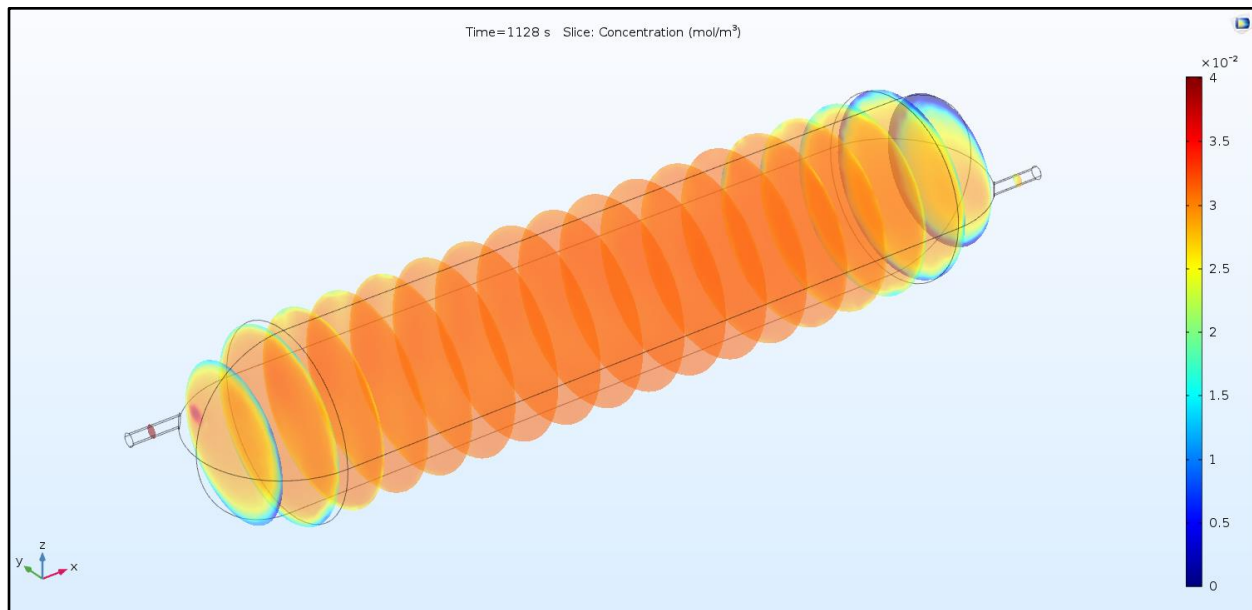


Figure 84: Slice Concentration 8mL/min, $k=8.80\text{E-}7$, 1128 seconds (COMSOL® v. 5.2. 2017)

Original Geometry, 36.42 cm³, Pure Water $k=3.15\text{E-}$ at 8 mL/min

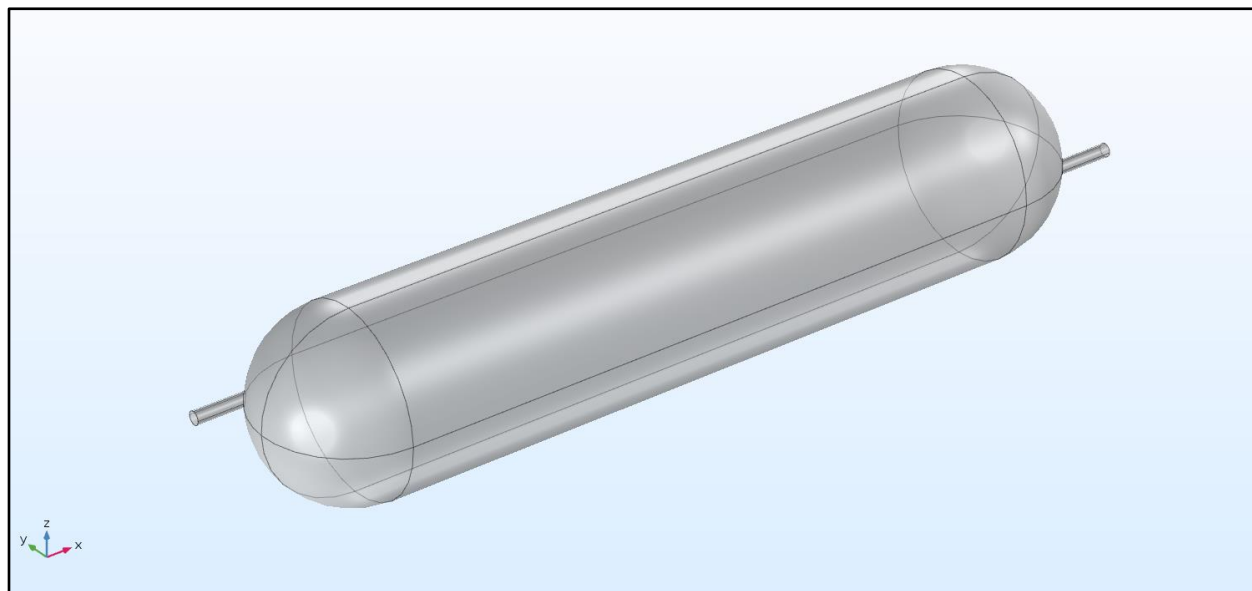


Figure 85: Original Geometry 8 mL/min, Isometric (COMSOL® v. 5.2. 2017)

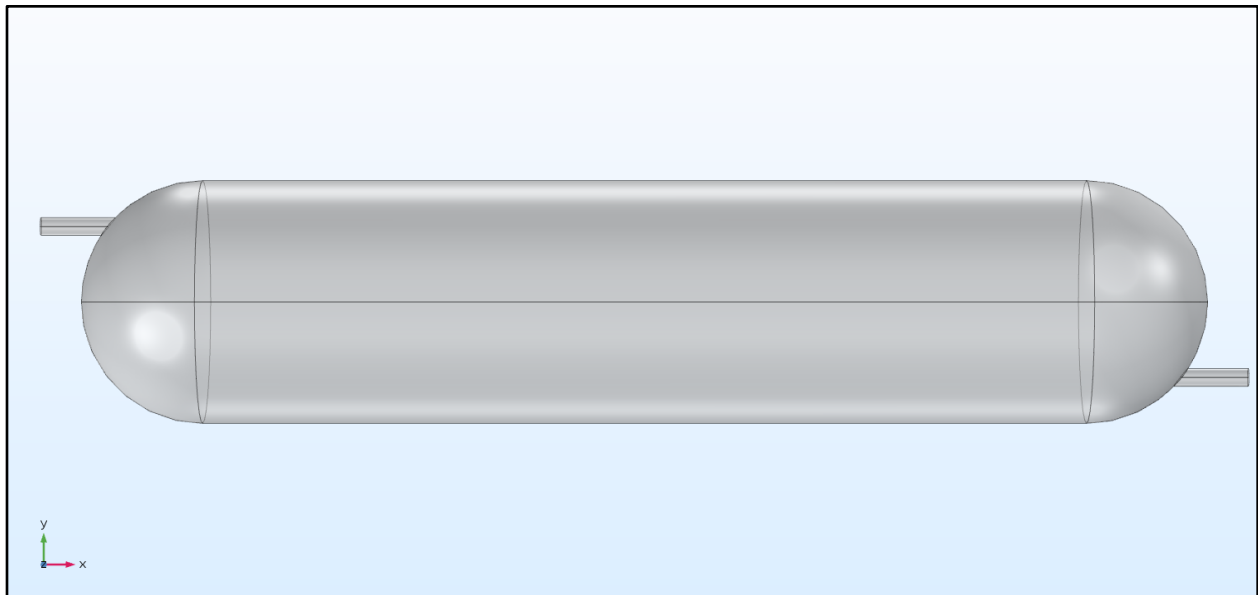


Figure 86: Original Geometry 8 mL/min, X-Axis (COMSOL® v. 5.2. 2017)

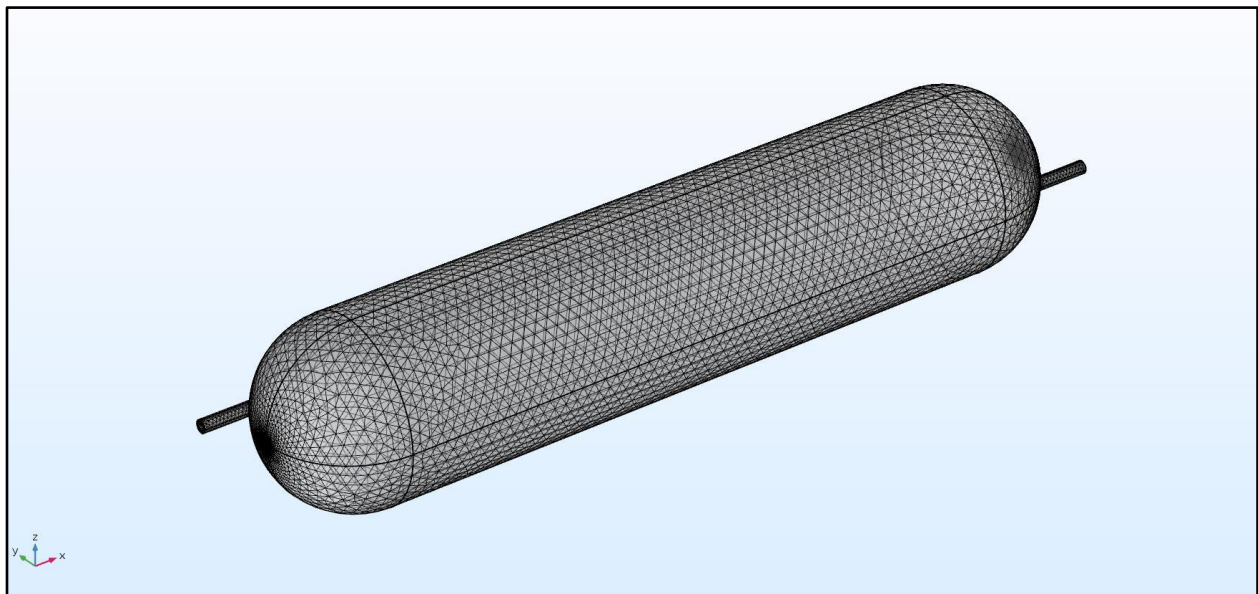


Figure 87: Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)



Figure 88: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)

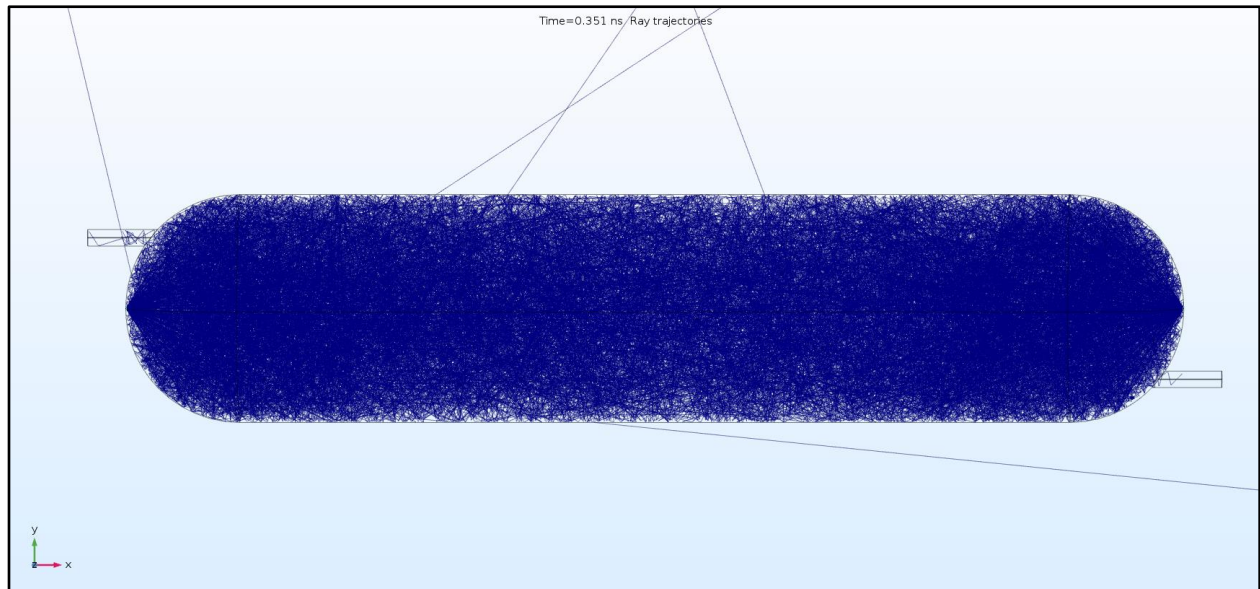


Figure 89: Ray Propagation at 4.0 ns, $k=3.15E-8$ (COMSOL® v. 5.2. 2017)

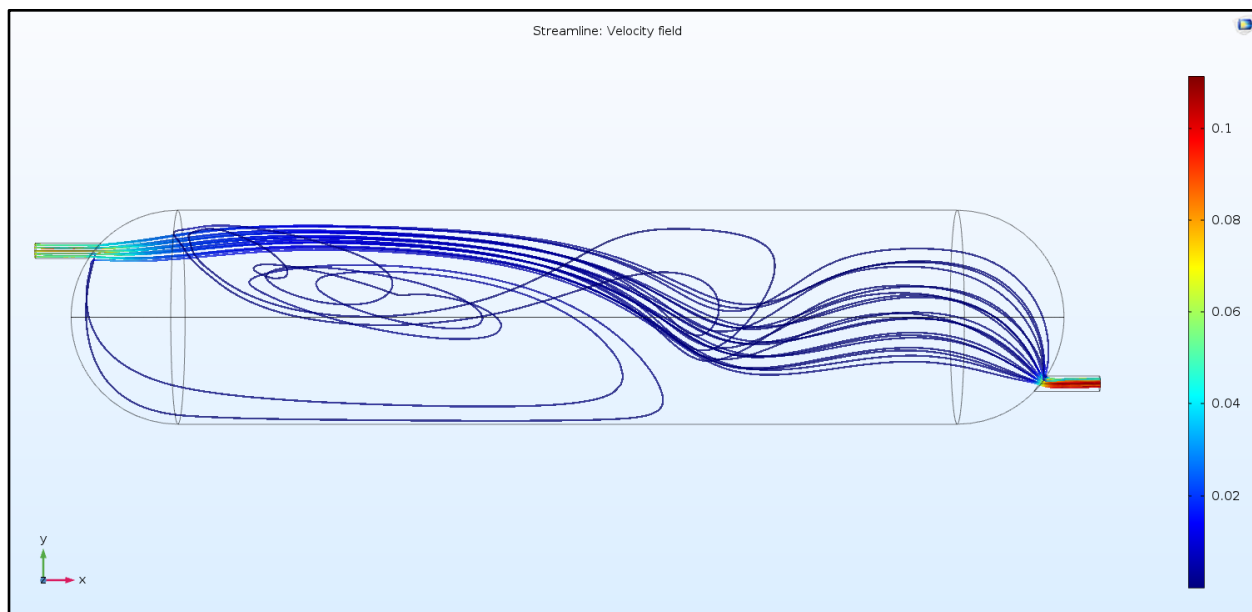


Figure 90: 8 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

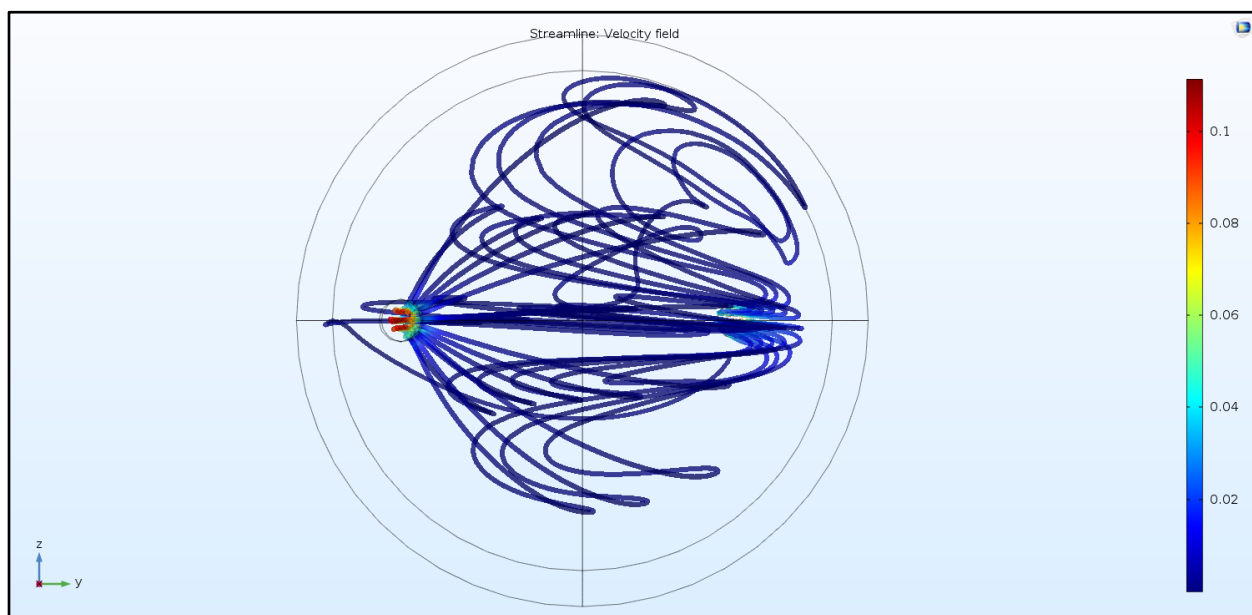


Figure 91: 8 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

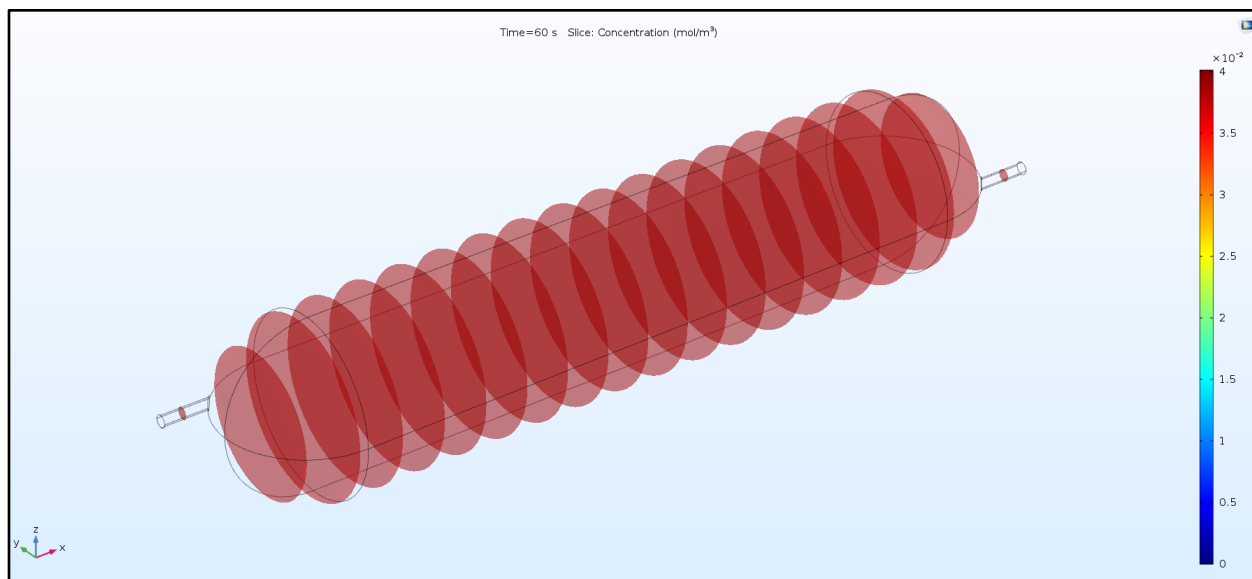


Figure 92: Slice Concentration 8mL/min, $k=3.15\text{E-}8$, 60 seconds (COMSOL® v. 5.2. 2017)

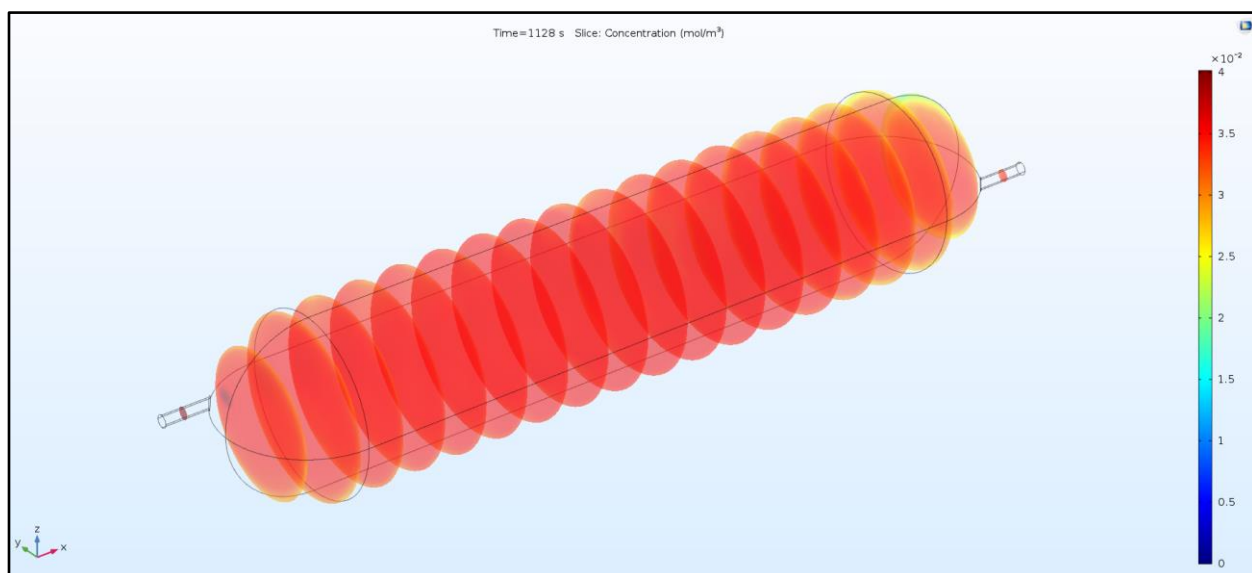


Figure 93: Slice Concentration 8mL/min, $k=3.15\text{E-}8$, 1128 seconds (COMSOL® v. 5.2. 2017)

Original Geometry, 36.42 cm³, Brilliant Blue k=8.80E-7 at 10 mL/min

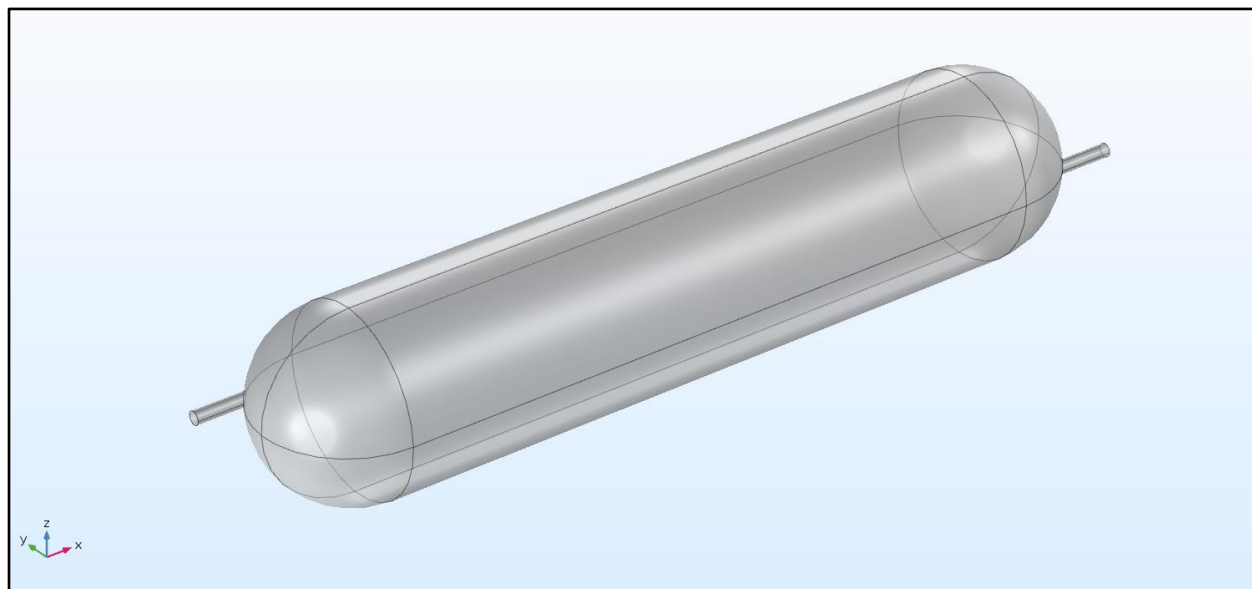


Figure 94: Original Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017)

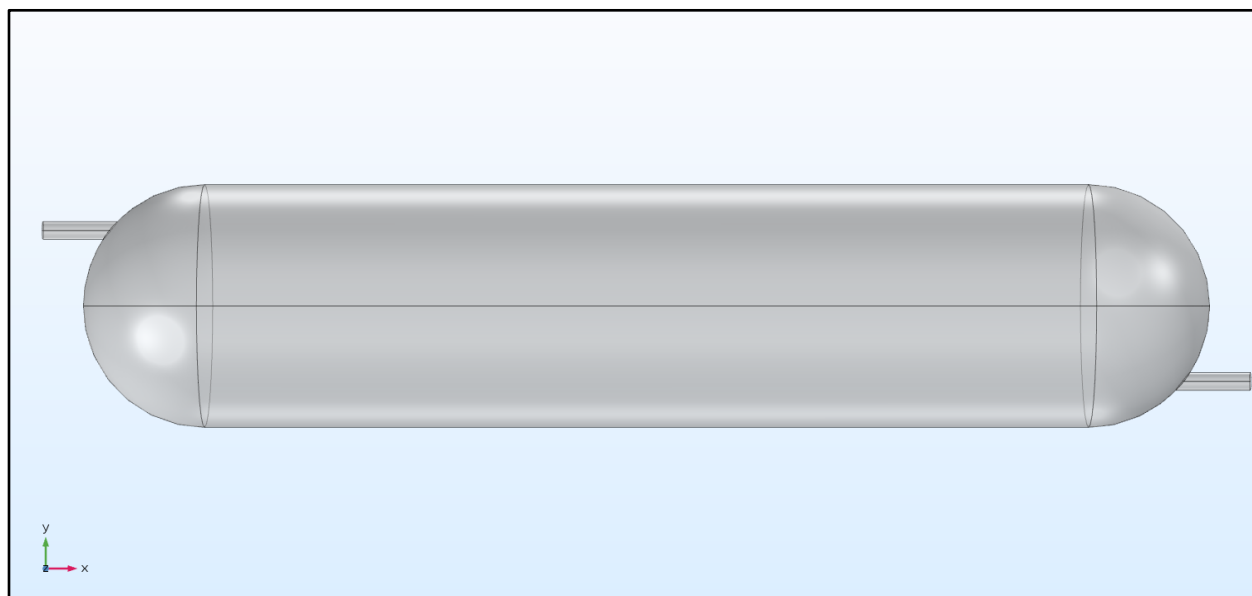


Figure 95: Original Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017)

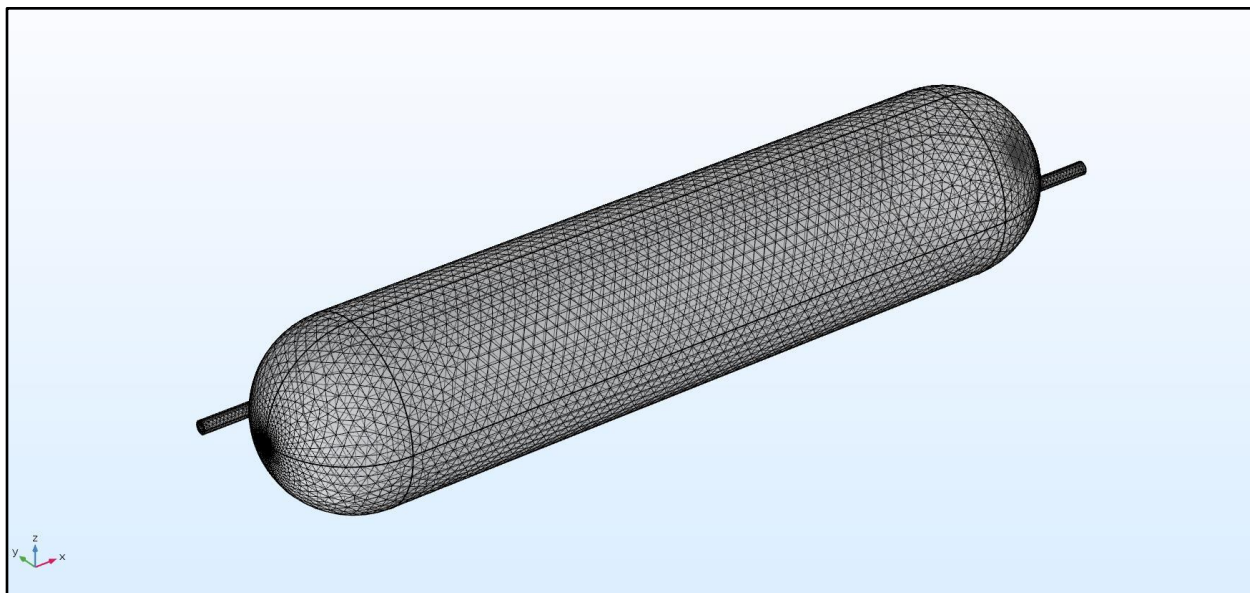


Figure 96: Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)



Figure 97: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)

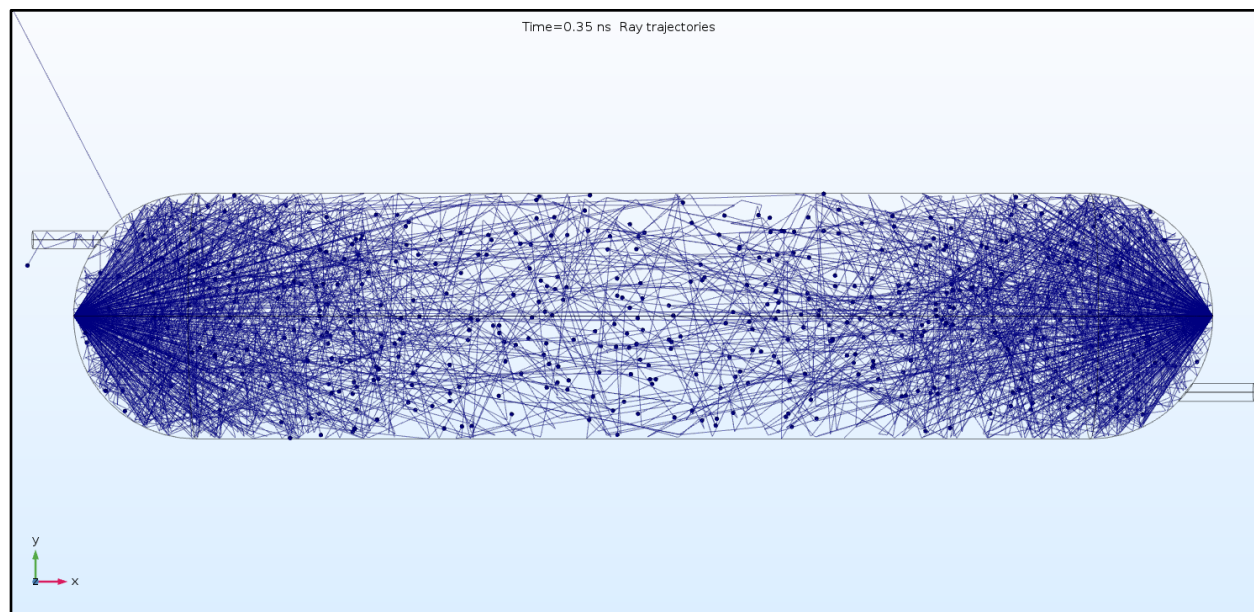


Figure 98: Ray Propagation at 0.35 ns, $k=8.80E-7$ (COMSOL® v. 5.2. 2017)

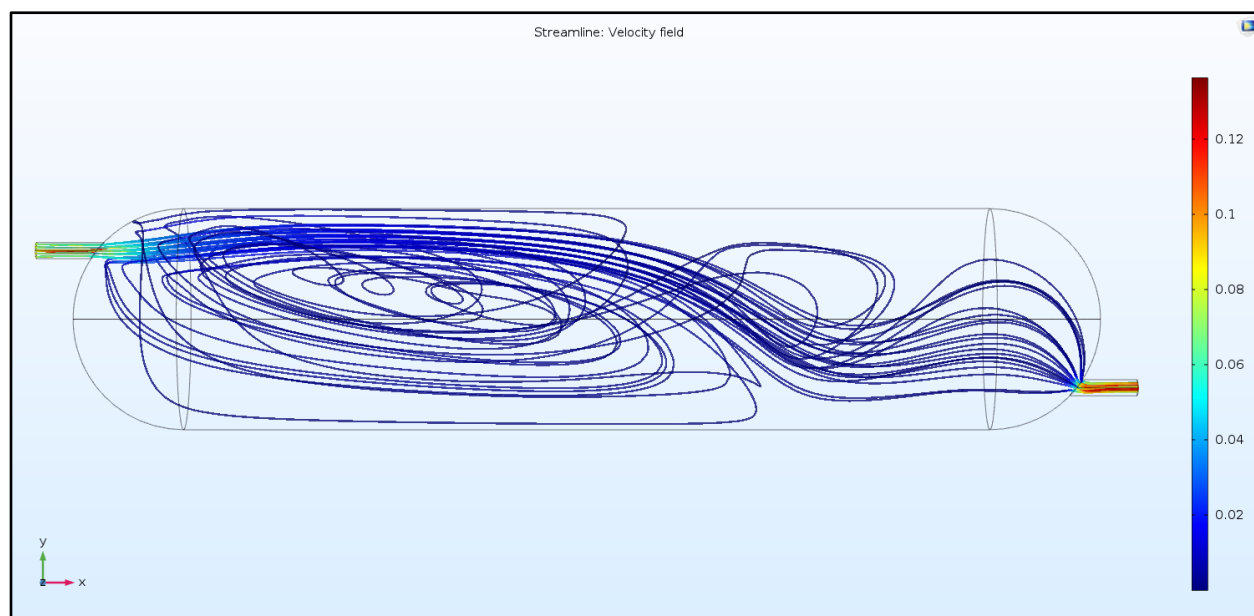


Figure 99: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

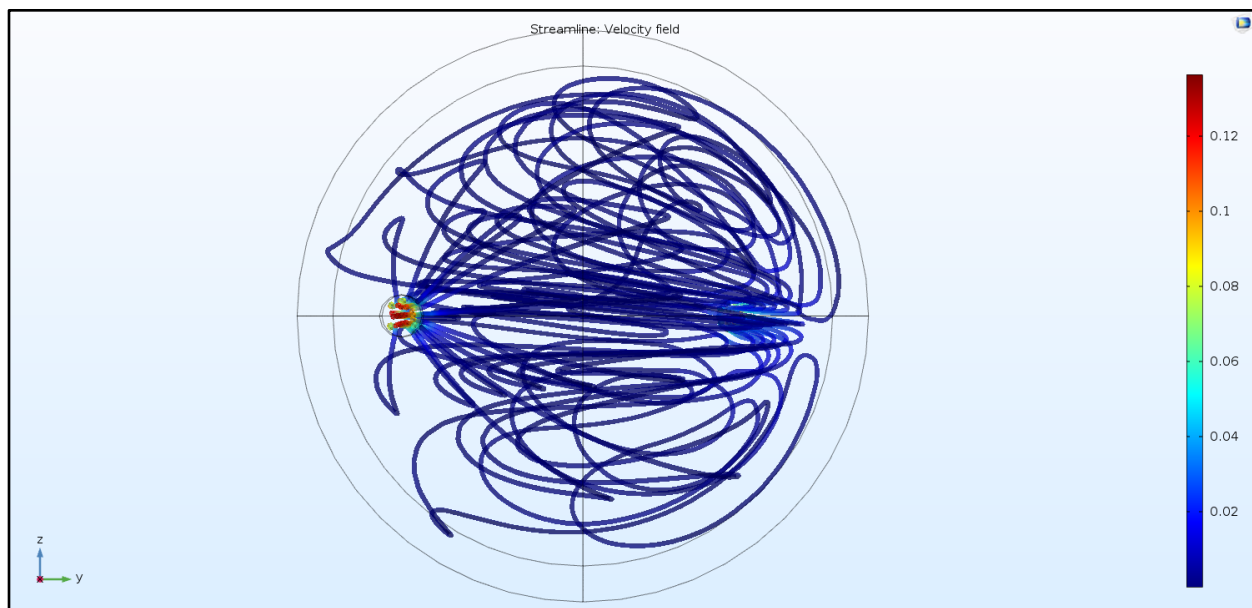


Figure 100: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

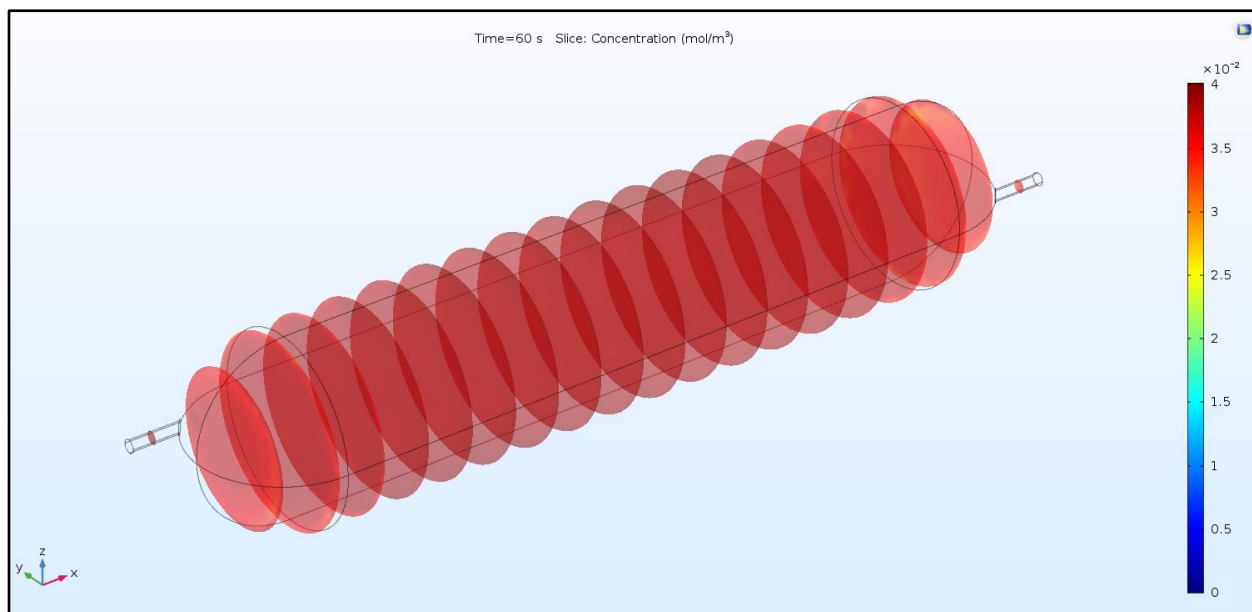


Figure 101: Slice Concentration 10mL/min, $k=8.80\text{E-}7$, 60 seconds (COMSOL® v. 5.2. 2017)

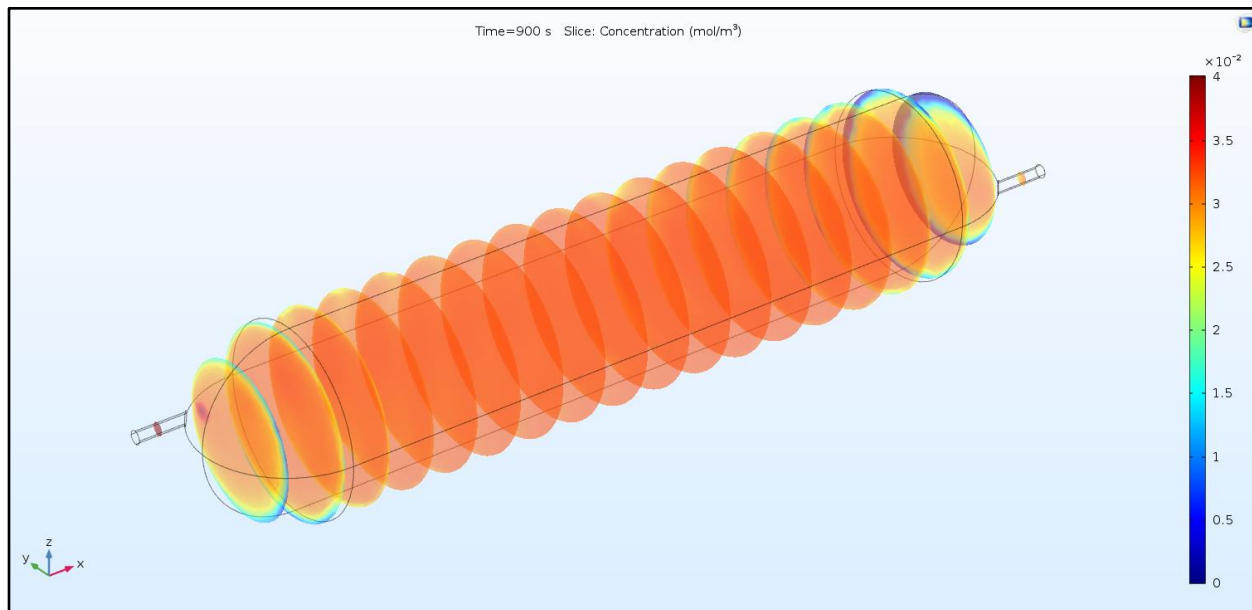


Figure 102: Slice Concentration 10mL/min, $k=8.80\text{E-}7$, 900 seconds(COMSOL® v. 5.2. 2017)

Original Geometry, 36.42 cm³, Pure Water $k=3.15\text{E-}$ at 10 mL/min

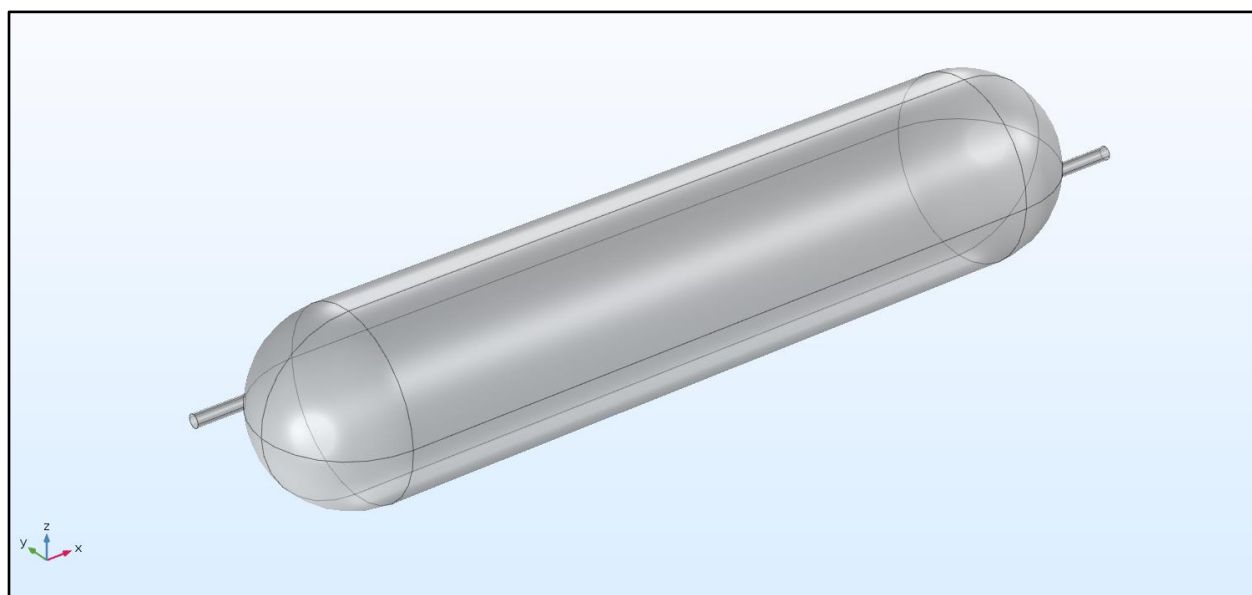


Figure 103: Original Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017)

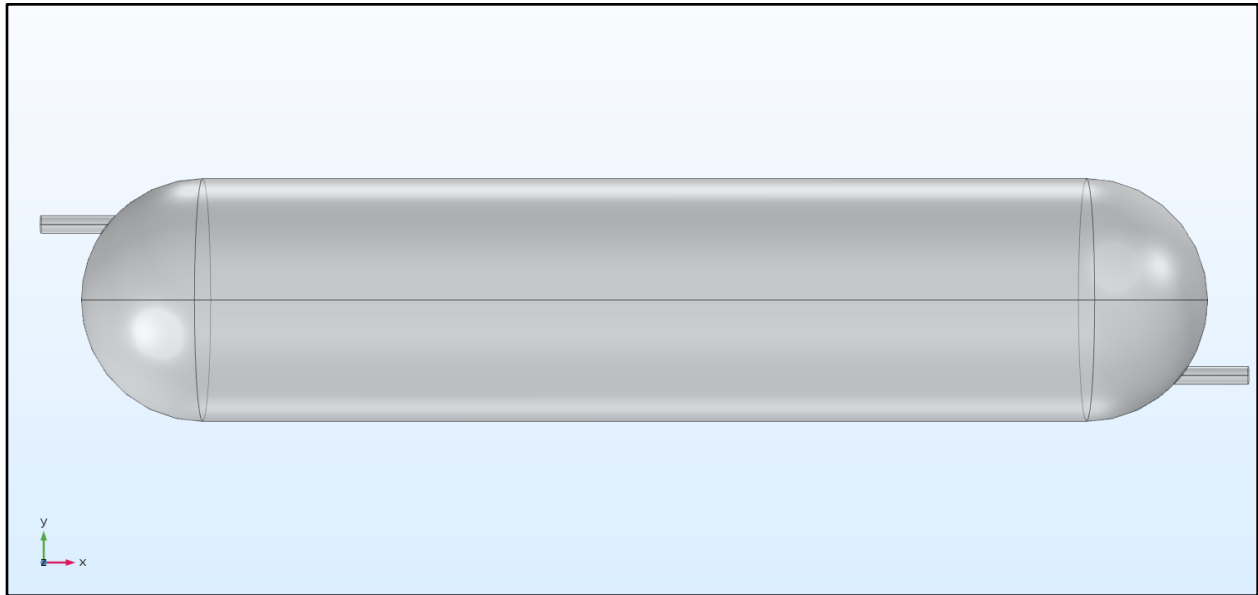


Figure 104: Original Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017)

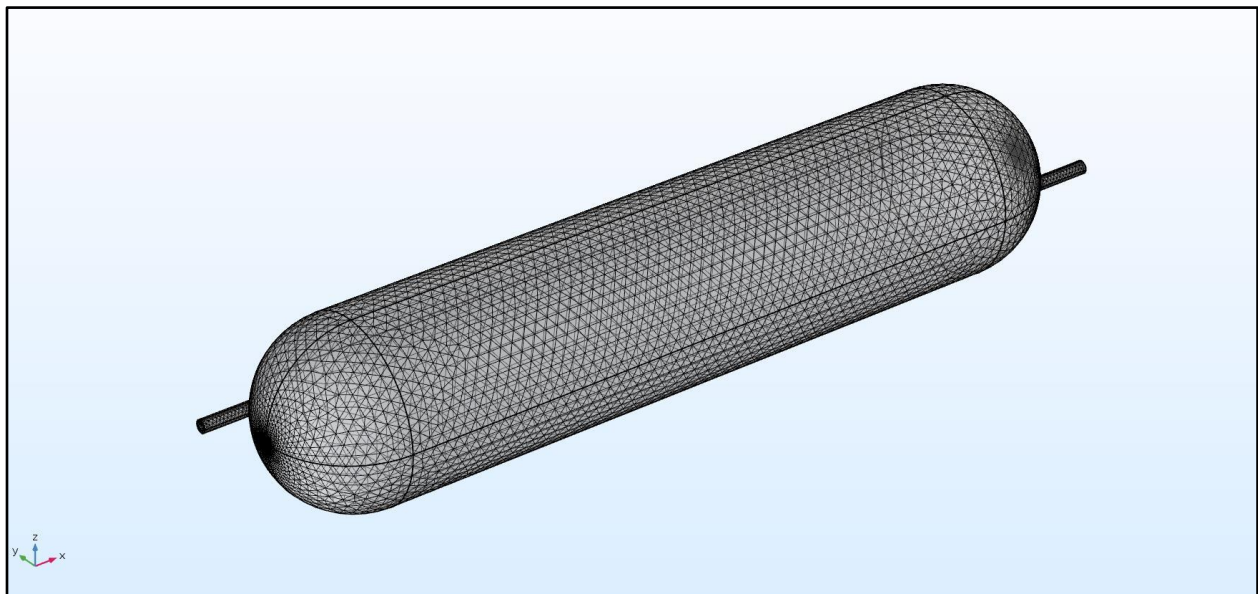


Figure 105: Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)



Figure 106: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)

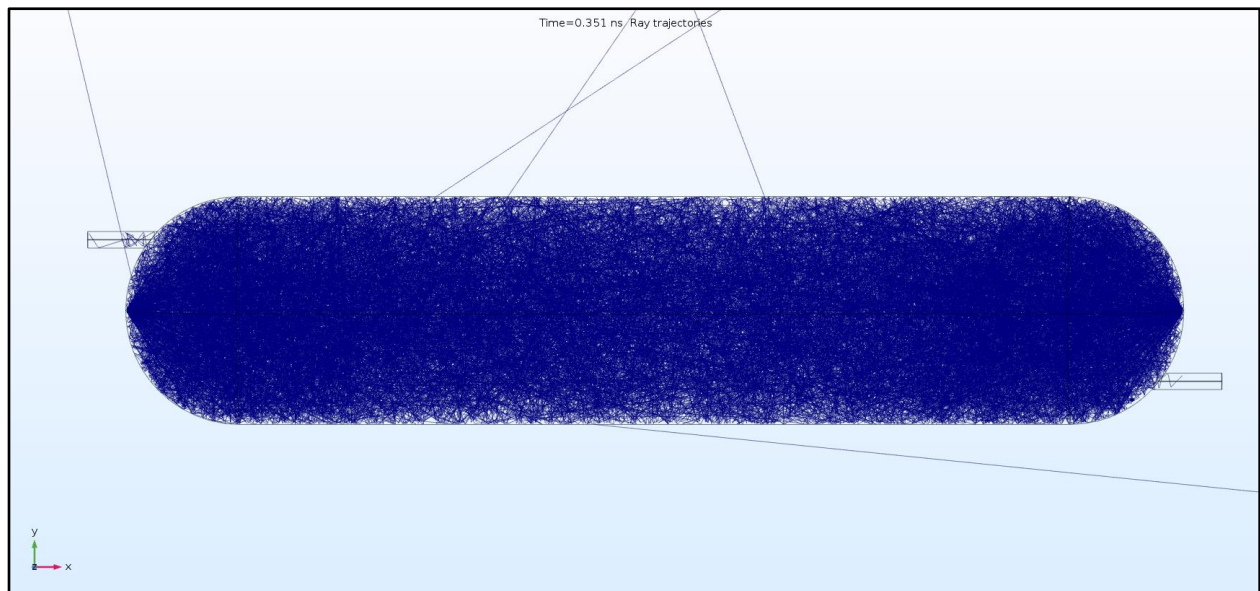


Figure 107: Ray Propagation at 4.0 ns, $k=3.15E-8$ (COMSOL® v. 5.2. 2017)

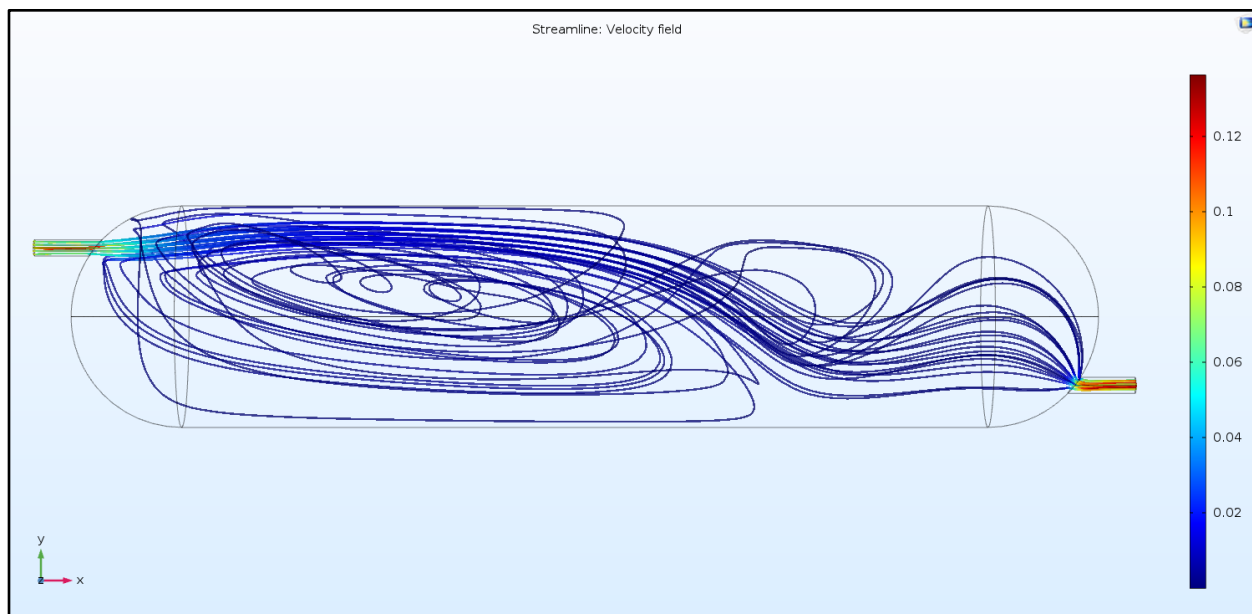


Figure 108: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

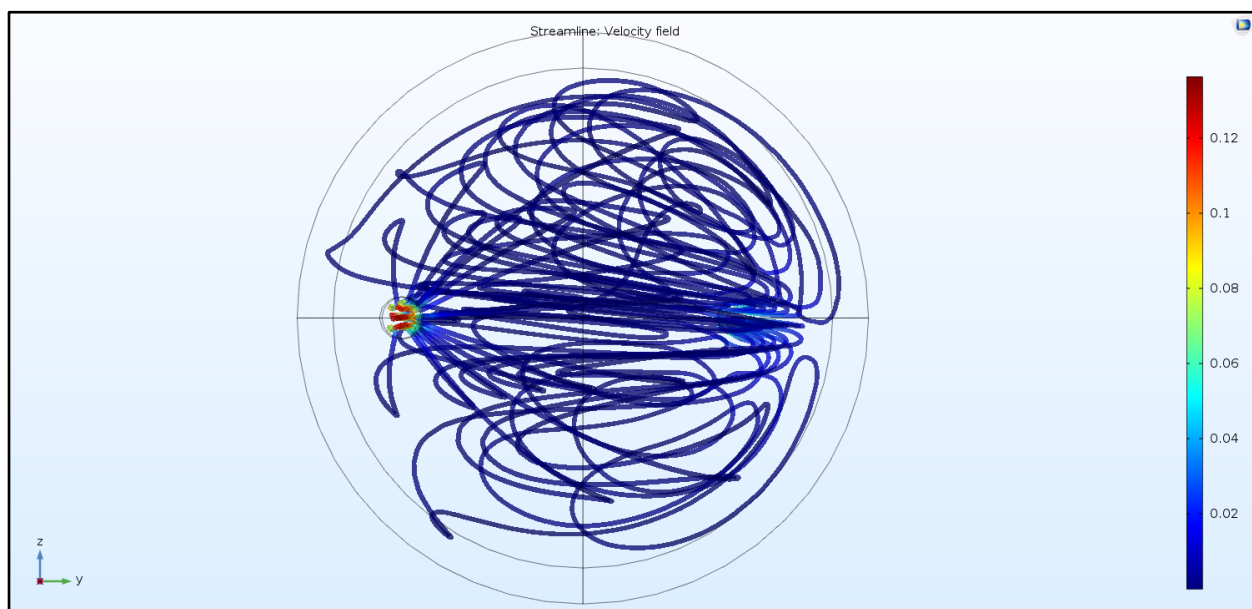


Figure 109: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

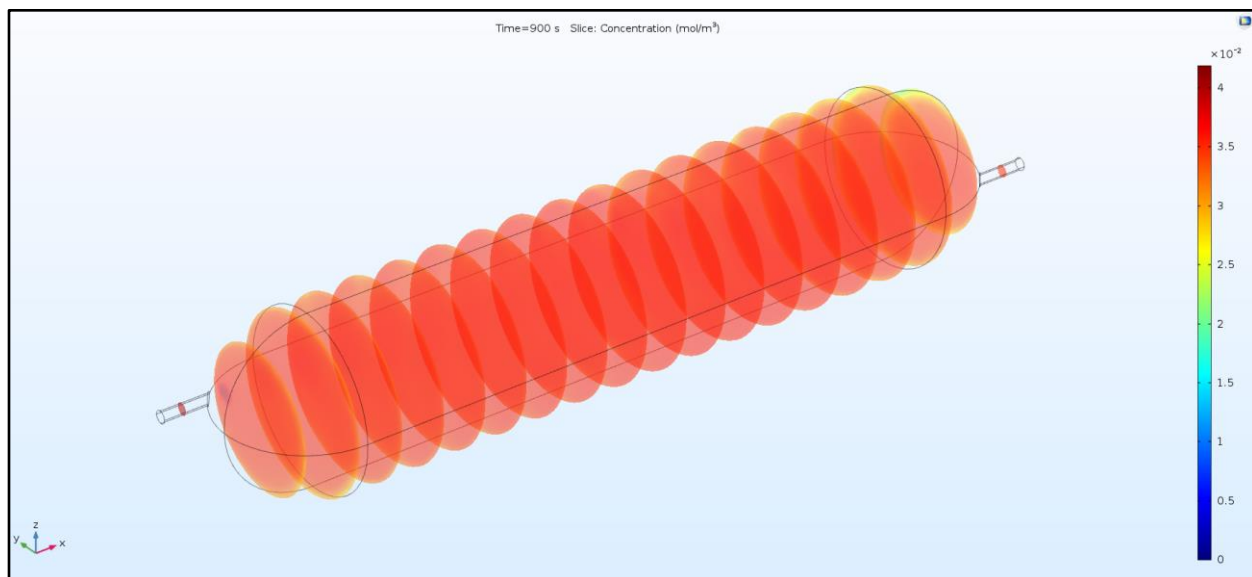


Figure 110: Slice Concentration 10mL/min, $k=3.15\text{E-}8$, 900 seconds (COMSOL® v. 5.2. 2017)

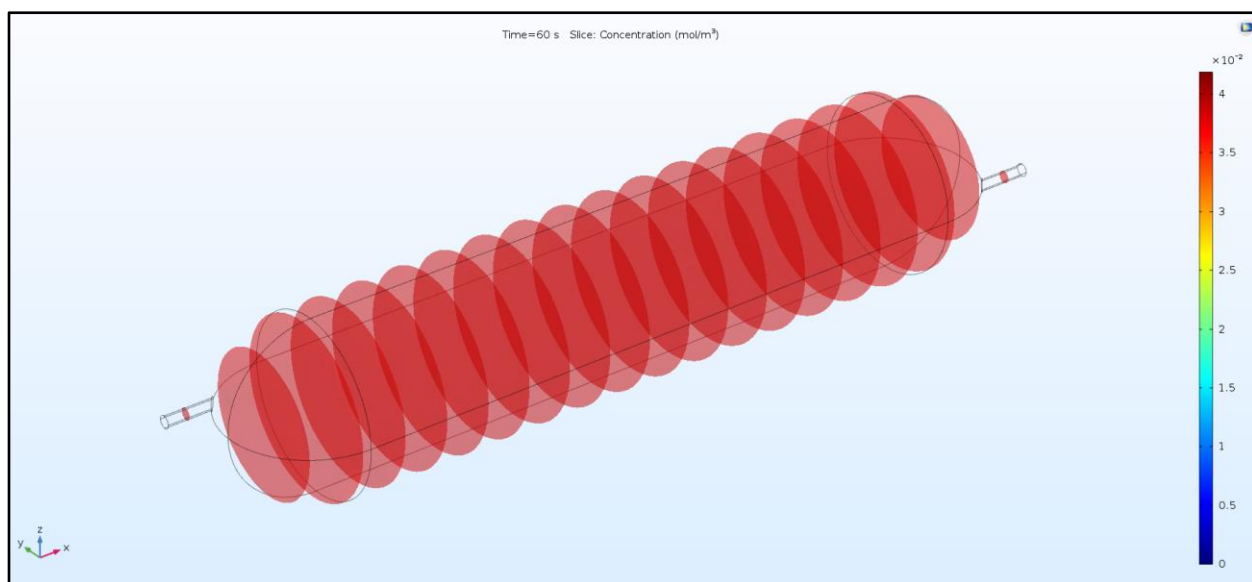


Figure 111: Slice Concentration 10mL/min, $k=3.15\text{E-}8$, 60 seconds (COMSOL® v. 5.2. 2017)

Original Geometry, 36.42 cm³, Pure Water $k=3.15E-$ at 10 mL/min, 100% Reflectance

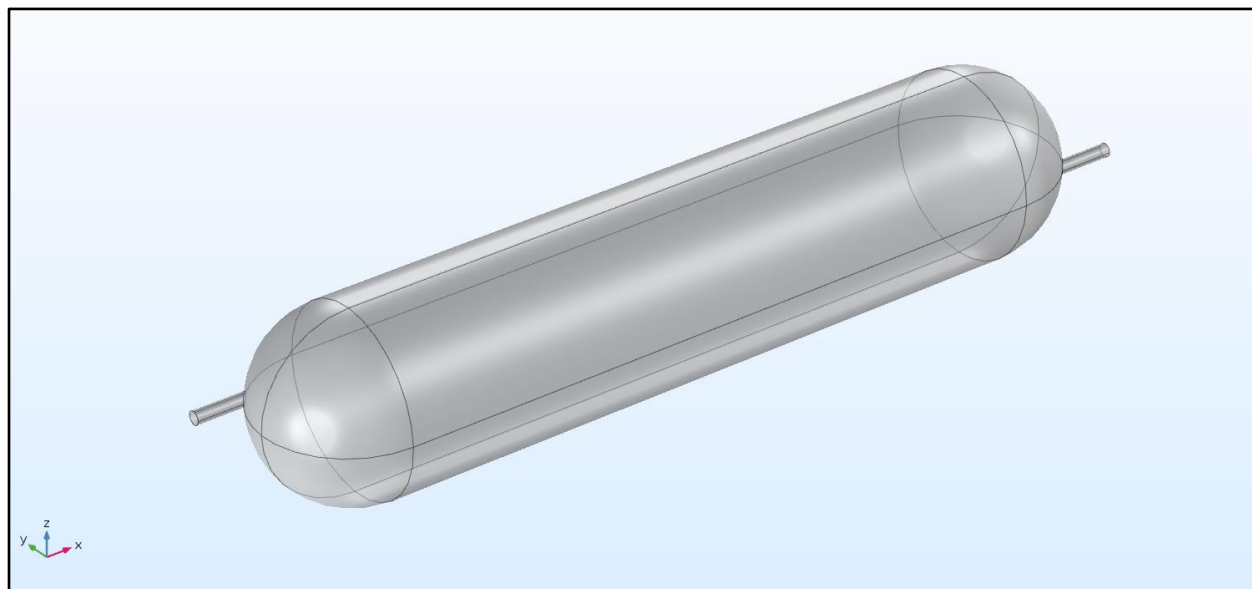


Figure 112: Original Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017)

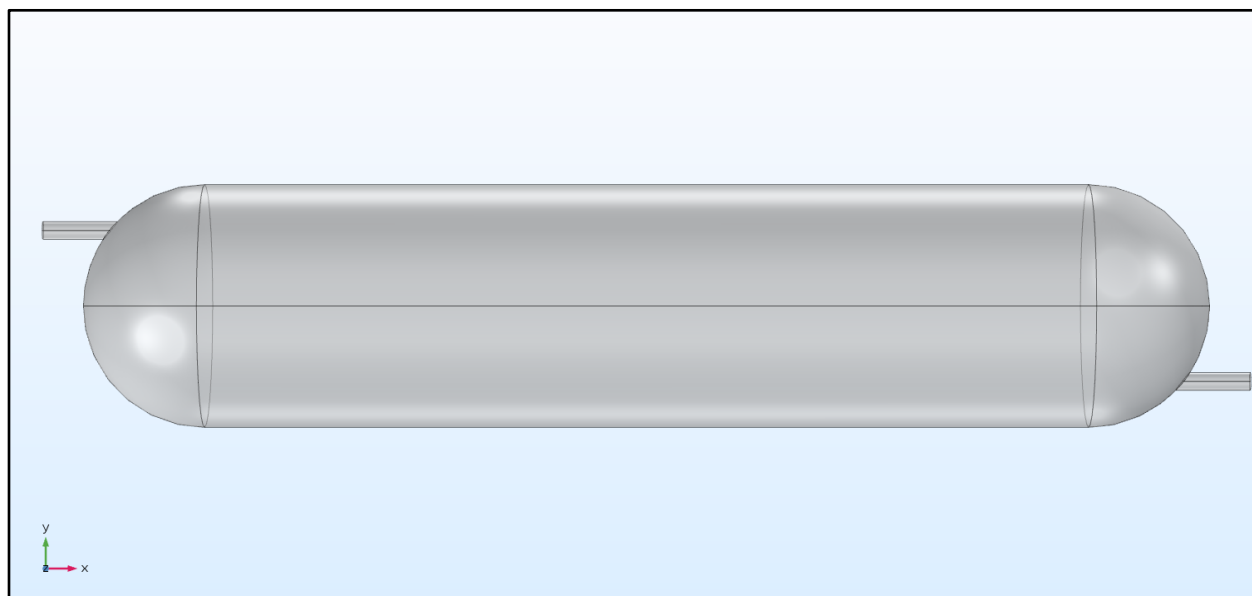


Figure 113: Original Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017)

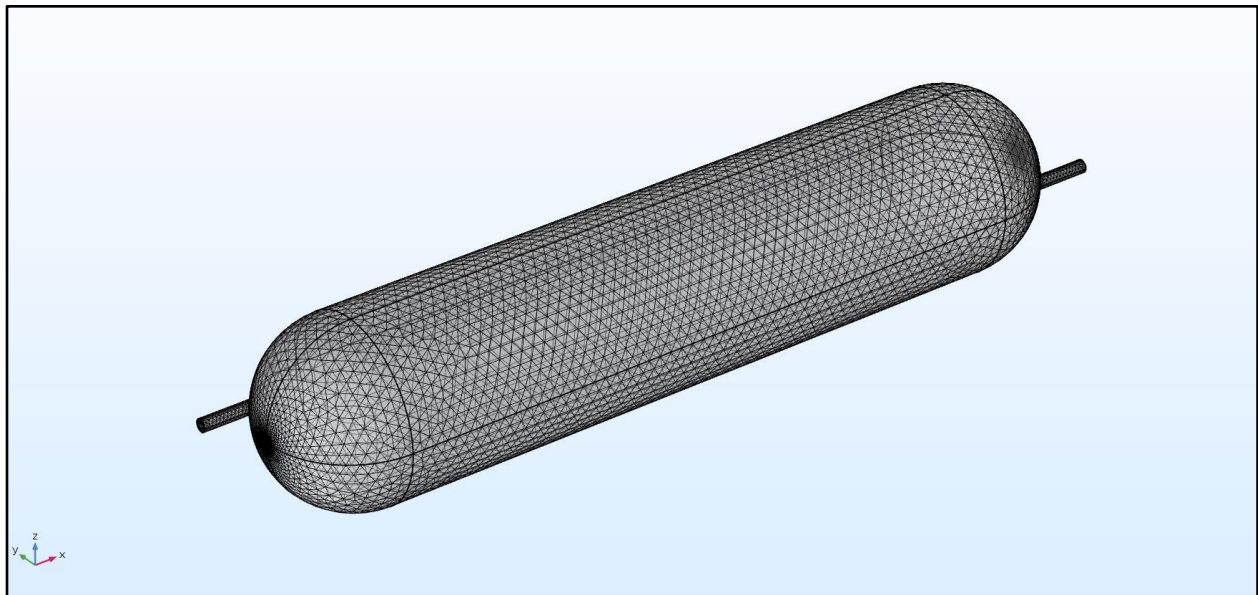


Figure 114: Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)



Figure 115: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)

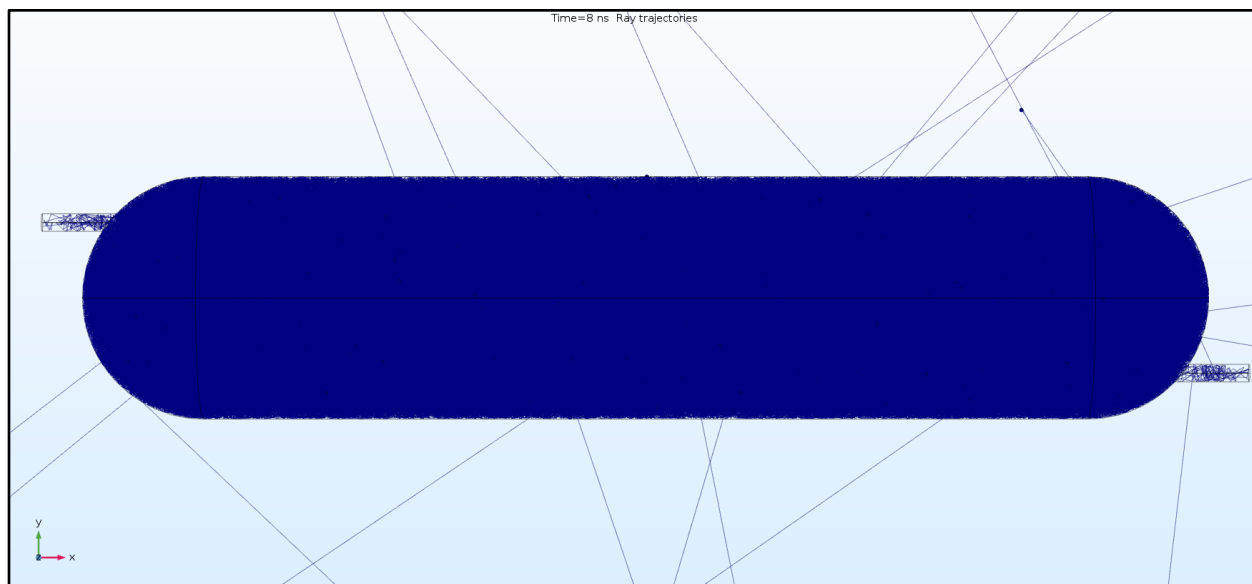


Figure 116: Ray Propagation at 8.0 ns (COMSOL® v. 5.2. 2017)

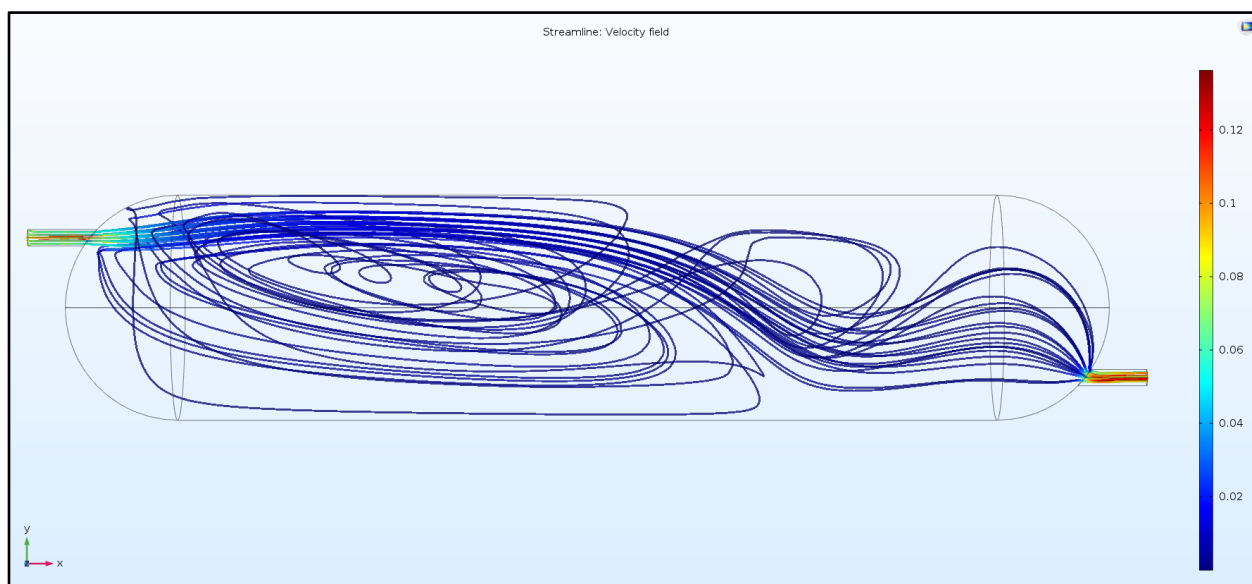


Figure 117: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

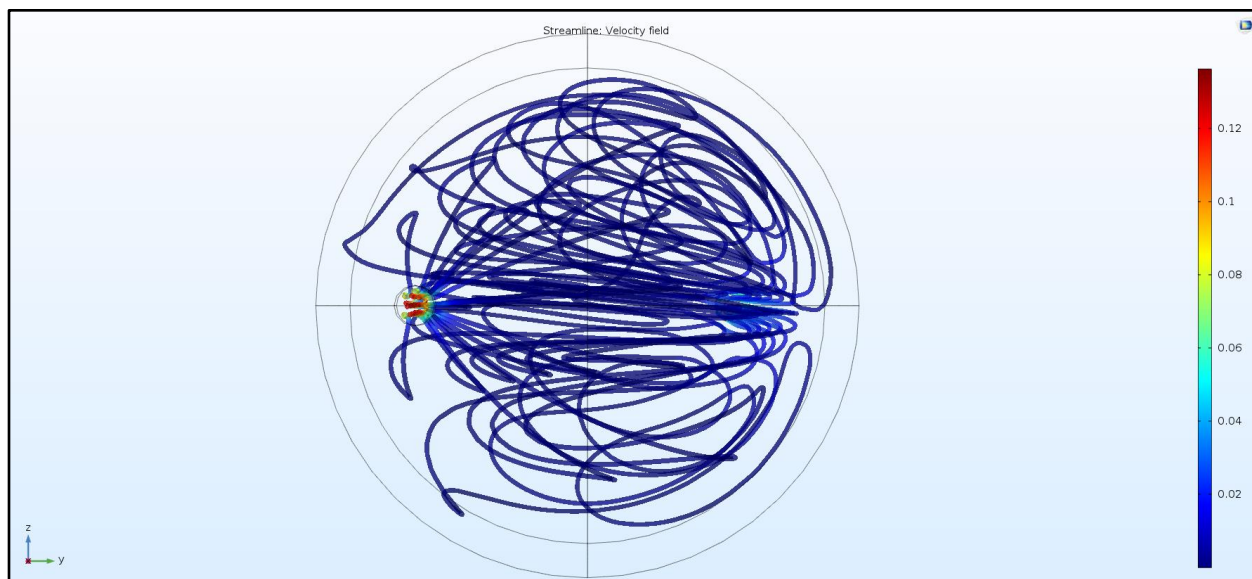


Figure 118: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

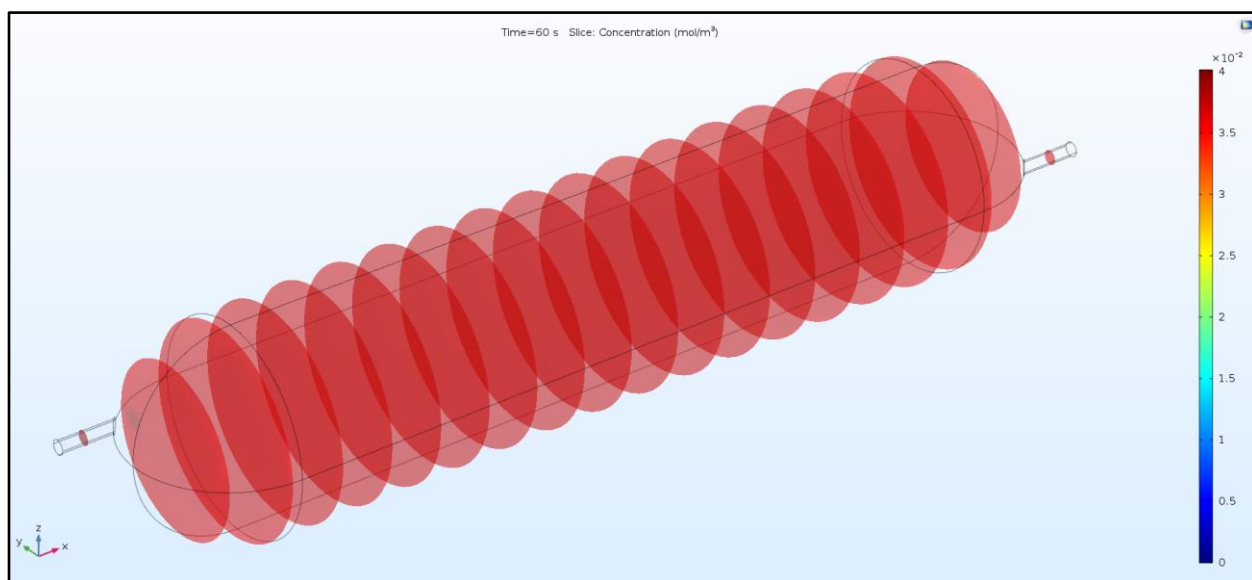


Figure 119: Slice Concentration 10mL/min, $k=8.80E-7$, 60 seconds (COMSOL® v. 5.2. 2017)

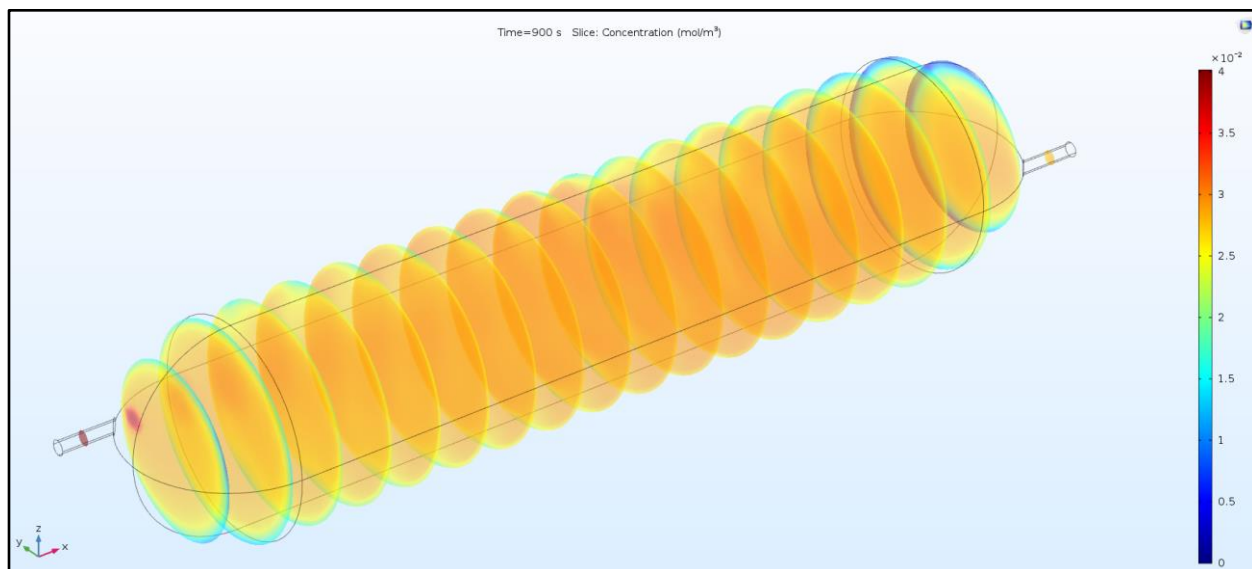


Figure 120: Slice Concentration 10mL/min, $k=8.80\text{E-}7$, 900 seconds (COMSOL® v. 5.2. 2017)

Half Scale Original Geometry, 4.546 cm³, Brilliant Blue $k=8.80\text{E-}7$ at 10 mL/min

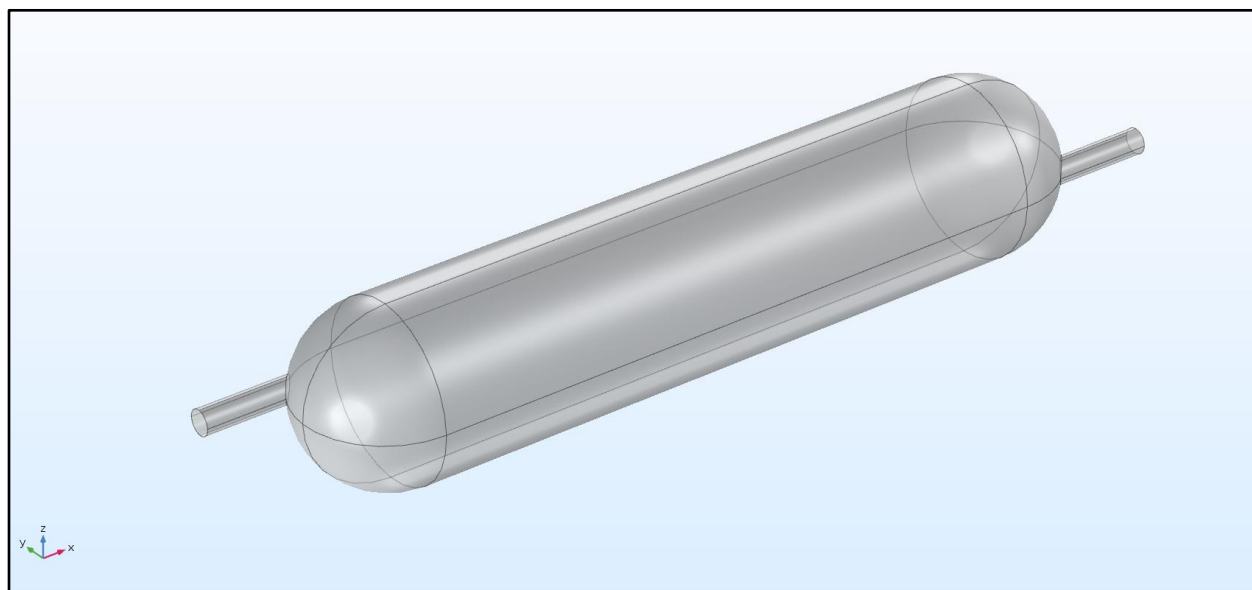


Figure 121: Half Scale Original Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017)

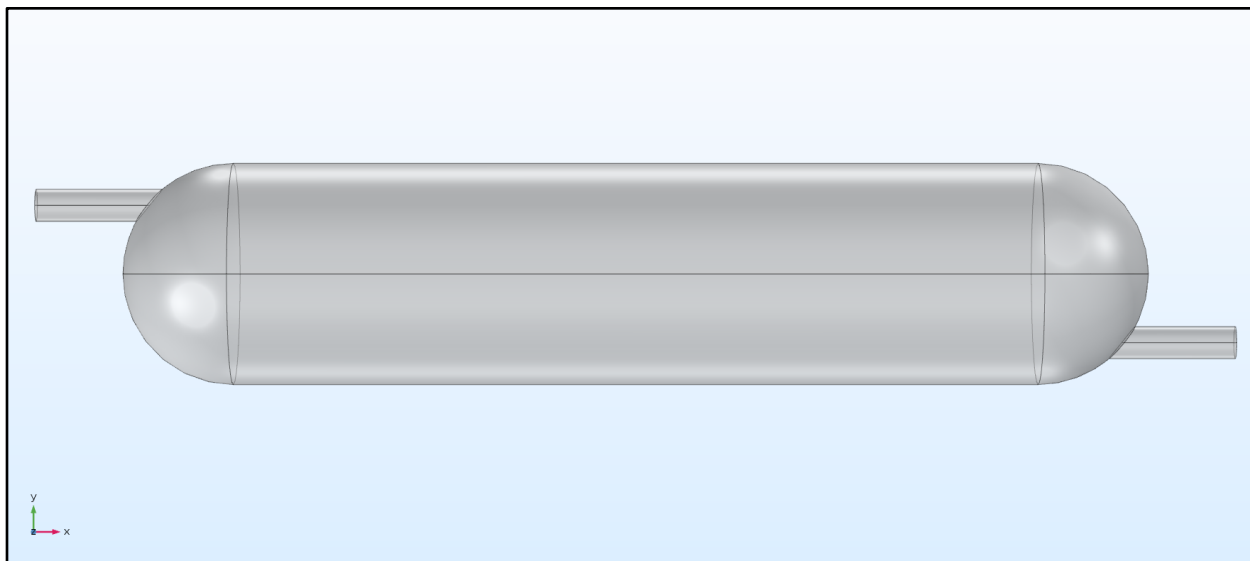


Figure 122: Half Scale Original Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017)

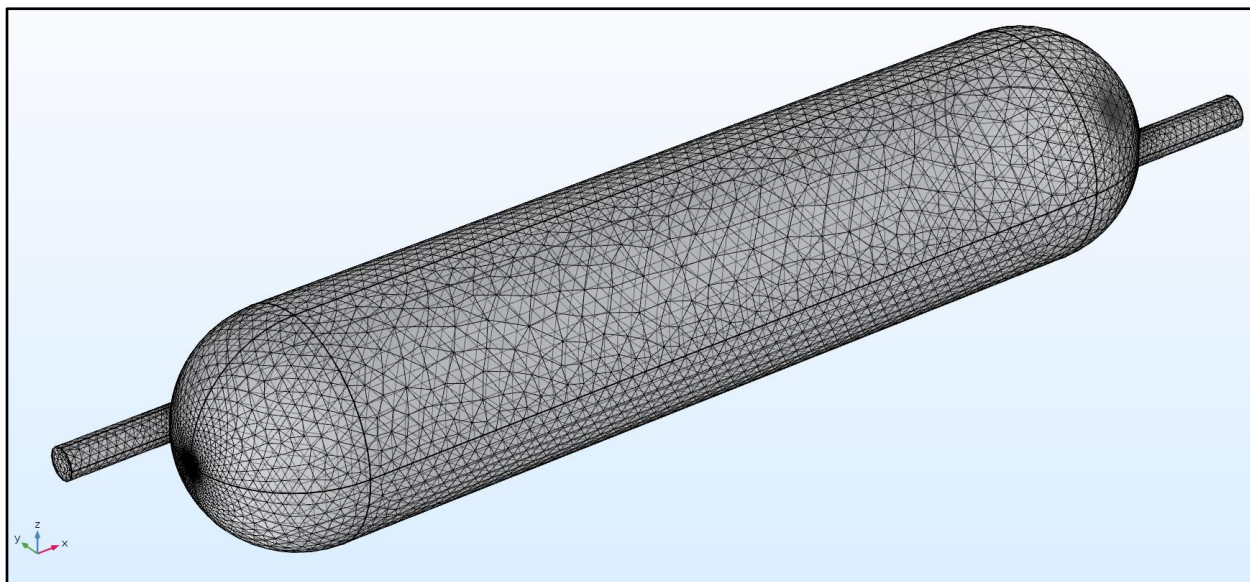


Figure 123: Half Scale Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)



Figure 124: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)

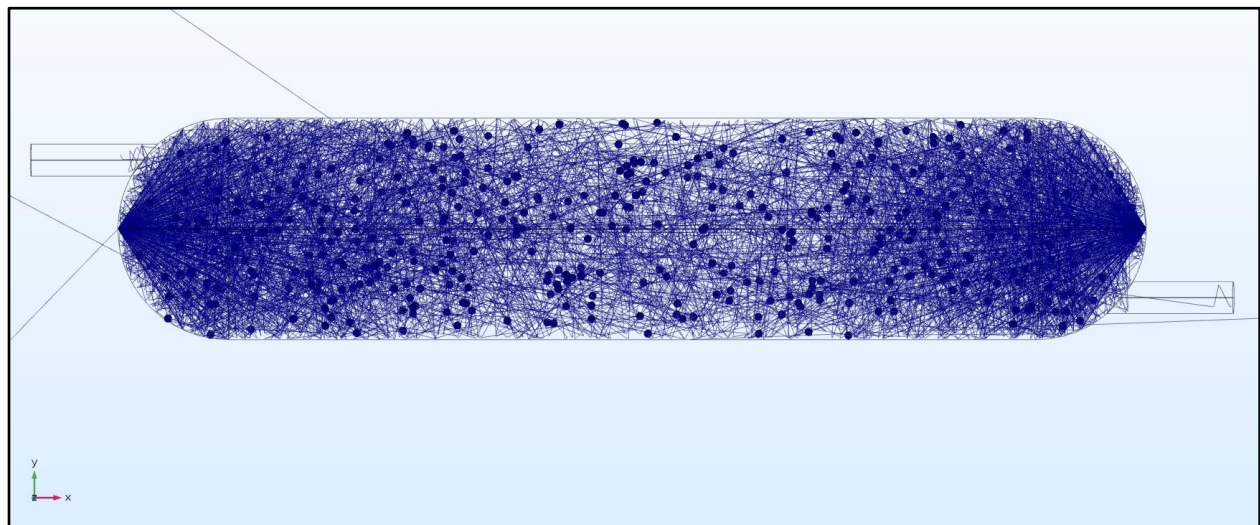


Figure 125: Ray Propagation at 0.35 ns, $k=8.80E-7$ (COMSOL® v. 5.2. 2017)

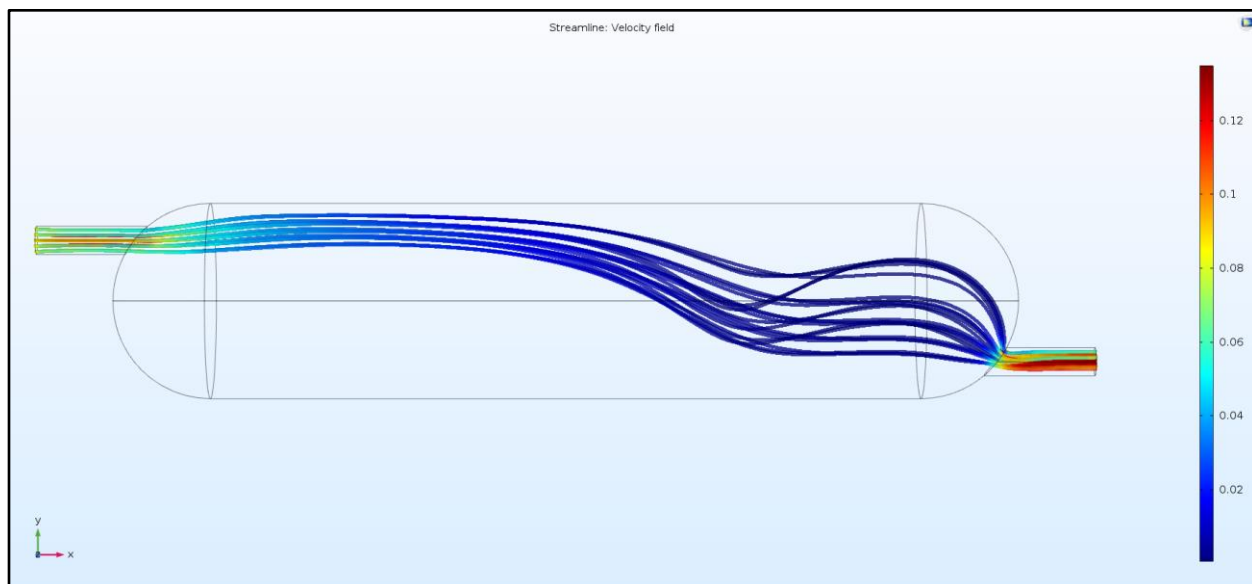


Figure 126: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

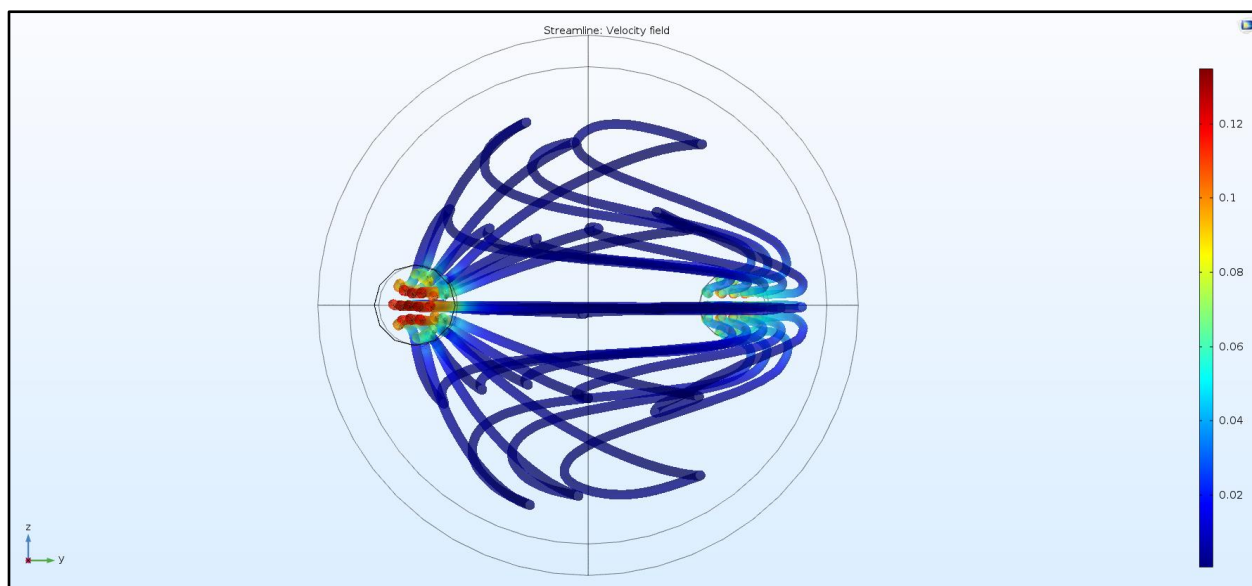


Figure 127: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

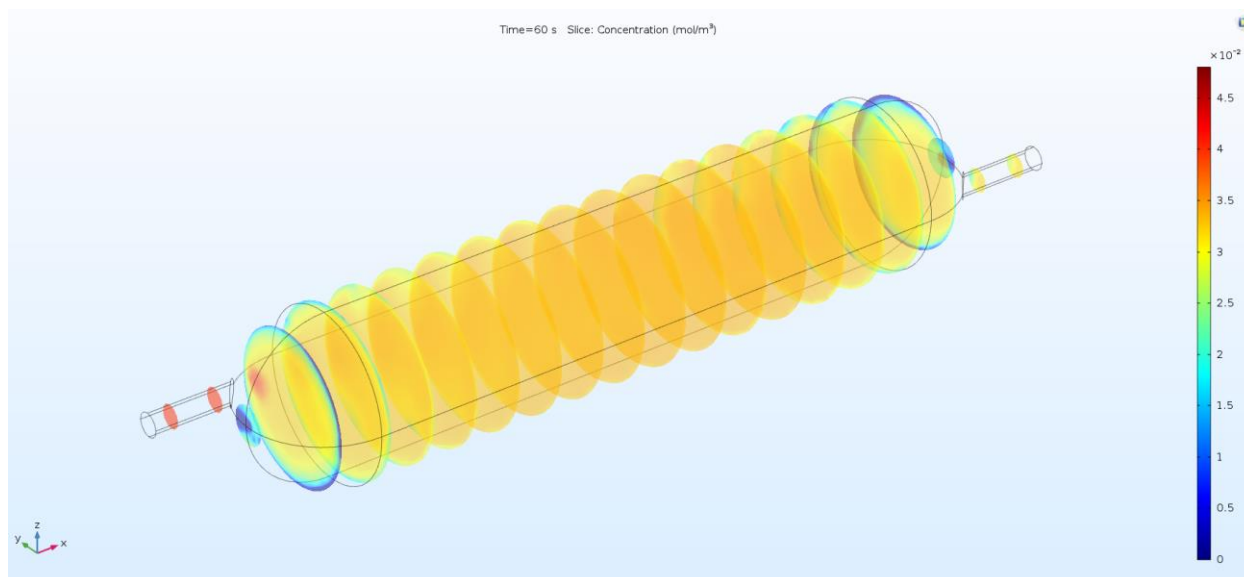


Figure 128: Slice Concentration 10mL/min, $k=8.80E-7$, 60 seconds (COMSOL® v. 5.2. 2017)

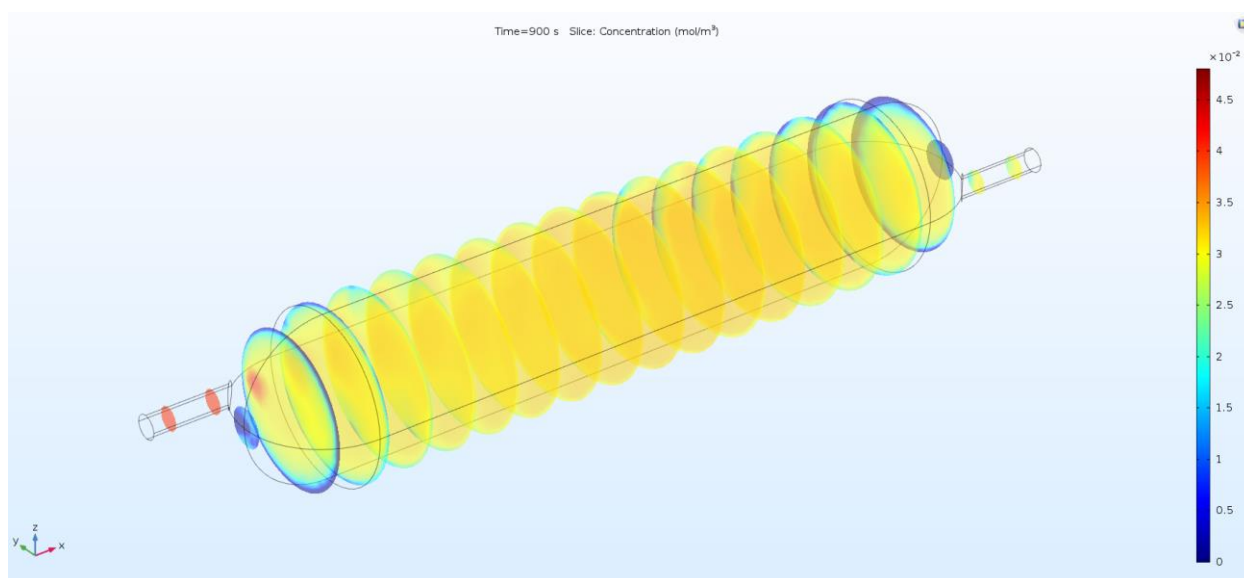


Figure 129: Slice Concentration 10mL/min, $k=8.80E-7$, 900 seconds (COMSOL® v. 5.2. 2017)

Half Scale Original Geometry, 4.546 cm³, Pure Water $k=3.15E-$ at 10 mL/min

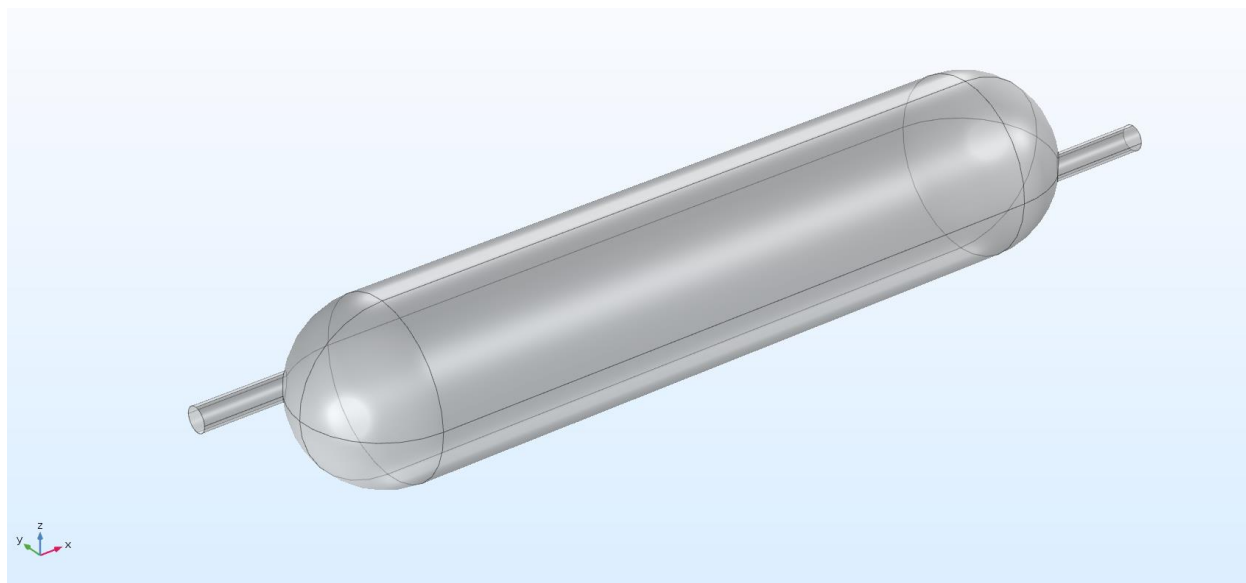


Figure 130: Half Scale Original Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017)

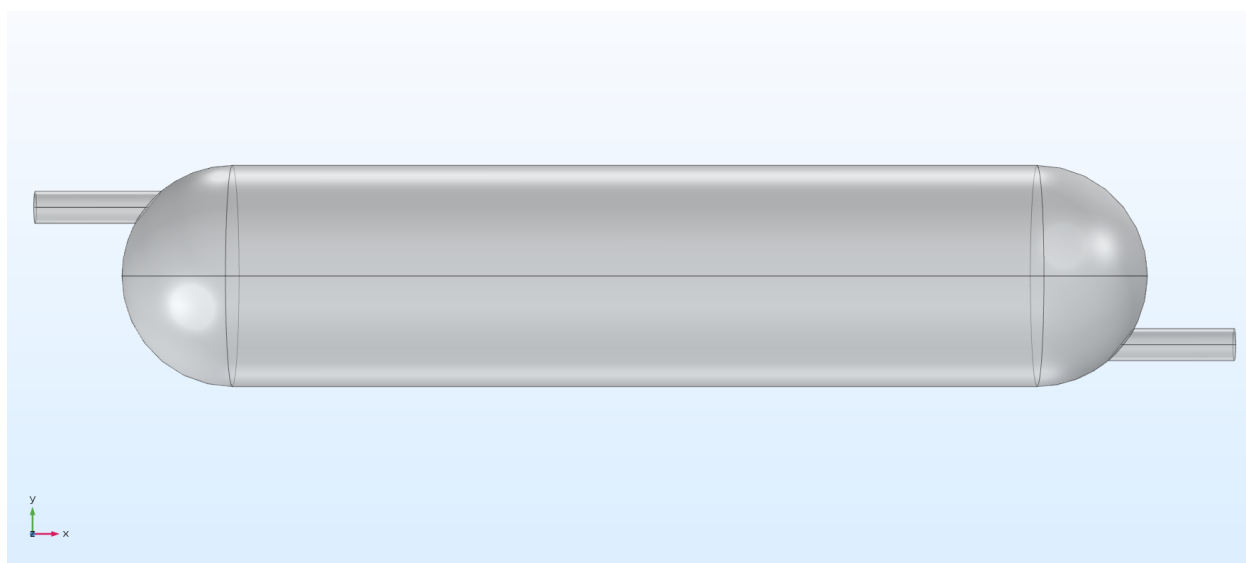


Figure 131: Half Scale Original Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017)

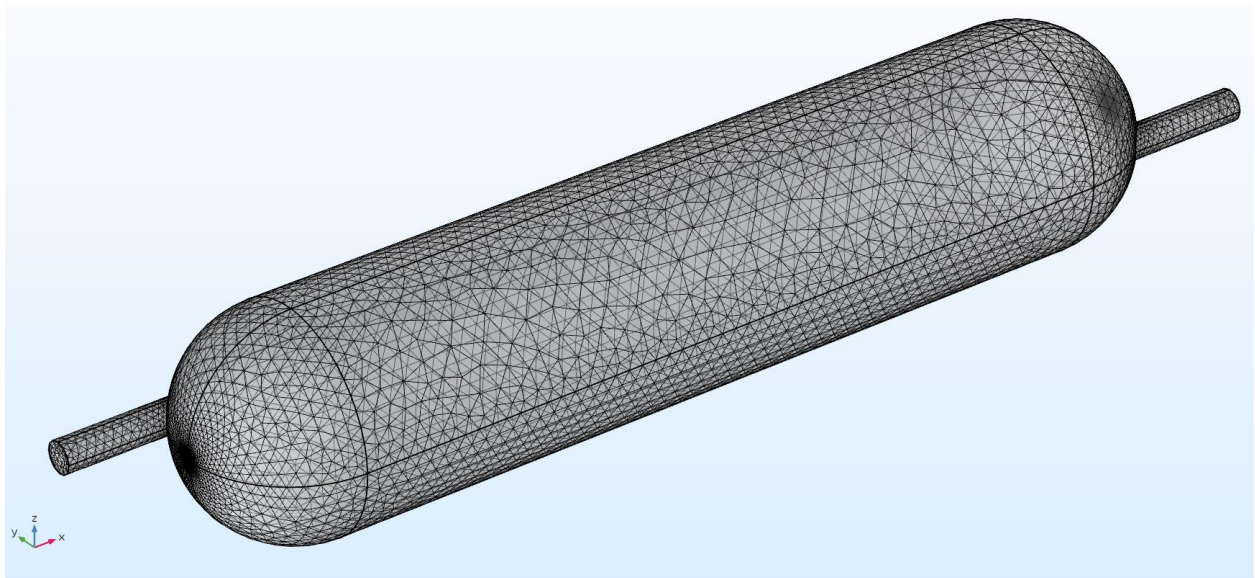


Figure 132: Half Scale Original Geometry Mesh Layout (COMSOL® v. 5.2. 2017)

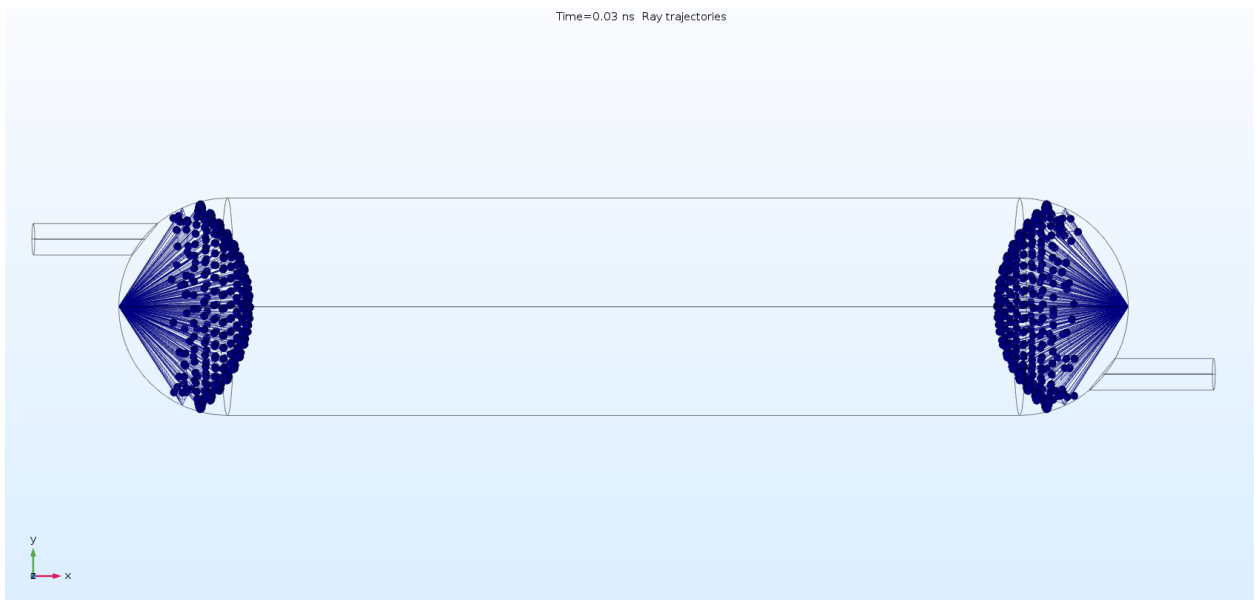


Figure 133: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)

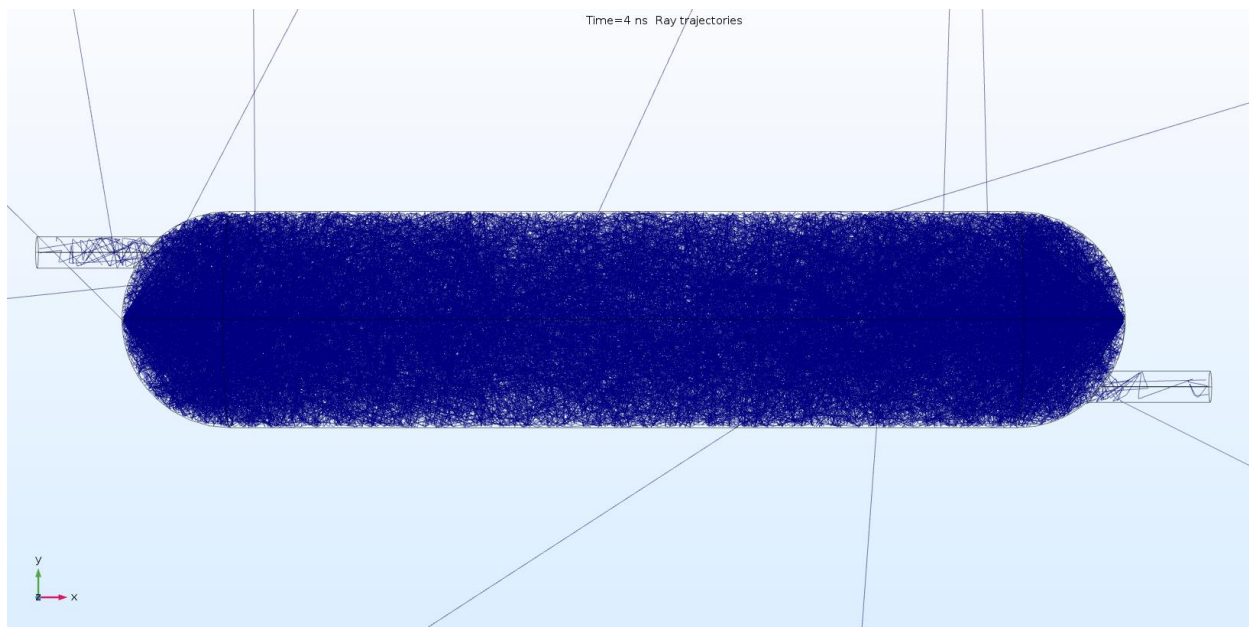


Figure 134: Ray Propagation at 4.0 ns, $k=3.15E-8$ (COMSOL® v. 5.2. 2017)

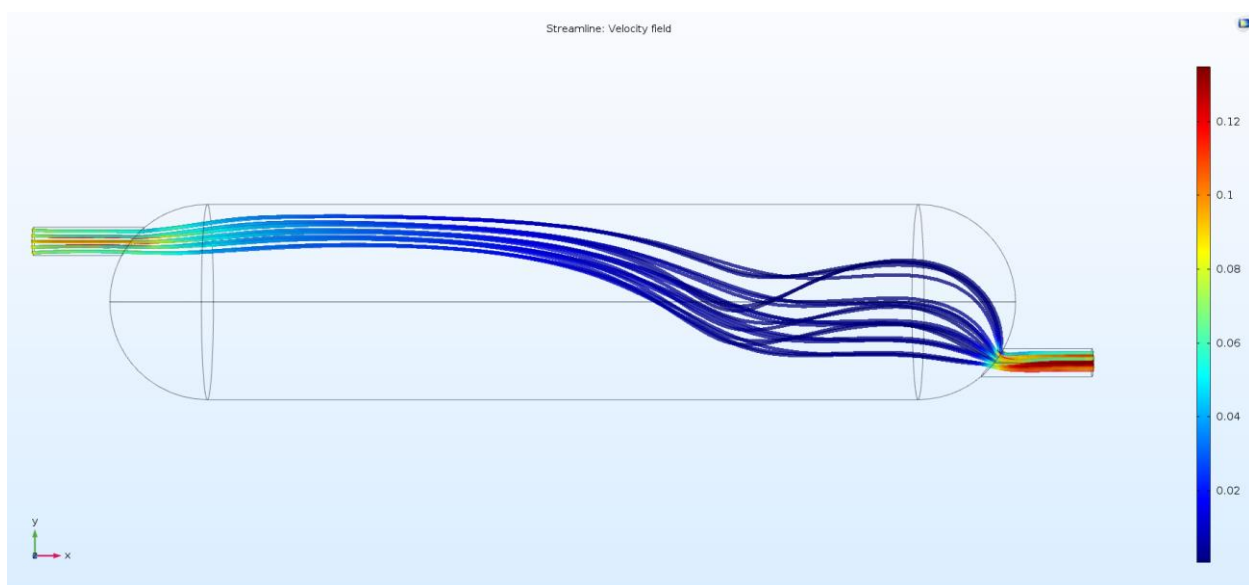


Figure 135: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

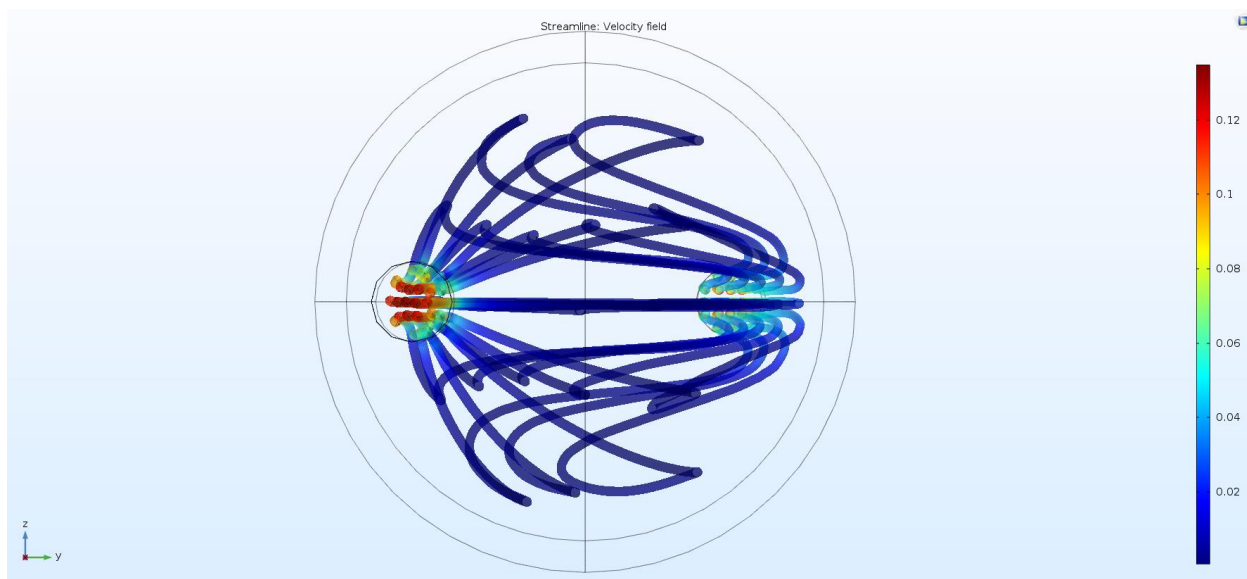


Figure 136: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

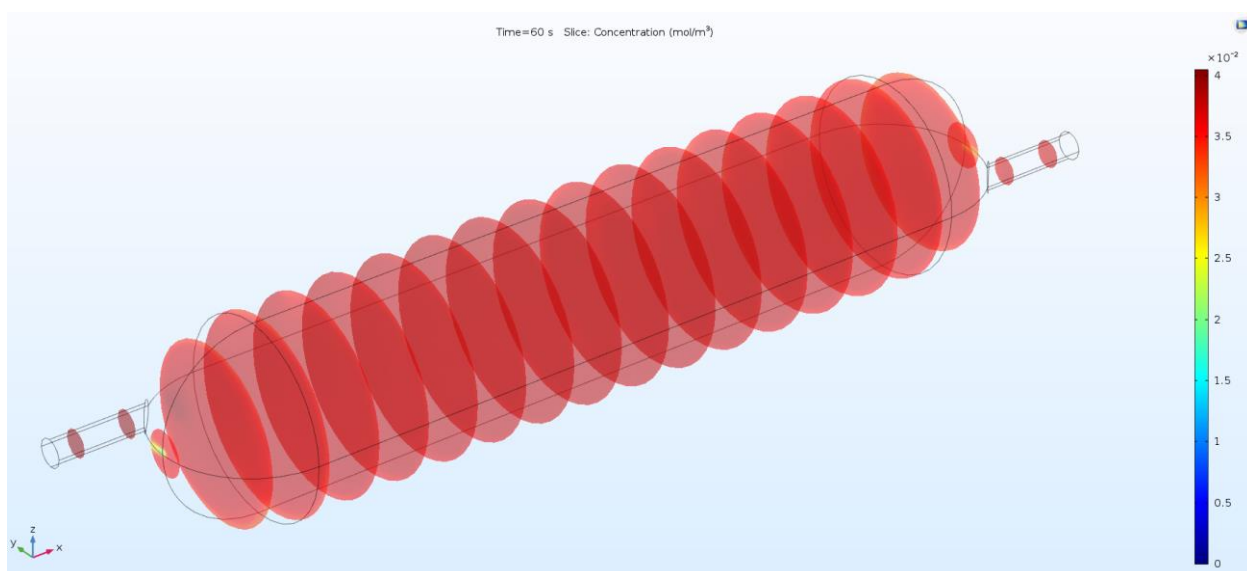


Figure 137: Slice Concentration 10mL/min, $k=3.15\text{E-}8$, 60 seconds (COMSOL® v. 5.2. 2017)

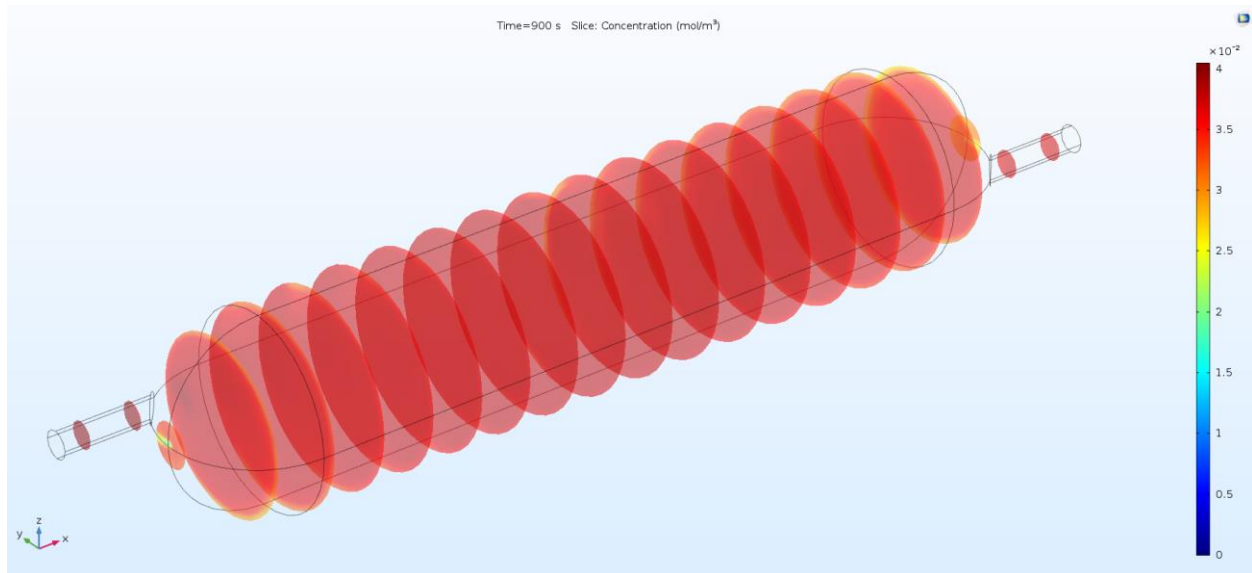


Figure 138: Slice Concentration 10mL/min, $k=3.15\text{E-}8$, 900 seconds (COMSOL® v. 5.2. 2017)

Half Scale Original Geometry with Separator Plate, 4.546 cm^3 , Brilliant Blue $k=8.80\text{E-}7$ at 10 mL/min

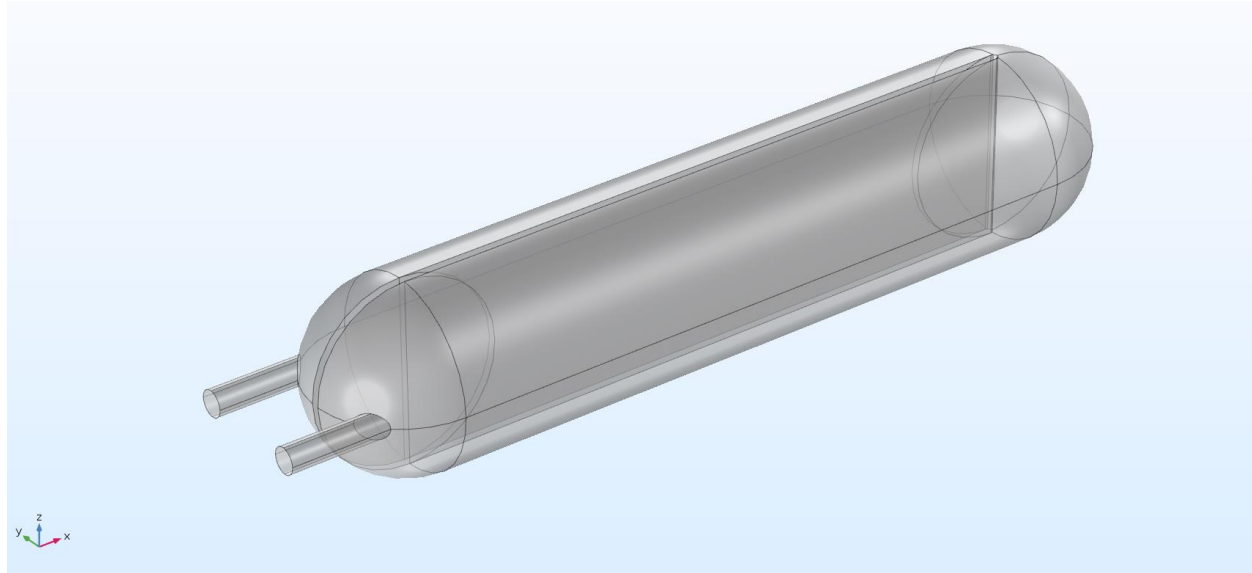


Figure 139: Half Scale Original Geometry with Separator Plate 10 mL/min, Isometric (COMSOL® v. 5.2. 2017)

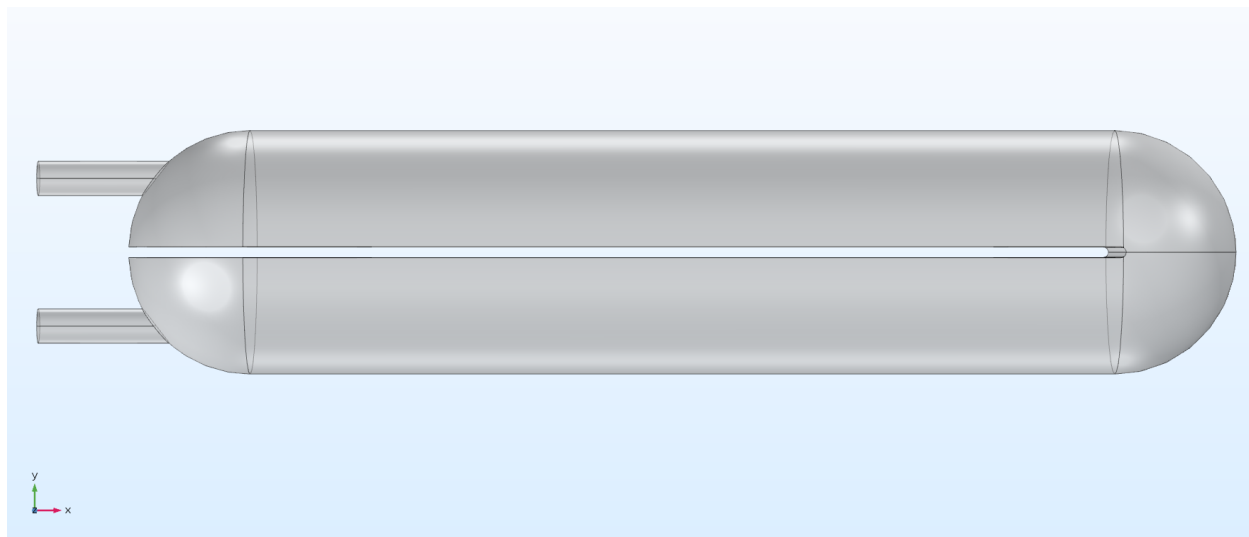


Figure 140: Half Scale Original Geometry with Separator Plate 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017)

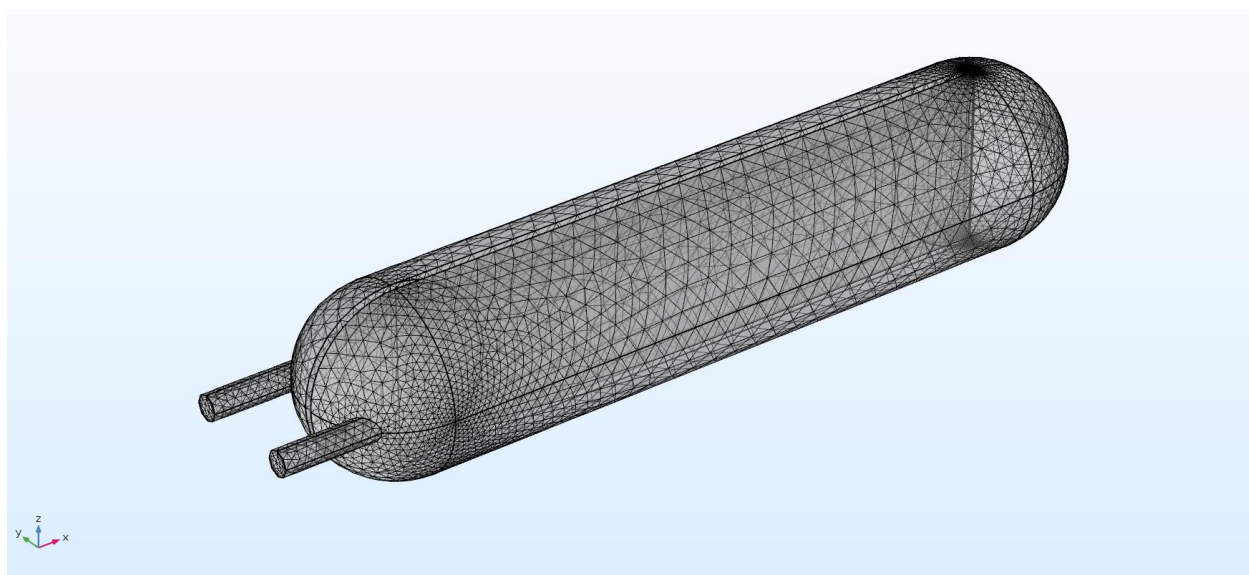


Figure 141: Half Scale Original Geometry with Separator Plate Mesh Layout (COMSOL® v. 5.2. 2017)

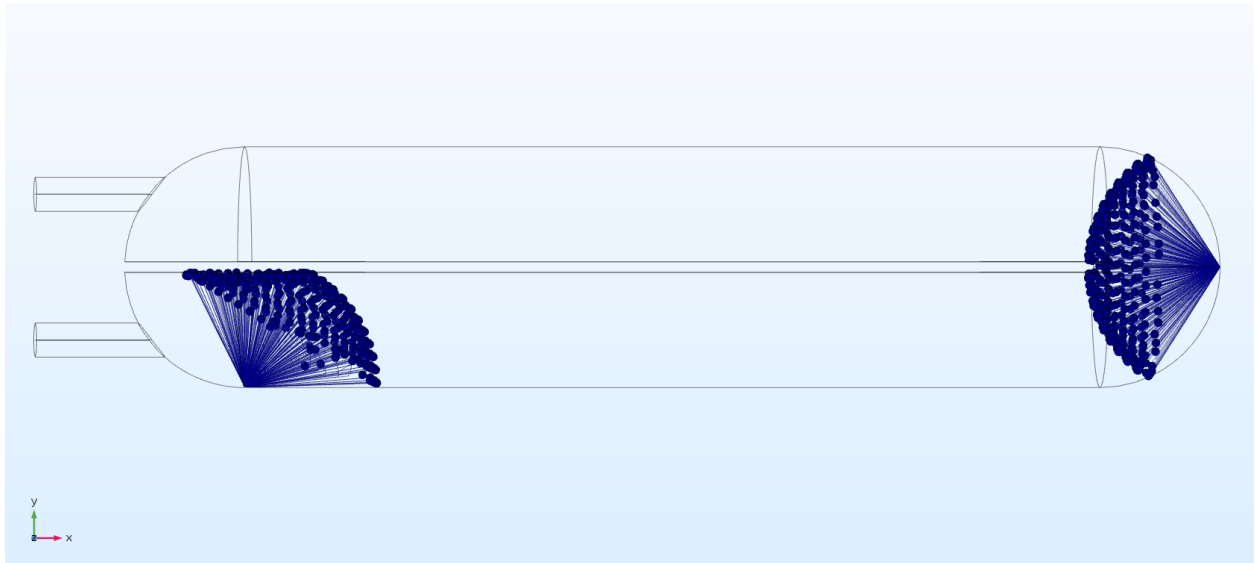


Figure 142: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)

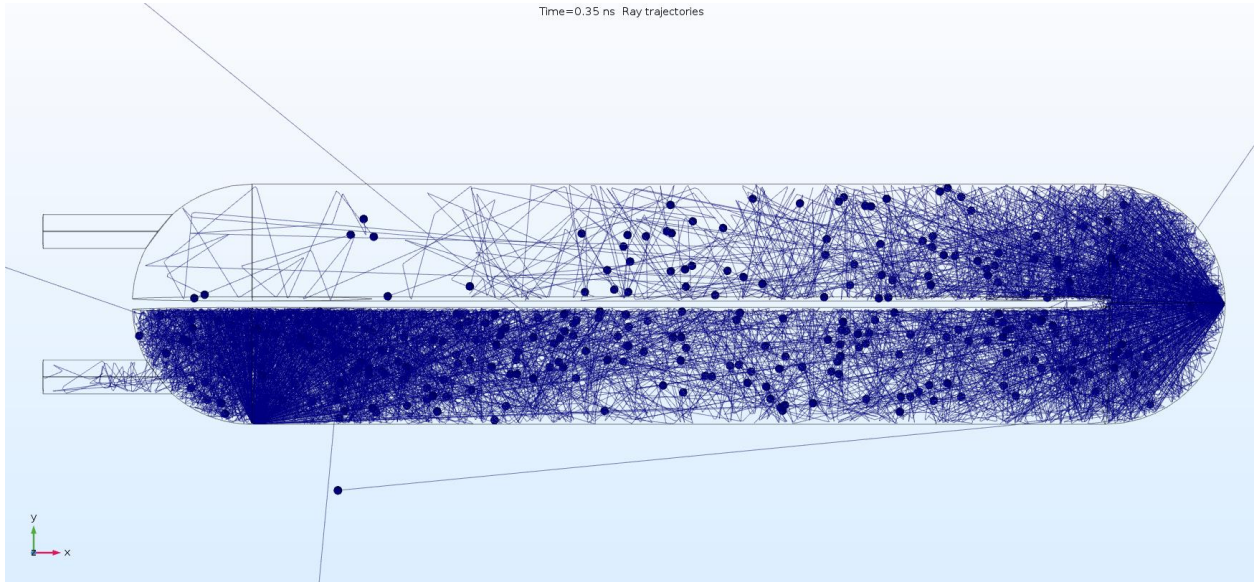


Figure 143: Ray Propagation at 0.35 ns, $k=8.80E-7$ (COMSOL® v. 5.2. 2017)

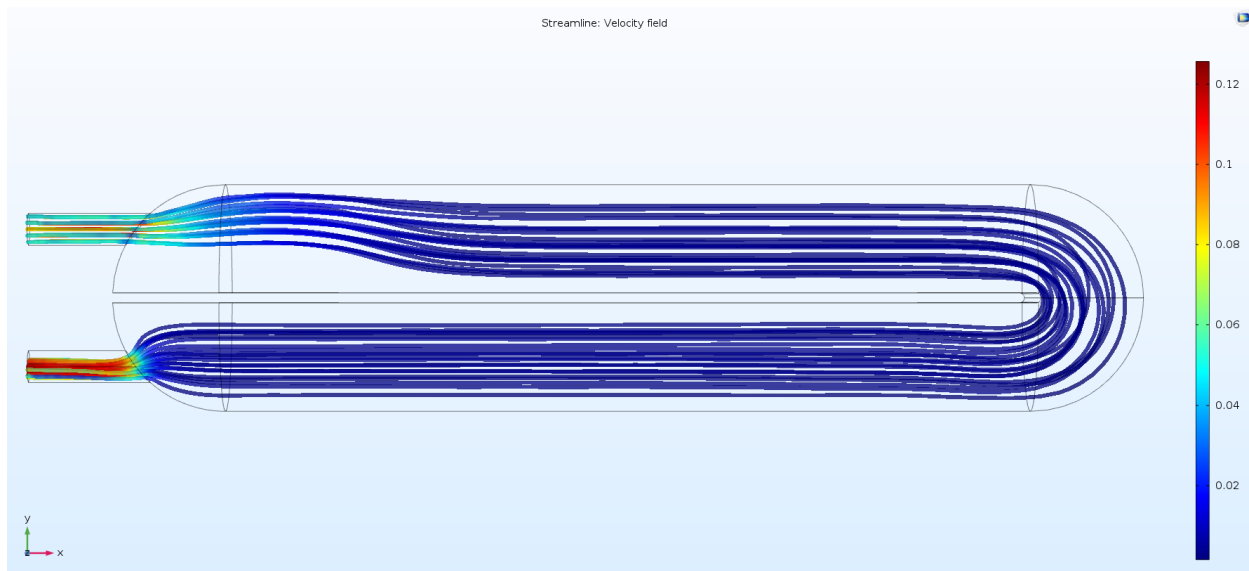


Figure 144: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

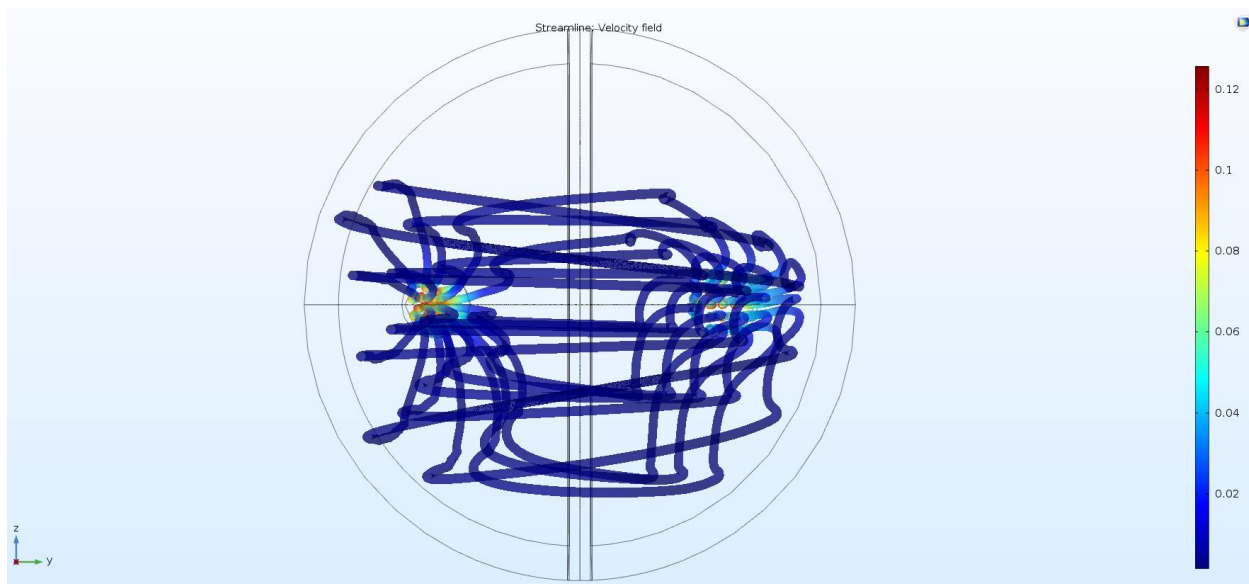


Figure 145: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

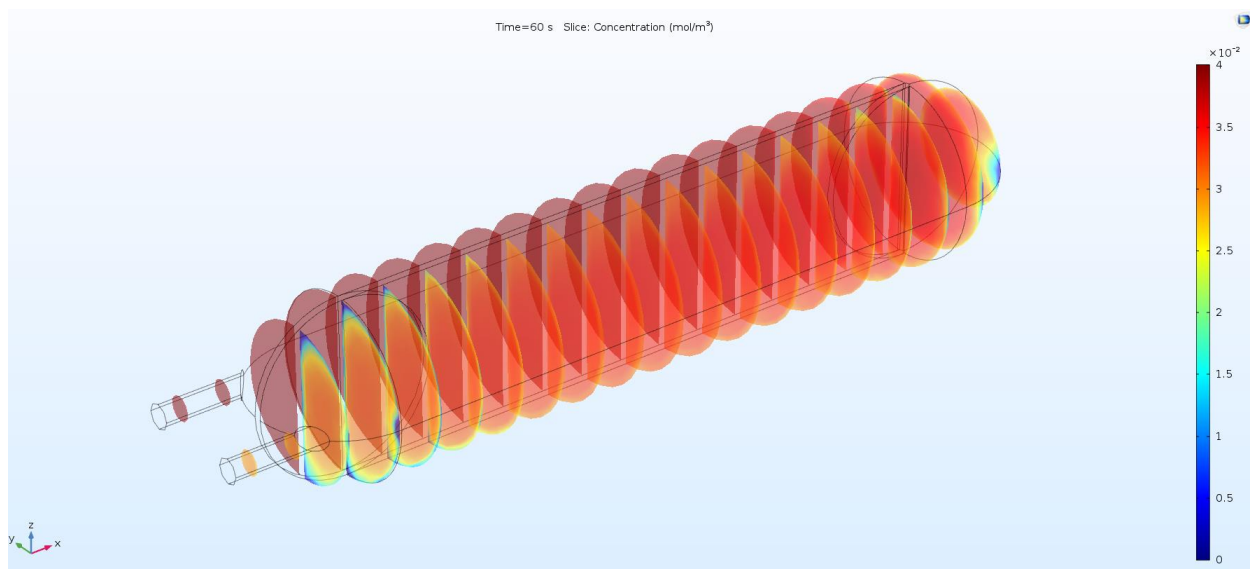


Figure 146: Slice Concentration 10mL/min, $k=8.80E-7$, 60 seconds (COMSOL® v. 5.2. 2017)

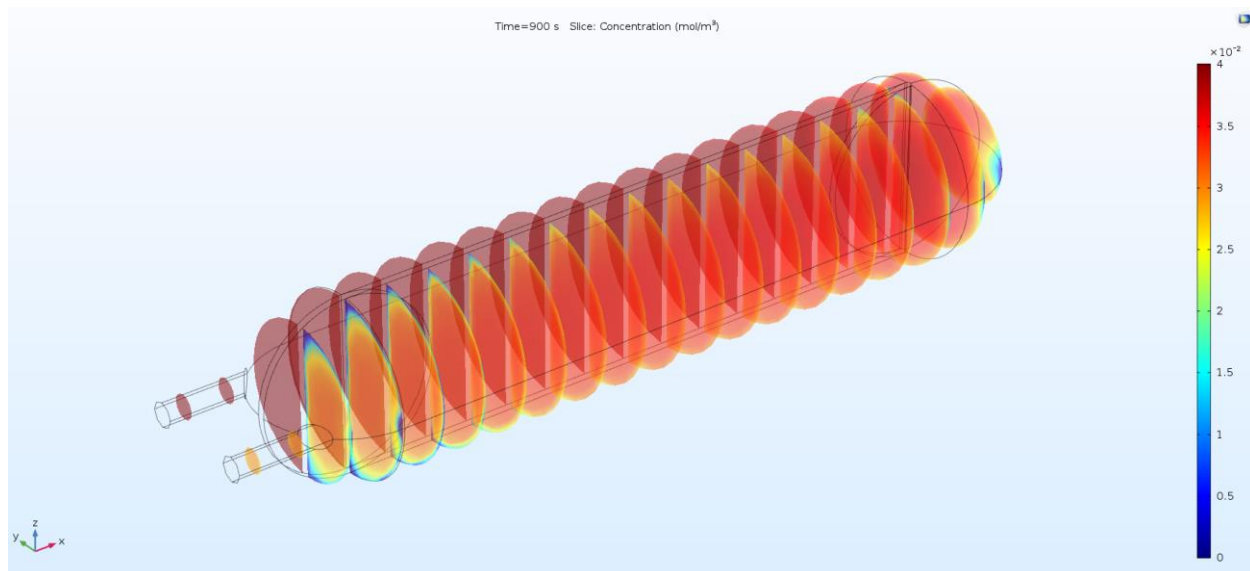


Figure 147: Slice Concentration 10mL/min, $k=8.80E-7$, 900 seconds (COMSOL® v. 5.2. 2017)

Half Scale Original Geometry with Separator Plate, 4.546 cm³, Pure Water $k=3.15E-6$ at 10 mL/min

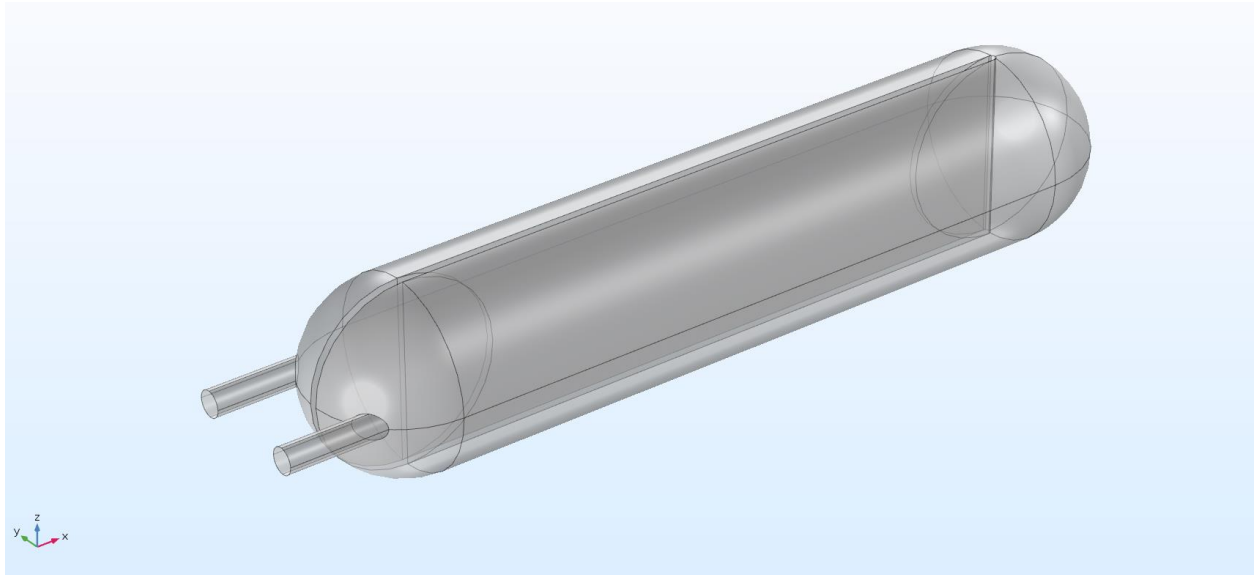


Figure 148: Half Scale Original Geometry with Separator Plate 10 mL/min, Isometric (COMSOL® v. 5.2. 2017)

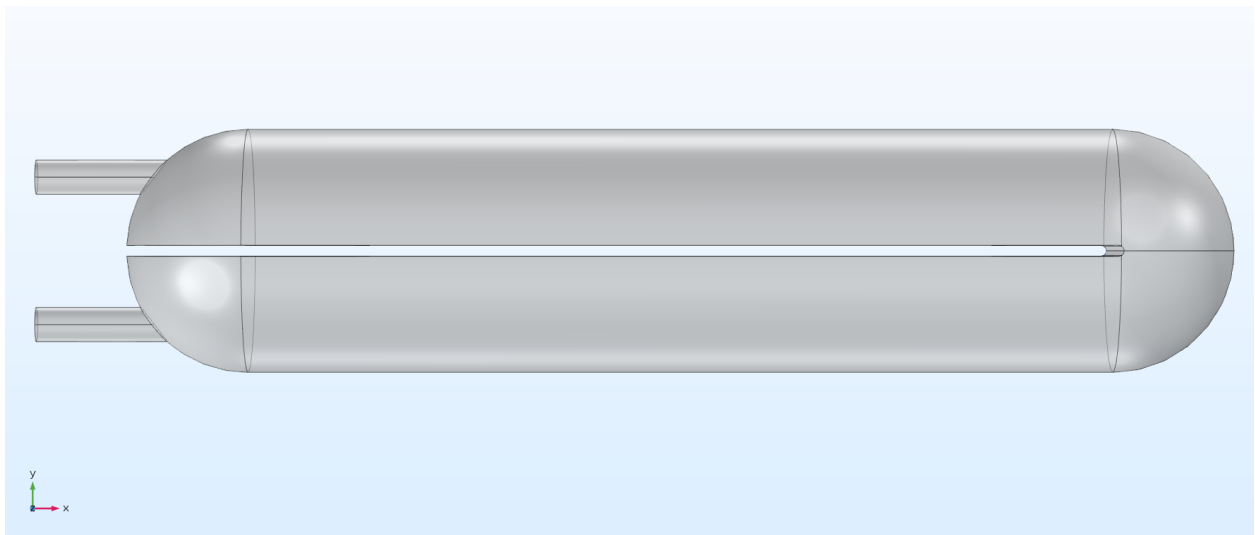


Figure 149: Half Scale Original Geometry with Separator Plate 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017)

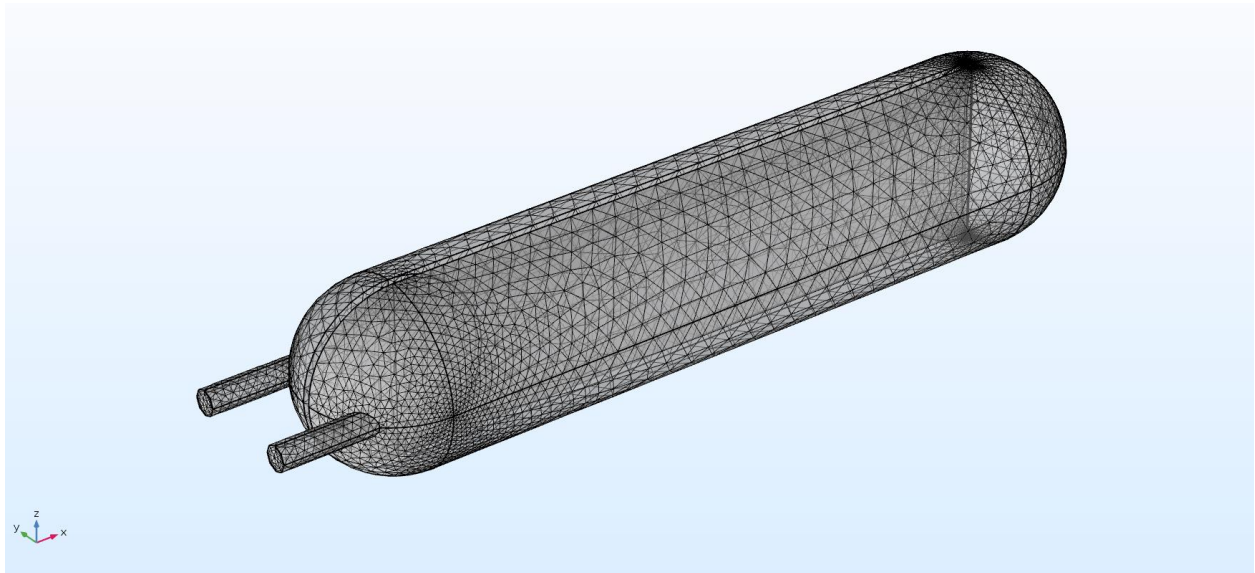


Figure 150: Half Scale Original Geometry with Separator Plate Mesh Layout (COMSOL® v. 5.2. 2017)

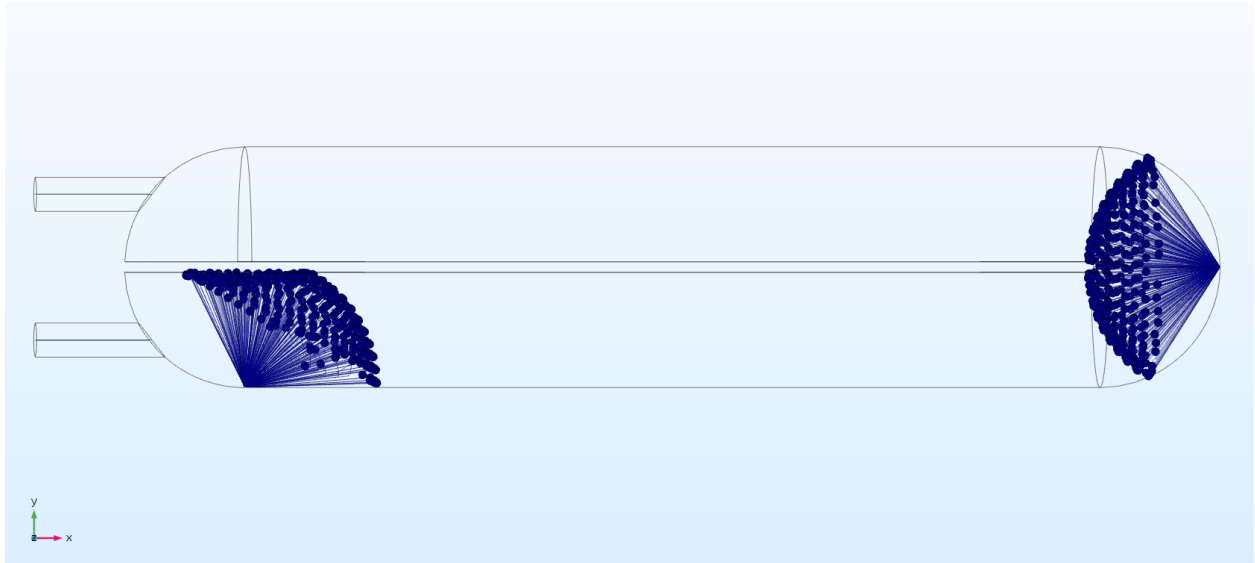


Figure 151: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)

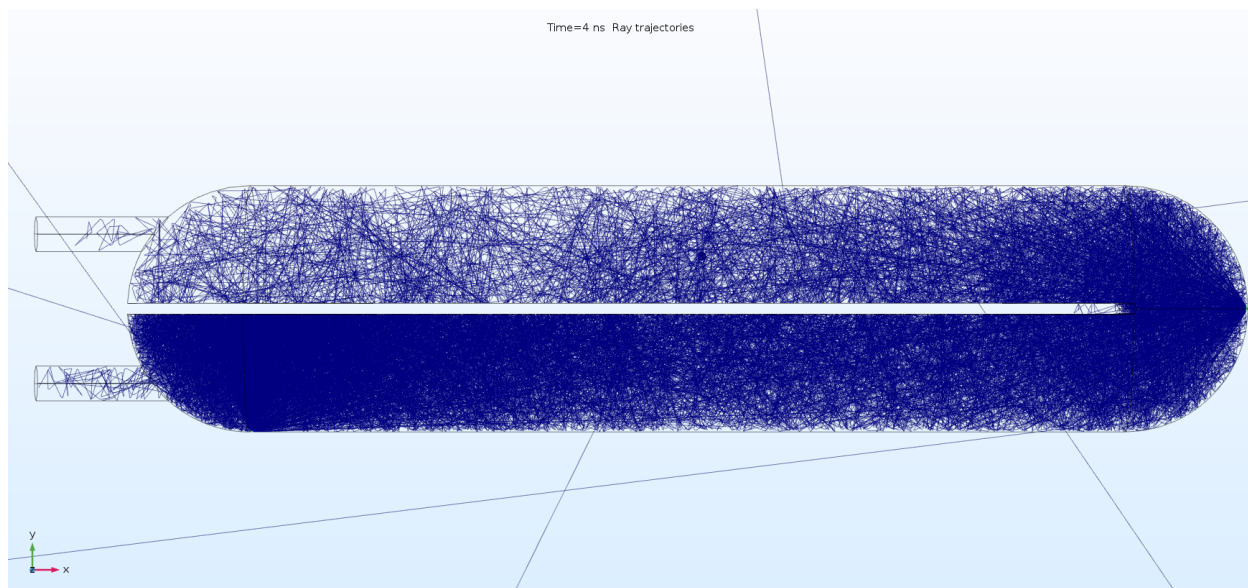


Figure 152: Ray Propagation at 4.0 ns, $k=3.15E-8$ (COMSOL® v. 5.2. 2017)

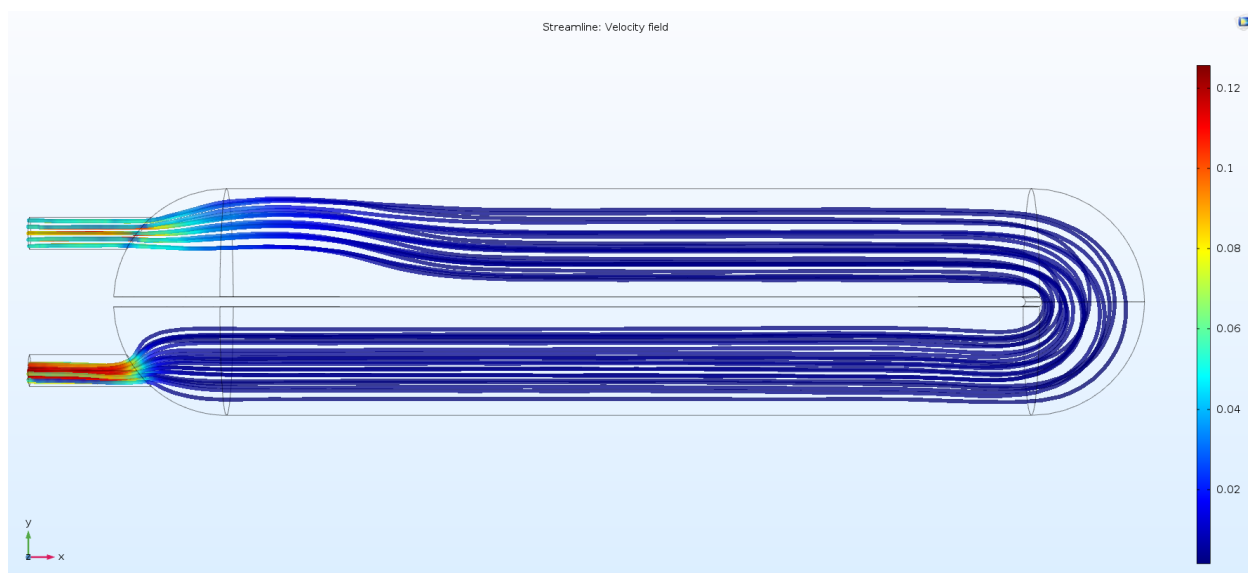


Figure 153: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

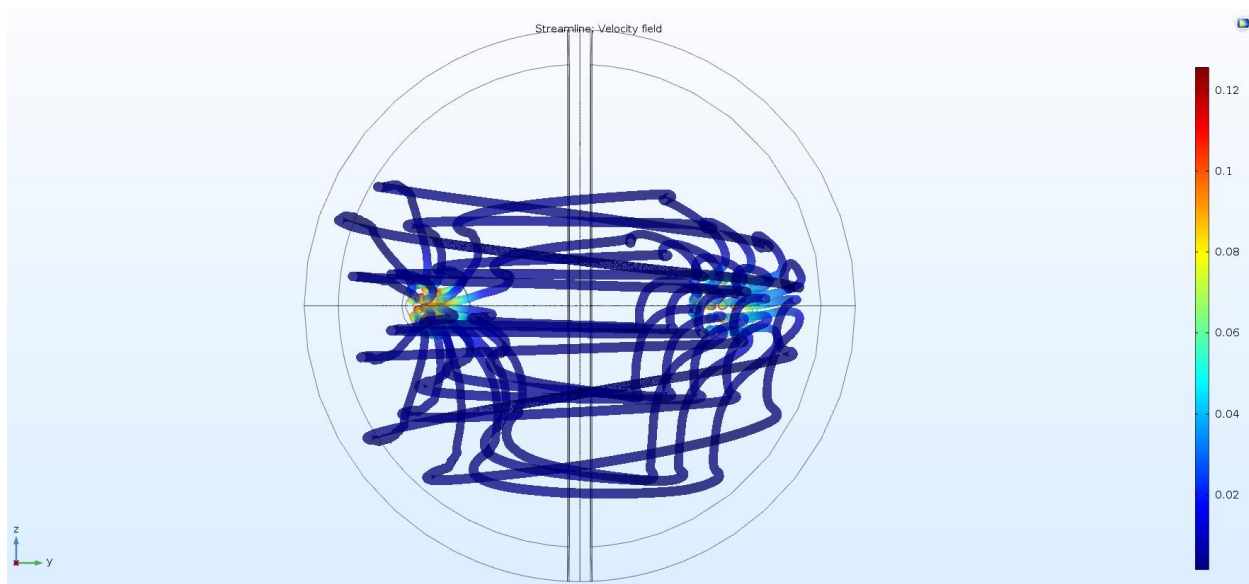


Figure 154: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

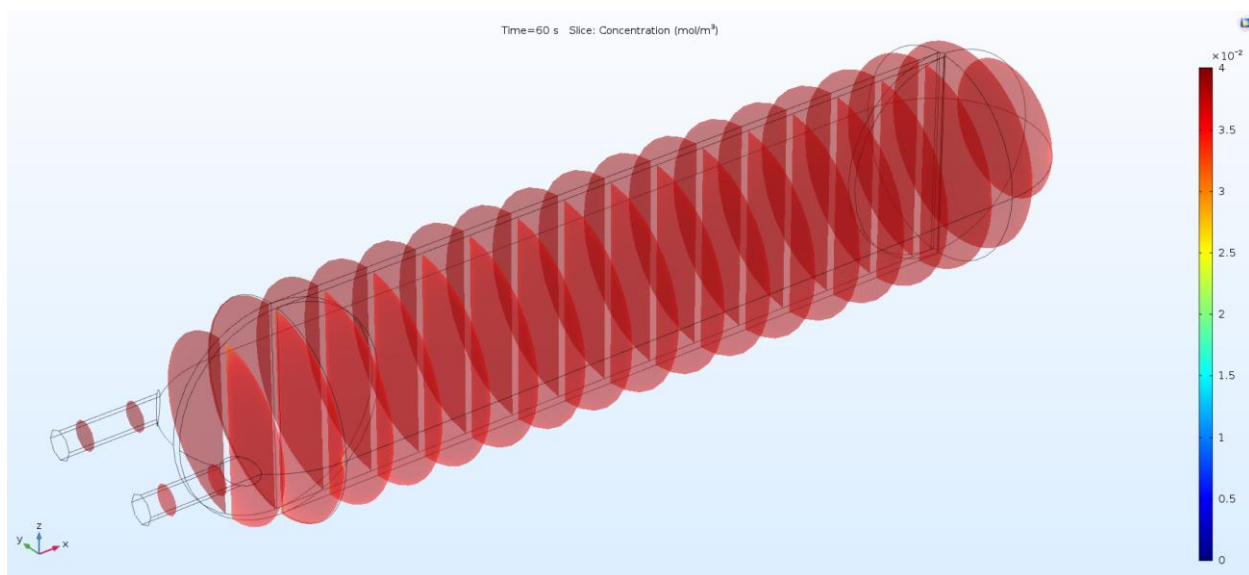


Figure 155: Slice Concentration 10mL/min, $k=3.15\text{E}-8$, 60 seconds (COMSOL® v. 5.2. 2017)

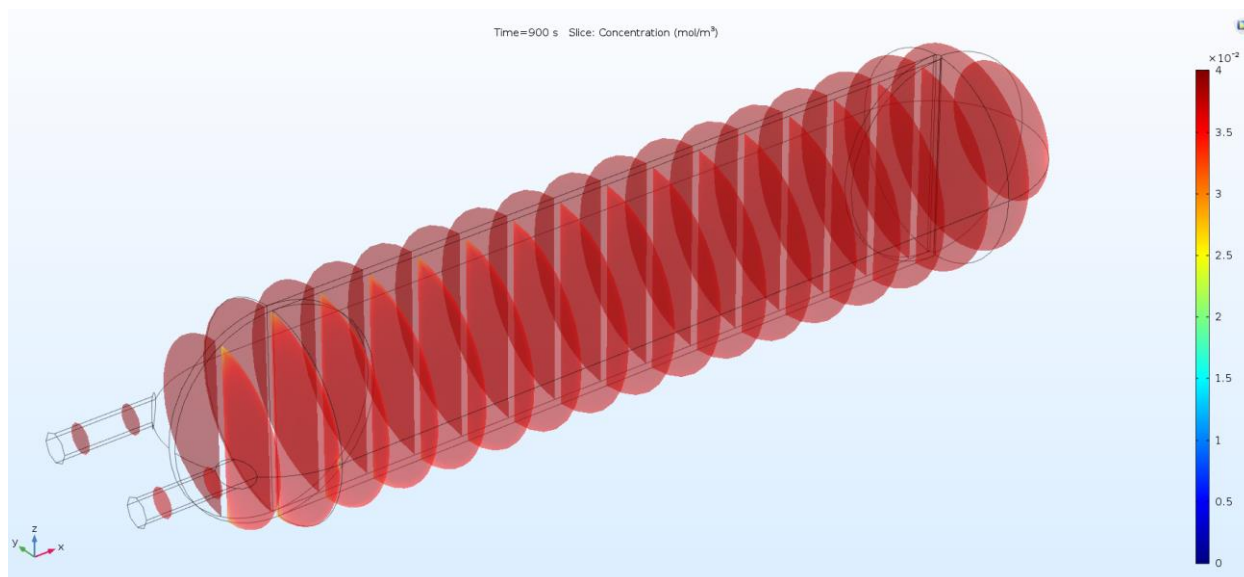


Figure 156: Slice Concentration 10mL/min, $k=3.15\text{E-}8$, 900 seconds (COMSOL® v. 5.2. 2017)

Sphere Geometry, 4.546 cm³, Brilliant Blue $k=8.80\text{E-}7$ at 10 mL/min

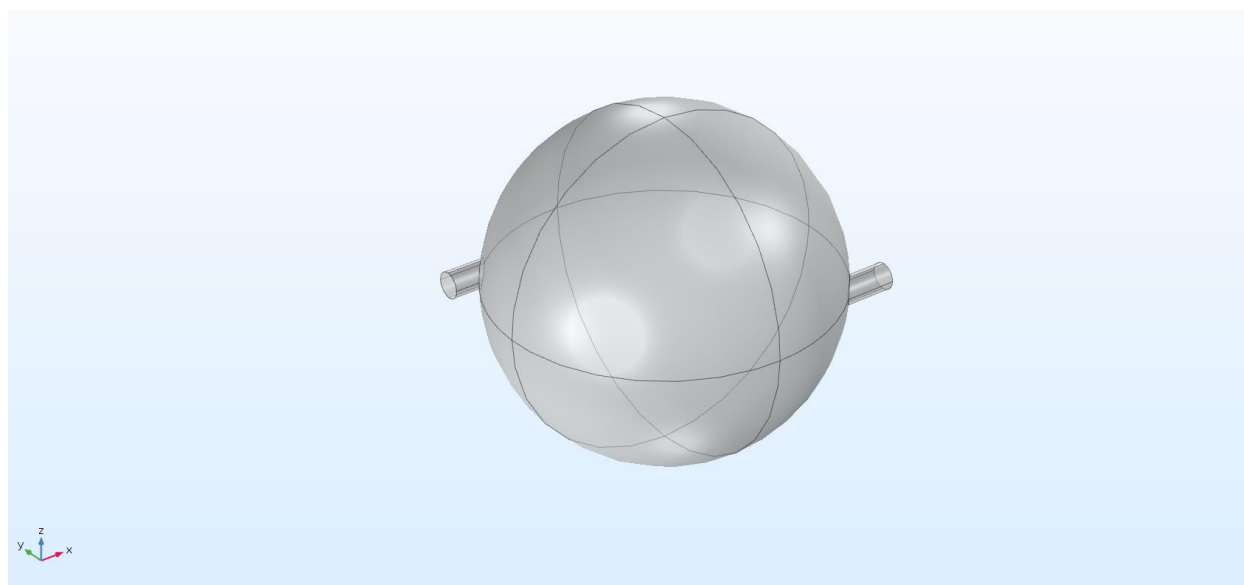


Figure 157: Sphere Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017)

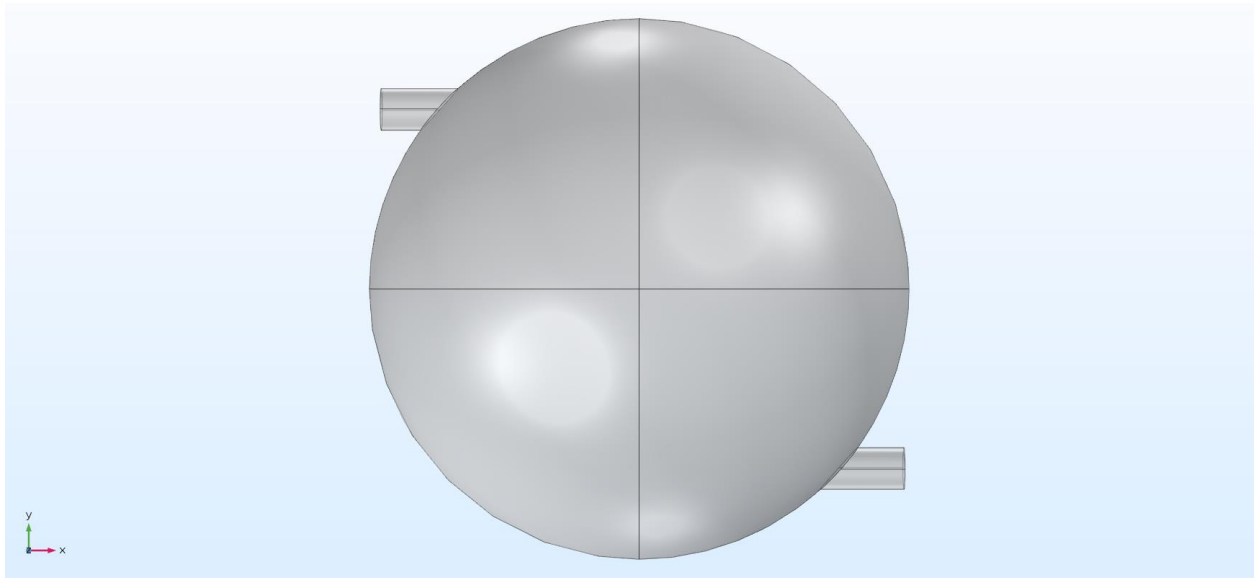


Figure 158: Sphere Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017)

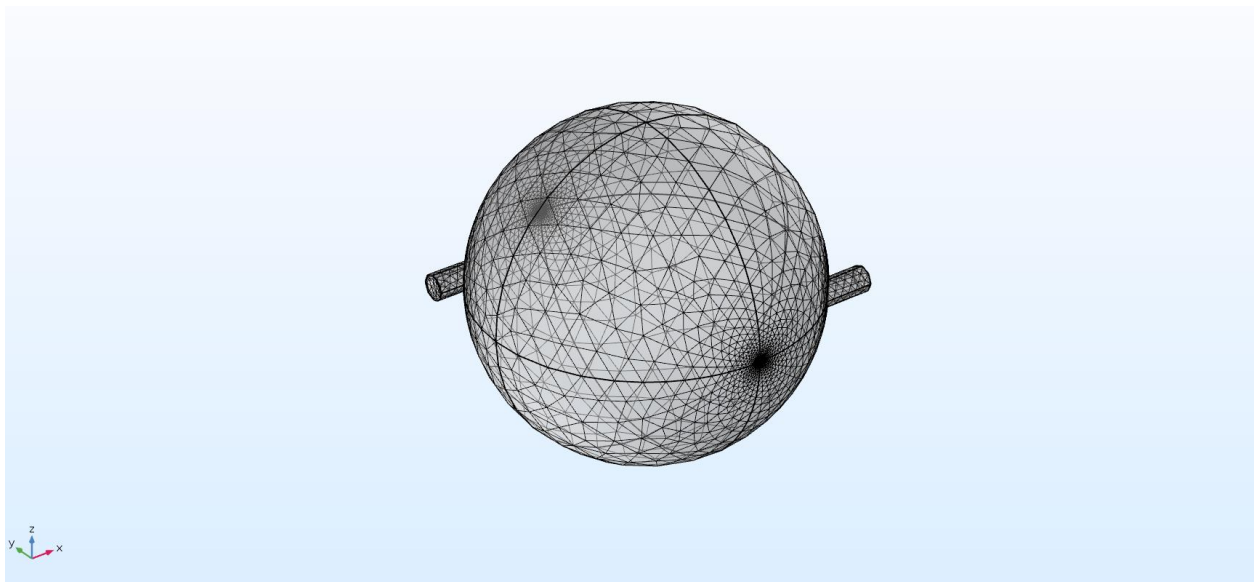


Figure 159: Sphere Geometry Mesh Layout (COMSOL® v. 5.2. 2017)

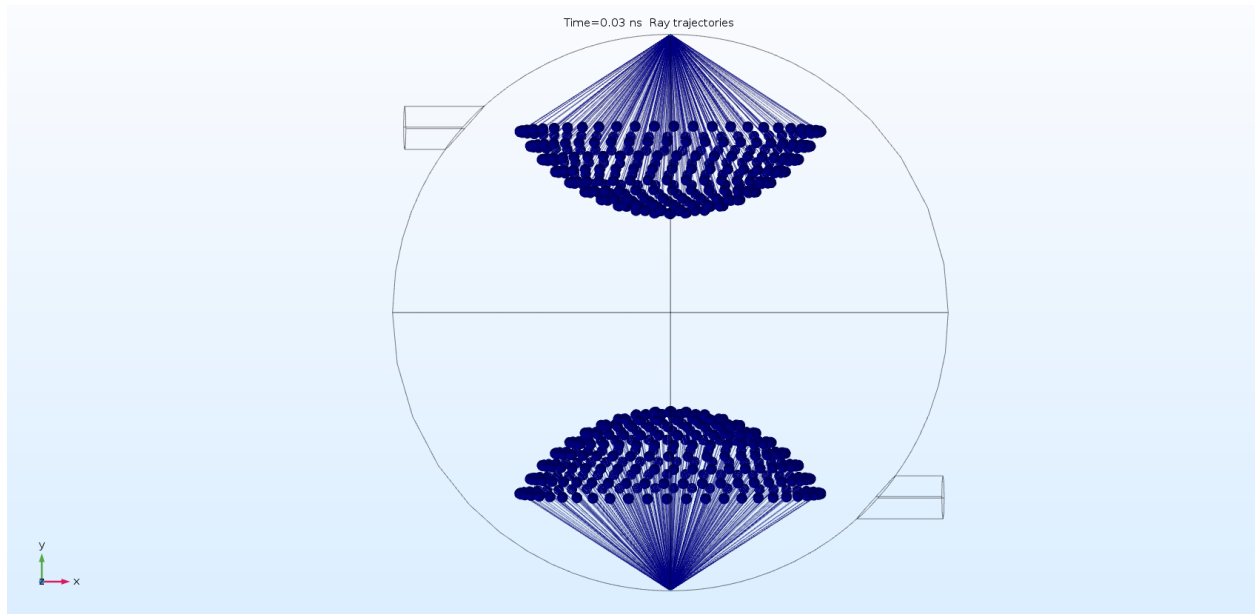


Figure 160: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)

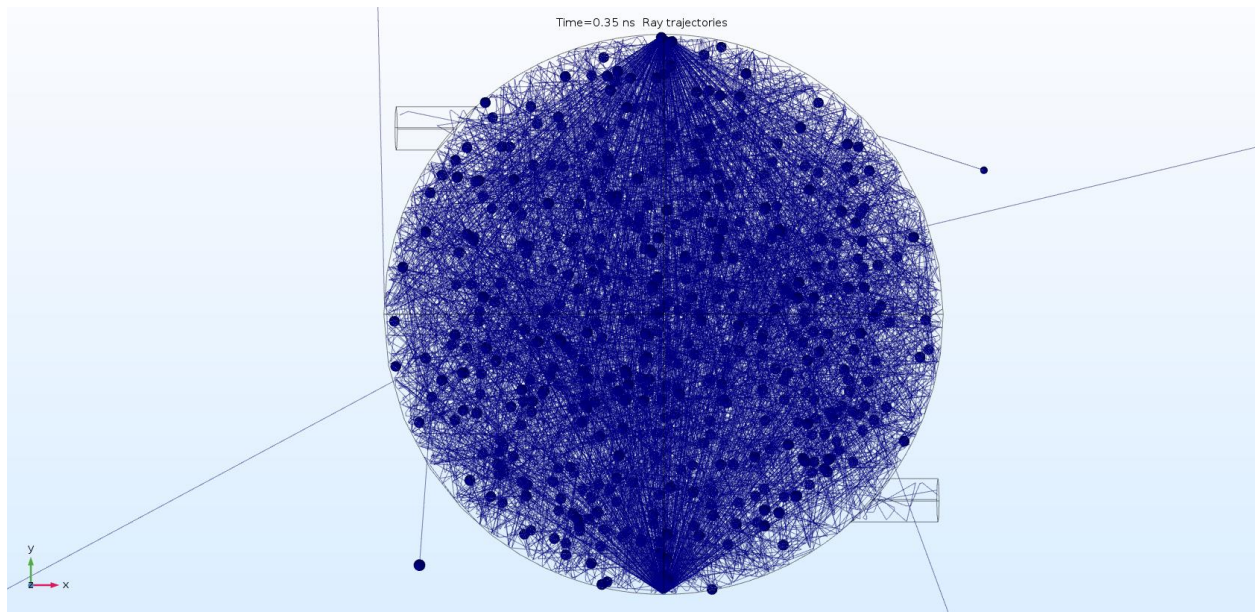


Figure 161: Ray Propagation at 0.35 ns, $k=8.80E-7$ (COMSOL® v. 5.2. 2017)

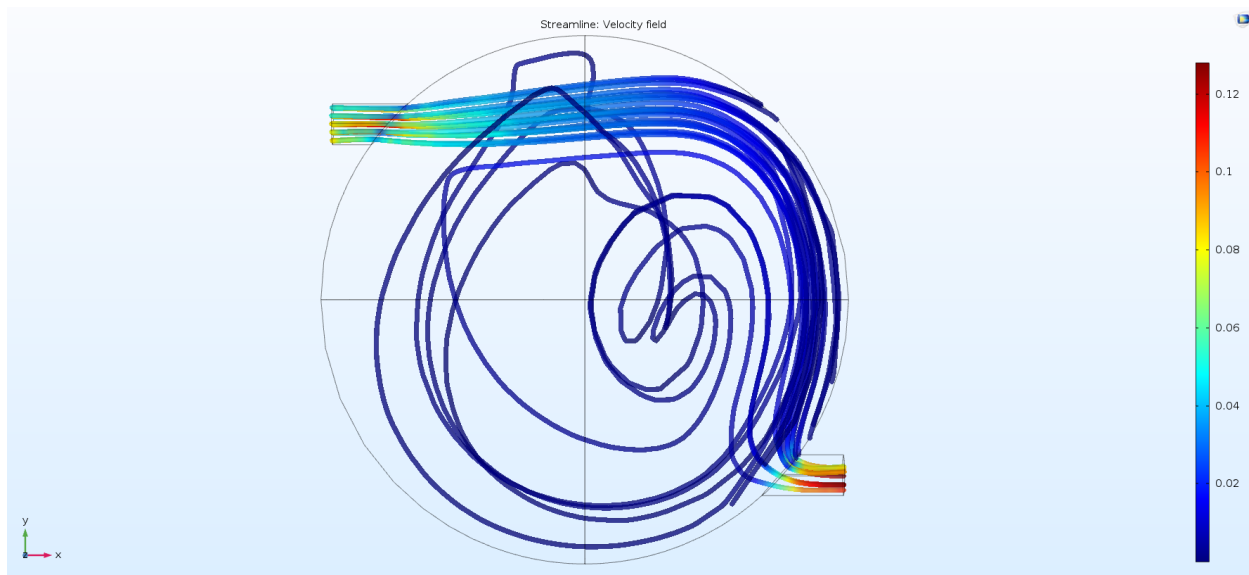


Figure 162: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

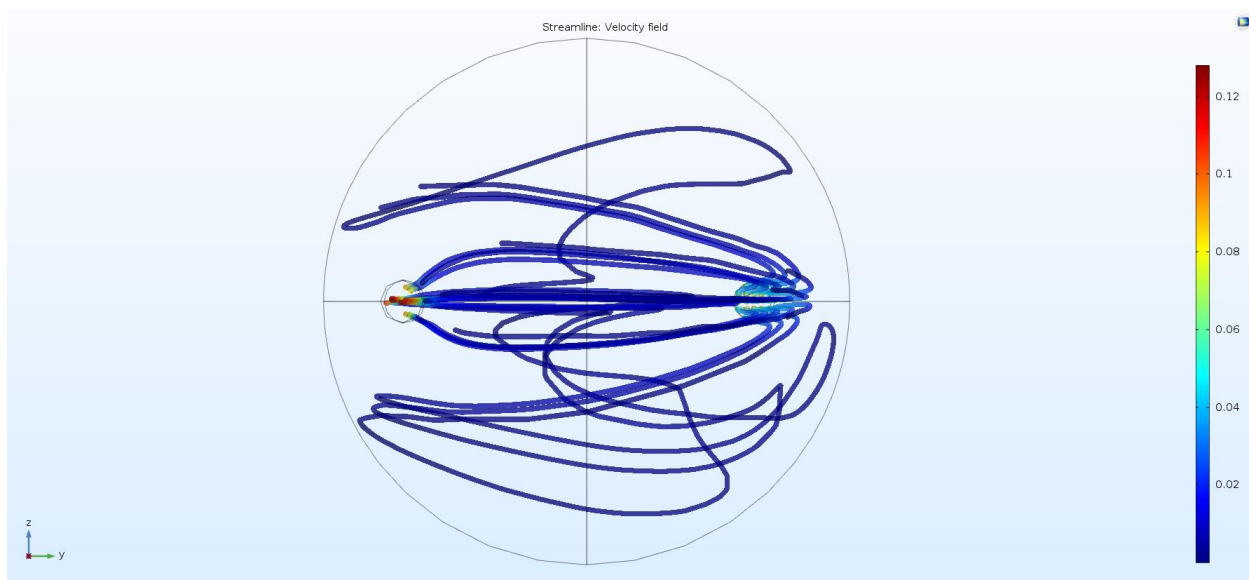


Figure 163: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

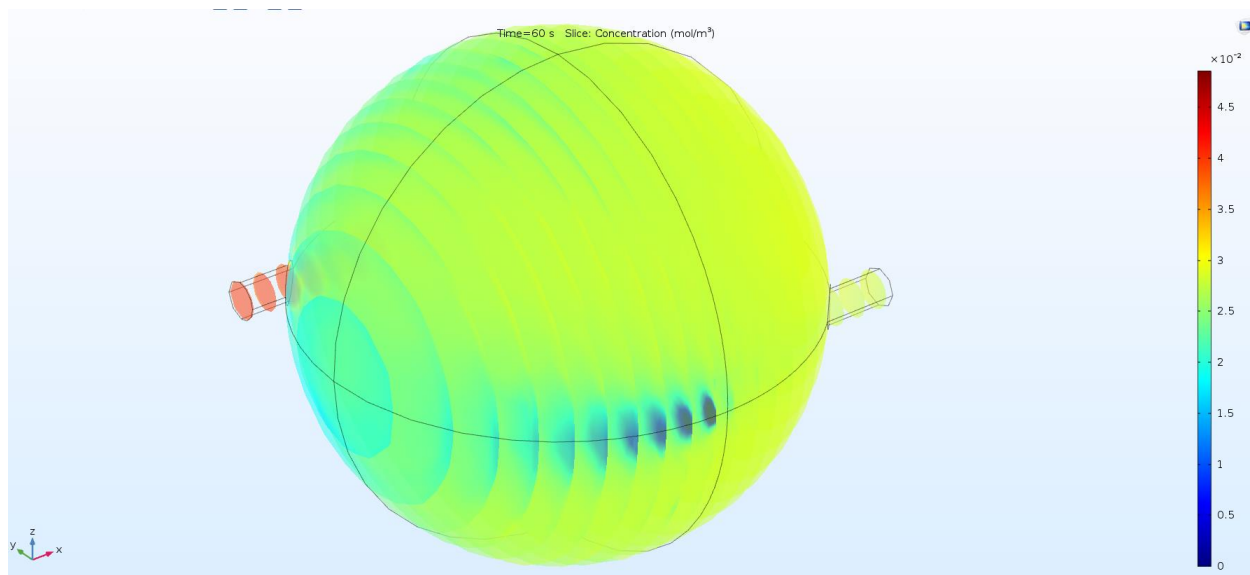


Figure 164: Slice Concentration 10mL/min, $k=8.80E-7$, 60 seconds (COMSOL® v. 5.2. 2017)

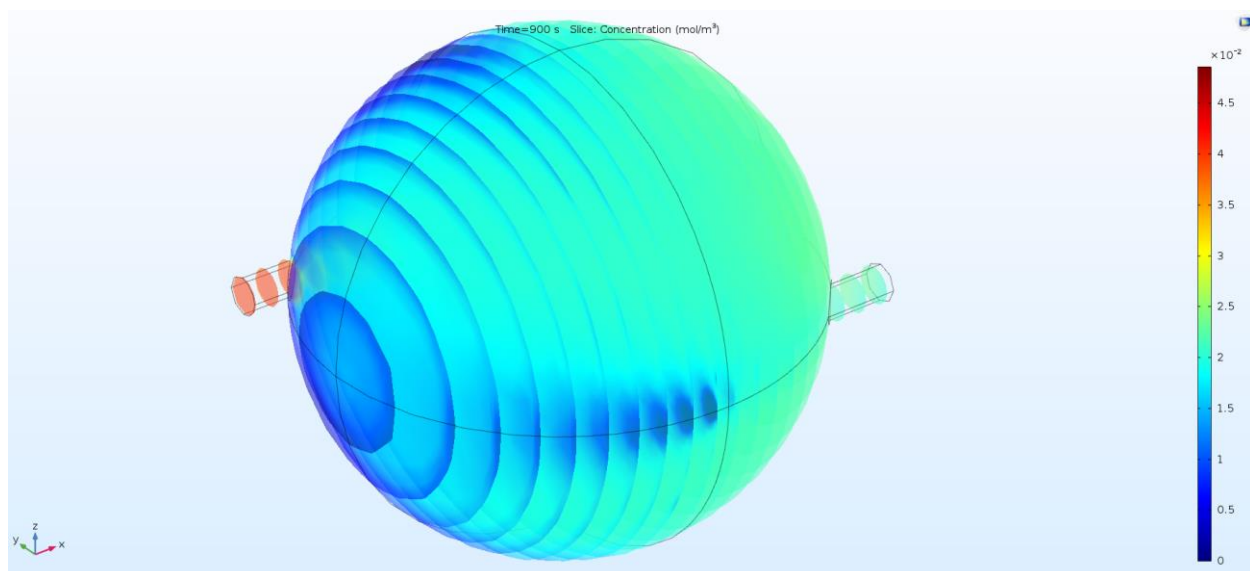


Figure 165: Slice Concentration 10mL/min, $k=8.80E-7$, 900 seconds (COMSOL® v. 5.2. 2017)

Sphere Geometry, 4.546 cm³, Pure Water k=3.15E- at 10 mL/min

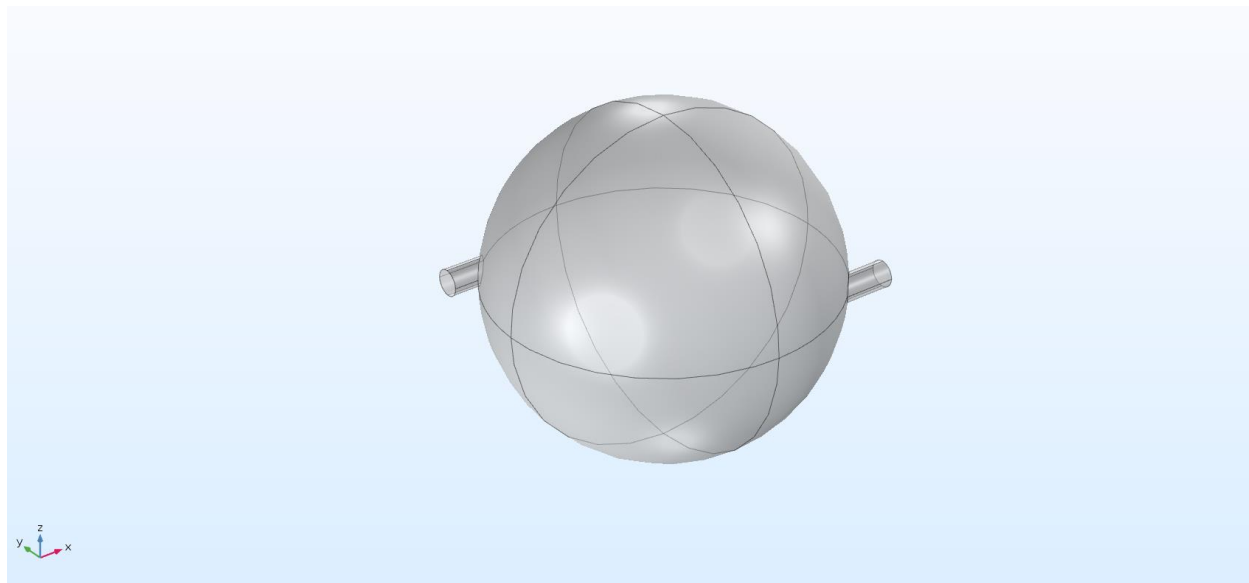


Figure 166: Sphere Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017)

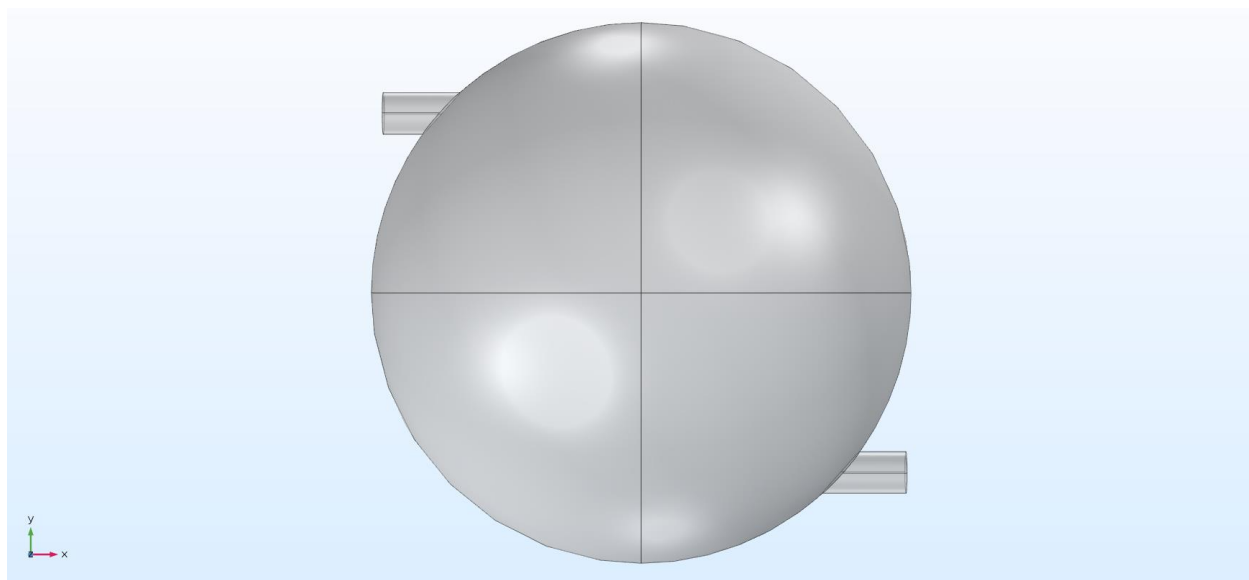


Figure 167: Sphere Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017)

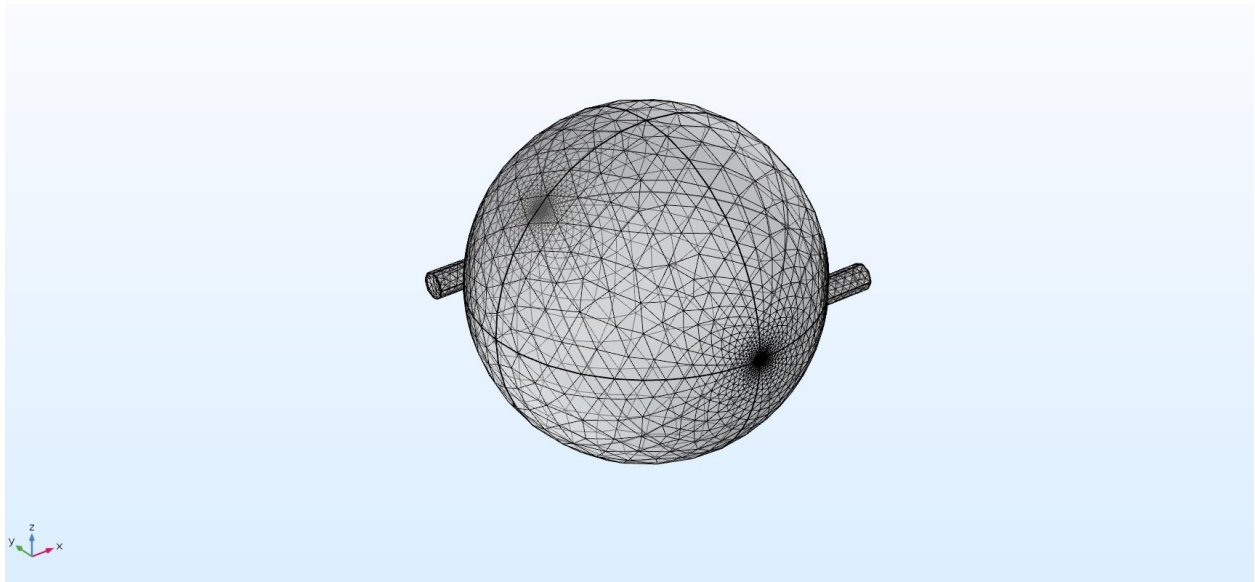


Figure 168: Sphere Geometry Mesh Layout (COMSOL® v. 5.2. 2017)

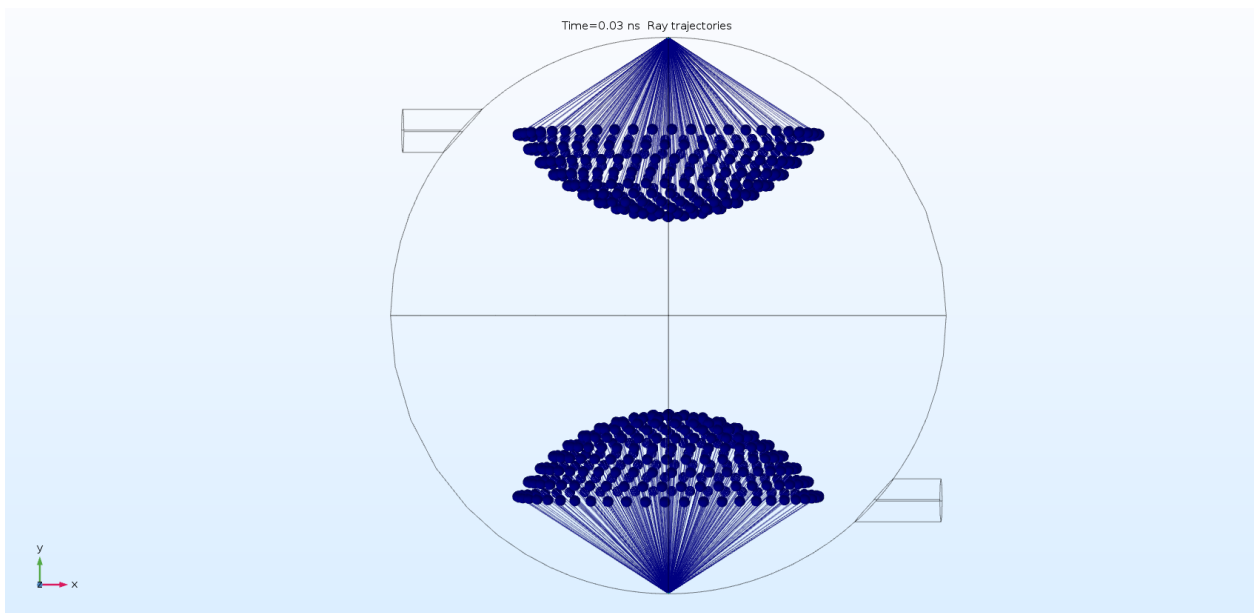


Figure 169: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)

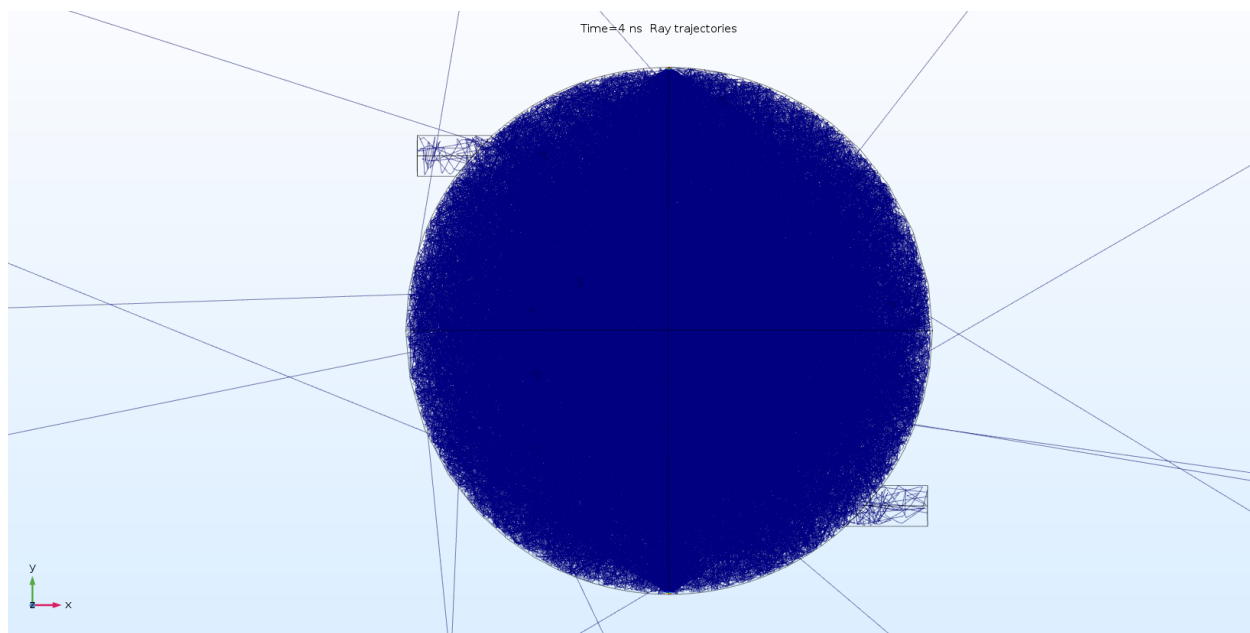


Figure 170: Ray Propagation at 4.0 ns, $k=3.15E-8$ (COMSOL® v. 5.2. 2017)

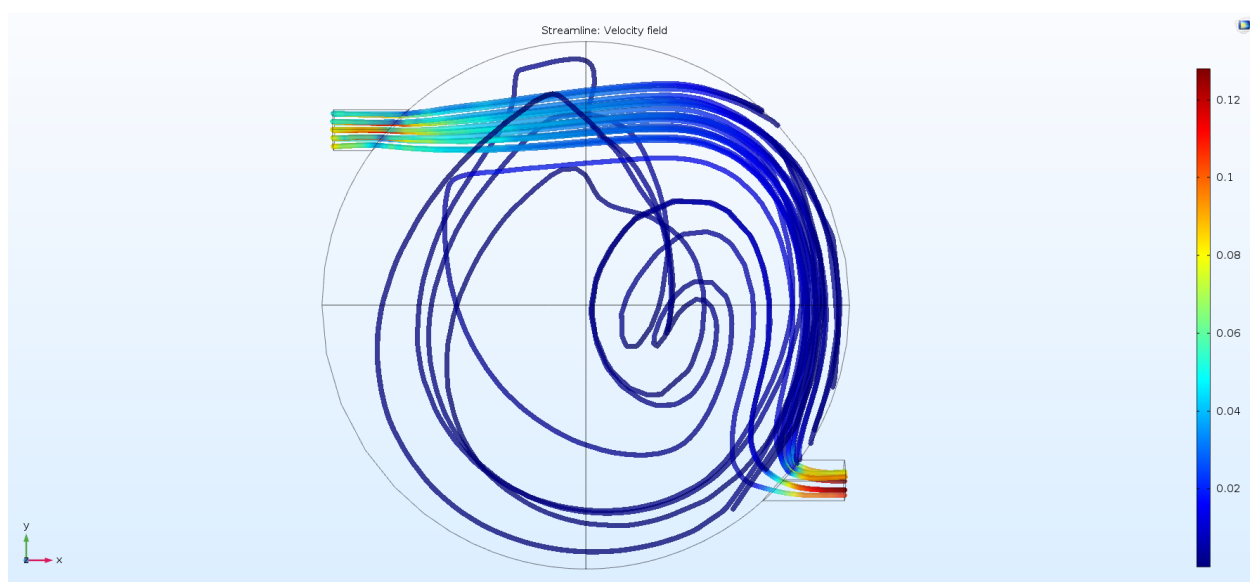


Figure 171: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

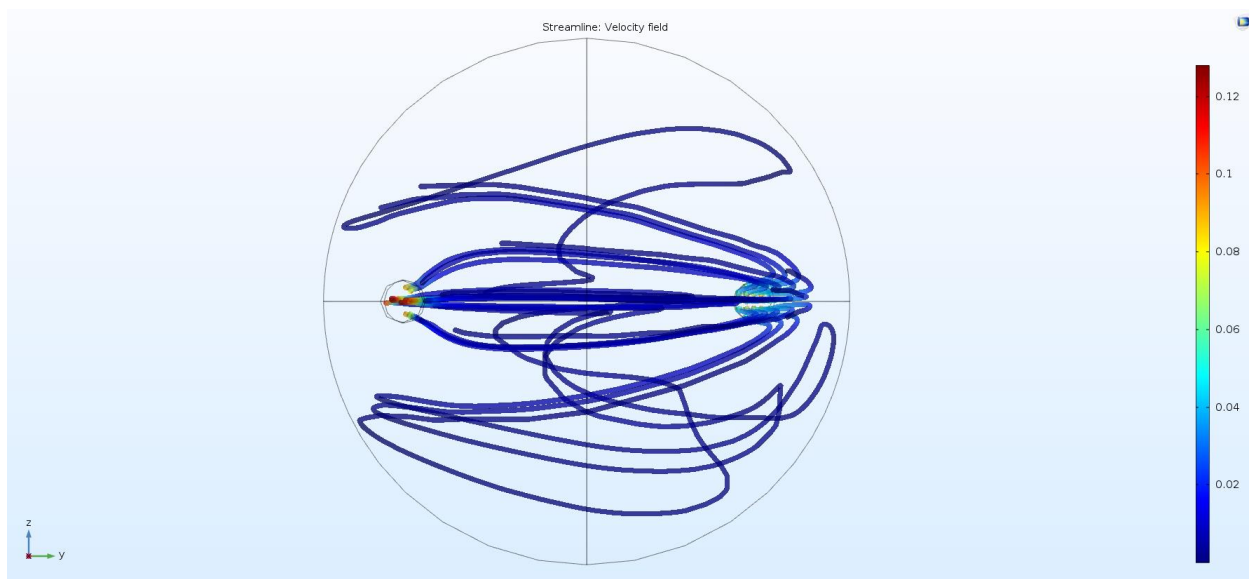


Figure 172: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

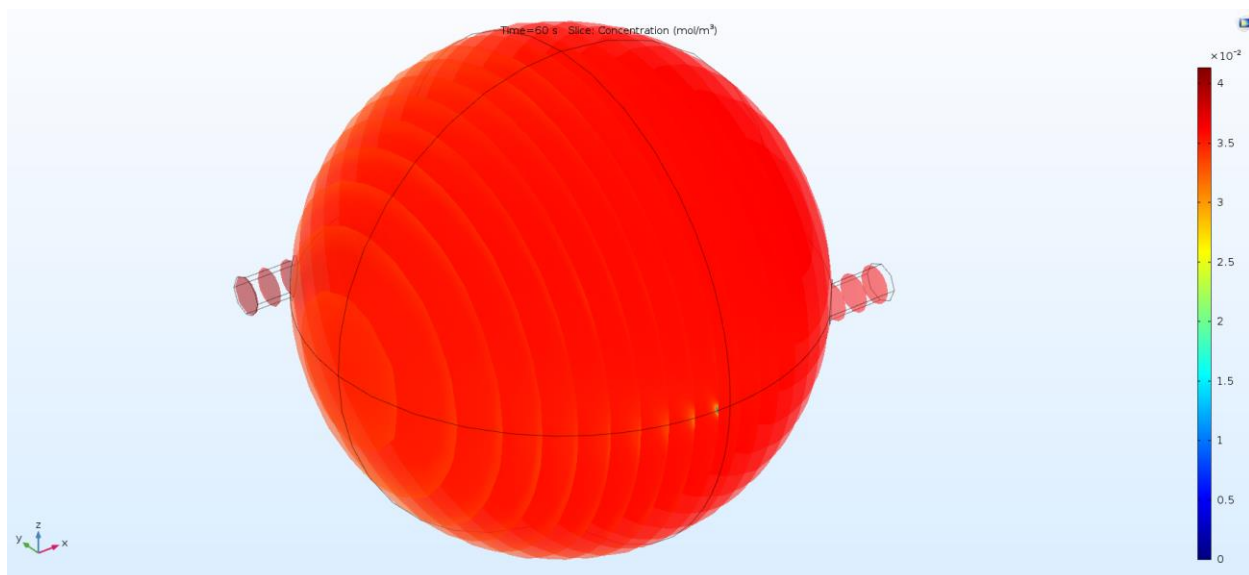


Figure 173: Slice Concentration 10mL/min, $k=3.15E-8$, 60 seconds (COMSOL® v. 5.2. 2017)

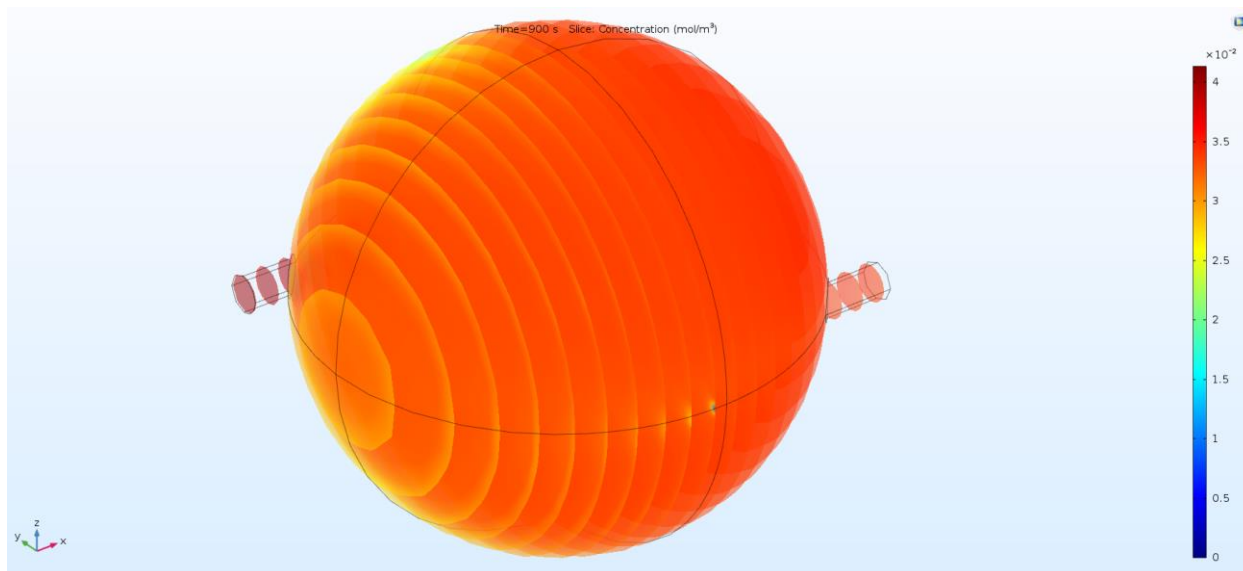


Figure 174: Slice Concentration 10mL/min, $k=3.15\text{E-}8$, 900 seconds (COMSOL® v. 5.2. 2017)

Sphere Geometry, 36.42 cm³, Brilliant Blue $k=8.80\text{E-}7$ at 10 mL/min

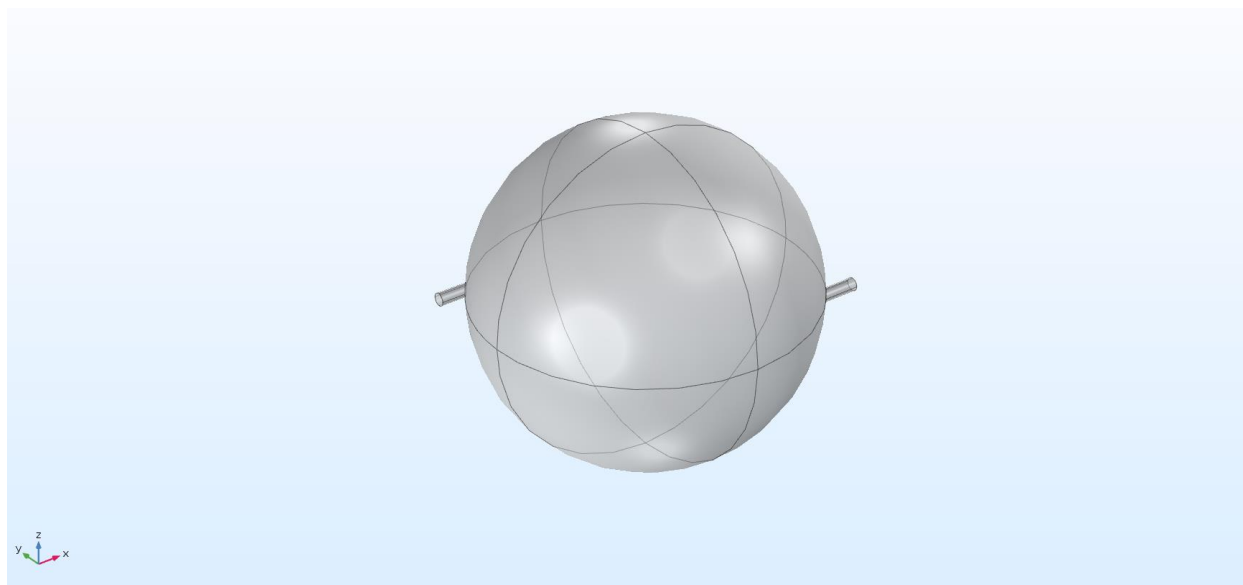


Figure 175: Sphere Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017)

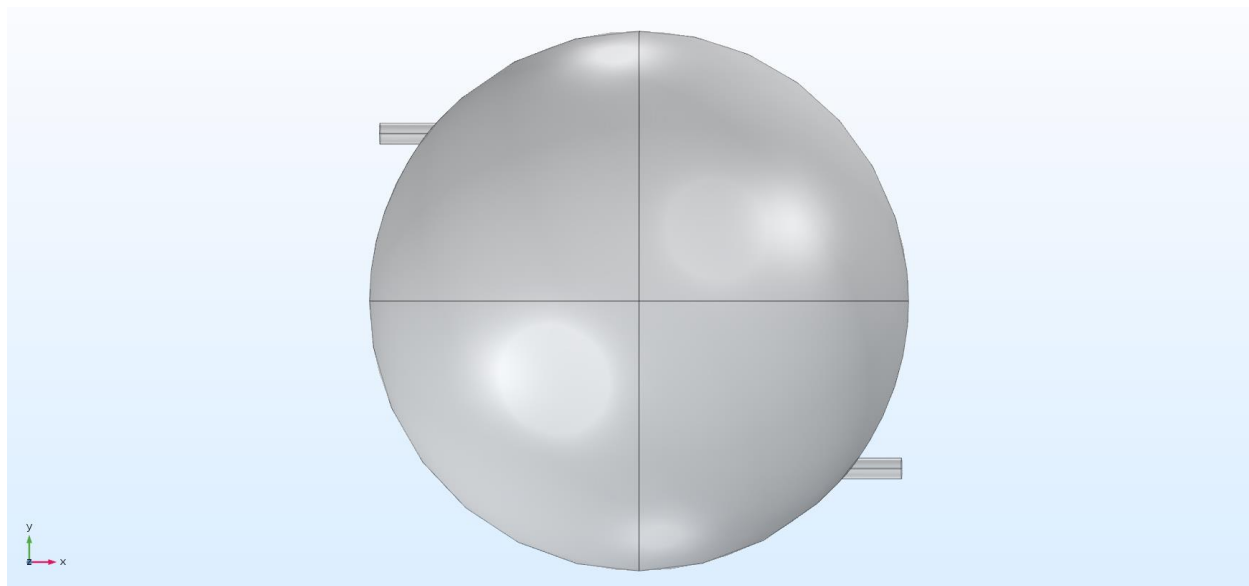


Figure 176: Sphere Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017)

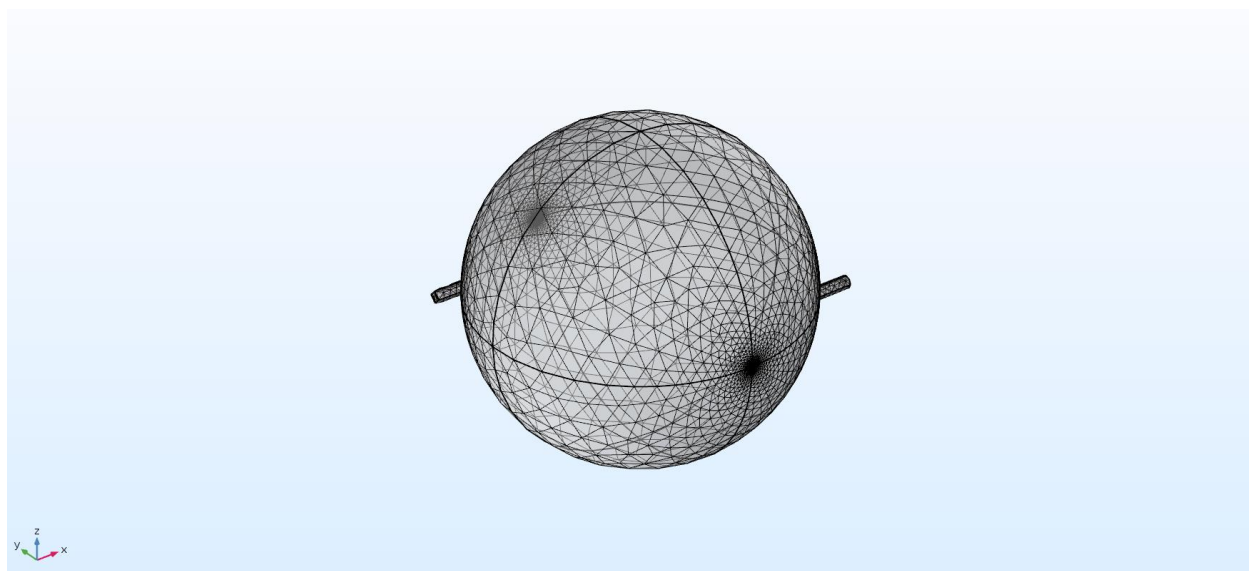


Figure 177: Sphere Geometry Mesh Layout (COMSOL® v. 5.2. 2017)

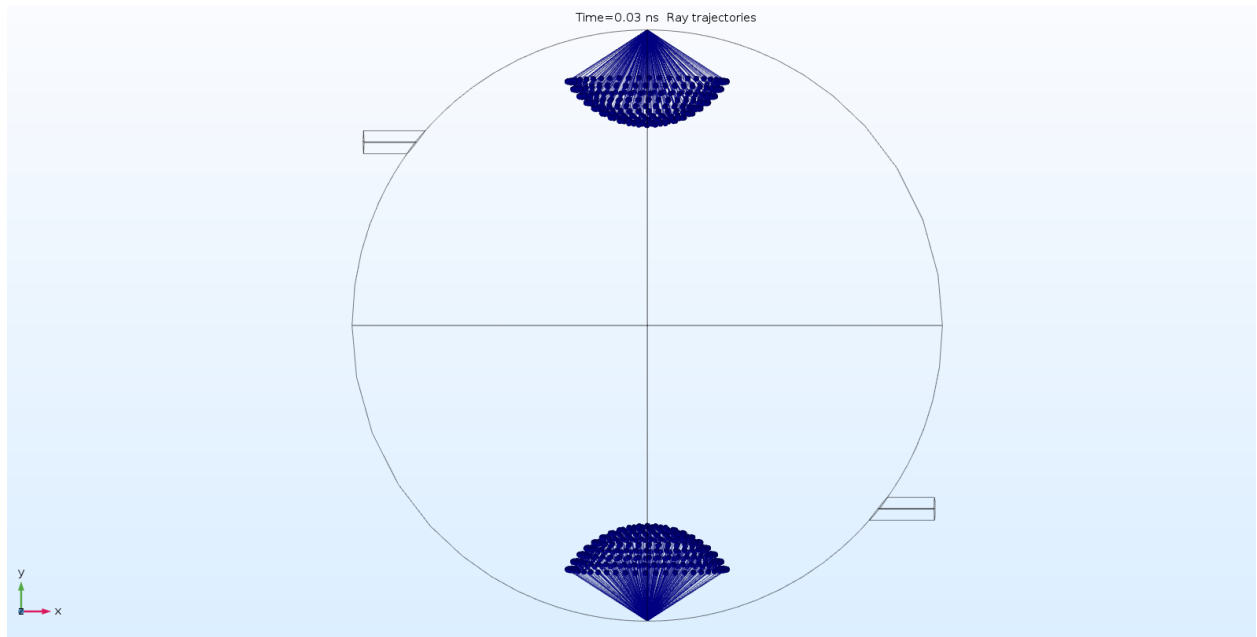


Figure 178: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)

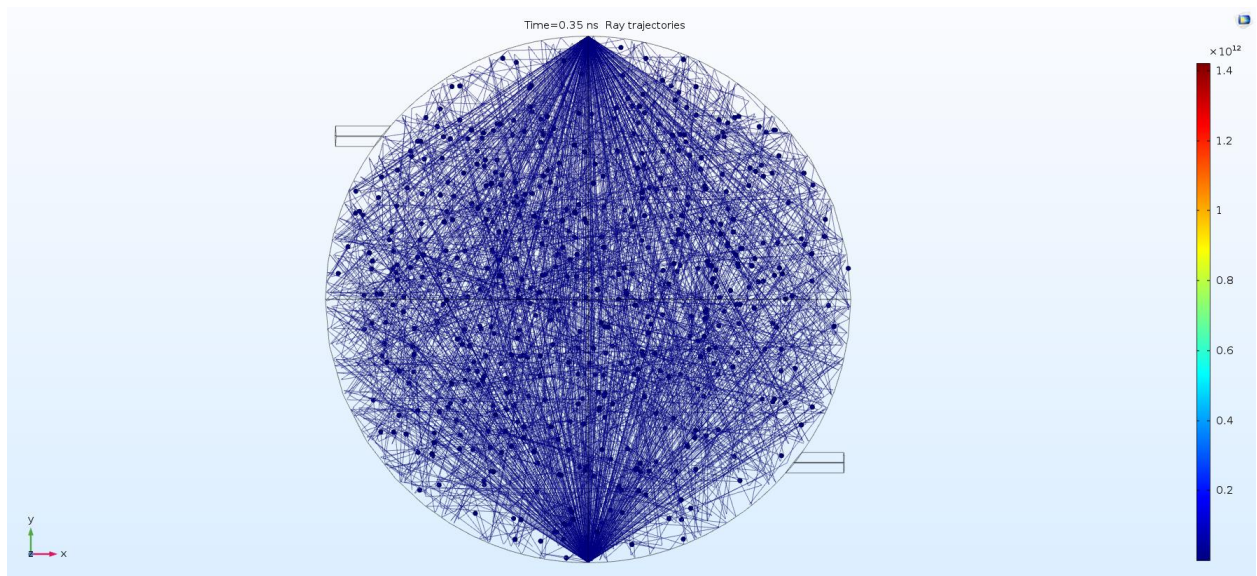


Figure 179: Ray Propagation at 0.35 ns, $k=8.80E-7$ (COMSOL® v. 5.2. 2017)

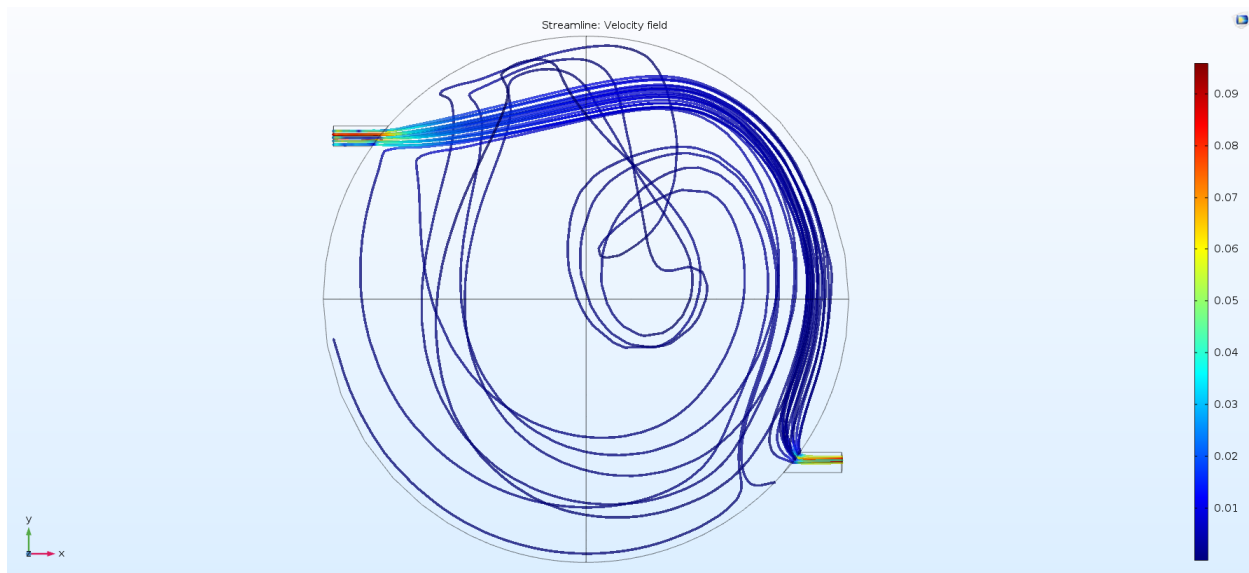


Figure 180: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

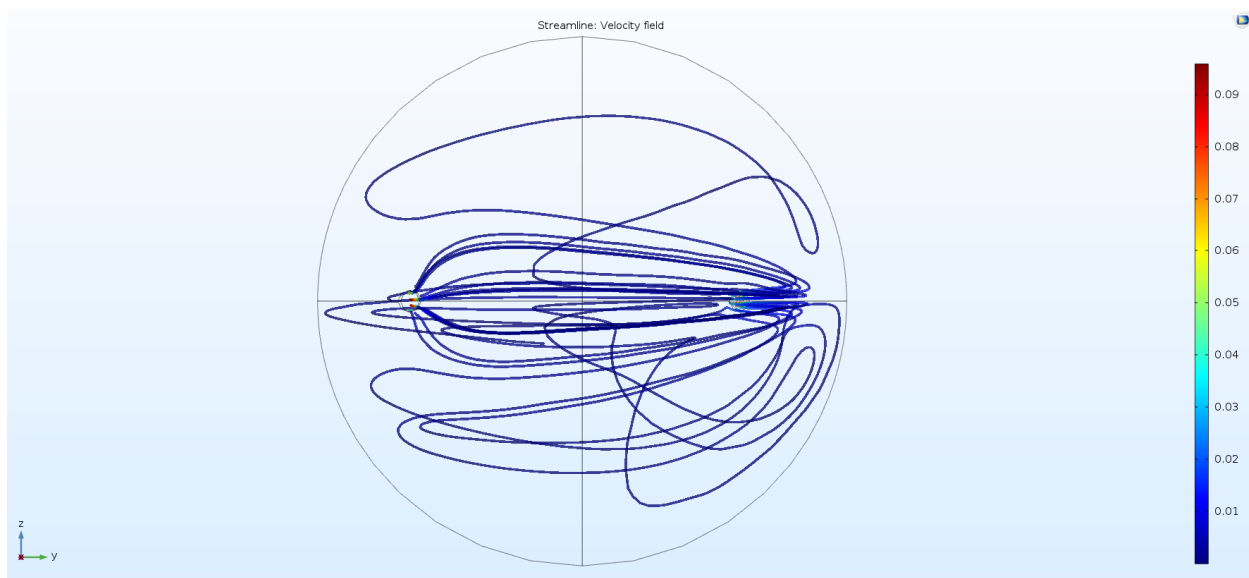


Figure 181: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

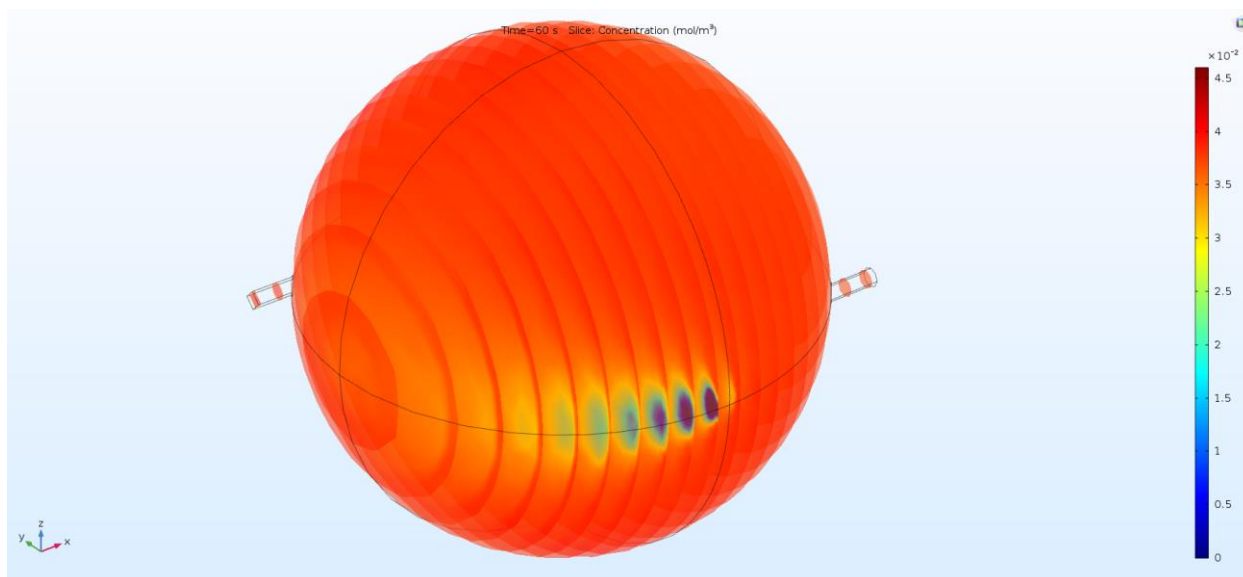


Figure 182: Slice Concentration 10mL/min, $k=8.80\text{E-}7$, 60 seconds (COMSOL® v. 5.2. 2017)

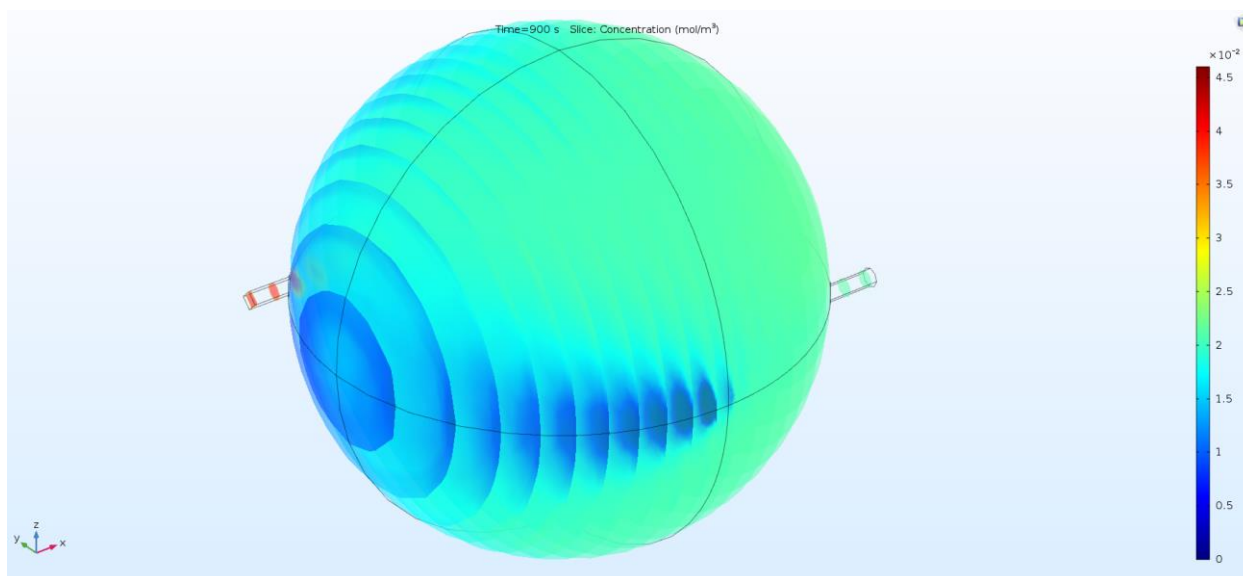


Figure 183: Slice Concentration 10mL/min, $k=8.80\text{E-}7$, 900 seconds (COMSOL® v. 5.2. 2017)

Sphere Geometry, 36.42 cm³, Pure Water k=3.15E- at 10 mL/min

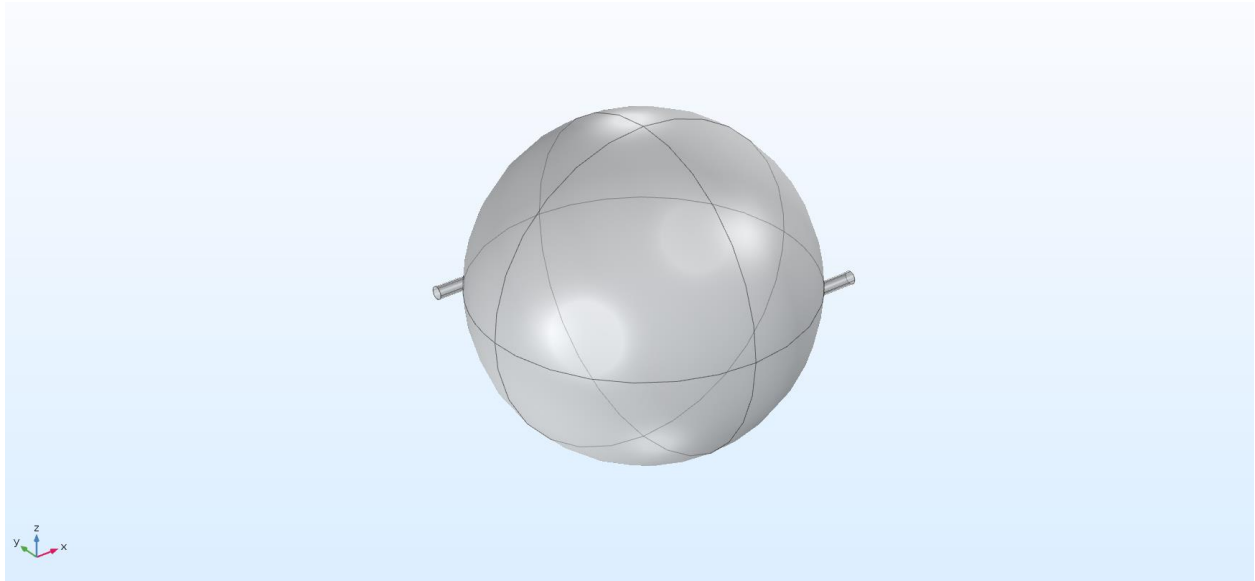


Figure 184: Sphere Geometry 10 mL/min, Isometric (COMSOL® v. 5.2. 2017)

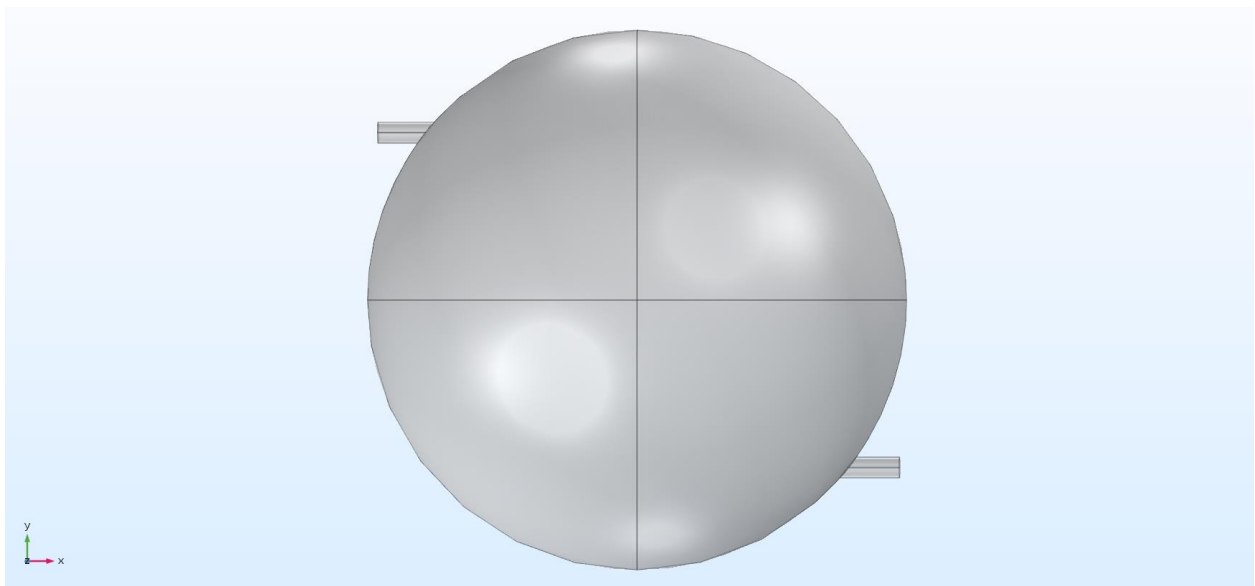


Figure 185: Sphere Geometry 10 mL/min, X-Axis (COMSOL® v. 5.2. 2017)

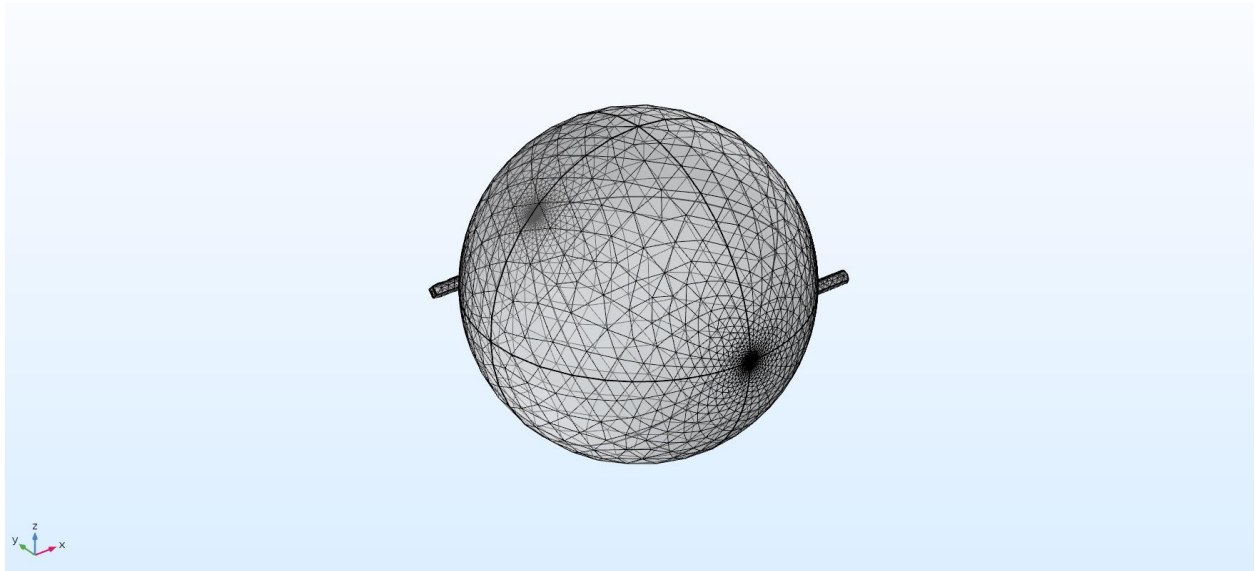


Figure 186: Sphere Geometry Mesh Layout (COMSOL® v. 5.2. 2017)

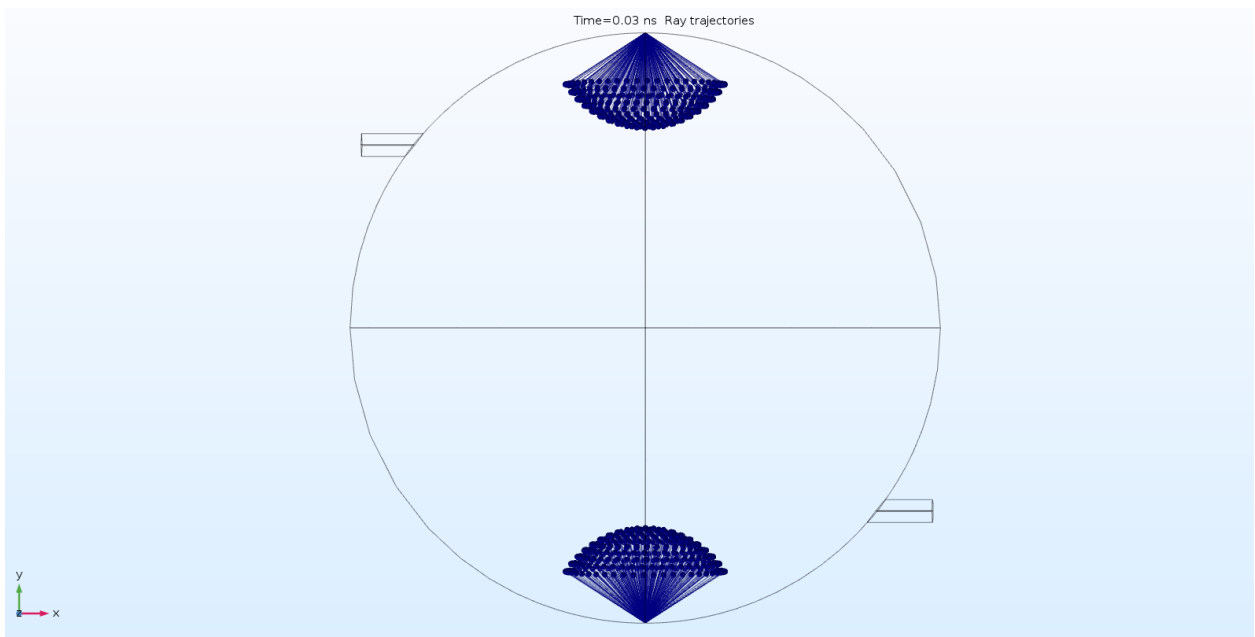


Figure 187: Ray Propagation at 0.03 ns (COMSOL® v. 5.2. 2017)

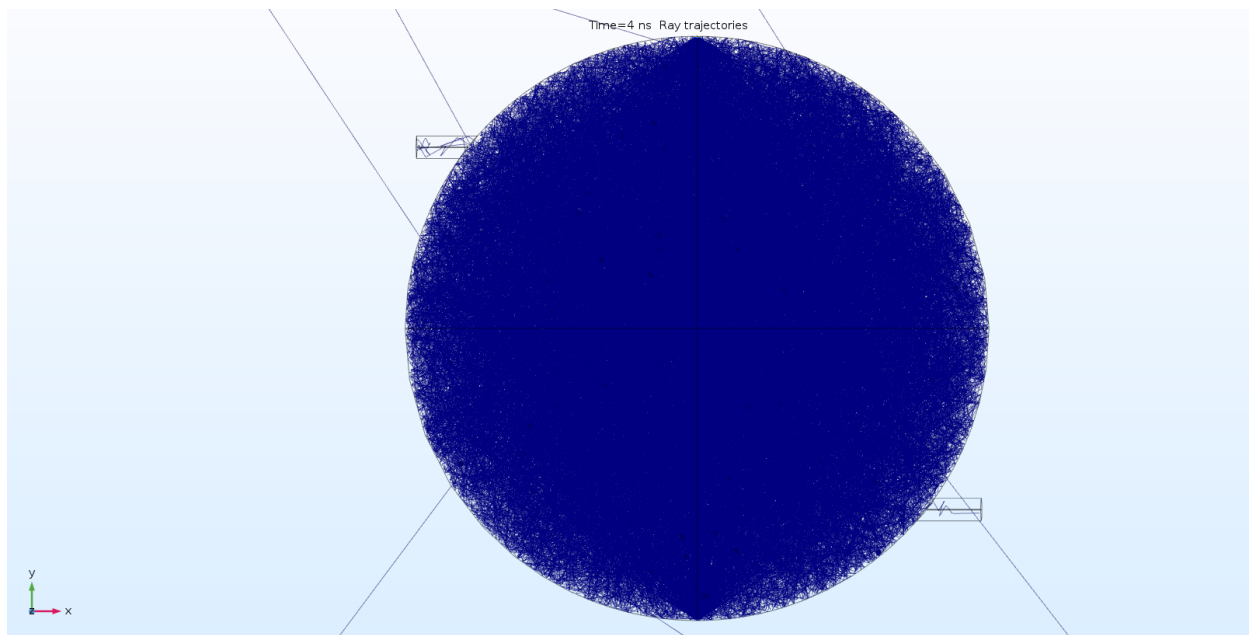


Figure 188: Ray Propagation at 4.0 ns, $k=3.15E-8$ (COMSOL® v. 5.2. 2017)

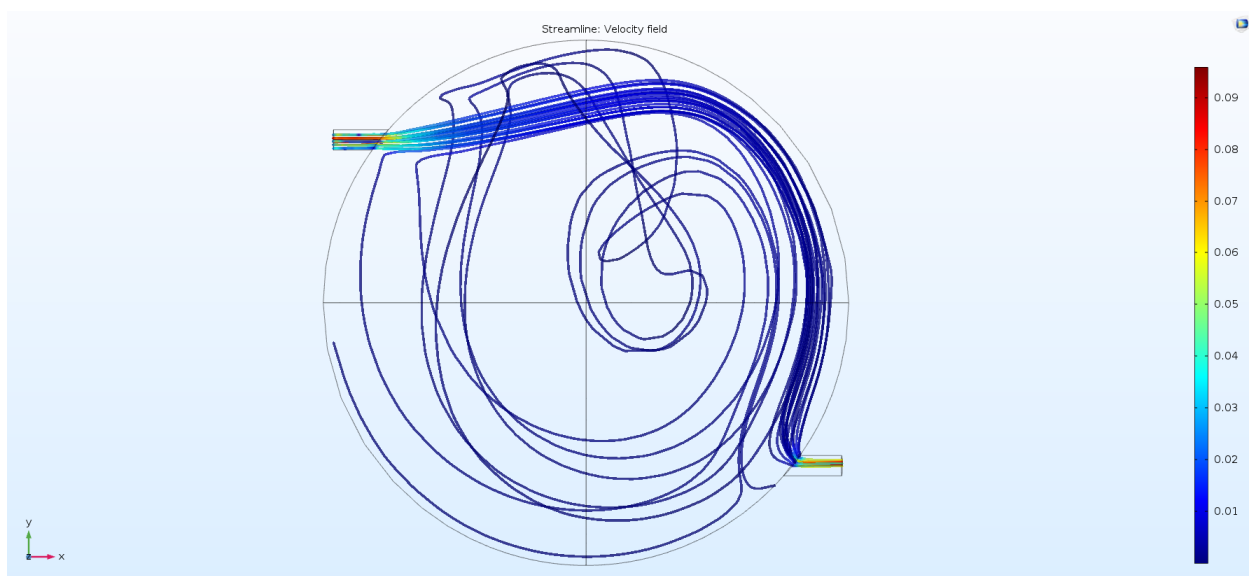


Figure 189: 10 mL/min Velocity Field, X and Y-Axis (COMSOL® v. 5.2. 2017)

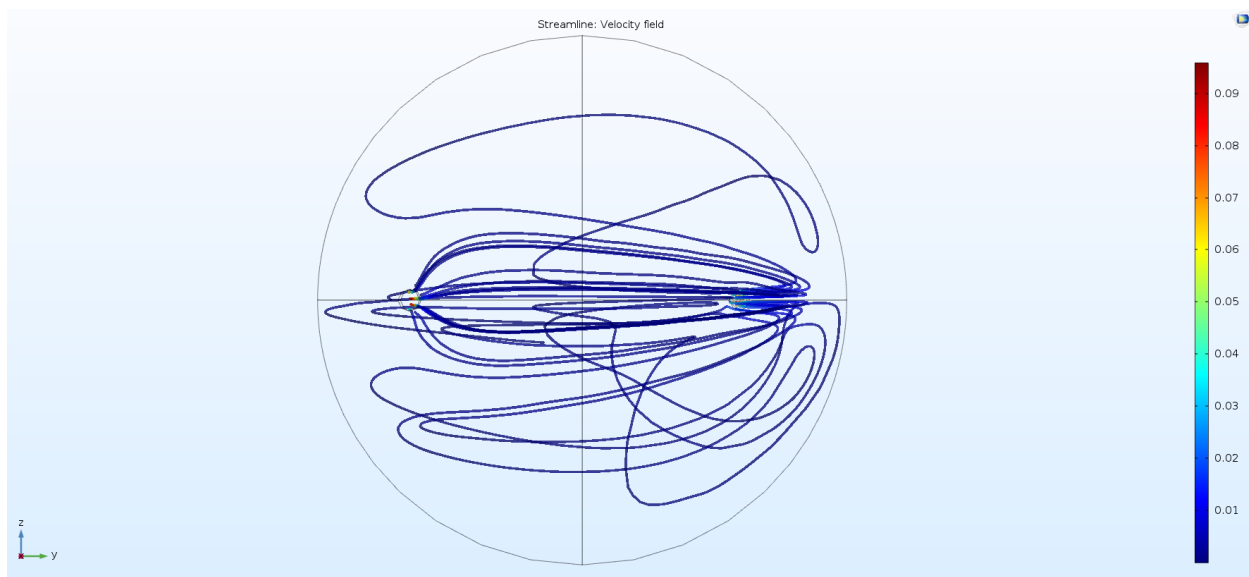


Figure 190: 10 mL/min Velocity Field, Y and Z-Axis (COMSOL® v. 5.2. 2017)

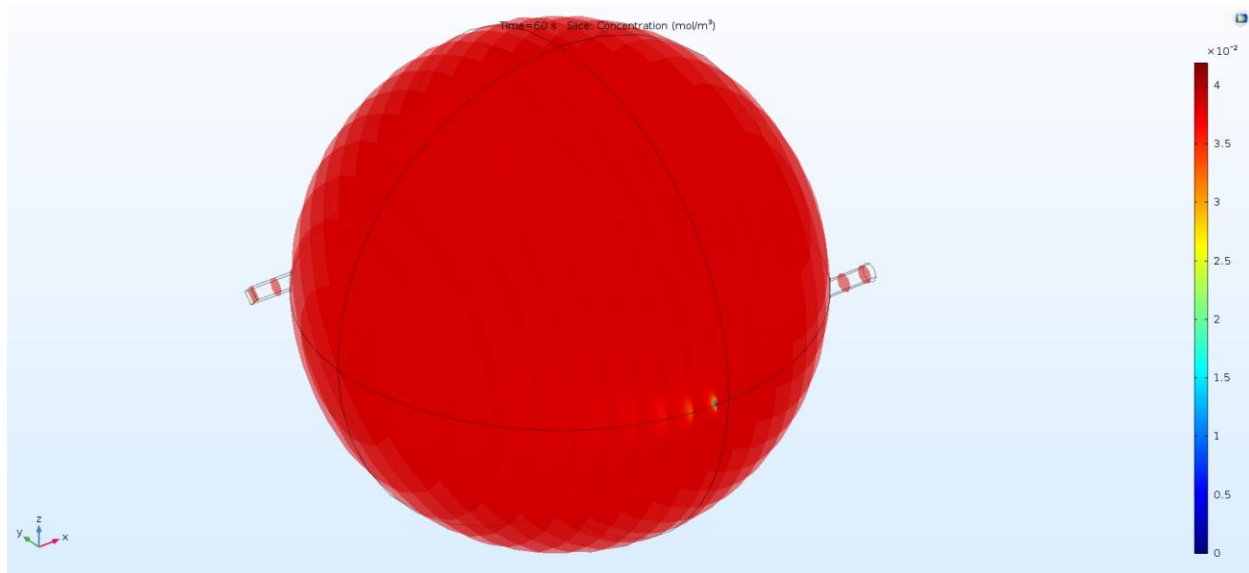


Figure 191: Slice Concentration 10mL/min, $k=3.15\text{E-}8$, 60 seconds (COMSOL® v. 5.2. 2017)

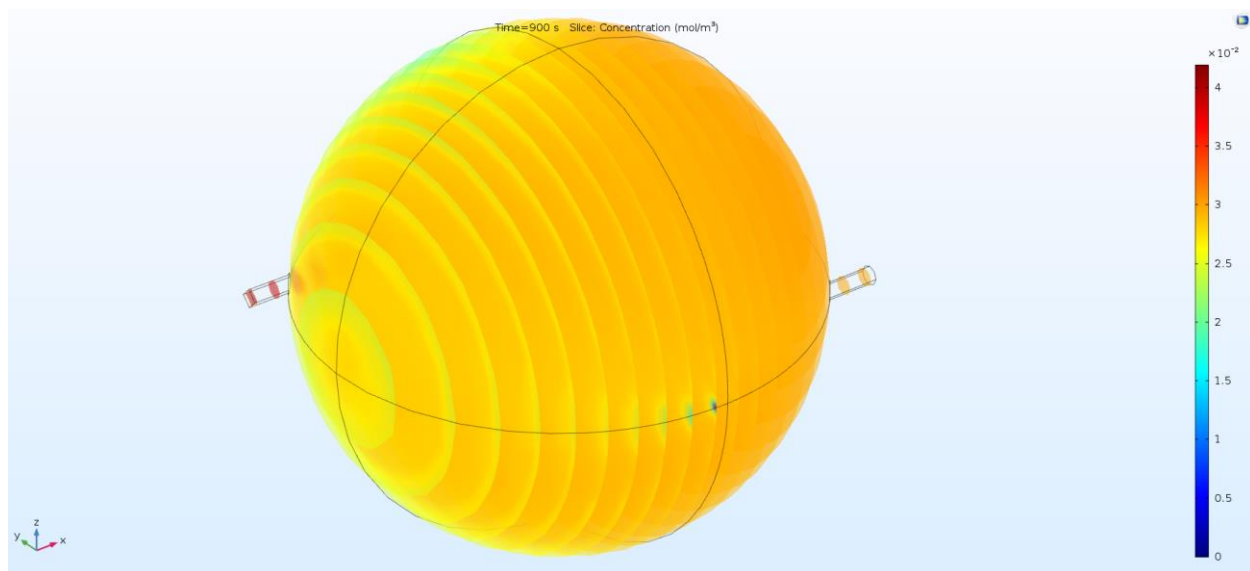


Figure 192: Slice Concentration 10mL/min, $k=3.15\text{E-}8$, 900 seconds (COMSOL® v. 5.2. 2017)

Appendix C – Supporting Data

Refractive Imaginary Index Power Conversion Table

Refractive Imaginary Power Conversion Table			
Measured Absorbance		0.1906	
Measured Transmittance		64.48%	
Target Percent Loss		35.52%	
Ref_Img	Input (W)	Output (W)	Percent Loss
0.00000E+00	1	1.0000	0.00%
3.35000E-08	1	0.9834	1.66%
2.00000E-07	1	0.9052	9.48%
1.01000E-06	1	0.6041	39.59%
9.50000E-07	1	0.6226	37.74%
8.00000E-07	1	0.6711	32.89%
8.50000E-07	1	0.6545	34.55%
8.70000E-07	1	0.6480	35.20%
8.74000E-07	1	0.6467	35.33%
8.79000E-07	1	0.6451	35.49%
8.80000E-07	1	0.6448	35.52%
Sample	Absorption at 255 nm		
1	0.1907		
2	0.1910		
3	0.1901		
4	0.1908		
5	0.1909		
6	0.1911		
7	0.1903		
8	0.1902		
9	0.1909		
Average	0.1906		

Appendix D - COMSOL[®] Utilized Modules and Sub-nodes

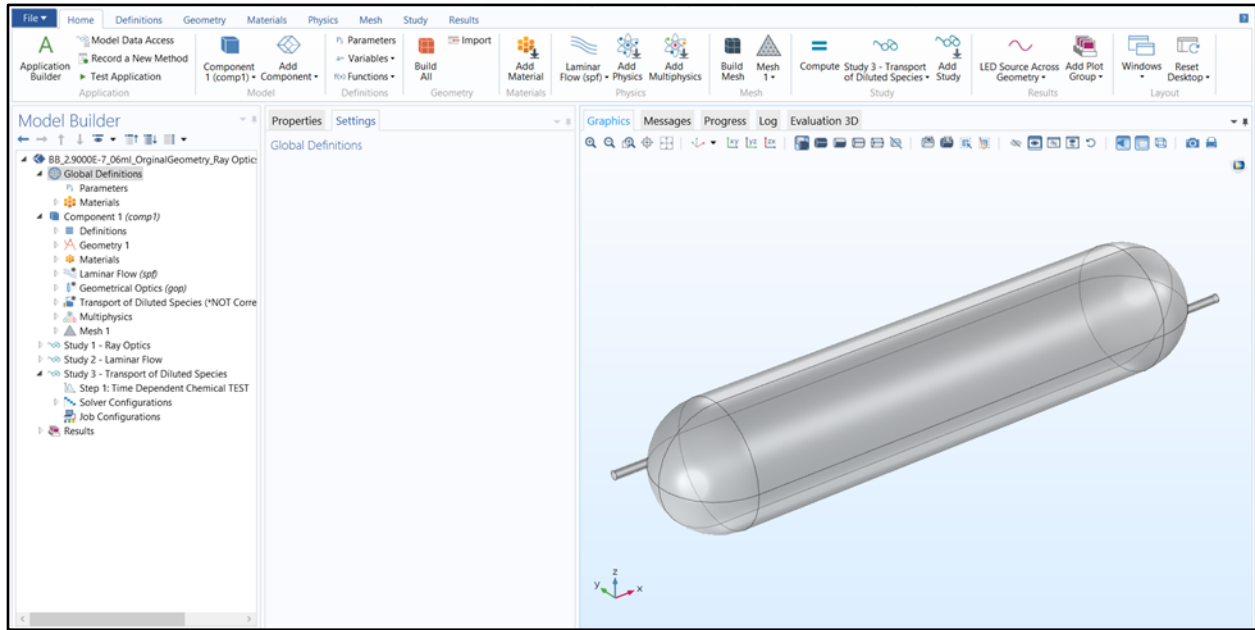


Figure 193: COMSOL[®] Operating System (COMSOL[®] v. 5.2. 2017)

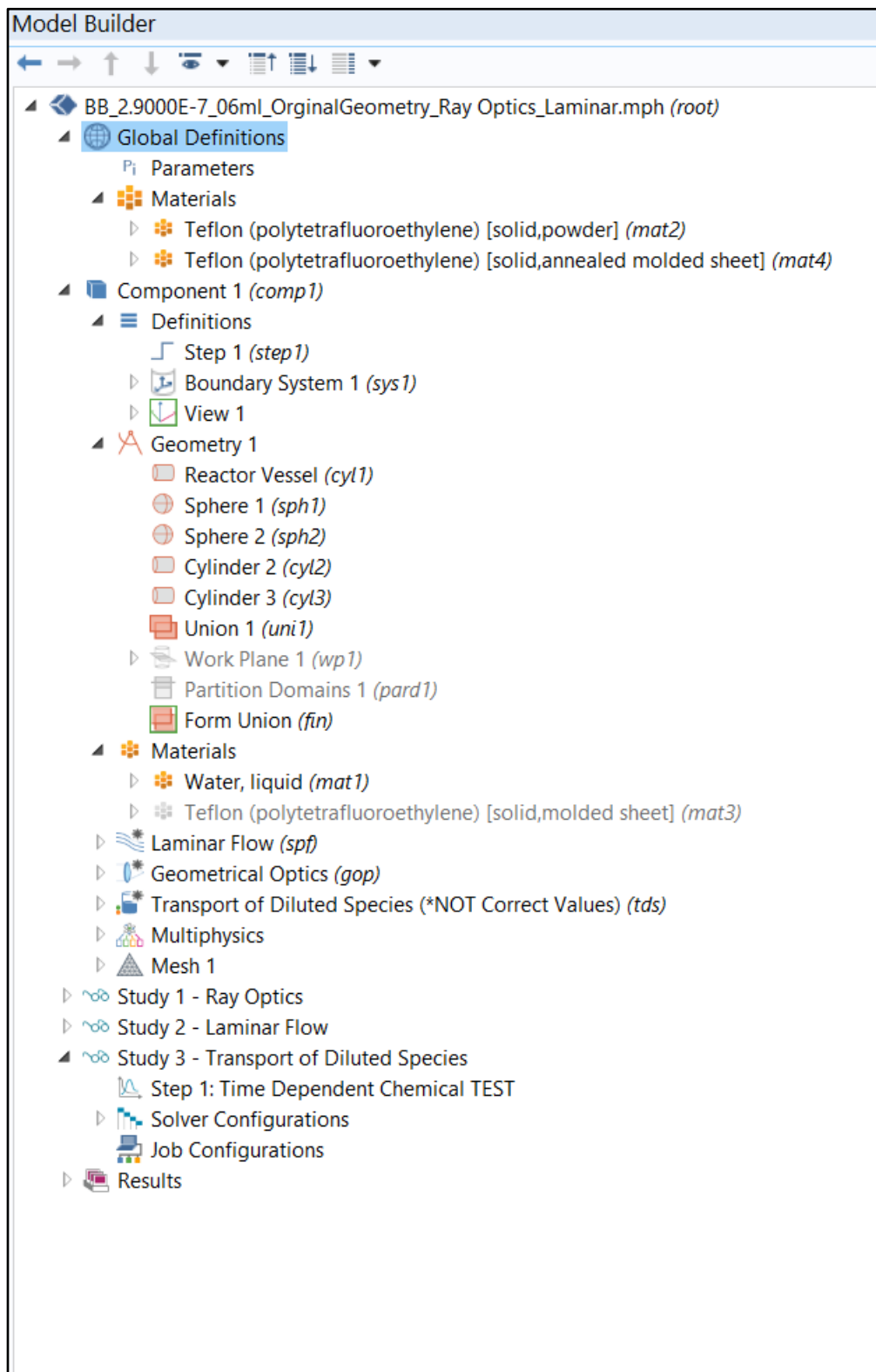


Figure 194: COMSOL® Modules and Sub-Nodes Utilized (COMSOL® v. 5.2. 2017)

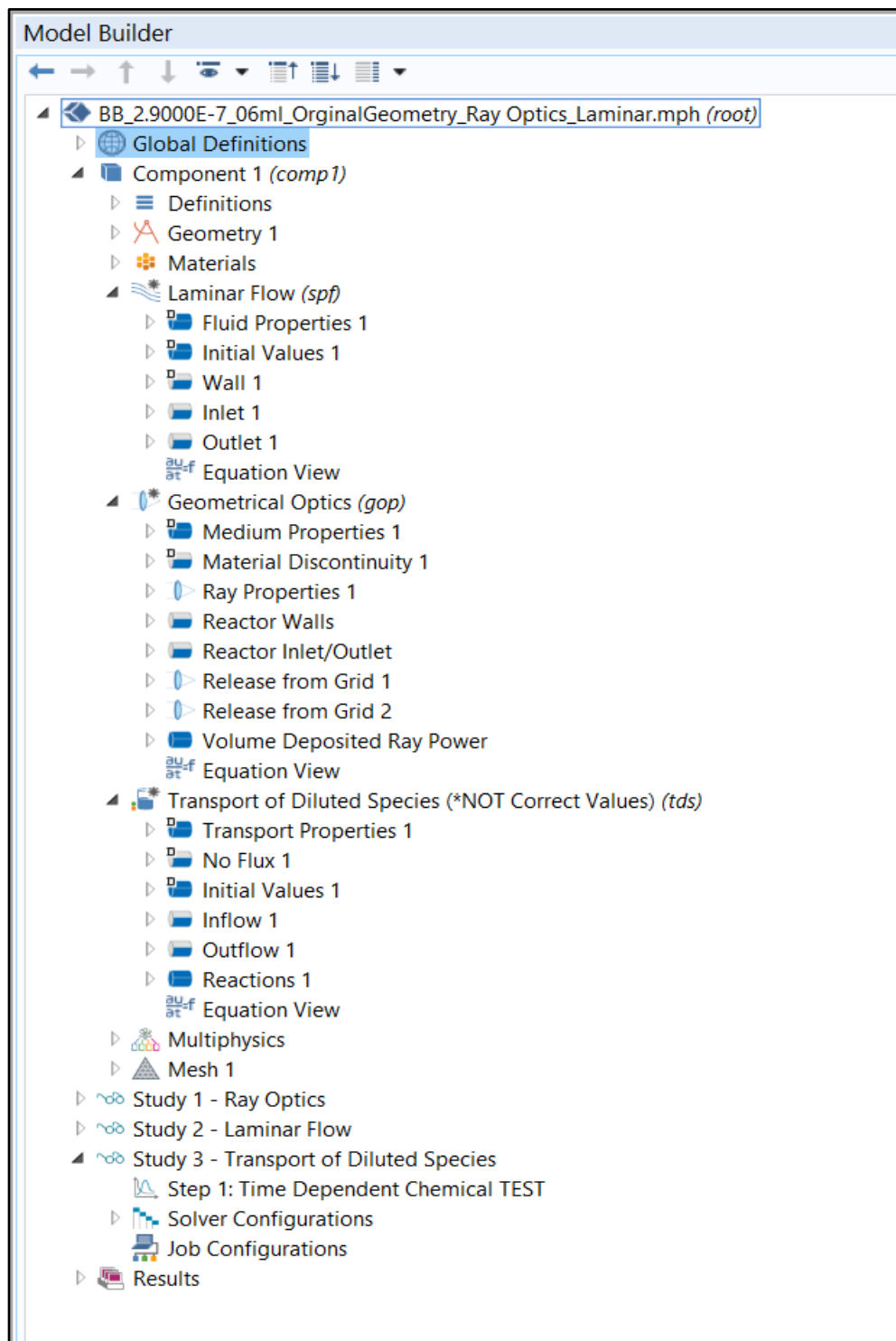


Figure 195: COMSOL® Ray Optics, Laminar Flow, Transport of Diluted Species Modules and Sub-Nodes (COMSOL® v. 5.2. 2017)

Bibliography

- Baker, Moses N. 1948. *The Quest for Pure Water; the History of Water Purification from the Earliest Records to the Twentieth Century*. American Water Works Assn., New York.
- Bates, Christopher. 2014. "UltraViolet Light Emitting Diode Optical Power Characterization." Air Force Institute of Technology.
- Block, S. S. 2001. *Disinfection, Sterilization, and Preservation*. Lippincott Williams & Wilkins.
- CamelBak. 2017. "All Clear UV Microbiological Water Purification Device."
<http://shop.camelbak.com/all-clear-bottle/d/1208>.
- Cargill, K. L., B. H. Pyle, R. L. Saure, and G. A. McFeters. 1992. "Effects of Culture Conditions and Biofilm Formation on the Iodine Susceptibility of *Legionella Pneumophila*." *Canadian Journal of Microbiology* 38 (5): 423–29.
- CAWST. 2017. "Biosand Filter Construcion Manual." *Washtion Education and Training Resources*.
http://resources.cawst.org/package/biosand-filter-construction-manual_en.
- CDC. 2017a. "CDC - Health Water Home - Healthy Swimming - Residential Pool or Hot Tub - Disinfection & Testing." *Centers for Disease Control and Prevention*.
<https://www.cdc.gov/healthywater/swimming/residential/disinfection-testing.html>.
- . 2017b. "CDC - Home - Yellow Book - Contents - Chapter 2 - The Pre-Travel Consultation." *Centers for Desease Control and Prevention*. <https://wwwnc.cdc.gov/travel/yellowbook/2016/the-pre-travel-consultation/water-disinfection-for-travelers>.
- . 2017c. "Safe Water System - Household Water Treatment - Chlorination - Disinfection By-Products." *Centers for Desease Control and Prevention*. <http://www.cdc.gov/safewater/chlorination-byproducts.html#four>.
- . 2017d. "Safe Water System - Household Water Treatment - Slow Sand Filtration." *Centers for*

Disease Control and Prevention. <http://www.cdc.gov/safewater/sand-filtration.html>.

Cecchine, Gary, Forrest E. Morgan, Michael A. Wermuth, Timothy Jackson, Agnes Gereben Schaefer, and Matthew Stafford. 2013. "The U.S. Military Response to the 2010 Haiti Earthquake." *RAND Corporation*. doi:10.1214/07-EJS057.

COMSOL®. 2017a. "COMSOL® Multiphysics Documentation." *COMSOL® Documentation*. COMSOL®.

———. 2017b. "COMSOL Ray Optics Module." *COMSOL®*. <https://www.comsol.com/ray-optics-module>.

———. 2017c. "The Platform for Physics-Based Modeling and Simulation." *COMSOL®*. <https://www.comsol.com/comsol-multiphysics>.

COMSOL® v. 5.2. 2017. "COMSOL Multiphysics®." Stockholm, Sweden: COMSOL AB. www.comsol.com.

Contributors, Wikipedia. 2017. "Brilliant Blue FCF." *Wikipedia, The Free Encyclopedia*. Accessed January 23. https://en.wikipedia.org/wiki/Brilliant_Blue_FCF.

Cray, Charlie. 2000. "Closing the Lid on Chlorine." *Public Health Reports* 115 (4): 378–81.

Curtis, Rick. 1998. *The Backpacker's Field Manual*. 1st Edition. Three Rivers Press.

Dankovich, Theresa A., and Derek G. Gray. 2011. "Bactericidal Paper Impregnated with Silver Nanoparticles for Point-of-Use Water Treatment." *Environmental Science and Technology* 45 (5): 1992–98. doi:10.1021/es103302t.

Dehghani, Mohammad Hadi, Gholam Reza Jahed, and Ahmad Zarei. 2013. "Investigation of Low-Pressure Ultraviolet Radiation on Inactivation of Rhabditidae Nematode from Water." *Iranian Journal of Public Health* 42 (3): 314–19.

DoD. 2010. *Technical Bulletin Med 577, Sanitary Control and Surveillance*. Departments of Army, Navy,

and Air Force.

Downes, a., and Thos. P. Blunt. 1877. “Researches on the Effect of Light upon Bacteria and Other Organisms.” *Proceedings of the Royal Society of London* 26 (179–184): 488–500.

doi:10.1098/rspl.1877.0068.

Duckworth, K. 2014. “UltraViolet Light Emitting Diode Use in Advanced Oxidation Processes.” Air Force Institute of Technology.

Dupuis, Russell D., and Michael R. Krames. 2008. “History, Development, and Applications of High-Brightness Visible Light-Emitting Diodes.” *Journal of Lightwave Technology* 26 (9): 1154–71.

doi:10.1109/JLT.2008.923628.

EPA. 2017. “Drinking Water Treatability Database.” *Environmental Protection Agency*.

<http://iaspub.epa.gov/tdb/pages/treatment/treatmentOverview.do>.

Fyda, S., N. Almquist, C. Harper, and M. Miller. 2015. “Investigation of the Use of Ultraviolet Light Emitting Diodes in Water Treatment Systems.” Air Force Institute of Technology.

Gallucci, Drew. 2016. “Material and Design Considerations for a Portable Ultra-Violet (UV) Light Emitting Diode (LED) Water Purification Device.” Air Force Institute of Technology.

Goh, Joon-chul, Hoon-ju Chung, Jin Jang, and Chul-hi Han. 2002. “Light Emitting Diodes.” *Simulation* 23 (9): 544–46. doi:10.1002/0471238961.1209070811091908.a01.pub2.

Goldstein, Sara, Dorit Aschengrau, Yishay Diamant, and Joseph Rabani. 2007. “Photolysis of Aqueous H₂O₂: Quantum Yield and Applications for Polychromatic UV Actinometry in Photoreactors.” *Environmental Science and Technology* 41 (21): 7486–90. doi:10.1021/es071379t.

Grunwald, A, Anastasia D Nikolaou, Spyros K Golfinopoulos, and Themistokles D Lekkass. 2002. “Formation of Organic by-Products during Chlorination of Natural Waters.” *Journal of Environmental Monitoring: JEM* 4 (6): 910–16. doi:10.1039/b202965k.

- Hijnen, Wim A M, J. F. Schijven, P. Bonné, A. Visser, and G. J. Medema. 2004. "Elimination of Viruses, Bacteria and Protozoan Oocysts by Slow Sand Filtration." *Water Science and Technology* 50 (1): 147–54.
- Hijnen, Wim, K W R Watercycle, Gertjan Medema, K W R Watercycle, Membrane Based Desalination, An Integrated Approach, Quantitative Microbial, and Risk Assessment. 2006. "Inactivation Credit of UV-Radiation for Viruses , Bacteria and Protozoan (Oo) Cysts : A Review (THESIS VERSION) Inactivation Credit of UV Radiation for Viruses , Bacteria and Protozoan." *Water Research* 40 (3–22): 122–58.
- Holonyak, Nick, and S. F. Bevacqua. 1962. "Coherent (Visible) Light Emission from Ga(As_{1-x}P_x) Junctions." *Applied Physics Letters* 1 (4): 82–83. doi:10.1063/1.1753706.
- Ibrahim, Mohamed a S, Jitka MacAdam, Olivier Autin, and Bruce Jefferson. 2014. "Evaluating the Impact of LED Bulb Development on the Economic Viability of Ultraviolet Technology for Disinfection." *Environmental Technology* 35 (1–4): 400–406. doi:10.1080/09593330.2013.829858.
- International, N S F. 2012. "NSF INTERNATIONAL NSF Protocol P248 Military Operations Microbiological Water Purifiers," no. February.
- Jenny, Richard M, Otto D Simmons III, Max Shatalov, and Joel J Ducoste. 2014. "Modeling a Continuous Flow Ultraviolet Light Emitting Diode Reactor Using Computational Fluid Dynamics." *Chemical Engineering Science* 116 (0): 524–35. doi:http://dx.doi.org/10.1016/j.ces.2014.05.020.
- Jones, Robert, Brandon Wills, and Christopher Kang. 2010. "Chlorine Gas: An Evolving Hazardous Material Threat and Unconventional Weapon." *The Western Journal of Emergency Medicine* 11 (2): 151–56.
- <http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=2908650&tool=pmcentrez&rendertype=abstract>.

- Kovac, J., L. Peternai, and O. Lengyel. 2003. “Advanced Light Emitting Diodes Structures for Optoelectronic Applications.” *Thin Solid Films* 433 (1–2 SPEC.): 22–26. doi:10.1016/S0040-6090(03)00314-6.
- Lara, Humberto H, Nilda V Ayala-Nuñez, Liliana Ixtepan-Turrent, and Cristina Rodriguez-Padilla. 2010. “Mode of Antiviral Action of Silver Nanoparticles against HIV-1.” *Journal of Nanobiotechnology* 8 (1): 1. doi:10.1186/1477-3155-8-1.
- Life is Water. 2017. “The Drinkable Book.” <http://waterislife.com/clean-water/new-technology>.
- Linden, Karl G. 1998. “UV Acceptance.” *Civil Engineering* 68 (3): 58.
- Miller, Micheal. 2016. Data Summary Small Reactor, issued 2016.
- Morita, Shigemitsu, Atsushi Namikoshi, Tsuyoshi Hirata, Kumiko Oguma, Hiroyuki Katayama, and Shinichiro Ohgaki. 2002. “Efficacy of UV Irradiation in Inactivating *Cryptosporidium Parvum* Oocysts.” *Applied and Environmental Microbiology* 68 (11): 5387–93. doi:10.1128/AEM.68.11.5387.
- Mudimbi, P. M. 2015. “Pulsed Ultraviolet Light Emitting Diodes for Advanced Oxidation of Tartrazine.” Air Force Institute of Technology.
- Muramoto, Yoshihiko, Masahiro Kimura, and Suguru Nouda. 2014. “Development and Future of Ultraviolet Light-Emitting Diodes ~uV-LED Will Replace UV Lamp~.” *2015 IEEE Summer Topicals Meeting Series, SUM 2015*, 13–14. doi:10.1109/PHOSST.2015.7248169.
- . 2015. “Development and Future of Ultraviolet Light-Emitting Diodes ~uV-LED Will Replace UV Lamp~.” *2015 IEEE Summer Topicals Meeting Series, SUM 2015*, 13–14. doi:10.1109/PHOSST.2015.7248169.
- Nakamura, Shuji, Takashi Mukai, and Masayuki Senoh. 1994. “Candela-Class High-Brightness InGaN/AlGaIn Double-Heterostructure Blue-Light-Emitting Diodes.” *Applied Physics Letters* 64 (13): 1687–89. doi:10.1063/1.111832.

- NY DOH. 2017. “Boil Water Response - Information for the Public Health Professional.” *New York Department of Health, Center for Environmental Health*.
https://www.health.ny.gov/environmental/water/drinking/boilwater/response_information_public_health_professional.htm.
- Percival, Steven L., Marylynn Yates, David Williams, Rachel Chalmers, and Nicholas Gray. 2013. *Microbiology of Waterborne Diseases: Microbiological Aspects and Risks*. Academic Press.
- Pirnie, Malcom, Karl G Linden, and James P Jr. Malley. 2006. “Ultraviolet Disinfection Guidance Manual for the Final Long Term 2 Enhanced Surface Water Treatment Rule.” *Environmental Protection* 2 (11): 1–436.
- Polyanskiy, Mikhail N. 2017a. “Refractive Index Database for C₂H₅OH (Ethanol).”
<http://refractiveindex.info/?shelf=organic&book=ethanol&page=Sani-formula>.
- . 2017b. “Refractive Index Database for C₃H₇OH (Propanol).”
<http://refractiveindex.info/?shelf=organic&book=propanol&page=Sani-formula>.
- . 2017c. “Refractive Index Database for H₂O.”
[http://refractiveindex.info/?shelf=main&book=H₂O&page=Hale](http://refractiveindex.info/?shelf=main&book=H2O&page=Hale).
- Pontius, F. 2003. *Drinking Water Regulation and Health*. John Wiley & Sons.
- Rahn, Ronald. 1997. “Potassium Iodide as a Chemical Actinometer for 254 Nm Radiation: Use of Iodate as an Electron Scavenger.” *Photochemistry and Photobiology* 66 (4): 450–55.
- Richwine, J. P. 2014. “Modeling UltraViolet Light Emitting Diode Energy Propagation in Reactor Vessels.” Air Force Institute of Technology.
- Russell, Morgan. 2017. “Low-Cost, Low Power Technology to Destroy Organic Pollutants in Water: Ultra-Violet Light Emitting Diodes and Photocatalysis.” Air Force Institute of Technology.
- Schaller, Robert R. 1997. “Moore’s Law: Past, Present, and Future.” *IEEE Spectrum* 34 (6): 52–55, 57.

doi:10.1109/6.591665.

- Scott, R. W. 2015. "The Use of Ultra-Violet Light Emitting Diodes in an Advanced Oxidation Process with Brilliant Blue FCF as an Indicator." Air Force Institute of Technology.
- Shao, Feng. 2014. "Toxicity of Silver Nanoparticles on Virus" 5 (2): 587–90.
- Shipway, Andy, and Steve Shipway. 2008. "Energy of a Photon."
http://www.calctool.org/CALC/other/converters/e_of_photon.
- Spencer, Micheal. 2014. "Design Considerations for a Water Treatment System Utilizing UltraViolet Light Emitting Diodes." Air Force Institute of Technology.
- Steele, Robert V. 2007. "The Story of a New Light Source." *Nature Photon.* 1 (January): 25–26.
doi:doi:10.1038/nphoton.2006.44.
- Stubbs, John. 2017. "Dynamics of Chemical Degradation in Water Using Photocatalytic Reactions in an Ultraviolet Light Emitting Diode Reactor." Air Force Institute of Technology.
- Teng, Weiping, Zhongyan Shan, Xiaochun Teng, Haixia Guan, Yushu Li, Di Teng, Ying Jin, et al. 2006. "Effect of Iodine Intake on Thyroid Diseases in China." *The New England Journal of Medicine* 354 (26): 2783–93. doi:10.1056/NEJMoa054022.
- Tran, Tho. 2014. "Comparison of Continuous Versus Pulsed UltraViolet Light Emitting Diode Use in Water Disinfection on Bacillus Globigii Spores." Air Force Institute of Technology.
- Tuncel, Ali Tunç, Thorsten Ruppert, Bei-Tzu Wang, Jürgen Günther Okun, Stefan Kölker, Marina Alexandra Morath, and Sven Wolfgang Sauer. 2015. "Maleic Acid - but Not Structurally Related Methylmalonic Acid - Interrupts Energy Metabolism by Impaired Calcium Homeostasis." *PloS One* 10 (6): e0128770. doi:10.1371/journal.pone.0128770.
- Vestergaard. 2017a. "Life Straw." <http://lifestraw.com/>.
- . 2017b. "Life Straw Specs." <http://lifestraw.com/products/lifestraw/>.

Walter, Frie. 2015. “Guide to Frequency Domain Wave Electromagnetics Modeling.” *COMSOL*®.

<https://www.comsol.com/blogs/guide-to-frequency-domain-wave-electromagnetics-modeling/>.

Whitby, Elliott G. 2004. “The History of UV and Wastewater.” *IUVA News* 6 (3): 15–26.

doi:10.3102/0013189X10392139.

World Health Organization. 2011. *Guidlines for Drinking-Water Quality*. 4th ed. Geneva: World Health Organization.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 23-3-2017		2. REPORT TYPE Masters Thesis		3. DATES COVERED (From - To) October 2015 – March 20176	
4. TITLE AND SUBTITLE INVESTIGATING POINT-OF-USE UV-LED WATER PURIFICATION DEVICE USING COMPUTATIONAL MULTIPHYSICS MODELING SOFTWARE			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) James, Shandon L., Captain, USAF			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Institute of Technology Graduate School of Engineering and Management (AFIT/ENY) 2950 Hobson Way, Building 640 WPAFB OH 45433-8865			8. PERFORMING ORGANIZATION REPORT NUMBER AFIT-ENV-MS-17-M-196		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) US Environmental Protection Agency 25 W. Martin Luther King Dr. Mailstop NG-16 Cincinnati, OH 45268 Matthew Magnuson, (513) 569-7321, magnuson.matthew@epa.gov			10. SPONSOR/MONITOR'S ACRONYM(S) US EPA/NHSRC		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION / AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.					
13. SUPPLEMENTARY NOTES This material is declared a work of the U.S. Government and is not subject to copyright protection in the United States.					
14. ABSTRACT The United States Air Force (USAF) often deploys personnel to remote locations or responds to disasters worldwide. Point-of-Use (PoU) ultraviolet (UV) water treatment could provide the DoD with the ability to provide water for small mobile entities that are incapable of providing the support network that larger water purification devices require. PoUs could be used as the water treatment system within the DoD for applications that include disaster response, austere locations, aircraft/helicopter survival kit or small unit for special operations teams. This research investigates the ability to use computer modeling software to predict and optimize the characteristics of a UV LED PoU water purification reactor for such applications. This research developed a working model using computational multiphysics software to predict reaction processes within a UV LED water purification reactor, and validated the model with laboratory data. The research also investigated the effect of altering the reactor geometry and the corresponding interactions with corresponding reactor rate effectiveness. The model demonstrated the ability to predict the reaction curves gathered from the lab data as well as illustrated trends in reactor geometry. When investigating the efficiency of various reactor geometries, minimizing the surface area:volume ratio was shown to result in the largest increases in efficiency. However the volume of the reactor, reflectance, and flow rates also played a role in reactor effectiveness.					
15. SUBJECT TERMS Ultra-Violet LED, Water Treatment, Advanced Oxidation, COMSOL®, Computational Modeling					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 192	19a. NAME OF RESPONSIBLE PERSON Dr. Michael E. Miller, AFIT/ENV
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER (include area code) (937) 785-3636, ext. 4651 (Michael.Miller@afit.edu)